UNIVERSITY OF ALBERTA

STUDIES OF THE MECHANISM OF ELECTROSPRAY IONIZATION MASS SPECTROMETRY

BY

LIANG TANG

A thesis submitted to the faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

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Tang Liang

September 27, 1993

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled STUDIES OF THE MECHANISM OF ELECTROSPRAY IONIZATION MASS SPECTROMETRY submitted by LIANG TANG in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY.

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To my parents, my wife and my son

ABSTRACT

The two major processes in electrospray mass spectrometry (ESMS) are the formation of charged droplets and the formation of gas phase ions.

Measurements of the total electrospray current, I, from solutions of the electrolytes HCl and NaCl, in methanol and water respectively, demonstrate that the current I increases with the conductivity σ of the solution. The relationship, $I = A\sigma^n = A(\lambda^{\circ}_{m}C)^n$, where A is a constant, λ°_{m} is the limiting molar conductivity of the given electrolyte at concentration C and $n \approx 0.22$ has been found. Thus, while electrolytes with higher λ°_{m} give higher ion currents for a given concentration, differences between electrolytes are small due to the low value of n. The applicability of this equation supports the electrophoretic mechanism in the formation of charged droplets in electrospray.

The dependence of the mass analyzed ion intensities, I_A and I_B, of analytes A^+ and B^+ for a variety of concentrations, $[A^+]$ and $[B^+]$, in the same methanol solution have been determined in several series of experiments. The equation $I_{(A^+ ms)} = pf \frac{k_A[A^+]}{k_A[A^+] + k_B[B^+]} I$ where p is a constant expressing the efficiency of the mass spectrometer for sampling the gas phase ions current and f is the efficiency of conversion of droplet charge to gas phase ions, is proposed and coefficient k values obtained for the ions, Li^+, Na^+, K^+, Cs^+, NH_4^+, several protonated alkaloids, $(Ethyl)_4N^+$, $(n\text{-}Propyl)_4N^+$, $(n\text{-}Butyl)_4N^+$, $n\text{-}C_7H_{15}NH_3^+$, $n\text{-}C_{11}H_{23}NH_3^+$, were obtained. The observed coefficients, k, depend on the surface activities of the analytes when $[A^+]$ and $[B^+]$ are in the range 10^{-8} to 5×10^{-6} mol/L and on the ion evaporation rate constants and surface activities for $[A^+]$ and $[B^+]$ in the

range 5 x 10^{-5} to 10^{-2} mol/L. Ion evaporation rates predicted by the Iribarne equation follow the same pattern as the experimental coefficients but the exact predictions of the equation could not be confirmed or disproved.

Rates of solvent loss from the droplets and the fission of the droplets due to Rayleigh instability are also included in the analysis. It is verified that charged droplets begin to produce gas phase ions after most solvent has evaporated.

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LIST OF SYMBOLS

12C4	12-Crown-4
18C6	18-Crown-6
c_p	molar heat capacity
d:	distance of capillary tip to planar counter electrode
dm / dt	rate of droplet mass change
f	fraction of droplet charge that gets converted into gas phase ions
h	Planck constant
k	Boltzmann constant (in equation 3-11)
k (k_A)	sensitivity coefficient (of ion A)
m	mass
p	sampling efficiency
p°	solvent vapor pressure
q	charge
r	radial distance
r_c:	capillary outer radius
t	time
$\bar{v}$	average thermal velocity
z	number of ion charges
A	relaxation function
Å	angstrom
AC	alternative current
APCI	atmospheric pressure chemical ionization
B_j	electrophoretic function
Bu	n-butyl

C	concentration
CB	cluster breaker
CE	capillary electrophoresis
CI	chemical ionization
CAD	collision activated decomposition
CocH$^+$	protonated cocaine
CodH$^+$	protonated codeine
D	dielectric constant
DC	direct current
E_{c}:	imposed electric field in vacuum at capillary tip
Et	ethyl
EI	electron impact ionization
ES	electrospray
ESMS	electrospray mass spectrometry
F	volume factor (V_o/V_f)
F	Coulombic force (in Chapter 5)
FAB	fast atom bombardment
FTICR	Fourier transform-ion cyclotron resonance
FTICRMS	Fourier transform-ion cyclotron resonance mass spectrometer
H	a constant in Hendricks equation
HerH$^+$	protonated heroin
HPLC	high performance liquid chromatography
I	electrospray current
I_{obs}	observed ion intensities
$I(A^+,g)$	gas phase analyte ion current
$I(A^+_{ms})$	mass spectrometrically detected analyte ion intensity

ID	inner diameter
K_s	equilibrium constant
L	ligand (crown ether) (in Chapter 4)
L	axial distance (in Chapter 5)
LC	liquid chromatography
LD	laser desorption ionization
M	mole L^{-1}
M	molar mass of the solvent (in equation 3-15)
MS	mass spectrometer
MW	molecular weight
$MorH^+$	protonated morphine
MALDI	matrix assisted laser desorption ionization
N	elementary charges on a charged droplet
OD	outer diameter
Pen	n-pentyl
R	radius of charged droplet
R_g	gas constant
R_R	Rayleigh fission radius
Q:	flow rate (volume/time)
Sl	solvent molecule
SCIEX	a trade name
SCIEX 6000E	name of a triple quadrupole mass spectrometer
T	temperature
T_m	mass transmission
TS	thermospray
TOF	time-of-flight
Tpy	tripyridine

V_c	capillary voltage
V_f	final volume of charged droplet (before ion evaporation)
V_o	initial volume of charged droplet
Xe	fast xenon atom
α	condensation coefficient
γ:	surface tension of liquid
ε:	permittivity of solvent
ε_o:	permittivity of vacuum
η_0	viscosity
λ_m	molar conductivity
λ_m°	limiting molar conductivity
μ_j	relative ionic strength of the ion species j
ρ	density
ρ	space charge density (in Chapter 5)
σ	electrical conductivity
Γ	ionic strength
$\Delta G^{\neq}$	free energy of the transition state
ΔG^{o}_{sol}	solvation energy
$\Delta H_{vap}(MeOH)$	molar vaporization enthalpy of methanol

Chapter 1. General Introduction

1.1 Electrospray phenomena

Although electrospray mass spectrometry (ESMS) is still considered to be a new technique in modern mass spectrometry, electrospray has origins which can be traced back to the era of the industrial revolution. The early study of the electrospray phenomena started with the work of pioneers in science such as Bose (1) and Kelvin (2). An interesting early experiment was the Kelvin water-dropper apparatus in which water dripping rate was controlled by electrostatic field. Bailey, in his book *Electrostatic Spraying of Liquids* (3), gave an extensive account of the early activities on electrospray.

Since the beginning of this century, more research work on ES has been conducted. The research interests in electrospray was spurred by the wide application fields that electrospray can find as a method for dispersing fluid. A version of electrospray, ink-jet technology (4), has been developed for printing. There are not only single-jet printers but also sophisticated multicolor ink-jet printers. The high-speed, silent printing capability of a modern ink-jet printer makes it an ideal output device for computer systems. The fact that there are no moving parts in most of the these printers means that they are inherently reliable.

The electrostatic crop spraying may be compared directly with electrostatic printing as identical principles apply. Several crop sprayers have been developed (5). The interest in electrospraying of crops is no doubt due to health and safety legislation and an acute awareness of environmental pollution considerations.

Fundamental study has been conducted on charged droplets. The early work on the observation of an evaporating charged droplet was carried out by a simple adaptation of the Millikan oil drop experiment (6). Later, some new techniques were developed, such as point-to-plane electrostatic precipitator (7, 8), quadrupole (9) and light scattering techniques (10). Recently, differential mobility analyzer and anemometer (11-13) have been used for the characterization of the fine charged droplets from electrospray. The development of methodology of droplet measurement provides strong support for the mechanism study of charged droplet formation. Research work on the mechanism of charged droplet formation was initiated by physicists and engineers, among whom are Zeleny (14), Taylor (15, 16), Vonnegut and Neubauer (17, 18), Hayati, Bailey and Tadros (19, 20). Hendricks and his co-workers (21, 22) studied electrospray because of its possible application in an ion propelled rocket engine. They proposed an electrospray model, which is called the Hendricks Model in this thesis. It will be discussed later that the Hendricks Model gives a relation among the parameters involved in electrospray and gives a special insight into electrospray phenomena.

1.2 Ionization methods widely used in analytical mass spectrometry

Gas phase ions required for mass spectrometric analysis are difficult to produce when the analytes are polar compounds with high molecular weight. Most biochemical analyses involve such large compounds. Conventional methods like electron impact ionization (EI) or chemical ionization (CI) require gaseous analyte molecules but such molecules can not be produced by evaporation of highly polar and high molecular compounds. Several methods have been introduced, such as fast atom bombardment (FAB), laser desorption ionization (LD) and thermospray (TS), where gaseous analyte ions are created directly from analytes present in the solid or liquid state.

The pioneer work done by Barber and his colleagues (23) made FAB become a widely used ionization method. In FAB, the analyte is dispersed in a liquid matrix on the surface of a metal tip. The liquid matrix can be glycerol or other compounds, which have low melting points and low vapor pressures. The metal tip, with analyte sample on it, is subjected to the bombardment by fast atoms, typically Xe, which are obtained from an electric discharge and converted to atoms by charge-exchange neutralization of an ion beam accelerated to several kilovolts. This technique made accurate molecular weight measurement of peptides possible for the first time. Further development of FAB led to the related method of "continuous flow FAB" (24) which delivers a solution of analyte in matrix to the vacuum system through a probe that achieves a continuously refreshed surface for the bombardment of fast atoms.

The popular MS technique laser desorption is somewhat similar to FAB. In the modern version MALDI, matrix assisted laser desorption ionization, the analyte is in a liquid or solid matrix as in the case of FAB. MALDI was introduced by Karas and Killendamp (25). Karas and Killendamp's work showed that both the wavelength of the photons used and the composition of the matrix that contains the analyte play an important role. With this technique, it has become possible to ionize proteins with molecular weights over 200,000 dalton with little internal excitation energy in the desorbed ion.

Thermospray, developed by Vestal and his colleagues (26) has been widely used in the pharmaceutical industry. Because thermospray is a technique producing gas phase ions directly from analyte solution, it has been applied to the interfacing of LC to MS. In thermospray, the LC effluent is passed through a heated capillary which vaporizes the LC effluent into a superheated mist transported in a supersonic vapor jet. Most of the vaporized solvent and mist is pumped away by an auxiliary vacuum pump after it passes by the aperture to the mass spectrometer. The non-vaporized analyte molecules remain in the droplets of the mist as they diminish in size. The solution used for thermospray contains dissolved electrolyte such as ammonium acetate which leads to NH_4^+ and Ac^- ions in the solution. The droplets formed are observed to be charged (27). Both positive and negative charged droplets are observed. It is assumed that the droplet charging is due to a statistical unbalance of positive and negative ions present in the solution. This unbalance process of charging occurs during the fast droplet formation process (27). Finally, the rapidly evaporating charged droplets lead to formation of gas phase ions. The production of gas phase ions from charged droplets is a process that also occurs in electrospray. The mechanism involved will be discussed later. Thermospray is a good approach to HPLC/MS due to its capability of handling solvent flow rates which is useful in HPLC. It has been found suitable for the analysis of only relatively low molecular weight polar biological compounds.

1.3 Electrospray mass spectrometry

Electrospray mass spectrometry began to attract chemists and biochemists' attention world wide due to the successful work done by Yamashita and Fenn (28) in United States and Aleksandrov et al. (29) in the former Soviet Union. Their work demonstrated that ESMS might be the best technique for the mass analysis of biological compounds with high molecular weight. The idea of using ES dispersion of an analyte solution in a bath gas to produce solute ions for mass analysis originated with Dole et al. in the 1960s (30). Interested in the possibility of determining the molecular weights of polymers, they performed some pioneering experiments in which an acetone-benzene solution of polystyrene macromolecules was electrosprayed into a bath gas of nitrogen in a mass analyzer. They hoped that ES dispersion of a sample solution would result in the production of charged droplets, each of which contains only one charge and one solute molecules that gives rise to a macro-ion. Because the available mass analyzers at that time could not accommodate singly charged ions with molecular weights in his range of interest, 50000 to 500000 dalton, Dole only did ion retardation (31, 32) and ion mobility (33) measurements. However, the importance of Dole's contributions cannot be overstated. His research clearly suggested the facile ionization of macromolecules, the multiple charging phenomenon, as well as many of the instrumental methods currently utilized for ESMS technique. Stimpson and Evans (34) summarized the early activity in ESMS. Current activity of ESMS is focused mainly on the application of the ESMS technique on the analysis of biochemical compounds, which is the opinion expressed by recent review articles (35-39).

The ESMS instrumentation consists of three components, which are the electrospray source where charged droplets form by electrostatic nebulization of analyte solution; the atmosphere-to-vacuum interface where the charged droplets evaporate to produce gas phase ions and gas phase ion-molecule reaction may happen; and the mass spectrometer where mass analysis occurs. The ES source may consist simply of a metal capillary at elevated voltage relative to a counter electrode having an orifice where ions or ion-clusters enter the mass spectrometer entrained in a flow of gas. The solution with flow rate in the range of 1 ~ 20 μL/min delivered typically by a syringe or micropump moves through the silica capillary tubing to the spray tip where it is sprayed. The high DC voltage forms a high electric field at the capillary tip, causes charge accumulation on the liquid surface at the capillary terminus and disrupts the liquid surface, resulting in the formation of highly charged liquid droplets. Positively or negatively charged droplets may be produced depending upon the source voltage bias. Polar solvents such as methanol and/or water are usually electrosprayed. Usually, a concentration range of electrolyte in the range of $10^{-8} \sim 10^{-3}$ M is required at room temperature for a stable electrospray. Although higher voltage can improve ion detection sensitivity, a much higher voltage will generally cause a corona discharge and preclude analyte-ion detection. The corona discharge can be effectively suppressed by adding an effective electron scavenger such as O_2 (40, 41) or SF_6 (42, 43). The ES liquid nebulization process can be pneumatically assisted using a high-velocity annular flow of gas at the capillary terminus. This method is called "ionspray" (44) and has the advantage of accommodating high flow rate up to 100 μL/min.

At a short distance from the ES source, the nebulized liquid has a nearly monodisperse droplet diameter in the range of 1~2 μm (45, 46). Increased liquid flow rates only result in larger droplets (47), and the total electrospray ion current increases only slightly. Increased electrolyte concentration causes a decrease in the average droplet size.

Heating or ultrasound irradiation of the droplets is useful for manipulating the electrospray process. There is evidence that slight heating allows aqueous solutions to be readily electrosprayed (48, 49), presumably due to decreased viscosity and surface tension. The importance of viscosity and surface tension in the ES process will be discussed in Chapter 2. Irradiation of charged droplets by means of ultrasonic waves (50) also facilitates the electrospray process, particularly in the case of electrospray of aqueous solution. The introduction of the ultrasonic technique into ESMS is expected to attract more attention.

After the charged droplets leave the electrospray tip, they drift in the atmosphere and solvent is evaporated. The droplets undergo several fission processes, yielding smaller and smaller charged droplets. Finally, gas phase analyte ions form from these smaller droplets. The ions can be analyzed by a mass spectrometer. An atmosphere-to-vacuum interface is the common feature of ESMS instrumentation. An important attribute of an ion source operated at atmospheric pressure is the efficiency of sampling and transport of ions into the mass spectrometer. A simple design available in a commercial instrument from SCIEX utilizes an orifice with diameter ~100 μm to a vacuum region which is maintained by a cryopump with high pumping speed. Ions formed by ES drift against a countercurrent flow of dry N_2, which serves to exclude large droplets and aerosol particles and aids desolvation of solvated ions. As the ions pass through the orifice into the vacuum, further desolvation is accomplished by collisions as the ions are accelerated into a cluster breaker. In Chapter 3, a model of a SCIEX mass spectrometer SCIEX 6000E will be shown, where the configuration of atmosphere-to-vacuum interface is illustrated. Several other instruments can also be found on the market, which have been developed based on differentially pumped interfaces. The capillary inlet-skimmer interface developed by Fenn and his co-workers (51) is applied on the instrument produced by Analytica of Branford (Branford, CT). This interface uses a countercurrent flow of bath gas, which is typically N_2 at a pressure slightly above atmospheric pressure, to sweep away high m/z residual particles and solvent vapor from the mass spectrometer inlet. The glass capillary of this interface is metalized at both ends to establish well defined electric fields. Some fraction of ions is entrained in the gas flow entering the glass capillary. Ions can be transmitted through the capillary with high efficiency. Ions swept by the gas flow through the capillary emerge as a component of a free jet expansion in the first differentially pumped stage. Some fraction of the ions is then transmitted through a skimmer into the mass analyzer.

An atmosphere-to-vacuum interface called a "low pressure ion source" (52) takes advantages of both mentioned commercial interfaces and high pressure ion source in chemical ionization (53). This ion source allows ions formed by electrospray to be drawn through a metal capillary into a chamber at 10~100 torr, where they may react with a separately added gas for the study of ion-molecule reactions. The reaction products are then transmitted through the orifice of a SCIEX quadrupole instrument to be mass analyzed. A low pressure ion source is still at the stage of preliminary study, but it might be a potential new ion source in the study of gas phase ion-molecule reaction via electrospray.

After the ESMS work on a quadrupole mass spectrometer was reported, successful combination of an ES source with other types of mass spectrometers have been accomplished. The combination of ES with a magnetic sector machine demonstrates low ppm mass accuracy and high mass resolution for small proteins (54, 55). Initial results with a time-of-flight (TOF) instrument has also been reported (56). ESMS work done on an ion trap presents highly encouraging results (57), and the ion trap method shows significant advantage for MS/MS sensitivity in comparison with conventional tandem instruments. If ES is combined with Fourier transform-ion cyclotron resonance mass spectrometer (FTICRMS) (58-59), the potential for structural elucidation of proteins by multi-MS is quite promising. The coupling ES to FTICRMS makes the ESMS technique more powerful for the structural identification of nonvolatile molecules. The combination of ES with FTICR also appears to have potential for obtaining accurate molecular weights from high-resolution spectra.

ESMS produces charged droplets in a way that is much simpler than thermospray, and produces more abundant intact molecular ions. In particular, its feature of multiply charged macromolecules overwhelms other soft ionization techniques in biochemical analysis. Electrospray is a continuous process, which makes it suitable for LC-MS. The versatility of ESMS has resulted in its rapid development. ESMS quickly became commercially available after it was invented, and a large amount of ESMS literature has emerged in recent years. It is now not only an important tool in the structural study of polypeptides, proteins and carbohydrates but also a powerful apparatus in the combination of liquid chromatography (LC) and capillary electrophoresis (CE) separations with mass spectrometric analysis of organic compounds, especially peptides and proteins (60).

Although there were many research articles on ESMS available in the literature when I began my Ph.D program, most of the work described the applications of the method and explored the parameters that lead to improved performance. Little work dealing with the mechanism was available. The understanding of the ESMS mechanism was incomplete and out of pace with the rapid expansion in ESMS activity at that time. The lack of understanding of the mechanism may be expected to slow down the progress of ESMS. This thesis presents an investigation of the mechanism of ESMS.

Three important, mutually related topics are considered: the mechanism of charged droplet formation, the process of charged droplet evolution towards small highly charged droplets, and the gas phase ion formation from these droplets. The principal method in my study was the determination of mass analysed ion intensities of different analytes and the dependence of these intensities on the concentration of the analytes in the electrosprayed solution. These results were combined with available information in the literature on the electrospray mechanism and on the properties of small charged droplets. The combination of all the above information has provided, I believe, a useful synthesis leading to an advance in the understanding of the mechanism involved in ESMS.

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Chapter 2. Effect of the Conductivity of the Electrosprayed Solution on the Electrospray Current. Factors Determining Analyte Sensitivity in Electrospray Mass Spectrometry*

2.1 Introduction

Electrospray mass spectrometry (ESMS) is a new technique of extraordinary potential (1-3). The exciting applications of this technique have created also a great deal of interest in the mechanism by which the gas phase ions required for the mass spectrometric analysis are produced. The two main stages in the mechanism are the production of charged droplets and the production of gas phase ions from the charged droplets. Since the second stage depends on the first, it seems logical to examine the charged droplet formation first and this approach has been taken in the mechanistic work on ESMS (4-8).

The experimental work discussued in this chapter, which examines the dependence of the total current I produced by electrospray on the electrical conductivity σ of the solution, is connected directly with the charged droplet formation process. However, because the conductivity depends on the concentration of the ions in solution including that of the analyte ions, the findings also set the stage for a partial examination of the second stage, - the production of gas phase ions from the charged droplets and in particular the dependence of the gas phase analyte ion current on the concentration of analyte ions and other electrolyte ions in the electrosprayed solution.

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The formation of charged droplets in the electrospray process has been subject to intensive studies which predate the mass spectrometric applications. These studies were driven by a number of important technical applications of electrospray (9). This intensive effort has produced much valuable information; however, a complete understanding has not been achieved and complete equations relating the pertinent variables, are not yet available.

A number of authors (9-12) agree that the charging of the droplets is electrophoretic. Electrophoretic charging means that the external electric field induces a partial separation of positive from negative electrolyte ions which are present in the solution (i.e. "preformed" ions in the mass spectrometric nomenclature). Thus, when the capillary is of positive polarity, the liquid surface at the capillary tip becomes enriched with positive ions. This excess charge induces an instability of the surface which ultimately leads to a dispersal of the liquid into a fine mist of positively charged droplets. The charge of the droplets is due to an excess of positive electrolyte ions over the negative counter ions. The electrophoretic mechanism is of special importance to the mass spectrometrist since it indicates that the gas phase ions detected by the mass spectrometer will be due to electrolyte ions present in the solution (4-8).

Recently, it has been shown (8), in support of the electrophoretic mechanism, that the electrospray process may be viewed as an electrolysis cell of a special kind. When the metal capillary is at a positive potential, an electrochemical oxidation reaction occurs at the metal-liquid interface at the capillary tip. This oxidation either removes negative ions from the solution converting the charge to electrons transferred to the metal or produces positive ions in the solution from metal atoms of the capillary material. Thus, the reaction: $Zn_{(s)} = Zn^{++}_{(aq)} + 2e$ was identified when the capillary tip was made of Zn metal and $Fe_{(s)} = Fe^{++} + 2e$, when the tip was of the usual material - stainless steel. The rate of positive charge formation due to dissolution of the metal ions was found equal to I, the measured electrospray current (8). An electrochemical reduction reaction is expected to occur at the negative counter electrode and so, the electrospray device may be viewed as an electrolysis cell which exhibits a special feature, i.e. part of the transport of charge is achieved through the gas phase via charged droplets and gas phase ions.

Experimentally it is found that the charged droplet emission current I is dependent on the presence of ionized electrolytes in the solvent to be electrosprayed. No spray is observed with totally deionized solutions. The threshold conductivity σ, where the spray is still intermittent, occurs (6) for methanol containing dissolved electrolytes at a $\sigma \approx 10^{-7}\ \Omega^{-1}\ cm^{-1}$. For electrolytes like the alkali halides, the above σ corresponds to a total electrolyte concentration of $\sim 10^{-6}$ M (M = mole L^{-1}) (13).

As the conductivity is increased above the threshold, the ES current I increases and becomes stable. I is found to follow approximately a power law with the conductivity as shown in equation 2-1, where H is a constant.

$$I = H\,\sigma^{n} \qquad (2\text{-}1)$$

$$n \approx 0.2 - 0.4$$

Such a dependence was reported by Pfeifer and Hendricks (10) for glycerol solutions and was observed also for methanol solutions in previous work from this laboratory (6). For other measurements see (9, 11, 12).

When strong electrolytes like the alkali halides or strong acids like HCl are used at low concentrations $C < 10^{-3}$ M in a solvent like methanol, they are fully dissociated and ion-pairing effects are minimal. In this case equation 2-2 holds approximately,

$$\sigma \approx \overset{\circ}{\lambda}_m C \qquad (2\text{-}2)$$

where $\overset{\circ}{\lambda}_m$ is the limiting molar conductivity, corresponding to the molar conductivity λ_m at infinite dilution. Since ES is usually performed in this low concentration range, one can combine equation 2-1 and 2-2 to obtain equation 2-3.

$$I \approx H(\overset{\circ}{\lambda}_m C)^n \qquad (2\text{-}3)$$

The dependence of the electrospray current I on the conductivity has not been fully characterized and the functional form, equation 2-1, does not appear to be fully accepted in the literature. Another important point that has not been proven is the effect of the $\overset{\circ}{\lambda}_m$ of given electrolytes on the current I. Thus, according to equation 2-3, when two methanol solutions, each containing the same concentration C of two different electrolytes x and y, are electrosprayed, the current ratio measured should be given by,

$$\frac{I_x}{I_y} = \left(\frac{\overset{\circ}{\lambda}_m(x)}{\overset{\circ}{\lambda}_m(y)}\right)^n \qquad (2\text{-}4)$$

Most measurements have been performed with alkali halides, for which $\overset{\circ}{\lambda}_m$ changes very little (13), $\overset{\circ}{\lambda}_m \approx 100 \pm 20\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$. These small changes, combined with the facts that the exponent n is small, the electrospray currents I are not perfectly stable and the ES conditions are not perfectly reproducible, makes verification of equation 2-4 difficult.

Only electrolytes with a large $\overset{\circ}{\lambda}_m$ difference can be expected to lead to verifiable current differences. The obvious solution of this problem is to choose a strong acid like HCl as one of the electrolytes making use of the well known high mobility and thus also high conductivity of the hydrogen ion. Thus $\overset{o}{\lambda}_{m}(H^+) = 350$ while $\lambda^{\circ}(Na^+) = 50\ \Omega^{-1}\ cm^2\ mol^{-1}$ in water. ES of water solutions is difficult since high capillary voltages are required (8,11) and these may lead to a corona discharges which will make an unknown contributioned to the measured current (8).

ES of methanol-water solutions are easier to spray. The molar conductivity $\overset{o}{\lambda}_{m}$ of HCl and other electrolytes such as NaCl in the complete range of methanol-water mixtures has been determined previously by electrochemistry researchers (14). For the present ES experiments we chose the composition 40% by weight methanol. In this solvent the conductivity difference is still quite large, $\overset{o}{\lambda}_{m}(HCl) = 190$ versus $\overset{o}{\lambda}_{m}(NaCl) = 58\ \Omega^{-1}\ cm^2\ mol^{-1}$ (14).

As will be seen in Results and Discussion, section (a), the present measurements confirm the dependence of Ion $\overset{o}{\lambda}_{m}$ predicted by equation 2-4.

Pfeifer and Hendricks (10) have derived a theoretical equation which relates I to the parameters: capillary voltage and dimensions, flow rate, surface tension and conductivity of solvent. This equation defines the constants H and n in equation 2-1. In section (b) the present measurements of I were used for an examination of the degree of agreement between the experimentally measured and the theoretically predicted current.

The final section (c), utilizes the observed relationship between electrolyte concentration and ES current to make a quantitative prediction for the effect of concentration of the analyte and of electrolytes, such as impurities, on the sensitivity for mass spectrometric detection of the analyte.

2.2 Experimental

a. Total ion current measurement

The arrangement used for measurement of the total current I is shown in Figure 2-1. It was shown in earlier work from this group that the positive current leaving the capillary tip is equal to the positive current arriving at the plane electrode (6). The current to the plane electrode, which was at ground potential, was measured in the present experiments.

The 40% methanol-water solvent used in the present work requires a capillary voltage V_c of 5000 V for a stable ES spray. This voltage is higher than what is ordinarily used with methanol solutions ($V_c \approx 4000$ V). Therefore tests were made for the possible presence of a simultaneous corona discharge. These experiments were performed with our SCIEX API TAGA 6000E instrument, modified for ES, see references 4 and 8. The tests showed that the electrospray current I was the same in the absence and presence of discharge-suppressing SF_6 gas. This result means that no measurable discharge was occurring in the absence of SF_6 (8). The mass spectrometrically detected ions, when a NaCl containing solution was electrosprayed, were mostly Na^+ adducts to the solvent molecules. Significantly, the intensities of discharge indicating ions, i. e. protonated solvent molecules, were very low. This finding also supports that the absence of an electric discharge (8).

The stainless steel ES capillary had a diameter 0.004" ID and 0.010" OD. The distance from capillary tip to the planar counter electrode was 4 cm. All experiments were performed with a solvent flow

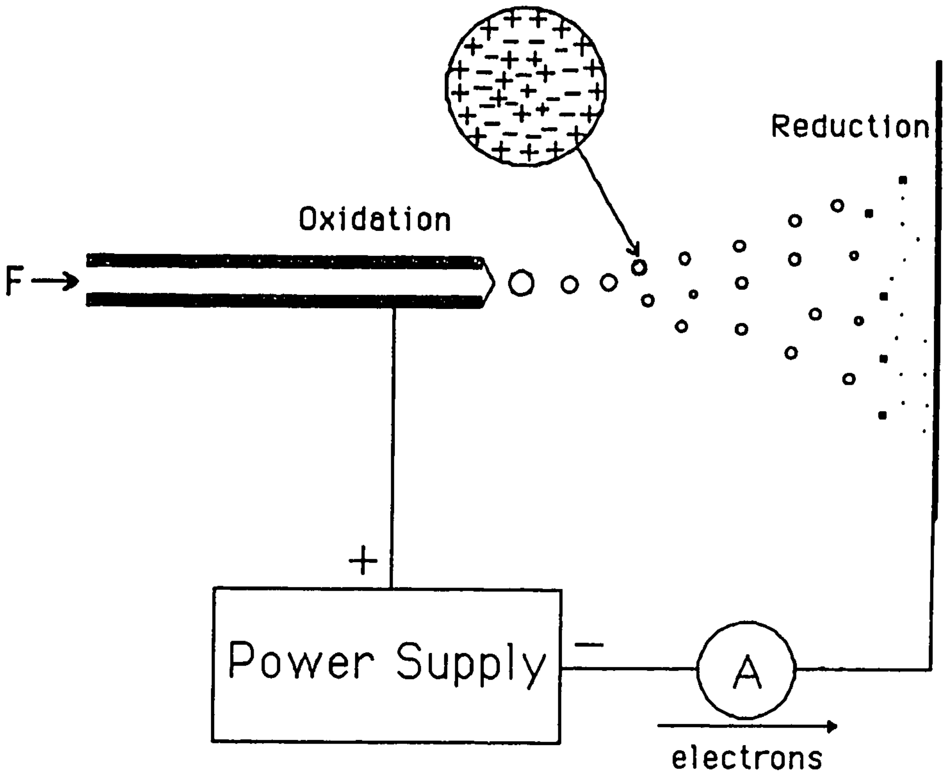

Figure 2-1 Schematic diagram of electrospray device. Capillary tip and droplets are highly magnified. Electrospray (ES) current A was measured with electrometer at ground potential. The operation of ES as an electrolysis cell is indicated by oxidation and reduction labels in figure.

20 μL/min.

b. Electrolyte solutions and conductivity measurements

Analytical grade methanol was fractionally distilled. Its conductivity after distillation was 1 x 10^{-7} Ω^{-1} cm^{-1}. The water used was deionized to a somewhat lower conductivity. The concentration of HCl in 40%, by weight, methanol was calibrated by titration as suggested by Johnson and Funk (15). Analytical grade NaCl was dissolved directly in the solvent. All experiments were made with freshly prepared solutions stored in Pyrex vessels under an argon atmosphere.

The conductance measurements were performed with a YSI model 31 conductivity bridge and a YSI 3402 dip cell.

2.3 Results and Discussion

a. Electrospray current. Dependence on conductivity of solution, limiting molar conductivity and concentration of electrolyte

The measured conductivities of solutions of NaCl and HCl, dissolved in 40% methanol-water solvent, are shown in Figure 2-2 plotted versus the concentration of the respective electrolyte. The data in the linear plot shown in 2A illustrate that in the concentration range 10^{-4}M to 10^{-2}M, the conductivity σ is very close to being proportional to the electrolyte concentration as assumed in equation 2-2. The slopes of the linear plots, Figure 2-2A, are 55 Ω^{-1} cm^2 mol^{-1} (NaCl) and 160 Ω^{-1} cm^2 mol^{-1} (HCl). These values are close to the λ_o values obtained by the more accurate and extensive measurements of Shedlovsky and Longsworth (14). λ_o(NaCl) =

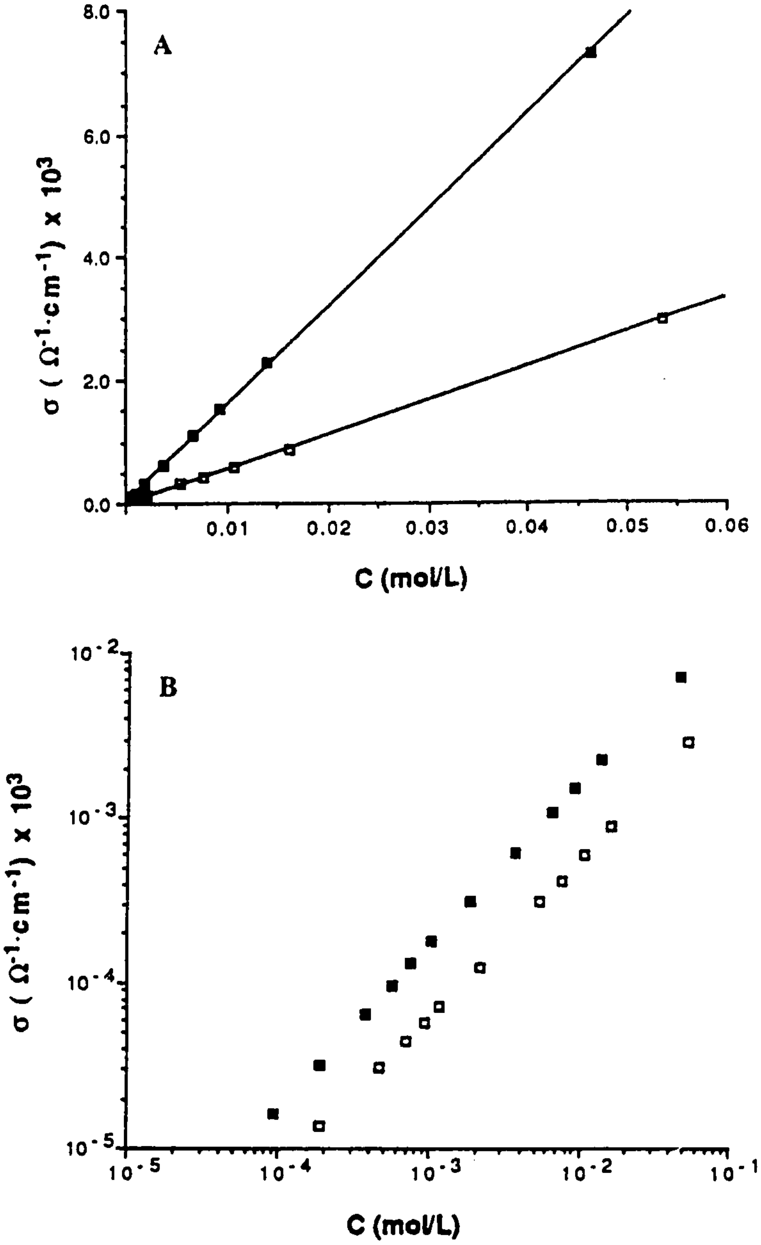

Figure 2-2 A. Plot of measured conductivity σ of solutions of HCl and NaCl respectively in solvent, 40% methanol, 60% water by weight versus concentration C of electrolyte, at 23°C. Linear plots indicate that equation. 2-2 holds in concentration range used. ■ HCl, □ NaCl.

B. Same data is in Figure 2-2A, but plotted as log σ versus log C.

58 and $\lambda_0(HCl) = 190\ \Omega^{-1}\ cm^2\ mol^{-1}$. The present data when plotted according to the Kohlrausch equation; $\lambda = \lambda_o - A\sqrt{C}$, led to λ_o values which are in closer agreement with the literature results (14). However, the point here is not to determine accurate λ_o values, but to show that equation 2-2 holds quite well in the concentration range of interest in ES and that the solutions used and the measured conductivities in this work are close to those expected from more specialized determinations.

The measured electrospray currents I with the above solutions are given in Figures 2-3 and 2-4. The current I plotted versus the conductivity σ is shown in Figure 2-3 for NaCl and HCl solutions. The experimental points for I versus σ for NaCl and HCl are seen to fall essentially on the same line. The straight line obtained in the log I versus log σ plot used provides a confirmation of equation 2-1. The slope of the plot is equal to 0.22 and can be equated to the exponent n in equation 2-1.

$$n \approx 0.22 \quad \text{(verified for NaCl and HCl solutions)} \qquad (2\text{-}5)$$

Since the linear plot in Figure 2-2A provided a confirmation of equation 2-2 for the systems used here, it follows that equation 2-3 which follows from equation 2-1 and equation 2-2, is also verified by the plots in Figures 2-2 and 2-3.

The measured log currents I for NaCl and HCl solutions plotted versus the log electrolyte concentration are shown in Figure 2-4. Two distinct straight lines with approximately the same slope are obtained in the log I vs log C plots used. The HCl line is displaced towards higher currents as expected from equation 2-3. The difference: log I_{HCl} – log I_{NaCl} is found to be equal to 0.11. According to equation 2-3 the relationship, equation 2-6, should hold.

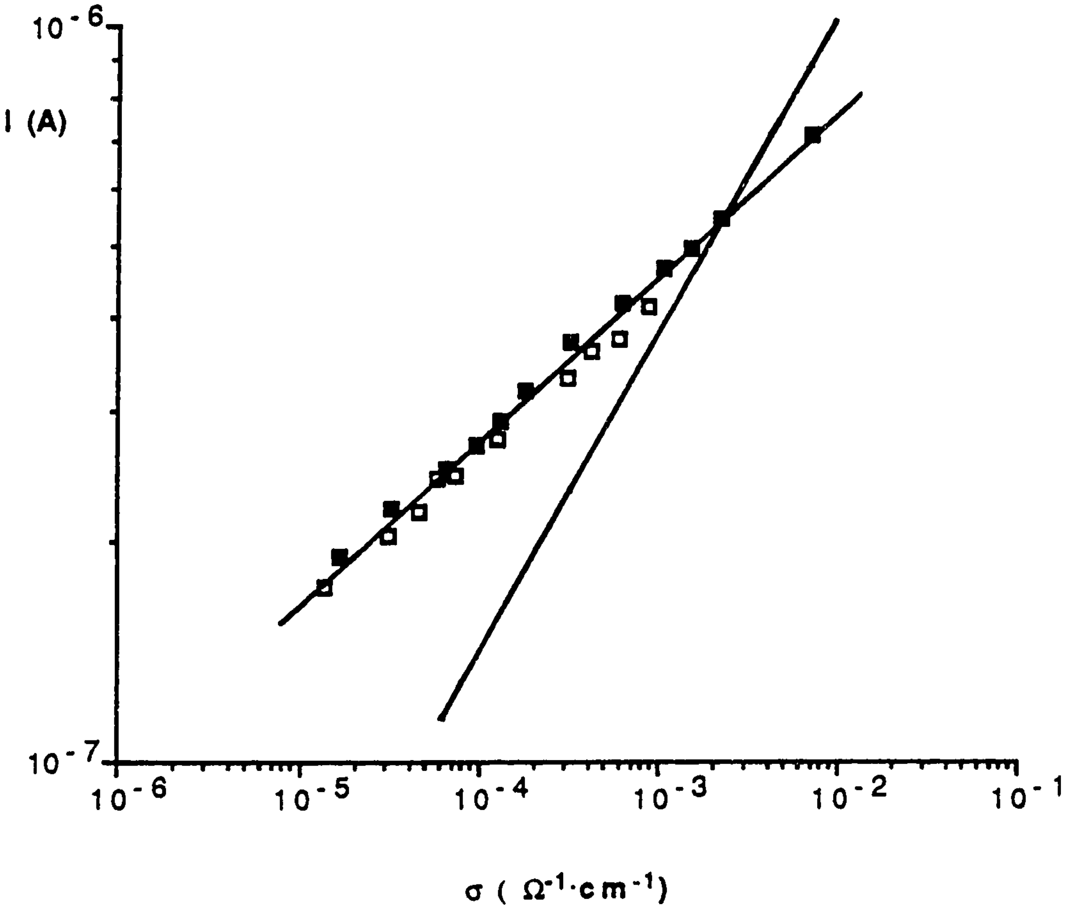

Figure 2-3 Logarithmic plot of electrospray current I versus conductivity of HCl and NaCl solutions in solvent 40% methanol, 60% water. The observation that currents I from NaCl and HCl fall on the same line confirms equation 2-3. Slope of present plot provides n = 0.22 for exponent n of equation 2-3 (R=0.98 in linear regression). ■ HCl, □ NaCl. Solid line with higher slope represents current I calculated with Hendricks expression, see equation 2-7.

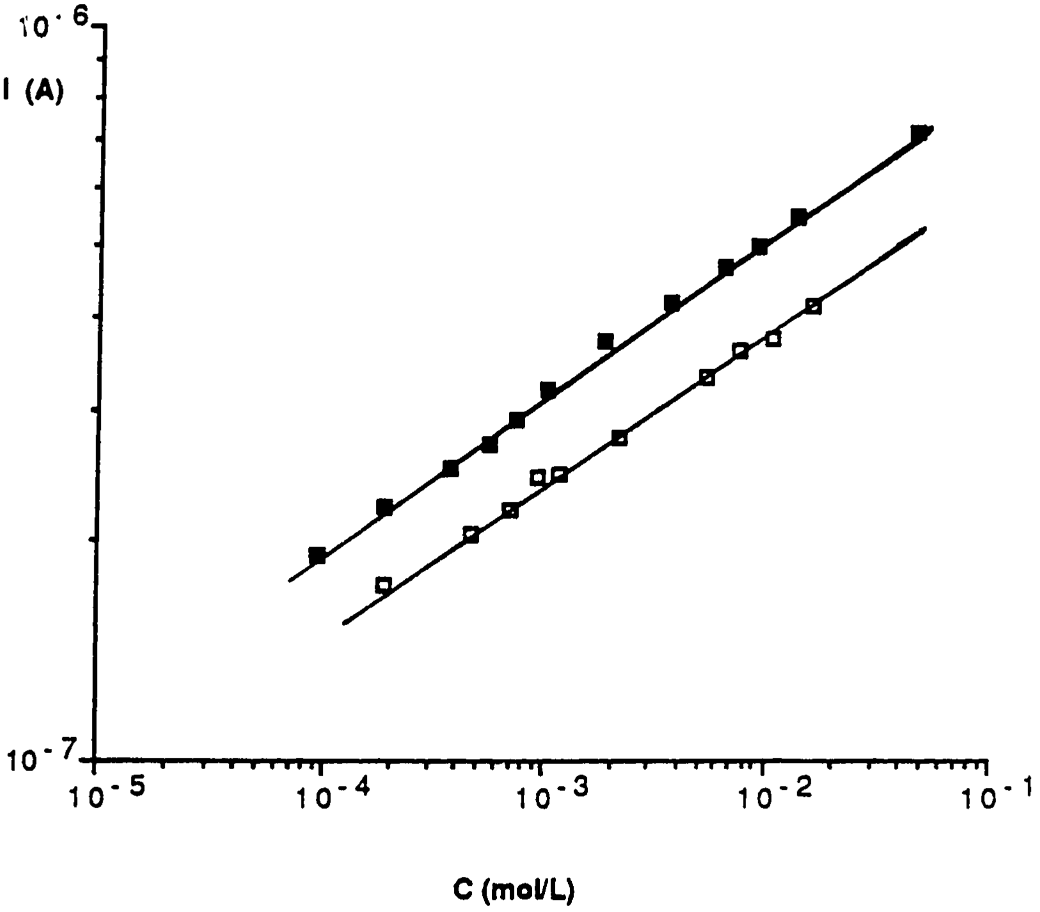

Figure 2-4 Logarithmic plot of measured ES current I versus concentration C of electrolytes HCl resp. NaCl in solvent 40% methanol, 60% water. Plots in Figure 2-3 and present figure confirm equation 2-3. ■ HCl, □ NaCl

$$\log I_{HCl} - \log I_{NaCl} = n(\log \overset{\circ}{\lambda}_m(HCl) - \log \overset{\circ}{\lambda}_m(NaCl) \qquad (2\text{-}6)$$

using n ≈ 0.22, see equation 2-5, and the log I difference of 0.11, one obtains from equation 2-6

$$\frac{\overset{\circ}{\lambda}_m(HCl)}{\overset{\circ}{\lambda}_m(NaCl)} \approx 3.2$$

This result is close to the ratio of 3 obtained from the conductivities measured in this work, see Figure 2-2 and the ratio of 3.3 obtained with the literature values (14).

Thus, the approximate equation 2-3 is fully confirmed by the plots in Figures 2-2 to 2-4.

b. Comparison with the Hendricks equation for the electrospray current I

In spite of considerable attention to the theoretical problem that the electrospray nebulization represents, there appear to be only two treatments (10, 11) which provide equations that predict the electrospray current I. The first treatment, that of Pfeifer and Hendricks (10) leads to the expression shown in equation 2-7. The treatment by D.P.H. Smith (11) is probably more realistic (6), but it does not provide a complete equation which explicitly predicts the functional dependence on the conductivity.

$$I = \left(\frac{4\pi}{\varepsilon}\right)^{3/7} (9\gamma)^{2/7} \varepsilon_0^{\,5/7} Q^{4/7} (\sigma E_c)^{3/7} \qquad (2\text{-}7)$$

ε_0: permittivity of vacuum	Q: flow rate (volume/time)
ε: permittivity of solvent	σ: conductivity of solution

γ: surface tension of liquid

E_c: imposed electric field in vacuum at capillary tip

E_c can be evaluated from the capillary voltage V_c applied to the capillary tip, with the use of the approximate equation 2-8, used by Hendricks (10) and Smith (11).

$$E_c = \frac{2\,V_c}{r_c \ln(4\,d/r_c)} \tag{2-8}$$

r_c: capillary outer radius

d: distance of capillary tip to planar counter electrode

Therefore, it is possible to evaluate the current I predicted by equation 2-7 for the experimental parameters used in the present work:
$Q = 20\ \mu L/min$, $\gamma = 3.4 \times 10^{-2}\ N\ m^{-1}$ for 40% w/w methanol water (16), $\varepsilon_0 = 8.8 \times 10^{-12}\ C^2\ N^{-1}\ m^{-2}$, $r_c = 1.27 \times 10^{-4}$ m; $d = 4 \times 10^{-2}$ m, $V_c = 5000$ V, $E_c = 1.1 \times 10^7\ V\ m^{-1}$ from equation 2-8.

The current I evaluated with these parameters for a range of conductivities is shown in Figure 2-3 and 2-5 together with the experimentally determined I. The experimental data for NaCl and HCl which were used for the plots in Figures 2-3 to 2-4 are used also in Figure 2-5. The agreement between the experimental and theoretical currents is fair. This was to be expected from the experimental plot in Figure 2-3 which gave an $n \approx 0.22$, while the predicted n by equation 2-7 is $n = 3/7 = 0.43$. The largest deviation occurs at low conductivities, i.e. below $10^{-4}\ \Omega^{-1}\ cm^{-1}$. This conductivity corresponds to concentrations below 10^{-3} M. Even in this range, the deviation is not large. Thus at $\sigma = 10^{-5}\ \Omega^{-1}\ cm^{-1}$ the current predicted by equation 2-7 is smaller by only a factor

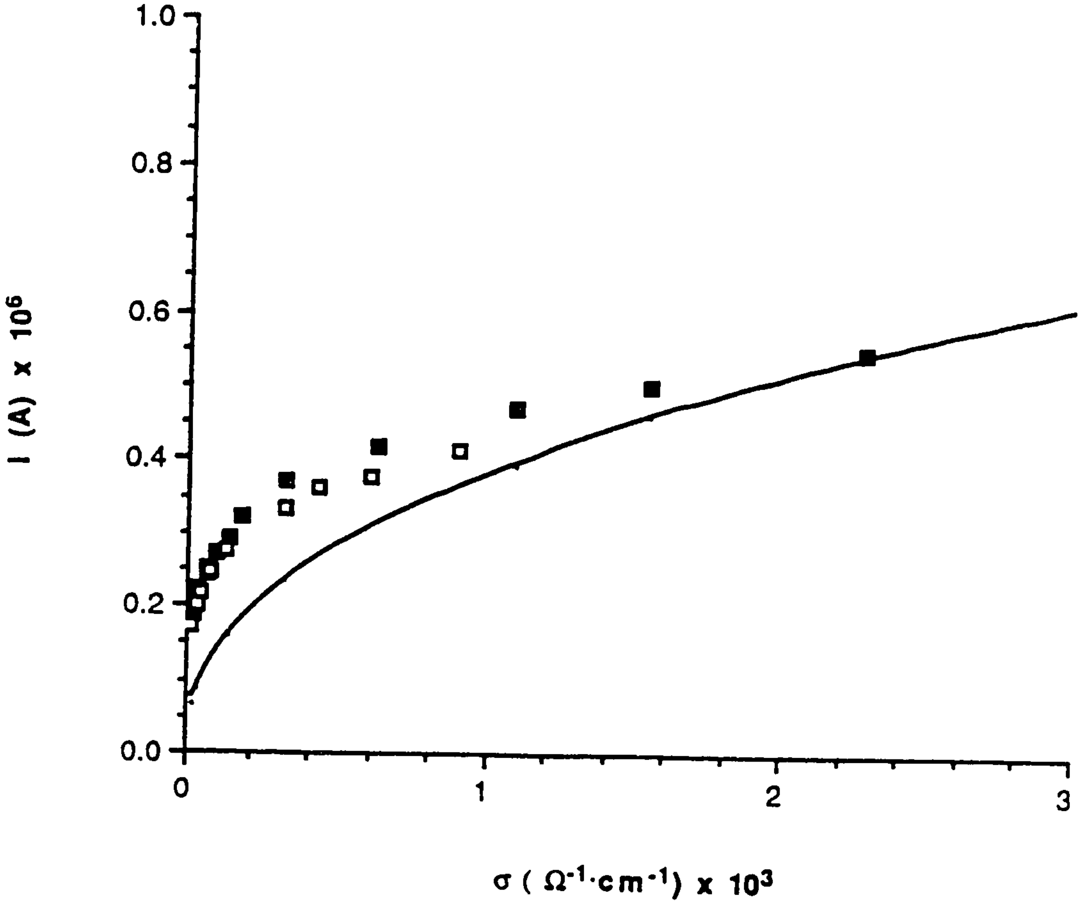

Figure 2-5 Linear plot of measured ES current I versus conductivity of solutions. Solid line represents calculated current predicted by the Hendricks [10] equation 2-7.

of 3 relative to the experimental I. Considering the complexities of the electrospray nebulization process (9-12) even an agreement within a factor of 10 between theoretical predictions and experiment might be considered a considerable success for the theory, when an equation like 2-7 is involved which has no adjustable parameters.

The experimentally observed exponent n for the concentration dependence appears to depend also on the type of capillary tip used. The earlier work in references 7 and 17 where a wider outer diameter capillary was used, produced electrospray currents I which depended on the conductivity with an exponent n which was higher, 0.37-0.42, and thus closer to the n = 0.43 predicted by equation 2-7.

The dependence of I on the flow rate Q of the solution was also examined and found to depend on an exponent close to the 4/7 power predicted by equation 2-7 in the earlier work.

The partial success of the Hendricks equation 2-7 need not mean that the assumptions used for the derivation are correct. However, the equation obviously makes some useful predictions.

Since the imposed external field E_c is very high, one might be concerned that the low field conductivities determined in the present work and used in the equations may not apply. This question is briefly examined in the Appendix where it is shown that use of the low field conductivities is justified.

c. Dynamic range of detected analyte ion intensity in ESMS

The preceding experimental and theoretical information shows that the electrospray current I and thus also the product between the average charge on the droplets and the rate of droplet emission is a function of the conductivity of the solution. However, the functional dependence is weak, i.e. I changes with the conductivity, see equation 2-3, 2-4 and 2-7, taken to the n ≈ 0.3 power.

Furthermore, because the limiting molar conductivities λ°_{m} for most electrolytes are within ~30% of each other, one might expect that the relative concentrations of the electrolytes in the charged droplets formed at the capillary tip will be very similar to those in the solution subjected to electrospray. By this we mean that no significant enrichment (fractionation) of one ionic species over another is expected for the initially formed droplets.

The assumption of no fractionation of ionic species must be qualified with regard to any new electrolyte species produced by the electrospray process. As shown in the work of Blades et al.(7), new ions, such as Fe^{++} can be produced by an electrolytic oxidation at the stainless steel capillary tip, when the capillary potential is positive. It is these ions that provide the charge balance for the extra positive charge on the droplets. However, at normal electrospray currents, I ~5 x 10^{-7} A, the concentration of these ions is in the 10^{-6} M range (7) and thus considerably lower than the typical impurity electrolyte concentration and very much lower than the concentration of electrolyte buffers that would be present in any liquid chromatography (LC) effluent. Thus, even though the electrosprayed droplets may contain one ionic species that was initially not present in the electrosprayed solution, the concentration of that species will be low (10^{-6} M) and of little significance unless the solvent used was deliberately deionized.

While the selectivity for one ionic species over another for the transfer of ions from the bulk solution to the droplets may be expected to be very low, the same need not be the case in the transfer of ions from the droplets to the gas phase. Thus, assuming that the Iribarne ion evaporation model (18) is the principle mechanism for the ion transfer to the gas phase, one may conceive of ionic species whose ion evaporation free energies might be especially low and lead to much higher ion evaporation rates.

To obtain a simple model, we propose that the ion evaporation rate from the droplets is proportional to the ion concentration in the droplet. Singling out analyte ions A^+ and lumping all other electrolyte ions as external electrolytes E^+, one can assume equation 2-9 to provide a prediction for the gas phase analyte ion current $I(A^+,g)$ in the vicinity of the planar counter electrode, see Figure 2-1.

$$I(A^+,g) = f \frac{k_A[A^+]}{k_E[E^+] + k_A[A^+]} I \qquad (2\text{-}9)$$

I is the total current, see equations 2-1, 2-3 and 2-7, and $I(A^+,g)$ is the current due to gas phase ions generated by escape of analyte ions from the droplets. k_A and k_E are rate constants which express the rate of transfer of ions from the droplets to the gas phase, $[A^+]$ and $[E^+]$ are the respective electrolyte concentrations in the droplets. The proportionality constant f represents the fraction of droplet charge that gets converted into gas phase ions.

Since $I(A^+,g)$ could not be determined in the present experiment and since the interest is in the mass spectrometrically detected analyte ion intensity $I(A^+_{ms})$, we assume a proportionality,

$$I(A^+,ms) = p\, I(A^+,g)$$

where p is a proportionality constant expressing the "sampling efficiency" of the system, and obtain

$$I(A^+,ms) = pf \frac{k_A[A^+]}{k_A[A^+] + k_E[E^+]} I \tag{2-10}$$

The predictions of equation 2-10 are compared in Figure 2-6 with previously reported experimental results from ESMS on cocaine hydrochloride solutions (6). Shown in Figure 2-6 is the measured total ES ion current I as well as the mass analyzed current I (A^+, ms) due to the analyte A^+ where A^+ is protonated cocaine. Also shown is the calculated I (A^+, ms) obtained with equation 2-10. This curve was obtained with the simplest assumption $k_{A^+} = k_{E^+}$. It was also assumed that the bulk solution concentrations can be substituted in equation 2-10. The presence of external electrolyte E was due to impurities in the solvent used. Conductivity determinations and mass spectrometric analysis of the ES produced ions with the pure solvent, had shown that the impurities E^+ were mostly NH_4X and NaX electrolytes with a total concentration of ~5 x 10^{-6} M and this value was used in equation 2-10. Since the factor pf in equation 2-10 is not known at this stage, the calculated A^+ intensities were obtained by adjusting pf to obtain agreement with the measured A^+ intensity at one experimental point, $[A^+] = 10^{-7}$ M.

Two regions in the analyte A^+ intensity curve can be recognized in Figure 2-6. The first is the important linear region of constant analyte sensitivity. It occurs where the external electrolyte concentration $[E^+]$ is much larger than the analyte concentration $[A^+]$. Under these conditions equation 2-10 reduces to

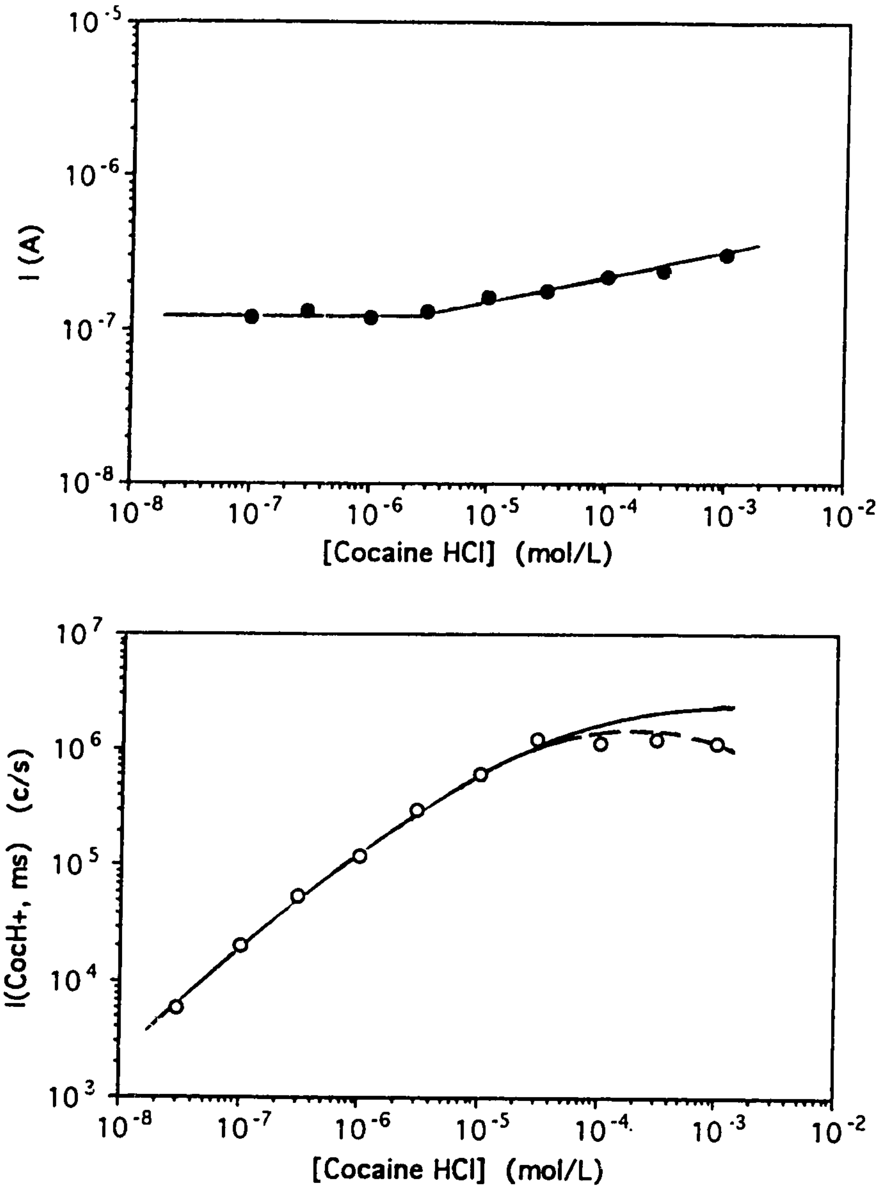

Figure 2-6 (Upper plot) Total electrospray current I as a function of added analyte concentration.

(Lower plot) Changes of mass analyzed ion intensity (counts/s) of analyte ion versus analyte concentration. Solid line: predictions of equation 2-10. ○: experimental points.

$$I(A^{+},ms) = \frac{pf\,k_A[A^{+}]}{k_E[E^{+}]}\,I \qquad (2\text{-}11)$$

Furthermore since $[E^+]$ is constant and E^+ is the dominant electrolyte, also I is constant, see Figure 2-6. Therefore, $I(A^+, ms)$ is proportional to the only variable, $[A^+]$.

In the second region, where $[A^+] >> [E^+]$, equation 2-10 assumes the limiting form:

$$I(A^{+}, ms) \approx pfI = pf\,H(\overset{\circ}{\lambda}_m)^n\,[A^{+}]^n \qquad n \approx 0.2 \qquad (2\text{-}12)$$

where the last equality involves use of equation 2-3, with A being the dominant electrolyte. $I(A^+, ms)$ increases very slowly in this region, see Figure 2-6, due to the slow increase of I with electrolyte concentration.

Above $[A^+] = 10^{-3}$ M, it is observed that the experimental points begin to deviate significantly from the calculated curve. The downward deviation indicates that either p or f or both decrease in this region. A decrease of the ion sampling efficiency p with increase of I may be expected particularly for conditions where the system is space charge dominated, see for example Sunner (19). However, the increase of I is small. Furthermore, evidence will be presented in next chapter that space charge effects become important only for $I > 10^{-6}$ A, i.e. currents considerably higher than those occurring in the present experiments.

A more probable cause for the downward experimental trend of $I(A^+, ms)$ is the decrease at high concentrations of the fraction f of charge evaporating from the droplets. It is known, that when the electrolyte concentration is increased at constant flow rate, there is an initial decrease followed by an increase of droplet radius (12). Unfortunately, quantitative data for flow rates and solvents used in ES mass spectrometry are not available. In the experiments with methanol solution at flow rates of ~20 μL/min it is generally observed that the counter electrode remains dry for electrolyte concentrations up to ~10^{-3} M but becomes wet at higher concentrations. Obviously this change indicates incomplete droplet evaporation presumably due to an increase of droplet size with concentration in this range. Therefore, a decrease of f in this range could well be expected from these results.

Activity coefficients of both electrolytes (A^+ and E^+) may vary dramatically when the concentration of A^+ is in the high concentration range. If one takes into account the solvent evaporation of charged droplet, which is necessary for the ion emission (see Chapter 3), the difference between the activity coefficients of both electrolytes would be bigger. However, the activity coefficients can not be predicted due to the lack of reliable solvent evaporation data. The use of concentration instead of activity will result in the deviation.

A totally different reason for the deviation observed in Figure 2-6 should be considered also. As is evident from equation 2-11, which gives the limiting condition at low $[A^+]$, the assumption $k_A = k_E$, taken together with the fitting procedure to one experimental point, amounts to lumping the real k_A/k_E ratio into the fitted pf product, i.e. the fitted product actually corresponds to: pf k_A/k_E. This fitted constant is not suitable for the regime of high $[A^+]$ where equation 2-12 applies, since in this region the fitting constant is only pf. For instance, assuming that the actual ratio is $k_A/k_E > 1$, which is a general case for two different ion species, the fitted constant at low $[A^+]$ will be too high for the high $[A^+]$ regime, i.e. the predicted A^+ intensity will be higher than the measured one.

The experimental A^+ intensity in Figure 2-6 is seen to actually decrease at the highest concentrations. The decrease would not be expected on the basis of the fitting constant argument and this suggests that a decrease of f at high concentrations is the most likely cause. However, the above discussion illustrates the fact that much more extensive measurements, involving a variety of pairs of A^+ and E^+ at different concentration regimes, should be performed in order to examine the range of validity of equation 2-10. Such work will be shown in Chapter 3.

The prediction of equation 2-10 for the situation where $[A^+]$ is kept constant and $[E^+]$ increases is for a decrease of the measured $A^+{}_{m,s}$ intensity. A degree of quantitative agreement is also observed and such data will be presented in section 3 as part of an extensive investigation dealing with the validity and limitations of equation 2-10. For the present, equation 2-10 could be considered as a promising but probably oversimplified approach to deal with the prediction of dynamic region of ion intensity in mass analysis.

2.4 Conclusions

The electrospray current I is a function of the conductivity σ of the electrosprayed solution and thus also a function of the concentration C and the nature of the electrolyte via the molar conductivity $\overset{\circ}{\lambda}_m$. However, because $\overset{\circ}{\lambda}_m$ changes by no more than a factor of 3 for the vast majority of electrolytes, and the functional dependence $(\overset{\circ}{\lambda}_m)^n$, where $n \approx 0.2\text{-}0.4$ is weak, changes of I for different electrolytes at the same concentration are minimal and hard to detect. The changes of I show also a weak dependence, C^n, on the concentration of the electrolyte. However, the practical concentration range increase, from 10^{-6} to 10^{-2} M, is very large and therefore the total change of I by a factor of $10^{4n} \approx 15$ is significant.

For the relative transfer rates of ions from the droplets to the gas phase one expects a proportional dependence on the relative concentrations of the ions in the droplets. This proportionality can be expressed by equation 2-10. The predictions of equation 2-10 are found to be in good agreement with the experimental data. In particular, equation 2-10 predicts a constant sensitivity for analyte at concentrations below about 10^{-5} M and a decreasing sensitivity above this value, which depends on the impurity level in the solution. It also predicts that the presence of electrolytes other than the analyte always leads to a decrease of the analyte sensitivity.

2.5 Appendix

Conductivity at high electric fields

Although the electric field E_c at the capillary tip in vacuo is very high, the electric field in the liquid at the tip need not be high. Apart from the reduction of E_c in the solvent by the ratio of the permittivities $\varepsilon/\varepsilon_0 = D$, where D is the dielectric constant of the solvent, the redistribution of electrolyte charges under the influence of the field, i.e. charge relaxation in the solution, may reduce the field to a very small value (9-12). Nevertheless, it is still of interest to know the dependence of the conductivity on the field. For example in the derivation of the Hendricks equation it is assumed (10) that each charged droplet removes the local charge, thus restoring the electrical field to its original high field value. Therefore, substitution of the low field conductivity in the Hendricks equation 2-7 may be inappropriate.

It is possible to show that the change of the conductivity with changing field will be small. Since the electrolytes used are strong, only the first Wien effect (20) due to the destruction of the "ion atmosphere" by the field (in modern terms, the reduction of ion pairing) will be important. Equation 2-11, developed by Onsager and Kim (21), provides predictions for the change of the equivalent conductivity λ_j of ionic species j with the field.

$$\lambda_j = \lambda_j^0 - 5.9420 \times 10^6 \frac{|z_1 z_2|}{(DT)^{3/2}} A \lambda_j^0 \Gamma^{1/2} - \frac{43.744 |z_1 z_2|}{(|z_1| + |z_2|) \eta_0 (DT)^{1/2}} B_j \Gamma^{1/2} \tag{2-11}$$

where λ_j^0: limiting equivalent conductivity of j-ion
$|z_1|$ and $|z_2|$: number of charges of ions j and counterions.
η_0: viscosity of solution [1.6×10^{-2} poise] (14a)
D: dielectric constant of the solution [60] (14a)
T: temperature of the solution [296°K]
A: relaxation function
B_j: electrophoretic function
Γ: ionic strength, $\Gamma = 2C$ (mole/L) for present, electrolyte

At the low concentrations used in the present ES work, i.e. $C \leq 10^{-2}$ M, the functions A and B_j are given (21) by,

$$A = \frac{1}{2a} \tag{2-12}$$

$$B_j = \frac{2\sqrt{\mu_j}}{2(1 - \mu_j)} + a^{-1} \log a \tag{2-13}$$

where a is defined by,

$$a = 1.63 \times 10^{-6} \left(|z_1| + |z_2| \right) \sqrt{\frac{D}{T}} \frac{E}{\sqrt{\Gamma}} \tag{2-14}$$

where E is the field strength in V/cm.

Substituting in equation 2-14 the values that apply for the present conditions, $z_1 = z_2 = 1$, $E = 1.103 \times 10^{-5}$ V/cm, for $V_c = 5000$ V, $\Gamma = 2C$ where C is concentration in mole/L, and the values for D and T given in square brackets under equation 2-11, one obtains,

$$a = 0.1146 \times \frac{1}{\sqrt{C}} \tag{2-15}$$

μ_j in equation 2-13 stands for the relative ionic strength of the ion species j which for the present 1:1 electrolytes leads to $\mu_j = 1/2$.

Equation 2-12 and 2-13 can now be evaluated and substituted into equation 2-11. The other numerical data required for equation 2-11 are given in square brackets beside each symbol, see definition of symbols under equation 2-11. Substitution of these values into equation 2-11 allows the evaluation of this expression. The high field molar conductivity due to the positive and negative counter ion will be,

$$\lambda_m = \lambda_+ + \lambda_-$$

Evaluating λ_+ and λ_- with equation 2-11 and adding the result one obtains,

$$\lambda_m(5\text{ kv}) = (1-15.491C)\overset{0}{\lambda}_m - 2\left[27.353 + 253.16\sqrt{C}\,\log\left(\frac{0.1146}{\sqrt{C}}\right)\right]\sqrt{C} \qquad (2\text{-}16)$$

The equivalent limiting molar conductivity $\overset{o}{\lambda}_m$ now stands for the sum: $\overset{o}{\lambda}_+ + \overset{o}{\lambda}_-$ of the positive and negative ion present in the 1:1 electrolyte.

Since, for the low concentration range used, the low field molar conductivity is essentially equal to the limiting molar conductivity $\overset{o}{\lambda}_m$, subtracting $\overset{o}{\lambda}_m$ from the expression in equation 2-16 one obtains the difference between the high and low field molar conductivity which in this concentration range is equal to the difference between the high and low field conductivity of the electrolyte;

$$\lambda_m(5\text{ kv}) - \overset{o}{\lambda}_m = [\sigma(5\text{ kv}) - \sigma]/C = \Delta\sigma/C \qquad (2\text{-}17)$$

The left side of equation 2-17 can be evaluated from equation 2-16 and the known λ_m° for the given electrolyte. $\Delta\sigma$ increases with concentration of the electrolyte. For the highest concentration, $C = 10^{-2}$ M used in the present experiments, $\Delta\sigma$ is found to correspond to an increase of 9% of the low field conductivity for NaCl and 2% for HCl. These are very modest changes which will have no effect on the magnitude of I evaluated with the Hendricks equation 2-7. The result of the $\Delta\sigma$ calculations could have been anticipated from the fact that the "ion atmosphere" becomes significant only at concentrations above 10^{-1} M, for 1:1 electrolytes.

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Chapter 3. Dependence of Ion Intensity in Electrospray Mass Spectrometry on the Concentration of the Analytes in the Electrosprayed Solution*

3.1 Introduction

On the basis of previous work (1-7) it has become clear that electrospray is a method by which ions present in solution, i.e. ions due to an electrolyte, are transferred to the gas phase. The presence of the very high electric field at the capillary tip leads to a partial separation of positive from negative ions present in the solution. For convenience we will in all subsequent discussions assume that the capillary is of positive polarity. At this polarity, the liquid near the meniscus becomes enriched in positive ions. The effect of the field on this positive charge leads to a destabilization of the meniscus, the formation of a liquid cone and the emission of charged droplets whose charge is due to an excess of positive electrolyte ions over the negative counter ions. The negative ions remaining in the solution are either electrolytically discharged on the wall of the capillary or electrolytically provided by positive counter ions by formation of positive ions from the capillary wall. Therefore, the electrospray process can be likened to an electrolysis cell of a special kind where oxidation occurs at the capillary anode and the positive current is carried away by the charged droplets (7).

In the present work we will examine how the analyte ion signal detected with the mass spectrometer depends on the concentration of the

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analyte ion in the solution and also how this signal is affected by the presence of other electrolytes. Other electrolytes are practically always present either as impurities in the solvent, as other coanalytes and particularly as buffers required in chromatographic separation or capillary electrophoresis.

The ions in the gas phase are originated from the excess charges on the droplets. Therefore, the current I leaving the ES capillary is a measure of the rate at which excess positive electrolyte ions leave the capillary. This current is easily measured and is found to depend on the conductivity σ of the solution (8). There is a minimum (threshold) conductivity below which there is no ES. The threshold occurs at $\sigma \approx 10^{-7}$ Ω^{-1} cm^{-1} (methanol) (6), which corresponds to a concentration of $\sim 10^{-6}$ M (M = mole/L) of electrolytes like NaCl or NH_4Cl (7, 8). As the conductivity is increased above this value, the current I leaving the capillary increases and becomes stable. I is only a very weak function of the conductivity (4, 6, 8):

$$I = H\sigma^n \qquad n \approx 0.2\text{-}0.3 \tag{3-1}$$

H is a constant which can be determined experimentally. A derivation of equation 3-1 in which H is given a functional dependence on experimental parameters such as electric field at the tip, radius of the capillary, surface tension of the solvent, flow rate etc. has been obtained (4).

When strong electrolytes are used at concentrations not exceeding 10^{-2} M, the conductivity σ follows the relationship

$$\sigma \approx \lambda_m^0 C \tag{3-2}$$

where C is the concentration of the electrolyte and λ_m is the limiting molar conductivity of the given electrolyte. Therefore, the current I depends on both the concentration and the nature of the electrolyte (8).

$$I = H\sigma^n = H\lambda_m^{\circ\,n}C^n \qquad (3\text{-}3)$$

$$n \approx 0.2\text{-}0.3$$

However, the changes of λ_m from one electrolyte to the other are generally not large. Due to the small value of n in equation 3-1, in practice, the changes of I with the nature of electrolyte are very small. Equation 3-1 is obeyed over the concentration range: $C = 10^{-5}$ M to $C = 10^{-3}$ M. At higher concentrations the current levels off and even decreases slowly with concentration (6, 8).

When two electrolytes such as A^+X^- and B^+Y^- are present in the solution, both A^+ and B^+ ions will be present amongst the excess positive ions that constitute the charges of the droplets. However, because of the very weak dependence of I on the total electrolyte concentration, see equation 3-3, addition of BY to AX will not materially increase the current, i.e. the total excess charge. On the other hand B^+ will compete with A^+ amongst the excess charges on the droplets. This means that the amount of gas phase ions A^+ produced from the charged droplets will decrease as BY is added to the solution.

On the basis of the above consideration, we proposed (8) the relationship:

$$I_{(A^+ms)} = pf\frac{k_A[A^+]}{k_A[A^+] + k_B[B^+]}I = \frac{pf[A^+]}{[A^+] + k_B/k_A[B^+]}I \qquad (3\text{-}4)$$

$$I_{(A^+ms)} = pI_{(A^+,g)} \qquad (3\text{-}5)$$

$I_{(A^+ ms)}$ is the mass spectrometrically detected ion current of A^+. p is a constant expressing the efficiency of the mass spectrometer for sampling the gas phase ions, see equation 3-5, and f is the efficiency of conversion of droplet charge to gas phase ions. $[A^+]$ and $[B^+]$ are the concentrations of the ions in the electrosprayed solution, which will be abbreviated as [A] and [B] in the following discussion. $I_{(A^+ ms)}$ depends on the ratio, k_A/k_B and not on the individual values of k_A and k_B. The ratio expresses a "fractionation" factor in the ES conversion of ions in solution to ions in the gas phase. The nature of the phenomena responsible for that ratio will be considered in the Results and Discussion section.

In the previous work (8) it was shown that equation 3-4 provided a good fit of limited, available experimental data. It was pointed out (8) that an examination involving a much wider variety of AX and BY partners as well as a greater change of relative concentrations of A^+ and B^+ would be required to establish the range over which equation 3-4 is applicable. The present work provides such experimental data and an examination of the validity of equation 3-4. Because the possible choice of concentrations is extremely wide, the comparisons were restricted to three types of experiments:

(a) [AX] was kept constant and [BY] was increased.
(b) [AX] = [BX] were increased simultaneously.
(c) [AX] was increased without BY being present.

Since the mass analysis was obtained with a quadrupole mass spectrometer and quadrupoles have strongly mass dependent ion transmission, all mass analyzed ion currents I(ms) were corrected for the mass dependent transmission. The method used to obtain the transmission is given in the Experimental part which includes also other details about the apparatus and methodology of the measurements.

The experimental results obtained have significance for the practicing ES mass spectrometrist. For example, they show that the suppression of a desired analyte ion by a buffer depends not only on the concentration but also on the nature of the buffer. Buffer cations with high coefficients, k, lead to strong suppression of the analyte and should be avoided.

In trying to correlate the observed relative values of the coefficients k with properties of the ionic species, such as surface activity and ion solvation, one has to consider not only models for the escape of gas phase ions from the charged droplets but also the fission processes through which the very small droplets are formed which lead ultimately to ions. The solvent evaporation rates from the droplets are also of great importance. In the treatment presented in the Discussion, we try to combine all these elements to present a relatively complete account.

3.2 Experimental

The instrument used was the SCIEX TAGA 6000E triple quadrupole atmospheric pressure mass spectrometer fitted with an electropsray interface, see Figure 3-1. The stainless steel electrospray capillary tip was 0.1 mm i.d. and 0.25 mm o.d. The capillary tip was ~4 cm from the opposing electrode (the interface plate) and at +4.35 kV relative to the interface plate. Gas phase ions produced by the electrospray in the 1 atmosphere plenum chamber [1] are accelerated towards a 4 mm orifice in the interface chamber [4]. The interface chamber contains dry N_2 gas at 1 atmosphere. The ions, M^+, have solvent molecules attached to them, i.e.

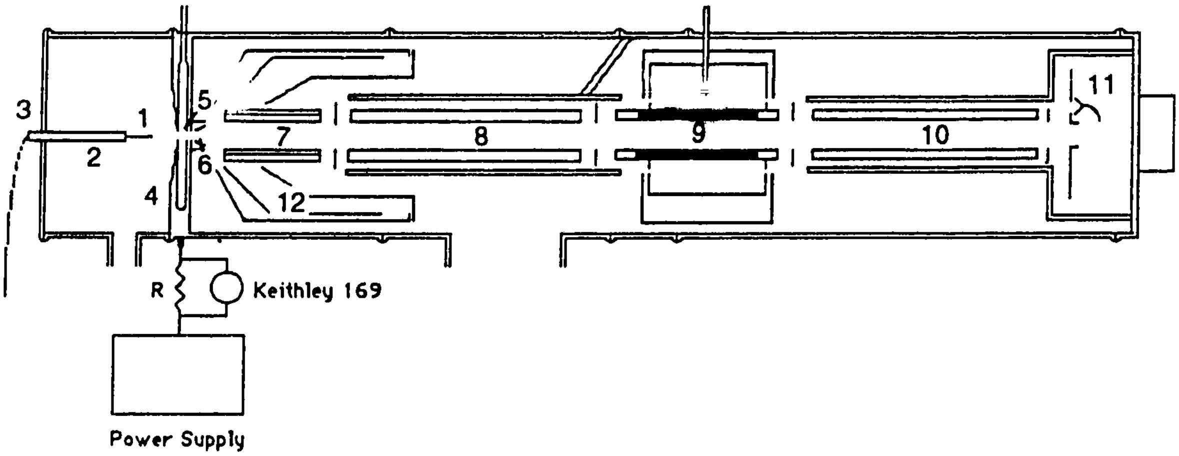


Figure 3-1 A schematic diagram of TAGA 6000E.

1. ES capillary tip (i.d. = 0.1 mm, o.d. = 0.25 mm) in plenum chamber at 1 atmosphere air pressure, 5 kV;
2. supporting rod;
3. front plate with jig which allows x, y, z motion of capillary;
4. interface plate (650 volts);
5. orifice to vacuum (100 μm diameter, 55 V)
6. cluster breaker CB (33 volts);
7. quadrupole 0 (30 volts);
8. quadrupole 1 (28 volts);
9. quadrupole 2 (20 volts);
10. quadrupole 3 (28 volts);
11. electron multiplier (-3.4 kV);
12. cryosurface at temperature ~20 K.

they are ion-solvent molecule clusters $M^+(CH_3OH)_n$. When they enter the dry N_2 chamber some of their solvent molecules are lost and other get replaced by H_2O due to residual H_2O in the N_2 gas. The gas phase ions drift, under the influence of the electric field in the interface chamber, to the aperture [5] where a sample of air and ions enters the vacuum of the mass analysis section. When the orifice [5] is at 55 V and the first electrode CB [6] is at 33 V, the ions are accelerated relative to the neutral gas beam in the space between the orifice and CB. The collisions of the ions with the gas lead to partial or complete cluster breakup so that the original $M^+(CH_3OH)_n$ ions are detected as M^+.

The rods in quadrupole 0 are made of wire mesh and operated in the AC mode only. It guides the ions while the gas molecules fly to the cryo-surfaces [12] where they are frozen, i.e. cryopumped. For our work no collision activated decomposition (CAD) was necessary. Therefore, in the present experiments quadrupole 1 was used for the mass analysis and quadrupole 2 and 3 were operated in the AC mode only. The ion detection was obtained with an electron multiplier [10] and the intensity was measured with an ion counting device.

Determinations of the mass dependent transmission were obtained with use of the corona discharge atmospheric pressure ionization (APCI) mode of the TAGA (9, 10). Ten different amines B were chosen for this purpose. When protonated by APCI these become BH^+. The masses of the bases were chosen so as to cover evenly the mass range to be calibrated. The typical assembly for this experiment is shown in Figure 3-2. A constant, low concentration of amine solution in a solvent was injected into a heated tube where the solution evaporated into the APCI source. Hexane

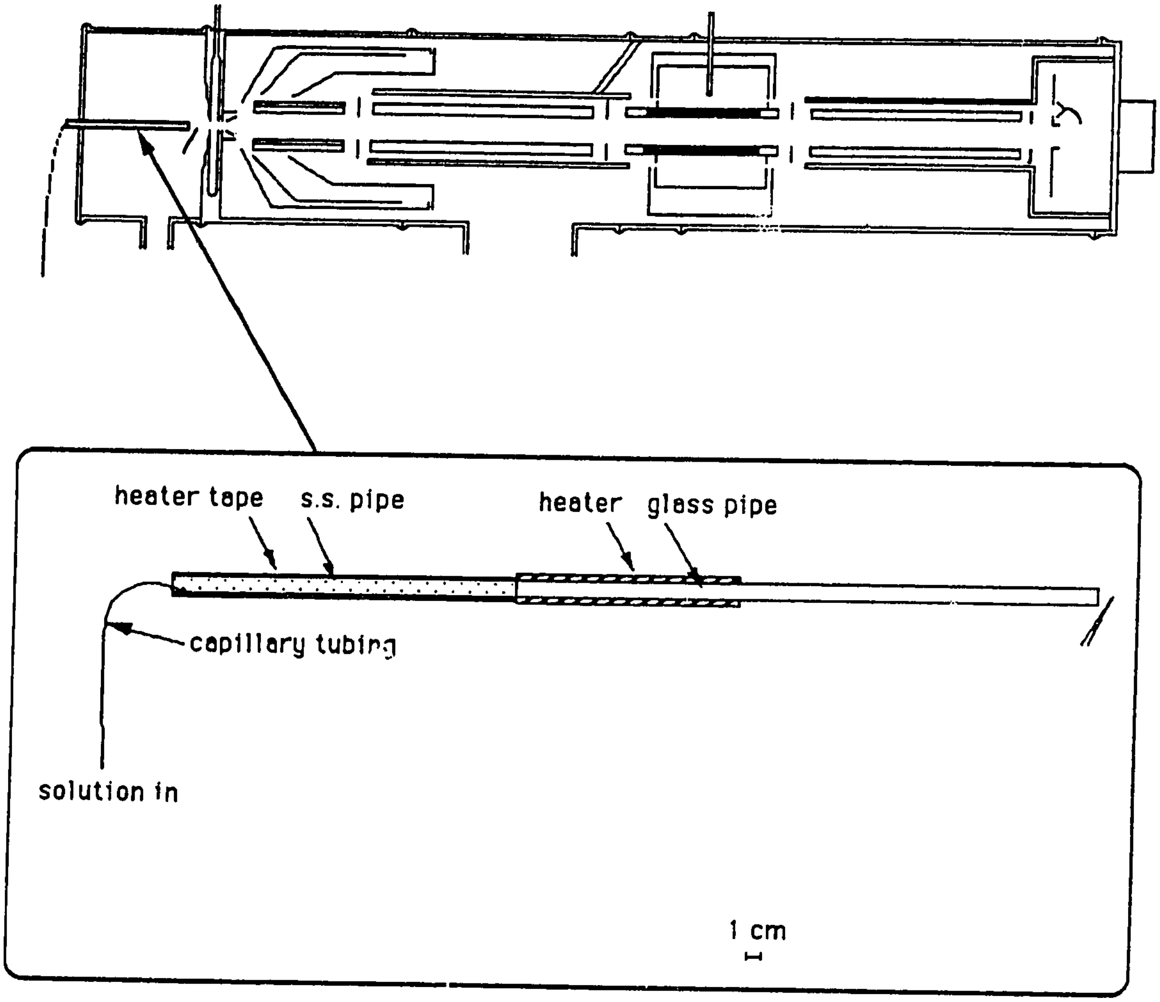


Figure 3-2 A special APCI set-up of TAGA 6000E for transmission determination.

(b.p 68.3 - 68.8 ^{o}C) was used as solvent for its low proton affinity, low boiling point and good solvent properties for amines. A 10^{-4} M concentration and 15 μl/min were used for each amine and were found to produce a stable amine BH^+ ion signal. Keeping APCI current constant as 2 μA, we could measure the ion intensity of each protonated amine signal. Because the generated B pressures are the same, the observed BH^+ signal should be the same in the absence of mass discrimination (9, 10). The measured relative BH^+ intensities are shown in Figure 3-3. They correspond to the relative transmissions at the given m/z.

The highest transmission was assigned as $T_m = 1$. To correct the observed ion intensities, I_{obs}, for mass dependent transmission, one has to divide I_{obs} by T_m for the given mass. Since T_m changes by more than a factor of 10 over the mass range that was used, errors in the corrected relative ion intensities are expected to increase with the mass difference of the two ions that are compared. For larger mass differences errors as large as a factor of two can not be excluded.

For the subsequent interpretation of the data, it is desirable to know the values of p and f which appear in equation 3-4. The product pf is easily determined. In general, the two mass analyzed ion intensities I_A and I_B dominate the mass spectrum. The total mass analyzed ion current corrected for transmission is thus $I_A + I_B$. The capillary ES current I is also measured and one obtains: $pf = (I_A + I_B)/I$. Generally for a typical I of 0.3 μA, the product was found to be $pf \approx 1 \times 10^{-6}$.

A determination of f, the fraction of droplet charge that is converted to gas phase ions, is much more difficult and would require specialized apparatus. A rough estimate, $f \approx 0.3$, was obtained in Figure 3-4 by measuring the total current, I_{CB}, reaching the first electrode, CB, located

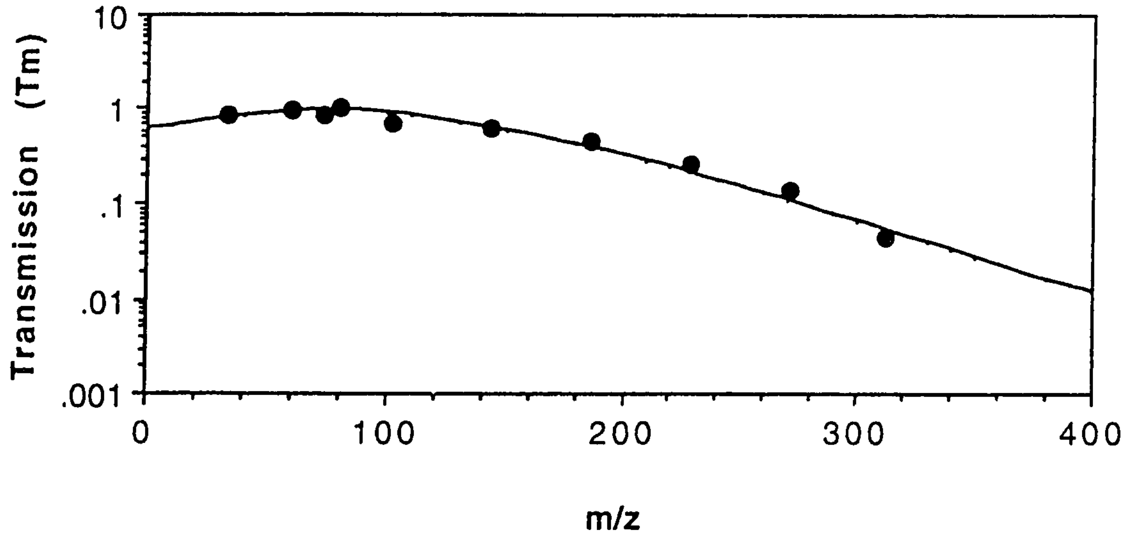


Figure 3-3 Experimental ion transmission curve which provides correction for mass dependent transmission of quadrupole used. The m/z with highest transmission T_m is given the value $T_m = 1$. Points shown are obtained from ion intensity measurements obtained with atmospheric pressure ionization using a technique described previously (9). Ten protonated amine ions are: $CH_3NH_3^+$ (m/z=33), i-$PrNH_3^+$ (m/z=60), n-$BuNH_3^+$ (m/z=74), PyH^+ (m/z=80), $Et_3NH_2^+$ (m/z=102), $Pr_3NH_2^+$ (m/z=144), $Bu_3NH_2^+$ (m/z=186), $Pe_3NH_2^+$ (m/z=228), $Hx_3NH_2^+$ (m/z=271) and $Hp_3NH_2^+$ (m/z=312)

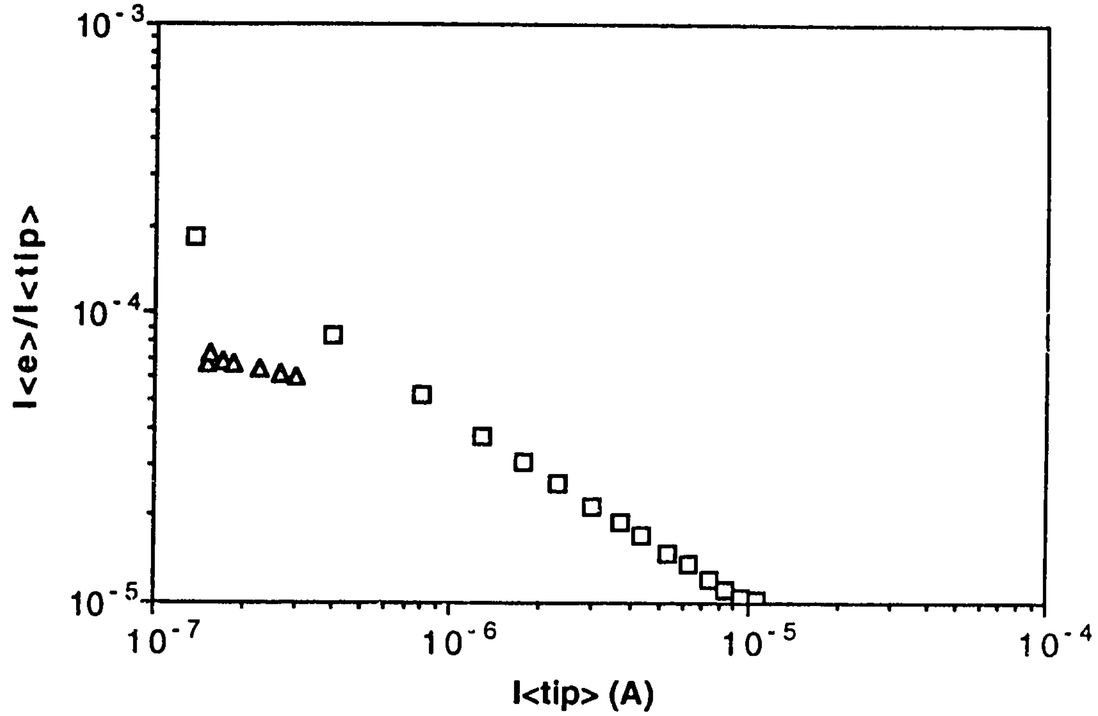


Figure 3-4 Ratio of total current on CB, I_{CB}, to total current fron the tip (ES tip or APCI tip), I_{tip}; □: APCI with room air; ▵: ES with CsCl in methanol.

in the vacuum of the mass analysis section. The electrode CB was closed off by spot welding a bit of metal foil to it. First, I_{CB} was obtained for an APCI electric discharge operated at atmospheric pressure with a total current, I = 0.1 μA. Then, I_{CB} was determined with an ES capillary placed in the same position as the API needle and electrospray current I = 0.1 μA. The ratios $I_{CB}/I = 2 \times 10^{-4}$ (API) and 0.7×10^{-4} (ES) were determined. Since APCI produces gas phase ions while ES initially produces charged droplets and later gas phase ions, the ratio: ES/API = 0.35, may be taken to give the yield of gas phase ions from the droplet charge in ES, if it is assumed that space charge effects, geometry and other conditions for the API and ES were the same. This assumption is probably not warranted and therefore, the estimate of the yield is very uncertain. However it may be taken to indicate that f is in the range: 0.5-0.1.

The flow rate of electrosprayed solution was 20 μL/min. Reagent grade methanol from the same bottle was used in all experiments. This methanol had a conductivity of $10^{-6}\Omega^{-1}$/cm which corresponds to an impurity level of NaCl or NH_4Cl of ~1.3×10^{-5} M. In previous work attempts were made to work with completely electrolyte free methanol solvent. It was found that the conductivity of such methanol increased rapidly on storage after purification. In order to obtain reproducible experiments, we chose to work with the reagent grade methanol which had a constant electrolyte impurity level.

3.3 Results and Discussion

I. Behavior when electrolytes are at higher, 10^{-5}-10^{-3} M, concentrations

a. Experiments where the analyte ion concentration is constant and a second electrolyte, B^+, is present in increasing concentrations

A series of experimental measurements were made in which the concentration of one of the compounds in solution was constant, $[A^+] = 10^{-5}$ M, and a second electrolyte $B^+ = NH_4^+$, was increased stepwise from 10^{-5} to 10^{-3} M. Used as A^+ were: Cs^+, $MorH^+$, $CodH^+$, $CocH^+$, $HerH^+$, $Ni^{++}(Tpy)_2$, $(Bu)_4N^+$, where Mor, Cod, Coc, Her, stand for the alkaloids morphine, codeine, cocaine, heroin, Tpy for tripyridine and Bu for n-butyl.

A typical result is shown in Figure 3-5 for $A^+ = CodH^+$. The top plot (a) in the figure gives the capillary current I. As pointed out in the Introduction, this current changes very slowly with electrolyte concentration, see equation 3-1. Thus, an increase of concentration by a factor of 50 increases the current by only a factor of 2. The relationship given in equation 3-1 predicts a straight line for the current I where a log plot is used and this is in agreement with the experimental result in Figure 3-5a.

The plot in Figure 3-5b gives the experimentally observed mass analyzed ion currents corrected for transmission efficiency. Addition of NH_4^+ decreases the ion intensity of $CodH^+$ as predicted by equation 3-4. The lines drawn through the experimental points are predicted changes calculated with equation 3-4. To obtain the parameter pf and k_B/k_A

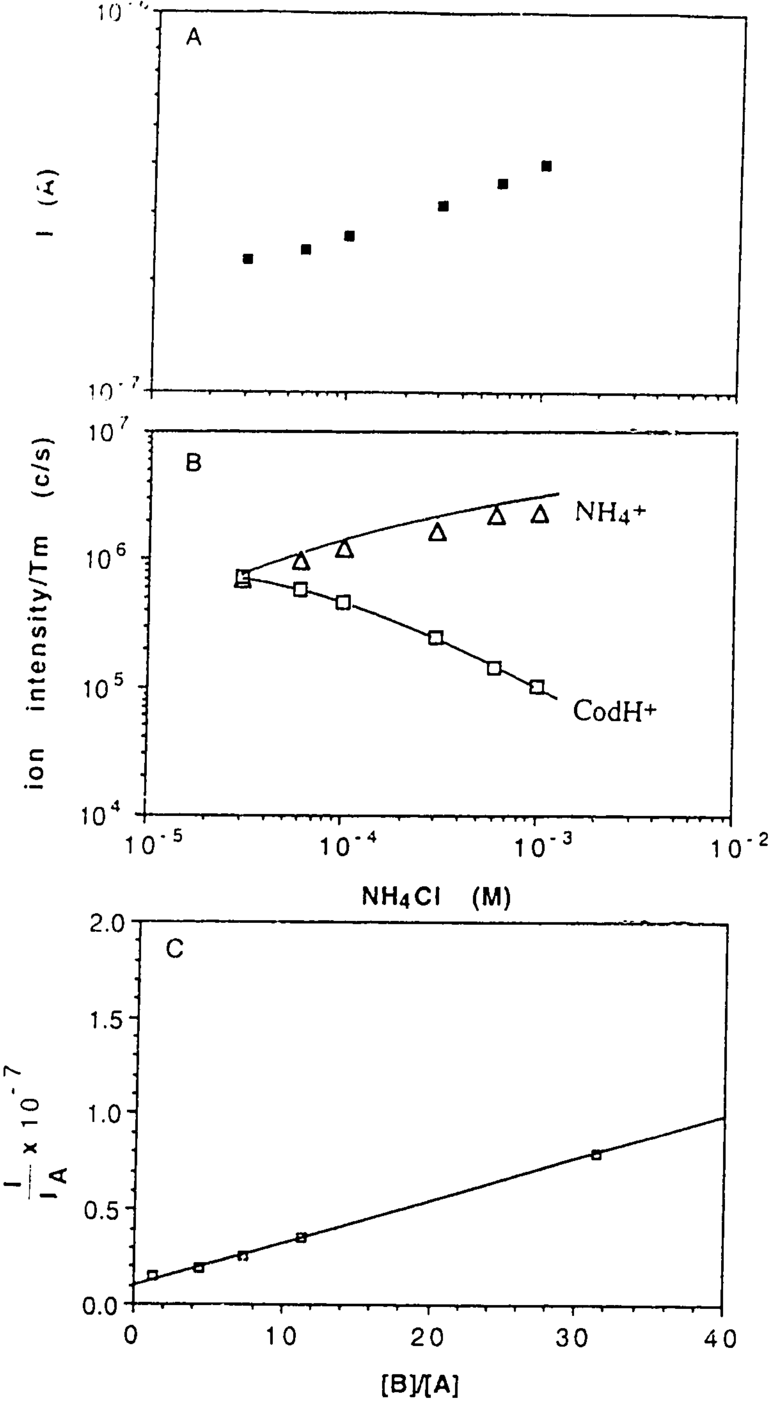


Figure 3-5 Results from ES where $[A^+] = [CodH^+] = 10^{-5}$ M and $[B^+] = [NH_4^+]$is increased as shown. (a) Measured capillary current I. (b) Ion intensities of NH_4^+ △ and $CodH^+$ □, corrected for transmission. Curves shown as solid lines are a calculated fit using equation 3-4. (c) Predicted linear plot based on equation 3-6 leads to ratio $k_A/k_B = 3.4$.

required for the fit, a rearranged form of equation 3-4 was used.

$$\frac{I}{I_A} = \frac{1}{pf} + \frac{1}{pf}\frac{k_B}{k_A}\frac{[B^+]}{[A^+]} \qquad (3\text{-}6)$$

I_A is the mass analyzed current of A^+, corrected for mass dependent transmission and converted from counts per second to amperes. Equation 3-6 predicts a straight line when I/I_A is plotted versus the solution concentrations ratio [B] / [A]. The predicted intercept is 1/pf and the slope is: $k_B/(k_A\ pf)$. The experimental plot shown in Figure 3-5c demonstrates that a good straight line relationship is observed. The intercept provides; $pf = 1.2 \times 10^{-6}$ and the slope $k_B / k_A = k_{NH_4^+} / k_{CodH^+} = 0.29$. These two parameters were used to obtain the predicted intensities in Figure 3-5b. For this system the agreement between the predictions of equation 3-4 and the experimental results can be considered as very good.

Similarly good agreement was observed for other AX electrolytes with $B^+ = NH_4^+$ in analogous plots as in Figure 3-5. A summary of these results is given in Figures 3-6 and 3-7. Figure 3-6 gives the plots obtained with the linearized form, equation 3-6, while Figure 3-7 gives the observed and predicted I_A as in Figure 3-5b but for all AX electrolytes used. The k_B / k_A ratios obtained are summarized in Table 3-1.

The pf values were found to be relatively close to each other and in the range: 1.2×10^{-6} and 2.5×10^{-6}. Considering the difficulties of the extrapolations to the intercept, see Figure 3-5c and Figure 3-6, the differences probably reflect experimental scatter rather than real trends. These pf values are in agreement with a $pf = 10^{-6}$ obtained with a more direct method, see Experimental section. An estimate of $f \approx 0.3$, refer to Experimental section, leads to $p \approx 3 \times 10^{-6}$. The very small p is mostly a

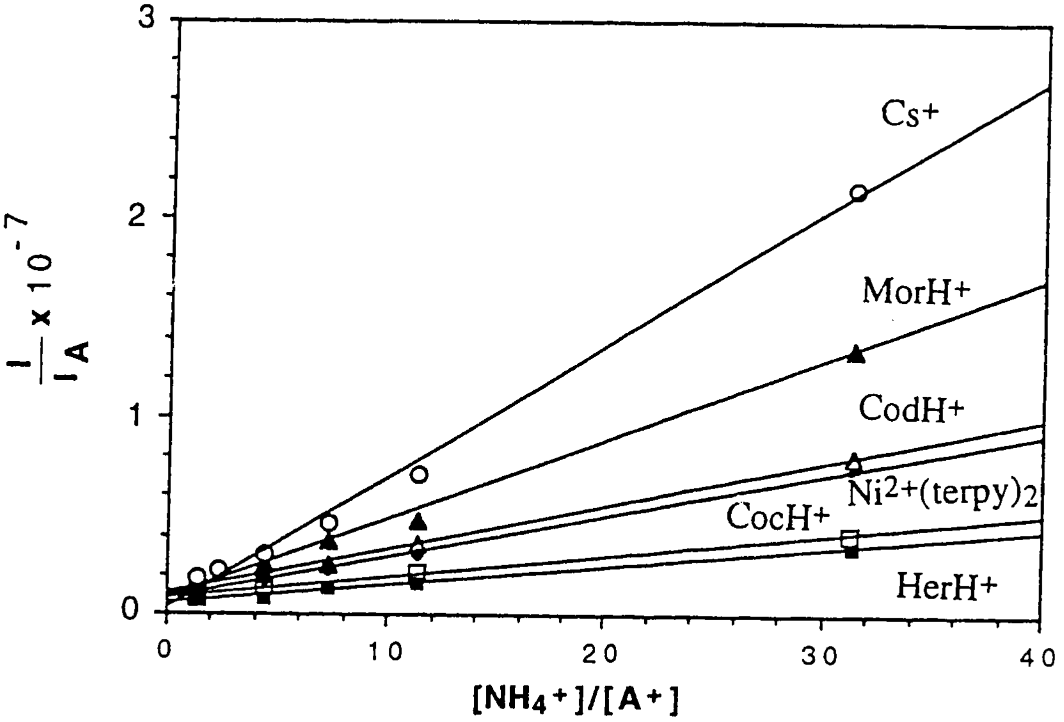


Figure 3-6 Linear plots based on equation 3-6, see Figure 3-5c, but for ions A^+ as shown.

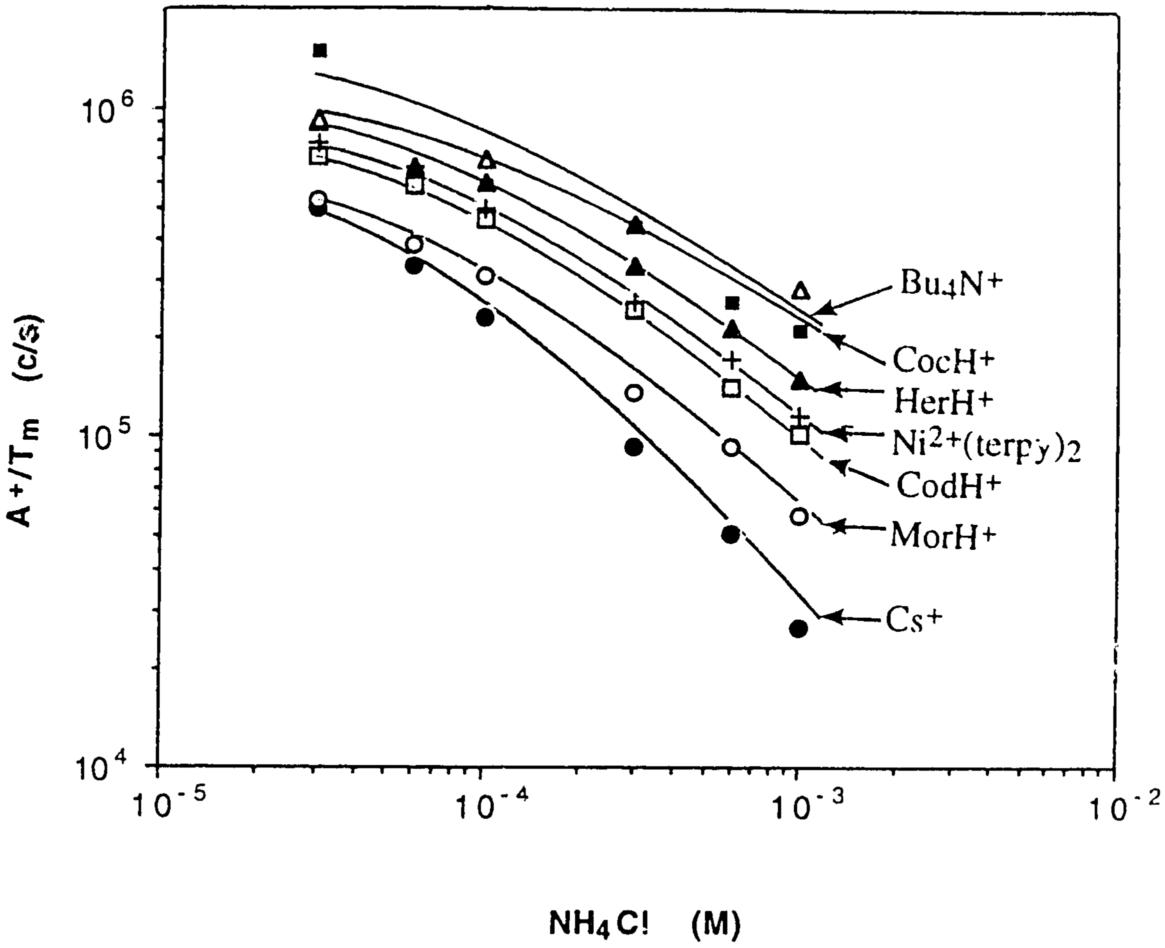


Figure 3-7 Ion intensities of A^+ (10^{-5} M) and with increasing concentration of B^+ (NH_4^+). Solid line curves are intensities of A^+ calculated with equation 3-4 and coefficients k from Table 3-1. ■ Bu_4N^+, △ $CocH^+$, ▲ $HerH^+$, + $Ni^{2+}(Terpy)_2$, ☐ $CodH^+$, ○ $MorH^+$, ● Cs^+.

Table 3-1. Experimentally determined Ratios of Coefficients k[a]

Ion	m/z	T_m	k^c	k^d	ion	m/z	T_m	k^d
Cs^+	133	0.6	1	1	Et_4N^+	130	0.72	$(3)^g$
Li^+	e	e	–	1.6	Pr_4N^+	186	0.38	$(5)^g$
Na^+	23	0.75	–	1.6	Pen_4N^+	298	0.064	$(16)^g$
K^+	39	0.90	–	1.0	$C_7NH_3^+$	115	0.83	8
NH_4^+	18	0.72	1.1	1.3	$C_{11}NH_3^+$	171	0.46	8
$MorH^+$	286	0.08	2.1	$(2.1)^f$				
$CodH^+$	300	0.065	3.8	$(3.8)^f$				
$HerH^+$	370	0.019	5.5	–				
$CocH^+$	304	0.06	8.3	$(8.3)^f$				
$Ni^{2+}(Tpy)_2$	262	0.72	4.9	–				
Bu_4N^+	242	0.17	9.1	$8.0(16)^f$				

a. The coefficients are defined in equation 3-4. All coefficients relative to $k_{Cs^+} = 1$. These coefficients are valid only at concentrations above 10^{-5} M.

b. T_m mass dependent ion transmission, see Figure 3-3.

c. From plots using equation 3-6 where $B^+ = NH_4^+$, see Figures 3-5 to 3-7.

d. Coefficients k obtained with $[A^+] = [B^+]$ experiments at high concentrations. Numbers without brackets measured for $B^+ = Cs^+$. For numbers in brackets A^+ and B^+ are identified in footnotes.

e. For Li^+ also clusters $Li(H_2O)^+$, $Li(H_2O)_2^+$, $LiCH_3OH^+$, $LiCH_3OH.H_2O$ and $Li^+(CH_3OH)_2$ were observed. k given refers to total intensity of all Li^+ ions corrected for respective transmission.

f. Coefficients based k values for $MorH^+$, $CodH^+$ and $CocH^+$ as in left umn. Ratios from plots Figure 3-10: on $Bu_4N^+/CocH^+ = 2$, $Bu_4N^+/CodH^+ = 5$, $Bu_4N^+/MorH^+ = 10$, lead to a high value for $Bu_4N^+ \approx 16$ when combined with above coefficients.

g. Coefficients based on ratios from Figure 3-11 and $Bu_4N^+ = 8$. These coefficients could be twice as high assuming that $Bu_4N = 16$, see footnote f.

consequence of the small orifice, 100 μm in diameter, which separates the atmospheric and vacuum region in the TAGA instrument.

It is clear from Figure 3-7 that the decrease of I_A is dependent on the nature of A. Thus Cs^+ experiences the largest decrease and $(Bu)_4N^+$ the smallest. At $[NH_4^+] = 10^{-3}$ M, the decrease of Cs^+ is 10 times larger than that for $(Bu)_4N^+$. The extent of decrease is dependent on the k_B / k_A ratio; the bigger the ratio, the bigger the decrease of analyte ion intensity, thus $k_B / k_A = 1.1$ for Cs^+ and 0.1 for $(Bu)_4N^+$, see Table 3-1.

Instead of working with the k_A / k_B ratios it is convenient to assign an arbitrary value to one of the constants and then evaluate the other relative to that value. We have assigned a normalization value $k = 1$ for Cs^+. The resulting other normalized values are given in Table 3-1

A^+ and B^+ in equation 3-4 can be interchanged and it is of interest to examine the validity of the equation for B different from NH_4^+.

On the basis of equation 3-1 one expects that replacing NH_4^+ ($k \approx 1$) with potassium, K^+ ($k \approx 1$), will lead to decreases in I_{A^+} with increase of [B] which are very close to those observed for $B^+ = NH_4^+$. The plots shown in Figure 3-8 for $A^+ = Cs^+$, $B^+ = K^+$ and $A^+ = Cs^+$, $B^+ = NH_4^+$ exhibit a nearly identical decrease of A^+ in agreement with the near equal k values for NH_4^+ and K^+.

A more interesting case is the replacement of NH_4^+ with an ion such as Bu_4N^+ with much larger k ($k \approx 10$). In this case a much larger decrease of the A^+ intensity with increasing concentration of $[Bu_4N^+]$ is predicted by equation 3-4. Experiments where $A = MorH^+$, shown in Figure 3-9, demonstrate that this prediction is upheld. At the highest concentration of $[B] = 10^{-3}$ M, the $MorH^+$ intensity with $B = Bu_4N^+$ is close to 50 times smaller than that with $B = NH_4^+$.

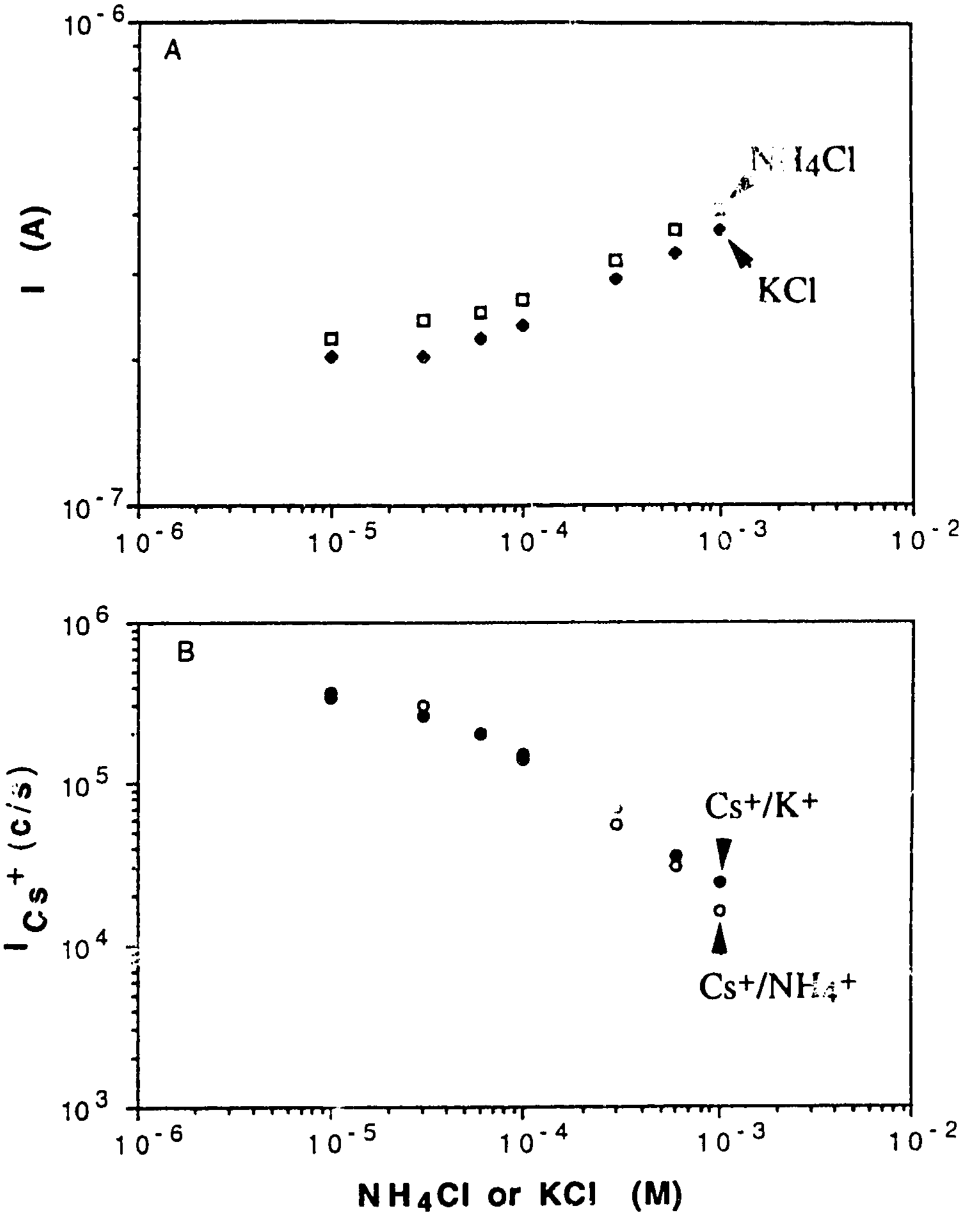


Figure 3-8 (A) Capillary current I. (B) Ion intensity for Cs^+ when $[Cs^+] = 10^{-5}$ M and $[B^+] = [NH_4^+]$ is increased ○, or $[B^+] = K^+$ is increased ● in separate experiments. Ions K^+ and NH_4^+ which have close to same coefficient k, Table 3-1, have the same effect in decreasing ion intensity of Cs^+.

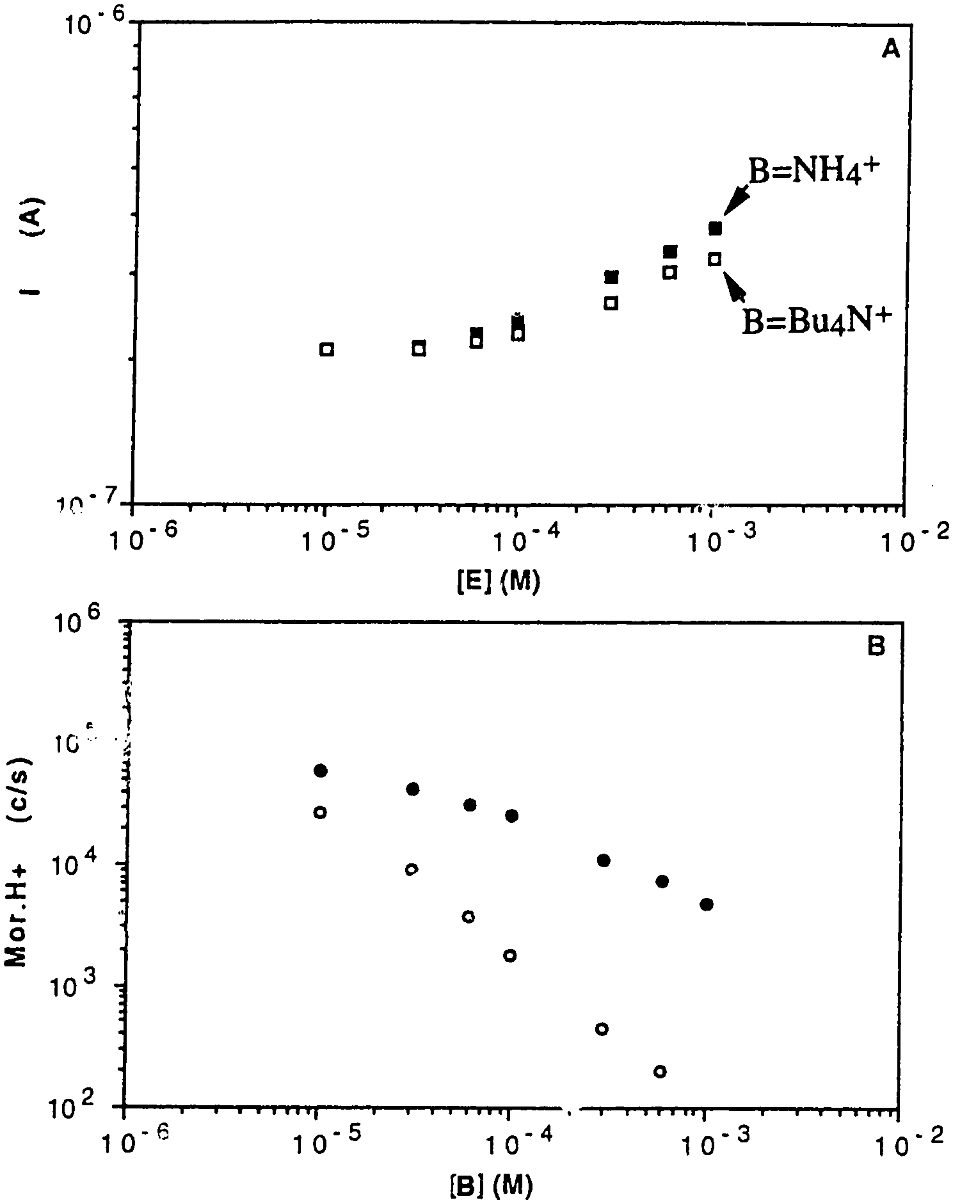


Figure 3-9 (A) Capillary current I. (B) Ion intensity for MorH+ when $[MorH^+] = 10^{-5}$ M and $[B^+] = [NH_4^+]$ is increased ●, or $[Bu_4N^+]$ is increased ○, in separate experiments. Data show that $B^+ = Bu_4N^+$ with high, $k = 9$, coefficient leads to much higher suppression of MorH+ intensity than $B^+=NH_4^+$ whose $k = 1$.

The results in Figure 3-8 and 3-9 illustrate that by choosing buffer cations with low sensitivity coefficients, k, one can minimize the adverse effect of the buffer on the sensitivity of the analyte. This effect was also observed on codeine, heroin and cocaine.

b. Experiments where concentration is increased and [A] = [B]

An alternative method of evaluating the k_A / k_B ratio is to use the I_A / I_B ratio whose concentration dependence predicted by equation 3-4 is given by

$$\frac{I_A}{I_B} = \frac{k_A[A]}{k_B[B]} \qquad (3\text{-}7)$$

Shown in Figures 3-10 to 3-12 are results where the concentrations of two electrolytes AX and BY, are kept equal [AX] = [BY] and increased from 10^{-8} to 10^{-3} M.

For the logarithmic plots shown, a constant ratio I_A/I_B corresponds to a constant distance: $\log I_A - \log I_B$. Because [A] = [B], a constant k_A/k_B requires a constant vertical distance in the intensity plots. This is observed at high concentrations $C > 10^{-5}$ M. At low concentrations, the two logI curves exhibit a different behavior which is considered in subsequent sections. The k_A/k_B ratio obtained from the high concentration region are given in Table 3-1. The coefficients are expressed relative to $k_{Cs} = 1$.

A comparison of the k values given in Table 3-1 obtained from the plots, Figures 3-5 to 3-8 and the $[A^+] = [B^+]$ results in Figures 3-10 to 3-12, shows that the data are in fair agreement and indicate the same trends. Differences between the two sets of data are to be expected. The

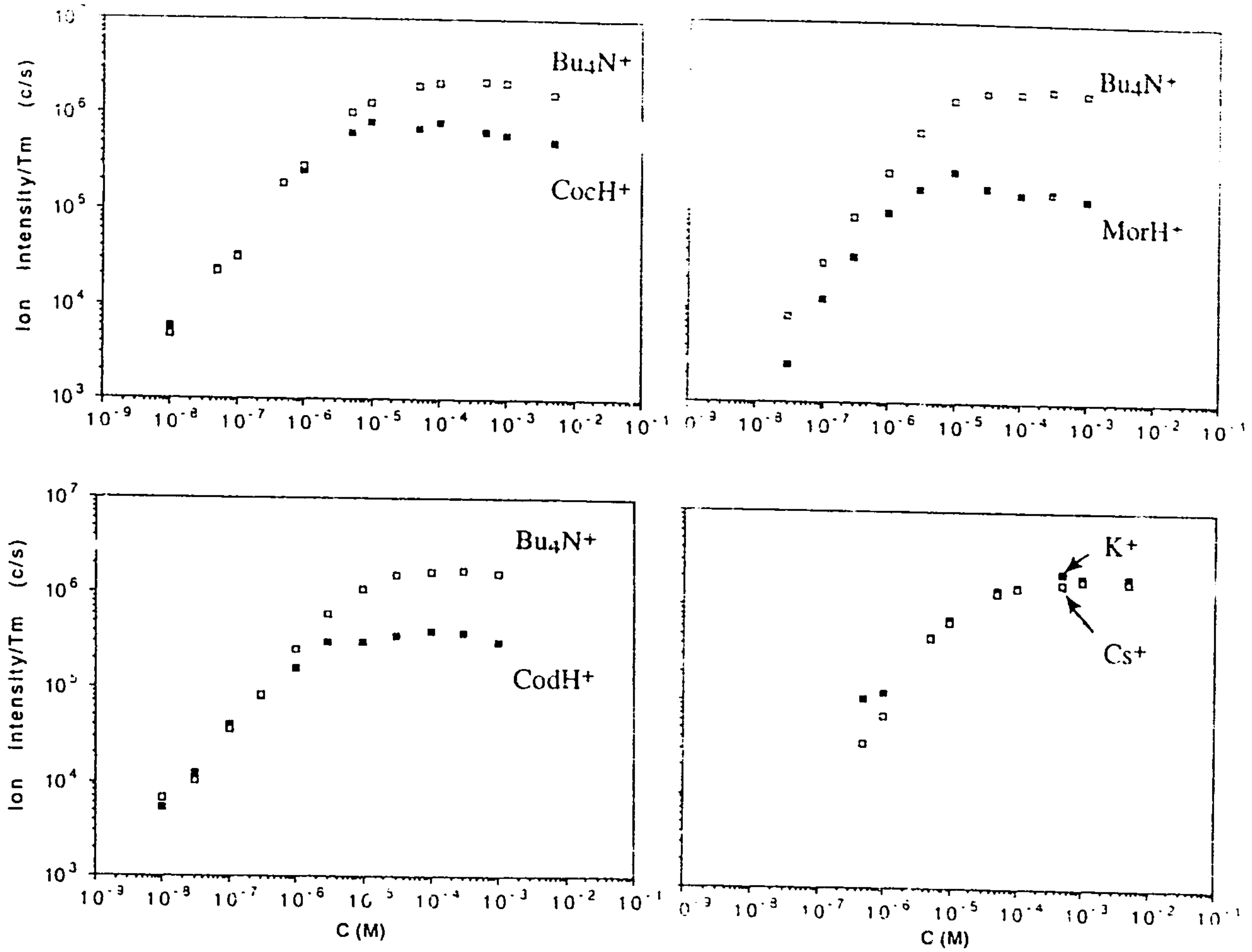


Figure 3-10 Ion intensities observed in experiment where [A+] = [B+] is increased from 10^{-8} to 10^{-2} M. I_A/I_B ratio is different at high and at low concentrations and this means that significance of k_A/k_B ratio is different at high and low concentrations.

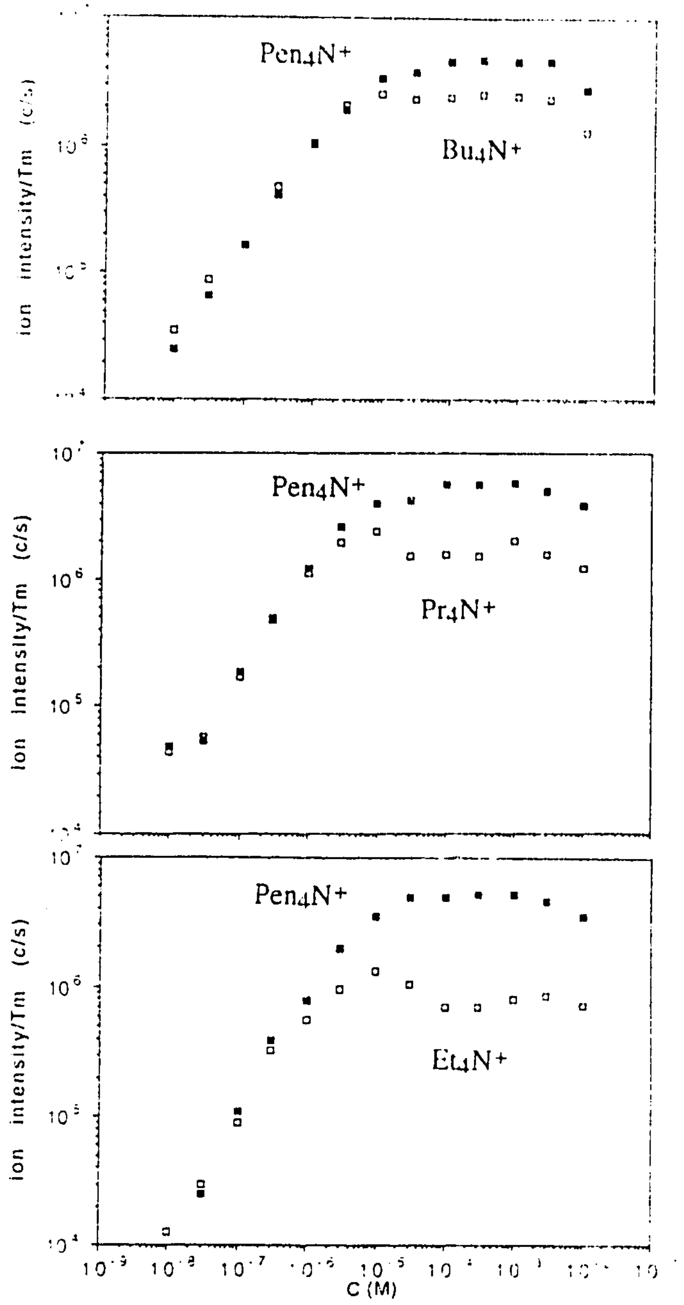


Figure 3-11 Ion intensities observed in experiment where $[A^+] = [B^+]$ is increased from 10^{-8} to 10^{-2} M. I_A/I_B ratio is different at high and at low concentrations and this means that significance of k_A/k_B ratio is different at high and low concentrations.

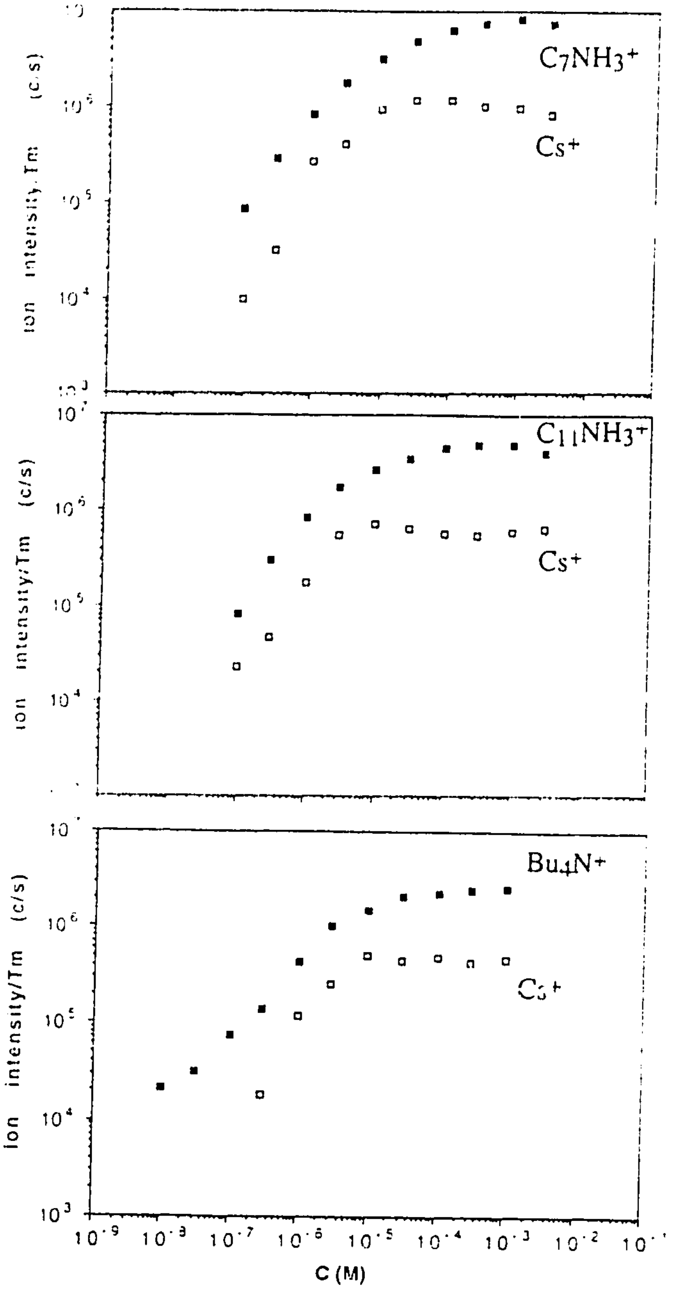


Figure 3-12 Ion intensities observed in experiments where $[A^+] = [B^+]$. In Figures 3-10 and 3-11, the intensity ratio approaches $I_A/I_B \approx 1$ at low concentrations. In present figure $I_A > I_B$ even at low concentrations.

plots, Figures 3-3 and 3-5 to 3-8, were obtained for $[A^+] = 10^{-5}$ M. This is a concentration that is at the low edge of the high concentration region. Therefore, these data are partly affected by phenomena which become important in the low concentration region, see next section.

The coefficients in Table 3-1 have their lowest values, $k \approx 1$, for the alkali and NH_4^+ cations. The tertiary ammonium ions, $MorH^+$ to $CocH^+$, have intermediate values and the quaternary ammonium ions like Bu_4N^+ have high values. The highest value $k \approx 16$ is observed for Pen_4N^+. An examination of the relationship between the structure and properties of the cations and their observed k values will be given in a later section.

II. Behavior when electrolytes are at low concentration, $<10^{-5}$ M. Indication for depletion of ions with high coefficient k and for surface activity effects.

The low concentration region 10^{-8}-10^{-5} M of the equal concentration plots [A] = [B], see Figures 3-10 to 3-12 exhibits very different behavior from the high concentration region 10^{-5}-10^{-3} M discussed in the preceding section. There are two important differences: (a) The ion intensities I_A and I_B experience a large decrease as [A] = [B] is decreased below 10^{-5} M; (b) The ratio $I_A : I_B$ gradually decreases and becomes close to unity, Figures 3-10 to 3-11, as the concentration is decreased much below 10^{-5} M.

The cause for the decrease of the intensities I_A and I_B, as [A] = [B] are decreased, was explained in Chapter 2. Due to the presence of an electrolyte impurity in the pure methanol used which is equivalent to 1.3×10^{-5} M NH_4Cl or NaCl = C, see Experimental, we have actually a three component system where the dominant electrolyte is the impurity electrolyte C whose concentration is constant. Therefore as [A] and [B] are decreased below 10^{-5} M, the presence of C becomes more and more important and since the C ions compete in the conversion process to gas phase ions, they lead to a decrease in the observed I_A and I_B. This type of behavior is analogous to that observed in section Ia and is in accord with equation 3-4 which can be extended in order to include a third electrolyte

$$I_A = \frac{k_A\,[A]}{k_A\,[A] + k_B\,[B] + k_C\,[C]}\,pf\,I \qquad (3\text{-}8)$$

Under conditions where [C] >> [A] = [B] equation 3-8 reduces to

$$I_A = \frac{k_A\,[A]}{k_C\,[C]}\,pf\,I \qquad (3\text{-}9)$$

and since pf, I and k_C [C] are constant, I_A becomes proportional to [A]. This equation predicts a linear region with a slope ≈1 for the logarithmic plots in the low [A] = [B] regions and such a region is observed in Figures 3-10 and 3-11. However, equation 3-9 and the ratio of I_A / I_B derived from it

$$I_A / I_B = \frac{k_A\,[A]}{k_B\,[B]} = \frac{k_A}{k_B} \qquad \text{when}\,[A]=[B] \qquad (3\text{-}10)$$

can not be valid because it predicts that $I_A \neq I_B$ since in general $k_A \neq k_B$, yet the observation is that the two ion currents become the same at low concentrations, see Figures 3-10 and 3-11.

The reasons for the failure of the equations are explored in the next section. It is shown there that the unipolar (+) ions on the surface of the droplets from which ion evaporation is assumed to occur (11) dominate over the charge paired electrolyte ions in the bulk of the droplet. Under these conditions of no resupply of the surface by ions from the bulk, a depletion of the surface ions A^+ with the higher ion evaporation coefficient, k_A, occurs which reduces the ratio, I_A / I_B, of the gas phase ion products.

The ion intensities I_A and I_B where $B^+ = Cs^+$ shown in Figure 3-12, do not become close to equal at very low concentrations. The ions A^+ can be expected to be surface active while Cs^+ is not. Under conditions where the surface ion population exceeds the bulk of droplet ion population, surface enrichment of A^+ due to surface activity will be especially important in leading to higher intensities I_A. As shown in section IIIf, it is probably differences in surface activities that lead to the observation that $k_A > k_B$ at low concentrations.

A somewhat simpler situation, where the same effects can be expected, occurs in experiments where there is only one added electrolyte AX, apart from the constant concentration impurity electrolyte C. In a series of experiments the concentration [AX] was varied over a wide range. Results from such experiments are shown in Figure 3-13 where AX = MorHCl, CodHCl, HerHCl, CocHCl and CsCl. The experimental points at low [A] show considerable scatter. This is unavoidable since absolute intensities I_A are difficult to reproduce exactly in separate electrospray experiments. Also shown in the figure are calculated I_A obtained with equation 3-4. The required parameters k_A, k_B, were taken from the data in Table 3-1 which were obtained from the linearized plots, equation 3-6, involving the same analyte A and the electrolyte, $B = NH_4^+$. Because the impurity C in methanol is mostly NH_4^+X and Na^+X and since the coefficients, k, for NH_4^+ and Na^+ are expected to be very similar, the k from Table 3-1 for $B = NH_4^+$ should be suitable. The current I required

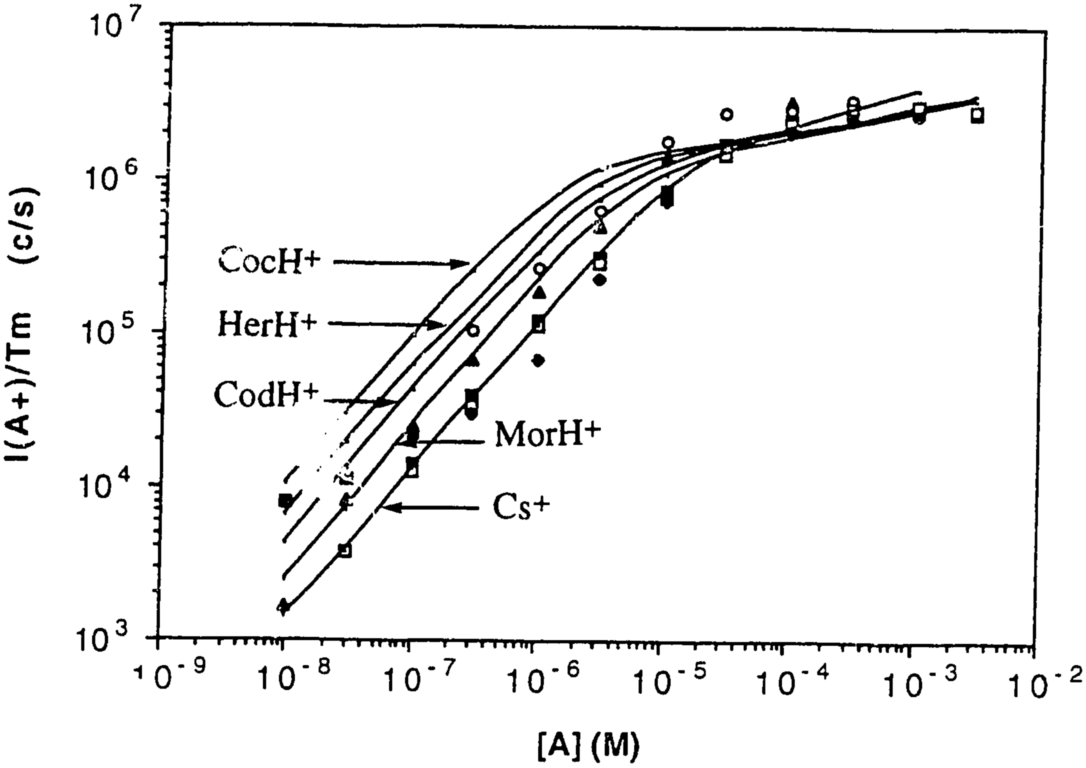


Figure 3-13 Observed ion intensities from separate experiments where [A+] is increased from 10^{-8} to 10^{-2} M. Solid lines are predicted intensities of A+ evaluated with equation 3-4 and coefficients in Table 3-1. Although no B is added, electrolyte impurity in the methanol used must be taken into account. □ MorH+, ■ CodH+, ○ HerH+, ▲ CocH+, ◆ Cs+.

for the evaluation of I_A, see equation 3-4, was measured in each experiment. It should be noted that I is constant for [A] 10^{-8}-10^{-6} M for all A since in this region C is the dominant electrolyte. Furthermore, I increases very slowly as [A] surpasses 10^{-5} M and is essentially independent of the nature of A, see equation 3-1 and Figure 3-5a.

The calculated curves in Figure 3-13 show clearly the predicted order of I_A dependent on the magnitude of k_A, Table 3-1, which is $CocH^+ > HerH^+ > CodH^+ > MorH^+ > Cs^+$. Despite the scatter in the experimental data it is very clear that the experimental data do not obey the predicted order and are much more compatible with nearly equal I_A currents at low [A^+]. This result is in agreement with the observations presented in Figures 3-10 and 3-11 which involved the simultaneous presence of two analytes [A] = [B] and the failure of equation 3-4 in the present case must be due to the causes already indicated for Figures 3-10 to 3-12.

III. Physical background and significance of coefficients k and equation 3-4

In this section we will examine phenomena concerning the mechanism of gas phase ion production by electrospray and their relationship to the present experimental findings and the significance of equation 3-4.

a. Properties of the Iribarne ion evaporation equation

It will here be assumed that the mechanism of ion evaporation from small highly charged droplets proposed by Iribarne and Thomson (11, 12) is at least qualitatively correct. After an examination of the properties of this equation, it will be shown that equation 3-4 can be derived from the Iribarne theory and that the coefficients k of equation 3-4 obtained at high concentrations should correspond to the (relative) ion evaporation rate constants of the Iribarne equation, when ions of similar surface activities are involved.

The ion evaporation rate constants of the Iribarne equation

$$k_I = (kT/h)\, e^{-\Delta G^{\neq}/RT} \qquad (3\text{-}11)$$

are based on Transition State Theory and $\Delta G^{\neq}$ stands for the free energy of the transition state where an ion solvent molecule cluster $M^+(Sl)_m$ leaves a small charged droplet. A basic assumption of the Iribarne treatment is that the transition complex occurs late, i.e. at a state where the ion cluster $M^+(Sl)_m$ is fully free of the droplet and at some distance x_m from it. The advantage of this assumption is that the free energy of this state can be evaluated with a closed classical expression:

$$\Delta G^{\neq} = \left(\frac{Ne^2}{4\pi\varepsilon_0(R + x_m)} - \frac{e^2}{16\pi\varepsilon_0 x_m}\right) - \left(\Delta G^{\circ}_{sol} + \frac{Ne^2}{4\pi\varepsilon_0(R - d)}\right) \qquad (3\text{-}12)$$

The terms in the first bracket give the energy of the transition state while the terms in the second bracket, give the energy of the initial state, see Figure 3-14. The zero level for both states is the charged drop and the ion cluster at infinite distance. The first term expresses the electrostatic potential energy due to the repulsion between the ion cluster and the charged droplet which has N elementary charges. The second term expresses the potential due to attraction between the charge of the ion and the polarizable drop. This term is approximated by the electrostatic attraction due to the image force. The third term represents the solvation

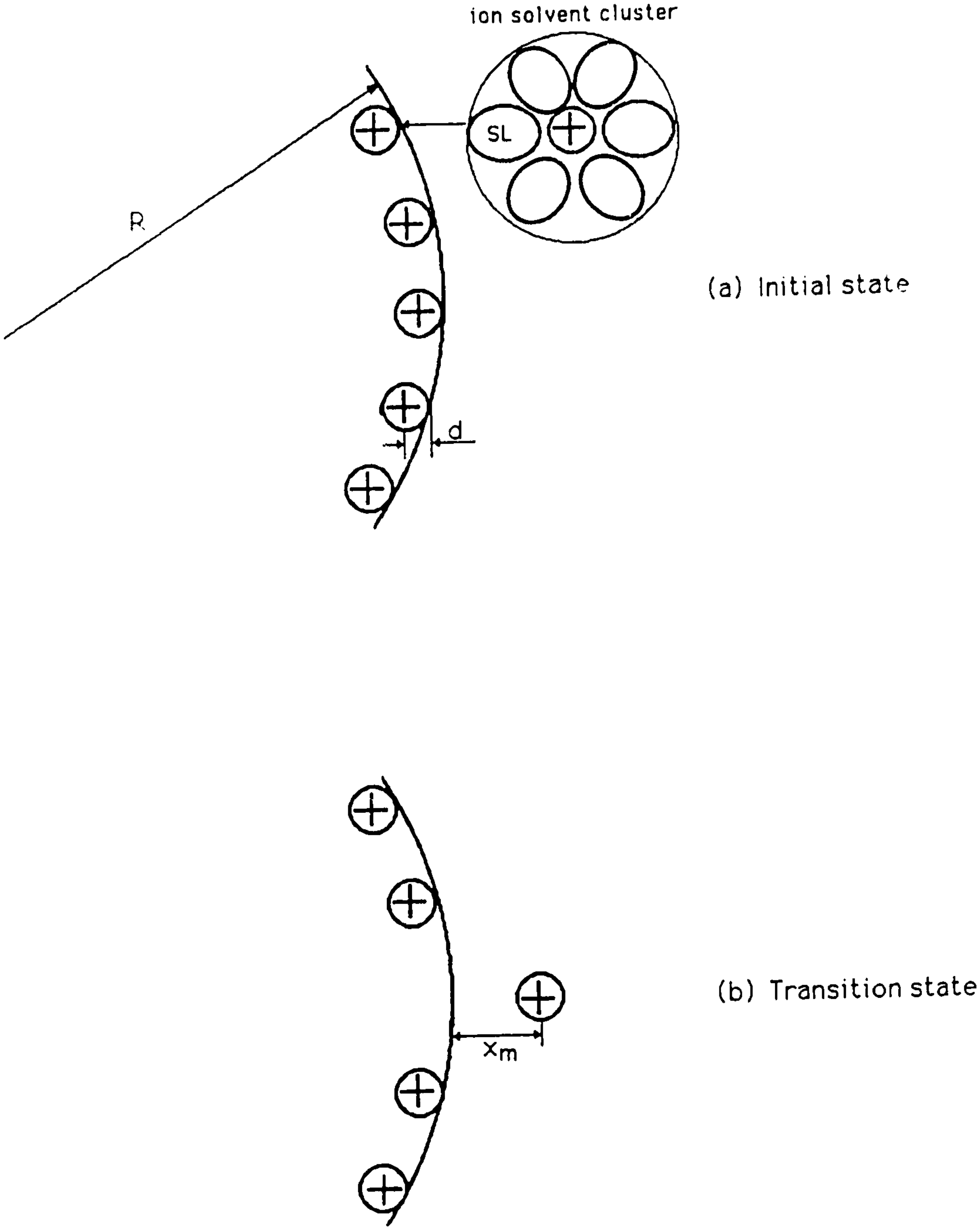


Figure 3-14 Schematic representation of initial state (a) and transition state (b) proposed by Iribarne and Thomson (11). Evaporating ion leaves as a cluster $M^{+}(Sl)_m$ where Sl are solvent molecules.

energy of the ion cluster $M^+(Sl)_m$ in the neutral drop, while the last term corrects for the fact that the drop is not neutral but has N elementary charges. Thus, $Ne^2 / 4\pi\varepsilon_0 (R - d)$ corresponds to the electrostatic repulsion energy required to bring the cluster from infinity to a distance d inside the drop, where the ΔG°_{sol} is released.

$\Delta G^{\neq}$ can be obtained by treating the distance x as parameter and finding the value x_m for which $\Delta G^{\neq}$ is maximum. Iribarne and Thomson (11) provide a very useful figure that gives the charge of the droplet N and the radius R for $\Delta G^{\neq} = 9$ kcal/mol, which leads to the rate constant $k = 10^6\ s^{-1}$ at T = 298, see equation 3-11. Iribarne reasoned that ion evaporation would become important only after k_I reaches such large values corresponding to µs lifetimes for ion evaporation. Two curves for, $\Delta G^\circ_{sol} = -56$ kcal/mol and $\Delta G^\circ_{sol} = -64$ kcal/mol were shown.

An additional illustration of results obtained with the Iribarne equation is given in Figure 3-15. The change of $\Delta G^{\neq}$ and k_I for constant ΔG°_{sol} (= −57 kcal/mol) and N (= 70) with the droplet radius treated as a parameter is shown in Figure 3-15a. These results illustrate the extremely rapid change of k_I with R. Thus, for a change from R = 100 Å to 70 Å, k_I increases from $3\times10^{-3}\ s^{-1}$ to $1.4\times10^{13}\ s^{-1}$, i.e. by 16 orders of magnitude! This very strong dependence on the radius of the droplet supports Iribarne's decision to assume that ion evaporation for a given charge N will be completely unimportant relative to Rayleigh fission for conditions where the Rayleigh fission radius R_R is larger than the radius R_I that leads to ion evaporation with $k_I = 10^6\ s^{-1}$. Iribarne showed that the ion evaporation condition, $R_I > R_R$, occurs when the droplets become very small, R = 80 Å and N ≈ 70 as typical values.

The results given in Figure 3-15b illustrate the change of $\Delta G^{\neq}$ and k_I

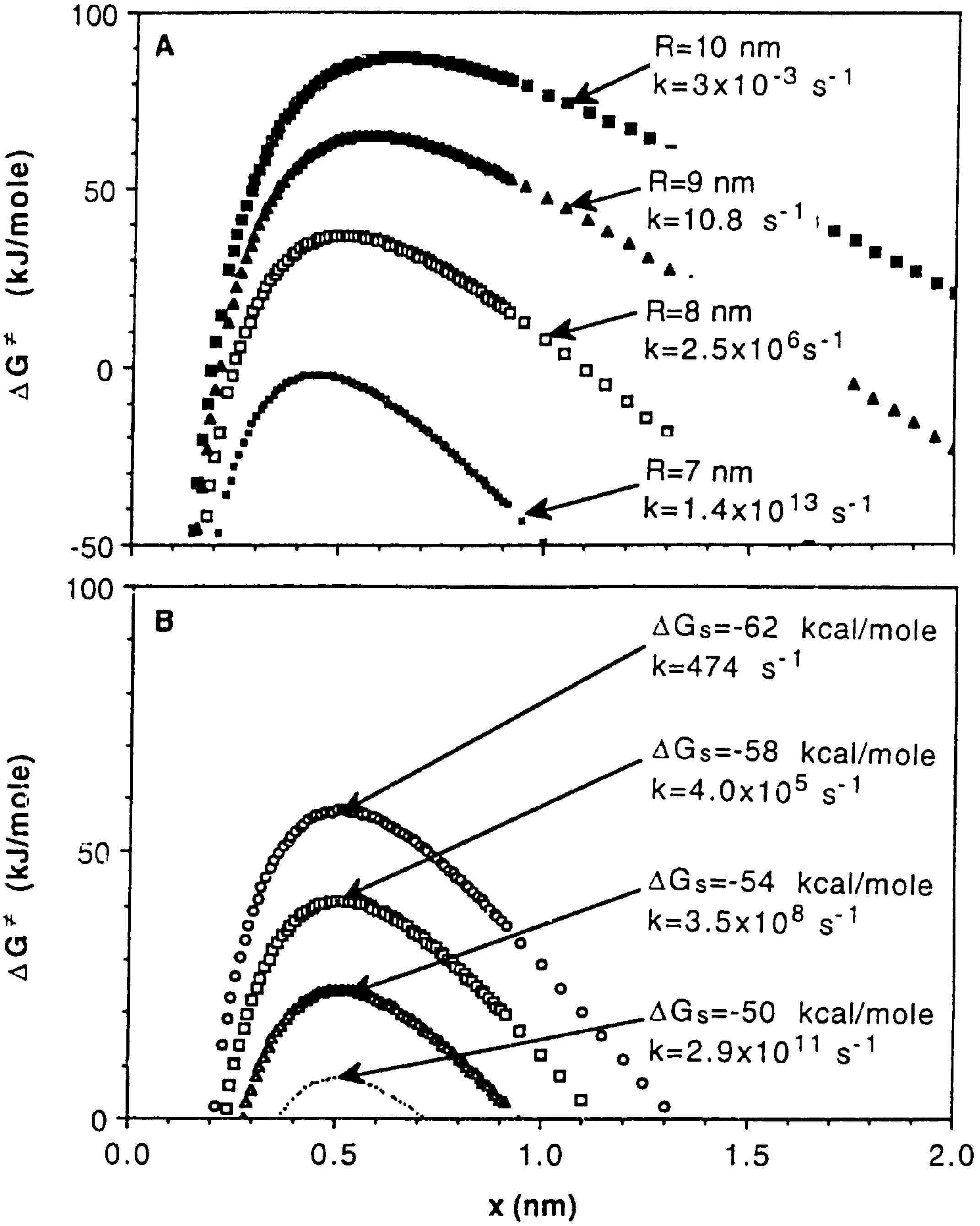


Figure 3-15 Free energy as a function of distance x of $M^+(Sl)_m$ from surface of drop predicted by equation 3-12. N = 70, d = 3.85 Å. (a) R is used as parameter and ΔG°_{sol} = −57 kcal/mol. (b) ΔG°_{sol} is used as parameter for R = 80 Å. Values of k_I obtained at ΔG°_{sol} are given beside each curve.

for constant N and d with ΔG°_{sol} as a variable parameter. It is interesting to note that the distance x_m which corresponds to the transition state remains essentially constant for different ΔG°_{sol}. An examination of equation 3-12 shows that for a constant x_m and constant d, the difference between $\Delta G^{\neq}$ for two given ΔG°_{sol} is given by

$$\Delta\Delta G^{\neq} = \Delta G^{\neq}_{a}(A^{+}) - \Delta G^{\neq}_{b}(B^{+}) = -\left(\Delta G^{o}_{sol}(A^{+}) - \Delta G^{o}_{sol}(B^{+})\right)$$

which means that the rate constant ratio for two different ion species which have different ion cluster solvation energies and the same value for d will be given by

$$\frac{k_{I(A^{+})}}{k_{I(B^{+})}} = e^{\left(\Delta G^{\circ}_{sol}(A^{+}) - \Delta G^{\circ}_{sol}(B^{+})\right)/RT} \qquad (3\text{-}13)$$

The plot shown in Figure 3-16a illustrates the change of $\Delta G^{\neq}_{I}$ and k_I when d is changed at constant R, N, ΔG°_{sol}. It is seen that also in this case x_m remains essentially constant for substantial changes of d. The independence of x_m on d and ΔG°_{sol} allows an important simplification.

$$k_{I,A}\left(N, R, d_A, \Delta G^{\circ}_{solA}\right) \approx k(R, N)\, k'_{A}\left(d_A, \Delta G^{\circ}_{solA}\right) \qquad (3\text{-}14a)$$

$$\approx k(R, N)\, k''_{A}\left(\Delta G^{\circ}_{solA}\right) k'''_{A}(d) \qquad (3\text{-}14b)$$

Thus, when more than one ion species is present in a droplet, k_I for each species can be factored into a function k(N, R), which represents the droplet state R, N and is independent of the nature of the ion and a constant $k'_{A}\left(d_A, \Delta G^{\circ}_{sol}(A)\right)$which expresses the nature of the ion A and is independent of R, N. Furthermore $k'_{A}\left(d_A, \Delta G^{\circ}_{solA}\right)$ can also be factored into two independent functions as shown in equation 3-14b. Equation 3-14 is based

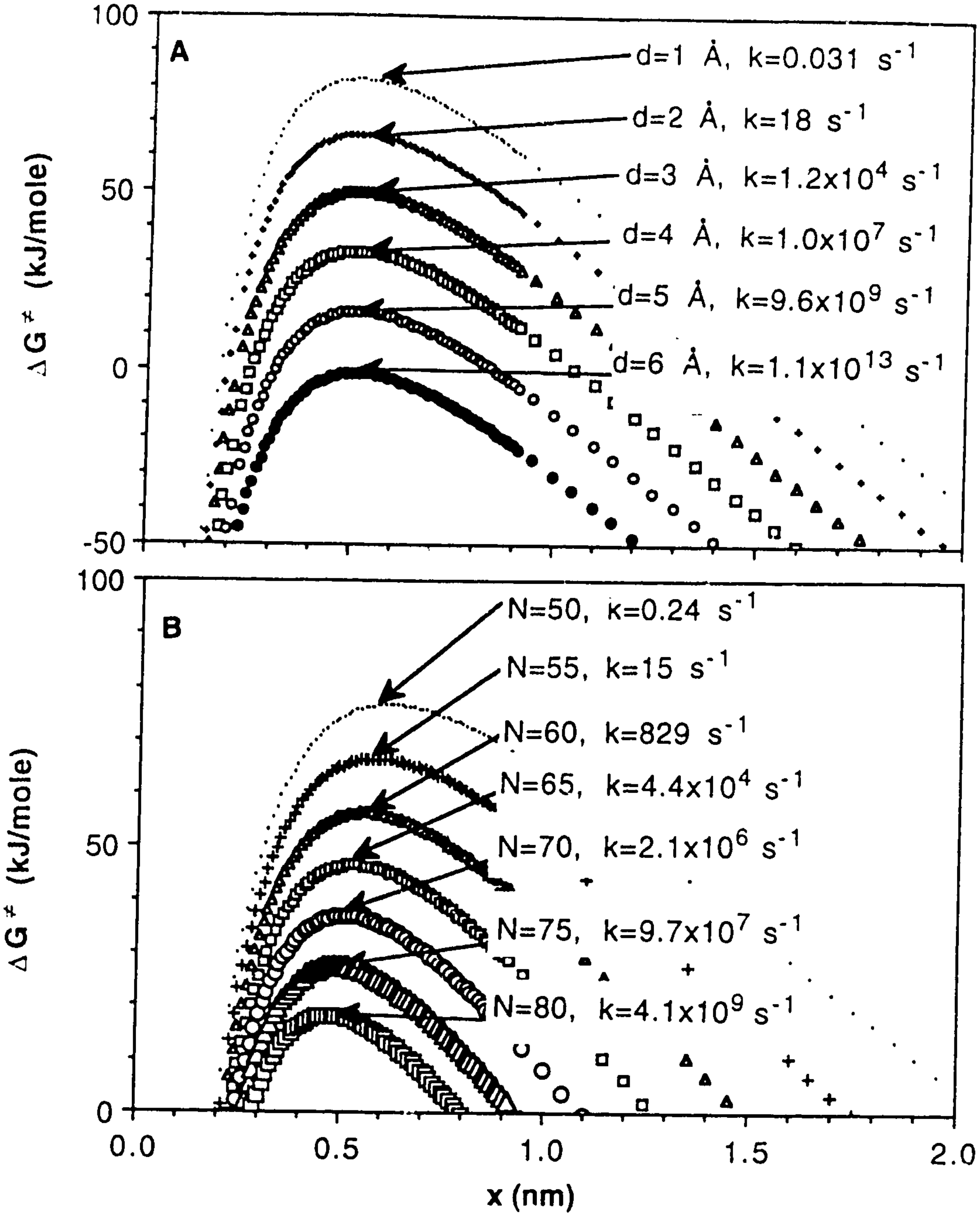


Figure 3-16 Same as Figure 3-15, (a) d is used as parameter while: R = 80 Å, N = 70, ΔG°_{sol} = –57 kcal/mol. (b) N is used as parameter while R = 80 Å, d = 3.85 Å, ΔG°_{sol} = –57 kcal/mol.

on the results given in Figures 3-15 and 3-16 and is valid for the range of parameters covered in these figures.

b. Ion evaporation and solvent evaporation

The results presented in Figure 3-16b illustrate the rapid decrease of the ion evaporation rate constant k_I with decrease of droplet charges N. Thus, the actual ion evaporation rates from a droplet will be controlled also by the solvent evaporation rate which will shrink the droplet and increase k_I. The droplets undergoing ion evaporation are very small and for the volatile solvents normally used, such as methanol and water, the evaporation rate will be under surface, rather than diffusion control (13). This means that the evaporation rate will be controlled by the rate of liquid to vapor conversion at the surface, since the recondensation of evaporated solvent molecules is negligible relative to the surface evaporation.

The rate of evaporation under surface control is expressed by equation 3-15 (13)

$$\frac{dm}{dt} = -\alpha \frac{\bar{v}}{4} 4\pi R^2 \frac{pM}{R_gT} \tag{3-15}$$

where the dm / dt is the rate of change of droplet mass, $\bar{v}$ is the average thermal velocity of the vapor molecules of the solvent, R is the radius of the droplet, p° is the vapor pressure of the solvent, M the molar mass of the solvent and R_g and T are the gas constant and temperature in K. α is the condensation coefficient equal to the fraction of solvent vapor molecules on collision with the droplet surface condense on the droplet. The value $\alpha = 0.04$ has been determined for water and ethanol (14). We make the assumption that the same value holds also for methanol.

Using the relationship between mass m, density ρ and volume of the droplet, $m = 4/3\ \pi R^3\rho$, equation 3-15 can be recast in the form

$$\frac{dR}{dt} = -\frac{\alpha\bar{v}}{4\rho}\frac{p^{\circ}M}{R_gT} \tag{3-16}$$

which on integration leads to a relationship between the radius R of the droplet and time t,

$$R = R_0 - \frac{\alpha\,\bar{v}\,p^{\circ}M}{4\,\rho\,R_gT}t \tag{3-17a}$$

$$R = R_0 - 1.2 \times 10^{-3}\,t \tag{3-17b}$$

where the numerical factor of equation 3-17b was evaluated for methanol ($p^{\circ} = 1.66 \times 10^4$ Pa, $M = 0.032$ kg/mol, $\bar{v} = 4.5 \times 10^2$ m/s, $\rho = 0.8 \times 10^3$ kg/m^3, $\alpha = 0.04$, $T = 298$ K). The radius of the droplet at $t = 0$ is R_0.

The temperature T to be used with equation 3-17a is the temperature of the droplet. The temperature of the droplet will be lower than the temperature of the surrounding air because of cooling of the droplet by solvent evaporation. The temperature difference can be evaluated as follows:

$$\frac{\text{collisions/s of drop with gas}}{\text{evaporating solvent molecules/s}} \approx \frac{p_g}{\alpha\,p^{o}} \approx 160 \text{ for MeOH}$$

$$p^{o}(\text{MeOH}) \approx 120 \text{ torr} \qquad \alpha = 0.04$$

Heat gained from ambient gas = Heat lost by evaporation

$$p_g\,c_p\,\Delta T = \alpha\,p^{o}\,\Delta H_{vap}(\text{MeOH})$$

where c_p is the molar heat capacity of air and ΔH_{vap}(MeOH) is the molar enthalpy of vaporization of methanol.

$$\Delta T = \frac{\alpha \, p^{o} \, \Delta H_{vap}}{p_g \, c_p} = \frac{9000}{7 \times 160} = 8^{o}C$$

$c_{p\ air} = 7/2\ R \approx 7$ cal/K mole $\Delta H_{vap}(MeOH) = 9000$ cal/mole

The assumption was made that every gas molecule assumes the temperature of the droplet on collision (i.e. accommodation coefficient = 1). A smaller accommodation coefficient will lead to higher ΔT. In the subsequent discussion, the temperature of the droplets is assumed to be $T = 298$ K. This means that the ambient gas in the electrospray was at $\sim 298+8 = 316$ K.

According to equation 3-17, the time required for the complete evaporation of an $R_0 = 100$ Å ($\approx 10^{-10}$ m) methanol droplet is $t = 8\ \mu s$, which is very short relative to the time scale of droplet residence between the ES capillary and the orifice to the mass spectrometer. Thus, once a droplet of Iribarne ion evaporation size is formed, it will evaporate and lead to gas phase ions within a few microseconds.

On the basis of equation 3-17 and the Iribarne rate constants it is possible to evaluate the gas phase ion yield as a function of time. The results shown in Figure 3-17a give the residual charge N on a droplet with $N = 70$, $R_0 = 80$ Å at $t = 0$. The data were obtained with the equation

$$\frac{\Delta N}{\Delta t} = -k_I N \qquad (3\text{-}18)$$

by selecting $\Delta N = -1$. The Δt_1, required for evaporation of the first charge is obtained with the $k_I(N_0, R_0)$ as predicted by the Iribarne equations, see Figures 3-15 and 3-16. Using Δt_1 the new radius for time $t = \Delta t_1$ was evaluated with equation 3-17. A new rate constant k_I was evaluated with the Iribarne equation using $N_1 = N_0-1$ and the new $R = R_1$.

Then Δt_2 was evaluated with equation 3-18. Proceding in this manner, the data shown in Figure 3-17 were obtained. The change of N with t is shown in Figure 3-17A, the change of R in 3-17B and the change of k with time in 3-17C. The results in Figure 3-17A indicate that about half of the charge N is converted to gas phase ions in ~1 µs. The solvent evaporation during the ion evaporation was found important as shown in Figure 3-17B.

c. Competitive ion evaporation

When the total charge N is due to two different ion species A and B, equation 3-18 can be reformulated with inclusion of equation 3-14a as shown

$$-\frac{\Delta N_A}{\Delta t} = k_{I_A} N \frac{N_A}{N} = k'_{(R,N)} k'_A N \frac{N_A}{N_A + N_B} \qquad (3\text{-}19)$$

where $N_A / (N_A + N_B)$ is the ratio of ions A to total ions N at the surface of the drop. There will be situations where the ratio $N_A / (N_A + N_B)$ will not change (significantly) during the ion evaporation process. This will be the case when the number of ions n_A and n_B in the bulk of the droplet, due to electrolyte in the droplets is very much higher than the number $N_A + N_B$ of ions at the surface. In this case the surface ratio $N_A : N_B$ will be maintained by rapid exchange with ions from the bulk. An approximate time constant for the exchange rate, time for diffusion of the ion to the surface, is given by

$$t_{Diff} \approx \frac{R^2}{\pi D} \qquad (3\text{-}20)$$

where D is the diffusion coefficient of the ion in the given solvent (23).

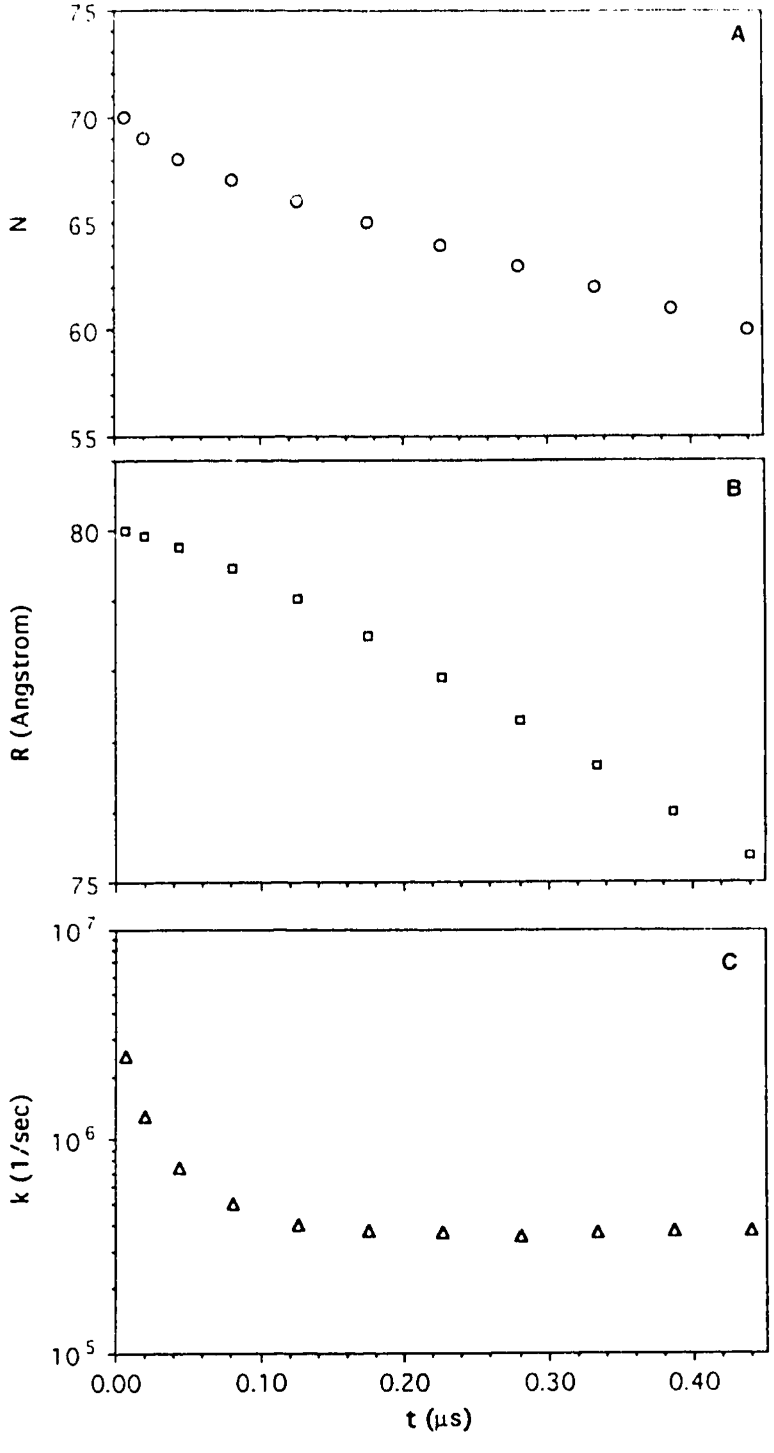


Figure 3-17 (a) Change of number of charges N with time for a droplet undergoing Iribarne ion evaporation and solvent evaporation. Evaluated with equation 3-17 and 3-18 for ΔG°_{sol} = −57 kcal/mol, d = 3.85 Å. Temperature of droplet is T=298 K. Ambient air temperature is ~316 K. (b) Change of radius of same droplet with time, evaluated with equation 317. (c) Change of rate constant, k, with time corresponding to the change of N and R.

Choosing R = 500 Å and a typical diffusion coefficient for alkali ions in water, $D = 1.7 \times 10^{-5}$ cm^2 s^{-1} one obtains $t_{Diff} \approx 1$ µs. The time required for smaller droplets will be much shorter. Furthermore, in methanol, the diffusion coefficients are higher. Since the Iribarne droplets are very small, diffusion will be able to maintain an approximately constant N_A / N_B ratio on a submicrosecond time scale. When the ions are not surface active, this ratio will be equal to the concentration ratio c_A / c_B in the bulk of the droplet.

For the condition where, $N_A / (N_A + N_B) = c_A / (c_A + c_B)$, remains constant during the Iribarne droplet evaporation one can obtain the total number of gas phase ions A^+ produced by the droplet by integration of equation 3-19 over a time, t_f, required for the complete evaporation of all ions from the droplet.

$$N_{A,g} = k_A' \frac{c_A}{c_A + c_B} \int_0^{t_f} k(R,N)\, N\, dt \qquad (3\text{-}21)$$

The value of the integral is the same for all ion species since k(R,N) is independent of the chemical nature of the evaporating ions. Assuming that the gas phase ion current $I_{A,g}$ is proportional to $N_{A,g}$ the number of gas phase ions produced in the average drop, the ratio of gas phase ion currents can be obtained with application of equation 3-21 and since the integrals cancel

$$\frac{I_{A,g}}{I_{A,g} + I_{B,g}} = \frac{k_A' c_A}{k_A' c_A + k_B' c_B} \qquad (3\text{-}22)$$

Furthermore, assuming that the droplet bulk ratio c_A / c_B equals the solution concentration ratio,

$$N_A / N_B = c_A / c_B = [A]/[B] \tag{3-23}$$

one obtains,

$$\frac{I_{A,g}}{I_{A,g} + I_{B,g}} = \frac{k'_A[A]}{k'_A[A] + k'_B[B]} \tag{3-24}$$

Equation 3-24 represents a derivation of the empirical equation 3-4 on the basis of the Iribarne relationships. It will be shown in the next section that the condition in equation 3-23 is valid only at higher electrolyte concentrations, i.e. $[A] = [B] > 5 \times 10^{-5}$ M. For that concentration range, and in the absence of differential surface activity between A and B, the experimental coefficient ratio k_A/k_B is predicted to be identical with the ion evaporation rate constants ratio k'_A/k'_B.

d. Charge, radius, concentration and time dependence for droplets evolving towards gas phase ion emission

An estimate of the charge Q, and radius R of the droplets from the time when they are produced by the electrospray to the point where they become gas phase ion emitters is possible on the basis of recent experimental observations of ES droplets by E.J. Davis et al. (16) and Gomez and Tang (17, 18). Reliable data are available only for droplets larger than 1 µm. The assumptions listed below are closely based on the work of Gomez and Tang (18).

(1) The initial droplets produced by ES, particularly at low flow rates, ~3 µL/minute, have a narrow size and charge per droplet distribution. Typical values are $R_0 = 1.5$ µm and $Q_0 = 8 \times 10^{-15}$C. This Q_0 corresponds to a charge that is ~40% of the charge, Q_R, required to lead to the Rayleigh droplet stability limit (19).

$$Q_R^2 = 64\pi^2 \varepsilon_0 \gamma R_R^3 \qquad (3\text{-}25a)$$

$$Q_R^2 = 1.25 \times 10^{-10} R_R^3 \qquad (3\text{-}25b)$$

where $\varepsilon_0 = 8.8 \times 10^{-12}$ is the permittivity of vacuum and γ is the surface tension. For methanol, $\gamma = 0.0226$ N/m^2, equation 3-25a leads to equation 3-25b.

(2) The droplets shrink due to solvent evaporation while the charge Q remains constant. Due to the decrease of radius, the droplets undergo fission when the radius has shrunk to a value for which Q equals 80% of Q_R. The parent droplet loses 15% of its charge and 2% of its mass producing several smaller, offspring droplets each of which has a radius which is ~10% of the radius of the parent droplet.

(3) Process (2) repeats itself when the parent droplet after radius shrinkage due to evaporation, is again at 80% of the Rayleigh stability limit. In this manner a succession of droplet emissions occur from the gradually shrinking parent droplet.

The graph given in Figure 3-18 illustrates the described process. The change of the parent droplet radius R with time was evaluated with equation 3-17. The radius of the parent droplet $R_0 = 1.5$ μm is small enough such that equation 3-17, which is based on surface controlled evaporation, should apply for solvents as volatile as methanol (13). The change of mass and thus also radius of the parent droplet when fission occurs is very small and therefore just perceptible for the data shown in Figure 3-18. The time required for the first fission is ~460 μs and at this point $R_1 = 0.94$ μm. A second fission occurs after a shorter time ~70 μs and further fissions occur at similar but gradually shortening intervals.

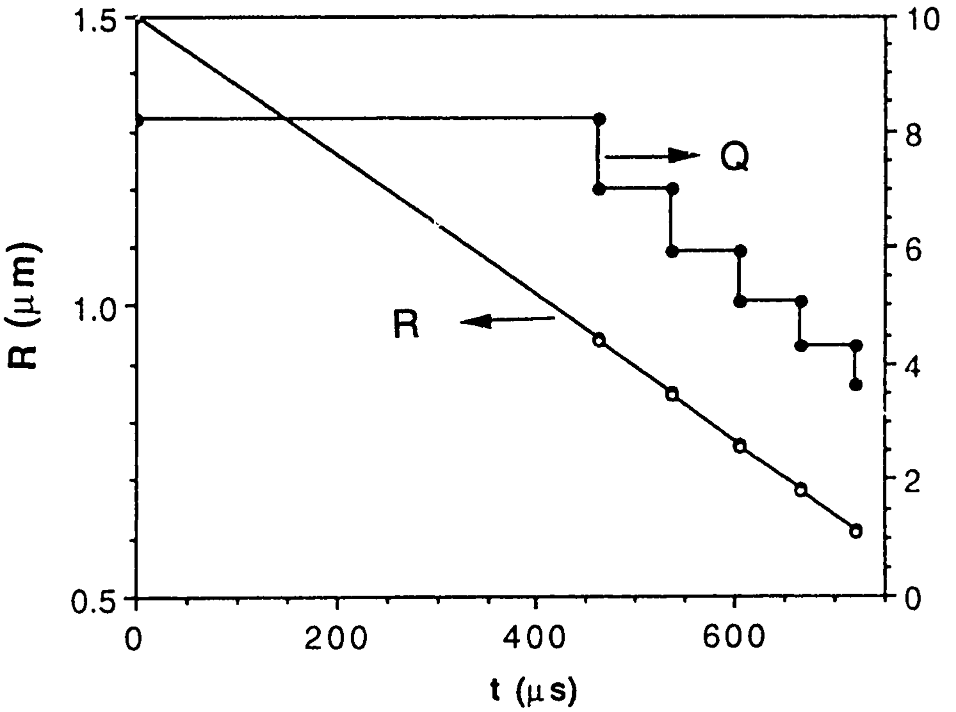


Figure 3-18 Changes of radius R and charge Q with time of a droplet produced by electrospray which undergoes successive not symmetric droplet fission, see Figure 3-19. Fission occurs at 80% of the Rayleigh limit and parent drop loses 2% of its mass and 15% of its charge.

The number n_S and the charge Q_S of the offspring droplets created from the parent droplet at a fission event can be estimated from the assumptions (2); i.e. the parent droplet uses 2% of its mass, 15% of its charge and the offspring droplet radius R_S is 10% of the parent radius R.

Applying conservation of mass where ρ is the density of the solvent

$$n_s \frac{4}{3} \pi R_s^3 \rho = 0.02 \frac{4}{3} \pi R^3 \rho$$

and since $R_S = 0.1$ R one obtains

$$n_S \approx 0.02 / (0.1)^3 = 20$$

The charge Q_S of each droplet is given by,

$$Q_s = \frac{0.15}{n_s} Q = 7.5 \times 10^{-3} Q$$

Thus, the first generation of ~20 droplets will have

$$Q_S = 6.12 \times 10^{-17} C \qquad R_S = 0.094\ \mu m$$

N_S = 382 elementary charges.

The Q_S and R_S of second, third, etc. litter of droplets can be evaluated in an analogous manner. In order to obtain an estimate of the process and properties leading to an "average" ion emitting droplet, we select a third generation of offsprings. At this point the parent droplet charge Q is down to 75% of the initial charge Q_0, see Figure 3-18 and 19. We do not select the litter where $Q = 0.5\ Q_0$ because it is likely that a full conversion of the parent droplet to offspring droplets does not occur due to time or other limitations.

The evolution of a third litter offspring droplet to an Iribarne ion emitting droplet is represented schematically in Figure 3-19. The

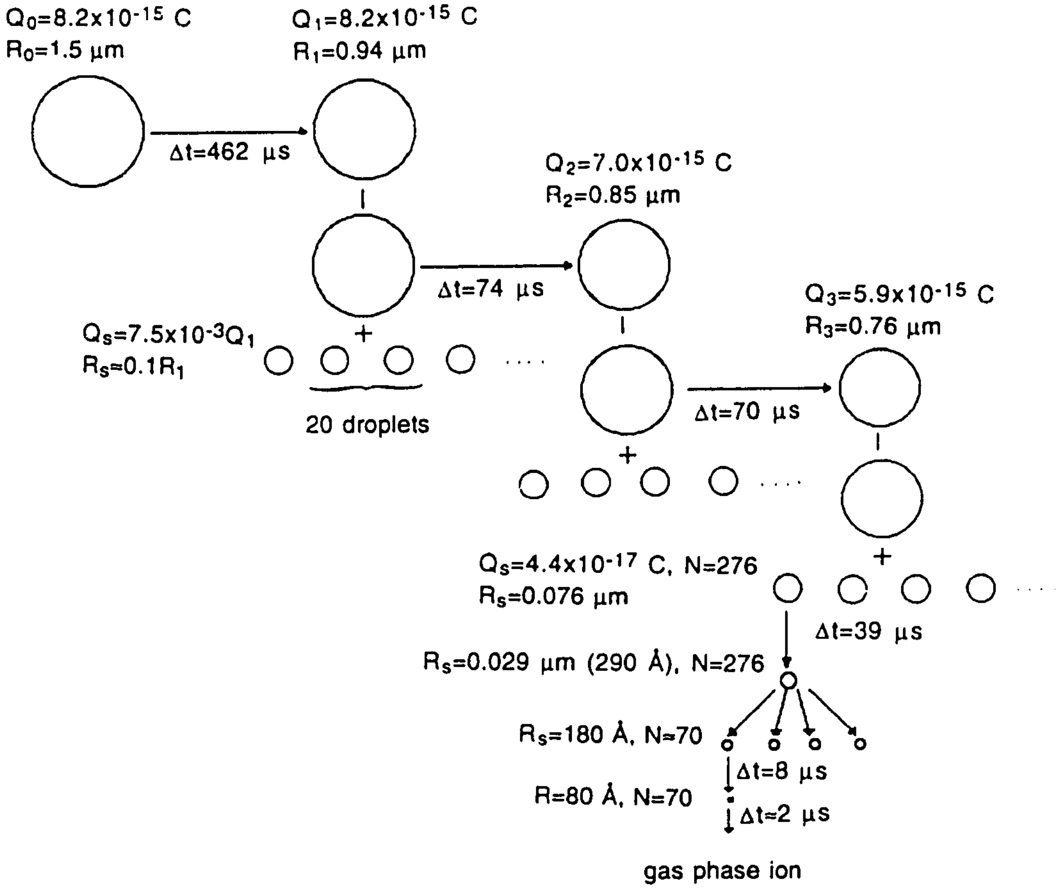


Figure 3-19 Changes of radius R, charge Q with time in droplet fissions of parent droplet and offspring droplets. Required time for solvent evaporation evaluated with equation 3-17. Time for ion evaporation involving Iribarne size droplet, from Figure 3-17.

offspring droplet shrinks through evaporation until it reaches 80% of the Rayleigh limit. At this point its radius is 290 Å and its charge consists of N = 276 elementary charges. The fission of such a small droplet has not been observed. For convenience we assume that the droplet splits into 4 droplets each carrying 1/4 of the charge. Then, each droplet shrinks through evaporation until it reaches the radius typically required for Iribarne ion emission, R = 80 Å for N = 70.

e. Prediction of the decrease of observed k_A/k_B ratio at low concentrations due to depletion of ions with higher evaporation coefficient

An estimate of the concentration of the electrolyte ions in the bulk of the Iribarne droplet can be obtained by assuming that the bulk electrolyte concentration in the offsprings at each fission is equal to the bulk concentration in the parent. With this assumption, because the volume shrinks due to evaporation, the concentration will have increased by the product of the volume ratios: $(V_i / V_f)_1 \times (V_i / V_f)_2 \times (V_i / V_f)_3 = F$ which can be evaluated from the data in Figure 3-18. The result is F = 7.6 x 17.3 x 11 = 1450. This means that the concentration in the Iribarne droplet has increased by a factor of ~1450 relative to the initial concentration. From the known volume V_I of the Iribarne droplet, Figure 3-18, one can evaluate n_M, the total number of paired electrolyte ions in the bulk of the droplet.

$$n_M = [M^+]\, F\, V_I\, L = 1.86 \times 10^6\, [M^+] \qquad (3\text{-}26)$$

where $[M^+]$ is the concentration of the electrolyte ions in the electrosprayed solution and L is Avogadros constant. The numerical factor given is for the droplet of 80 Å radius and $[M^+]$ in moles/L.

For $[M^+] = 10^{-5}$ mol/L the calculated number of bulk ions is $n_M = 18$. Since the number of ions on the surface is N = 70, the solution in the bulk has few additional ions to supply. It is easy to see that at such low initial concentrations the experimentally determined ratio k_A / k_B will be smaller than the theoretical ratio k'_A / k'_B (when $k'_A > k'_B$). To illustrate, we assume [A] = [B] and $k'_A / k'_B \approx \infty$. There will be 35 A and 35 B ions on the surface and 9 A and 9 B ion in the bulk. After all 44 surface and bulk A ions are used up due to the rapid evaporation of A also, 70-44 = 26 B ions will evaporate leading to $k_A / k_B = 44/26 = 1.7$ which is much smaller than $k'_A / k'_B = \infty$. Repeating the same type of calculation for different [A] = [B] concentrations one obtains the results shown in Figure 3-20, see curve $k'_A / k'_B = \infty$. It is possible to evaluate the change of the k_A / k_B with concentration also for other k'_A / k'_B ratios. Two such curves for the ratio 5 and 2 are also shown in Figure 3-20.

These data were evaluated with equation 3-19 using a numerical procedure similar to that used for the data shown in Figure 3-17. Δt for $\Delta N_A = -1$ was obtained for each step, then $\Delta N_A / \Delta N_B$ was evaluated for each Δt. The total A ions available for conversion to gas phase ions was taken as the sum of A ions on surface plus the A ions in the bulk of the droplet. For a complete numerical account see Appendix I.

Representative curves obtained with the experimentally obtained k_A / k_B, see Figures 3-10 and 3-11, are also shown in Figure 3-20. There is considerable correlation between the shapes of the experimental and calculated curves. It should be noted that the data shown in Figures 3-10 an 3-11 involve ions A^+ and B^+ whose surface activities are expected to be similar.

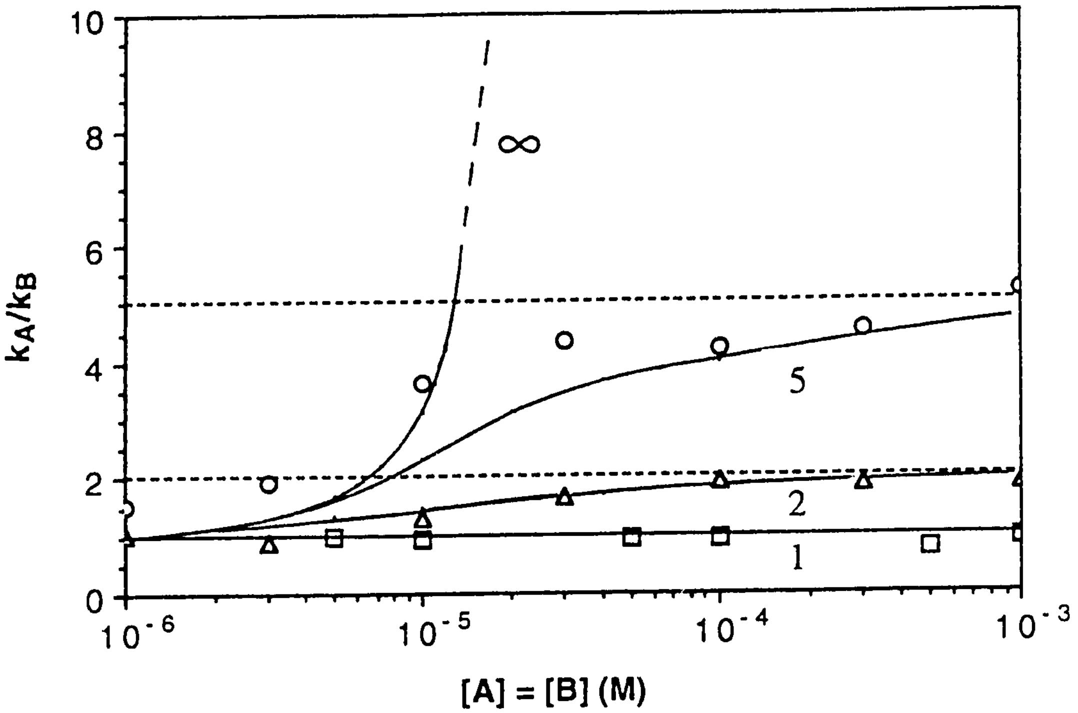


Figure 3-20 Predicted k_A/k_B ratio expected for a given ion evaporation ratio k'_A / k'_B in function of concentration [A^+] = [B^+]. Solid curves are predicted k_A / k_B for k'_A / k'_B values shown besides curves. Experimental points are from Figures 3-13 and 3-14 and give k_A / k_B for: $Bu_4N^+/CodH^+$ ○; Pen_4N^+/Bu_4N^+ Δ; Cs^+/K^+ □. Agreement between predicted and observed k_A/k_B supports proposed depletion mechanism. In calculated curves, A^+ and B^+ are assumed to have equal surface activity.

The agreement between predicted and experimental k_A / k_B in Figure 3-20 supports the depletion of faster evaporating ion interpretation proposed above.

f. Predictions of k'_A / k'_B from theory and experiment:

It was shown in the preceding section that the experimental k_A / k_B ratios obtained at high concentrations should correspond to rate constant k'_A / k'_B ratios for the evaporation of ions from the droplets when A and B have no surface activity or the same surface activity.

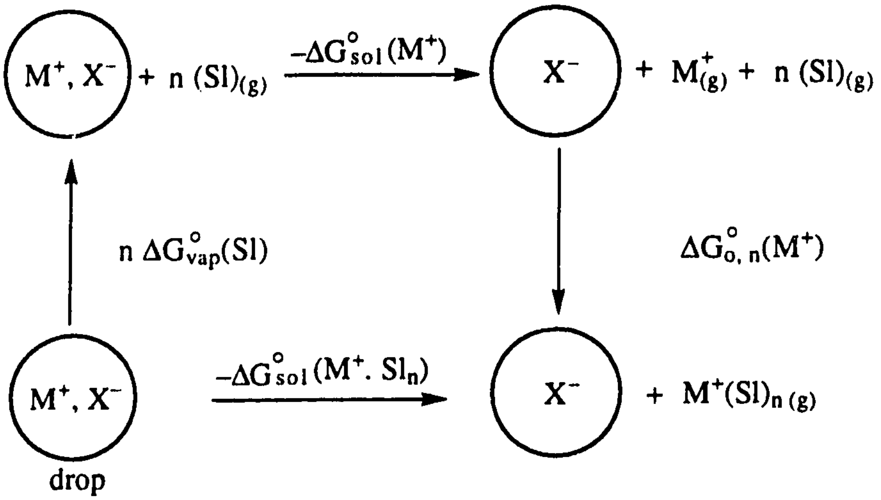
For the alkali cations, M^+ (Li^+, Na^+, K^+, Cs^+), the experimental results in Table 3-1 provide $k_A / k_B \approx k'_A / k'_B \approx 1$ which means that the $\Delta G^{\neq}$ for ion evaporation of these ions should be approximately equal, i.e.

$$\Delta\Delta G^{\neq} \approx 0 \qquad \text{for } Li^+ - Cs^+ \tag{3-27}$$

The characteristics of the ions enter $\Delta G^{\neq}$ through the solvation energy ΔG°_{sol} ($M^+(Sl)_m$) and the distance d, see equations 3-12, 3-14 and Figure 3-15. Assuming that the changes of d are small, equation 3-13 and 3-27 require that the $\Delta\Delta G^{\circ}_{sol}$ be small or close to zero.

$$\Delta\Delta G^{\circ}_{sol}\,(M^+(Sl)_m) \approx 0 \tag{3-28}$$

Fairly accurate estimates for $\Delta\Delta G^{\circ}_{sol}$ ($M^+(H_2O)_m$), in a small aqueous droplet, can be obtained from the thermodynamic cycle:



The cycle leads to:

$$\Delta G^\circ_{sol}(M^+.Sl_n) = \Delta G^\circ_{sol}(M^+) - \Delta G^\circ_{0,n}(M^+) - n\Delta G^\circ_{vap}(Sl) \qquad (3\text{-}29)$$

Data for the solvation of the naked ion, $\Delta G^\circ_{sol}(M^+)$, and for the solvation of the naked ion by n solvent molecules, $\Delta G^\circ_{0,n}(M^+)$, are available in the literature for Sl = H_2O, (20, 24). The vaporization energy of Sl = water from a small droplet, $\Delta G^\circ_{vap}(Sl)$, is also available for water. These data are summarized in Table 3-2. It is found that, $-\Delta G^\circ_{sol}(M^+(Sl)_n)$ decreases as n increases. A minimum is reached for n = m. These minimum values are given in Table 3-2. With these data we can evaluate the $\Delta\Delta G^\circ_{sol}$.

The $\Delta\Delta G^\circ_{sol}$ for Na^+ and Cs^+ is seen to be:

$- (\Delta G^\circ_{sol}(Na^+(H_2O)_m) - \Delta G^\circ_{sol}(Cs^+(H_2O)_m)) \approx 2.5$ kcal/mole

This difference is very much smaller than the difference of the solvation energy of the naked ions Na^+ and Cs^+ which is ~30 kcal/mol. However the $\Delta\Delta G^\circ_{sol}$ is still not equal to zero, see equation 3-28. It is not clear whether the disagreement is due to errors in the literature data used (20, 21). The

Table 3-2. Solvation Free Energies in Water

M^+	Li^+	Na^+	K^+	Cs^+	NH_4^+	$(CH_3)_4N^+$	$(C_2H_5)_4N^+$
$-\Delta G^\circ_{sol}(M^+)^a$	122	98.2	80.6	67.5	81^e	$(54)^f$	$(49)^f$
$-\Delta G^\circ_{o,m}(M^+)^b$	74.4	56.4	36.5	23.5	---	---	---
m^c	7	7	6	5	---	---	---
$-\Delta G^\circ_{sol}(M^+(H_2O)_m)^d$	61.2	56.5	55.8	54	55.6^e	$(52)^e$	$(48)^f$
$-R_{Ion}(\text{hydrated})^g$	3.82	3.58	3.3	3.29	3.3	---	---

a. Values in kcal/mol from Desnoyer (20).

b. Values in kcal/mol from Džidić (21).

c. m is the number of H2O molecules which lead to a minimum in $-\Delta G^\circ_{sol}(M^+(H_2O)_n)$.

d. Evaluated with equation 3-29 and $\Delta G^\circ_{vap}(H_2O)$= 1.95 kcal/mol, where $\Delta G^\circ_{vap}(H_2O)$= $RT\ln 760/p^\circ_R$ and p°_R is the vapor pressure of H2O in torr over a droplet with radius R. p°_R was obtained from p°, the vapor pressure over a flat surface with equation $\ln(p^\circ_R/p^\circ) = 2\gamma M/R\rho R_gT$ where γ is the surface tension, M the molar weight and ρ the density of water. R_g is the gas constant (22). $p^\circ = 23.8$ torr, $p^\circ_R = 28$ torr at 298 K.

e. Estimate based on near equality: $\Delta G^\circ_{0,5}(K^+) = \Delta G^\circ_{0,4}(NH_4^+)$, Kebarle (23) and value for K^+, see present table.

f. Rough estimates based on data from (23, 24).

g. Radii in Angstrom, from Conway (25)

literature data have expected errors in the ±3 kcal/mol range. Another problem is the use of water rather than methanol, for which the required supporting thermodynamic data are not available. However, the trend of higher $-\Delta G^{\circ}_{sol}(M^{+}(H_2O)_m)$ for the smaller ions in Table 3-2 is so consistent that a result of $\Delta\Delta G_{sol} = 0$ for all the alkali ions appears unlikely.

It is possible that differences in the parameter d might be also involved. d stands for the distance of the surface ion from the surface of the drop, see Figure 3-14. Iribarne assumed that this distance could be approximated by the radius of the ion plus the radius of one water molecule. This would mean that smaller d would have to be used for the smaller ions Li^+, Na^+. As evident from Figure 3-16a, this would lead to a correction in the wrong direction since smaller d lead to even lower k_I.

It can be argued that the d for the smaller ions should be larger and not smaller. Li^+, Na^+ are much more strongly solvated. Therefore, the electric field that forces the ions towards the surface will not be able to push the more solvated ions as closely to the surface. More suitable for the values of d should be the ionic radii obtained from ion mobility experiments in solution, the so called Stokes or hydrated ion radii (Conway) (25). These radii decrease in the order $Li^+ \rightarrow Cs^+$, see Table 3-2.

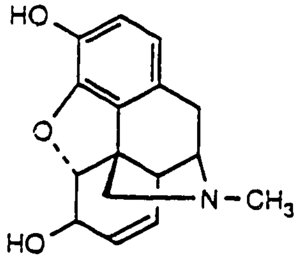
The $\Delta G^{\neq}$ for Na^+ and Cs^+ was evaluated with the Iribarne equation. using the $\Delta G^{\circ}_{sol}(M^{+}H_2O)_m)$ and d values given in Table 3-2 for a droplet with N = 70 charges and R = 80 Å. The result obtained was: $\Delta G^{\neq}(Na^+) = 9$ kcal/mol; $\Delta G^{\neq}(Cs^+) = 7.7$ kcal/mol at 298 K and $\Delta\Delta G^{\neq} = 1.3$ kcal/mol. This value is not equal to zero as required but sufficiently close to be consistent with the Iribarne treatment.

The tetraalkyl ammonium ions (TA) have experimental k values which are much larger than those for the alkali cations, see Table 3-1. This is consistent with expectation on the basis of the Iribarne theory. The solvation energies of the naked TA ions, $-\Delta G^{\circ}_{sol}(TA)$, can be estimated from available literature data (23, 24) and are found to be very much smaller than those for the alkali cations, see Table 3-2. In fact the $-\Delta G^{\circ}_{sol}$ for the naked $(C_5H_{11})_4N^+$ is smaller than the solvation energies for the alkali ion clusters, $\Delta G^{\circ}_{sol}(M^+(Sl)_m)$. The cluster $(C_2H_5)_4N^+(H_2O)_m$ is expected to have an $m \approx 1$, so that $\Delta G^{\circ}_{sol}((C_2H_5)_4N^+) \approx \Delta G^{\circ}_{sol}((C_2H_5)_4N^+(H_2O)_m)$.

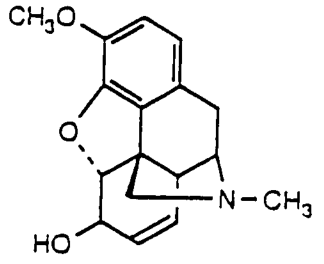
The low solvation energies for the TA ions given in Table 3-2 are in line with the observed high k values and with the order $Et_4N^+ < Pr_4N^+ < Bu_4N < Pen_4N$ of the experimental coefficients k in Table 3-1.

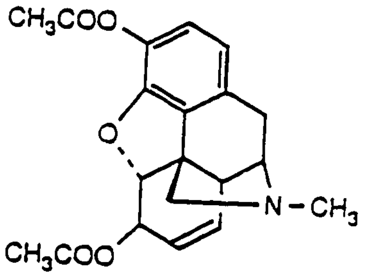
The structures of the alkaloids used in the present work are shown below:

Morphine

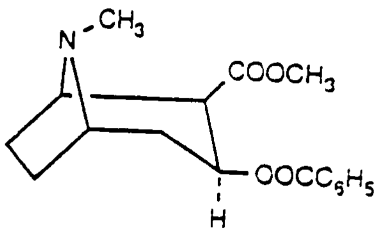


Codeine





Heroin



Cocaine

The experimental k values are: Morphine ~2, Codeine ~3.8, Heroin ~5.5, Cocaine ~8, see Table 3-1. Morphine, codeine and heroin are closely related. Morphine has two hydroxyl groups, codeine has one and heroin none. The hydroxyl groups, particularly in the presence of the positive charge on the nitrogen in the protonated compounds, will be somewhat acidic and therefore engage in stronger hydrogen bonding to the methanol or water solvent molecules (26). This will increase the solvation of the ion. Therefore, the observed order of k values for these three compounds follows the order of expected decreasing solvation and is in line with the ion evaporation theory. Although the cocaine structure is very different, this compound is also a tertiary amine. It is also devoid of hydroxyl groups and its high k value is consistent with expected relatively weak solvation.

g. Ion solvation and ion surface activity

It was shown in the preceding section that the magnitudes of experimentally observed coefficients k are, on the whole, consistent with the ion evaporation theory of Iribarne and Thomson. However, so far we have not taken into account the surface activity of the ions. Since surface active ions will have relatively higher concentrations on the surface than in the bulk of the droplet, it may be expected that the experimental k values for such ions will be found to be somewhat higher. Thus, the question may be asked: which is more important, surface activity or ion cluster solvation energies?

Unfortunately, due to the lack of accurate ion cluster solvation energies and of the parameters d, the k' values, see equation 3-14a, can not be predicted quantitatively with the Iribarne equations. Therefore, one has to resort to qualitative comparisons and with these the difficulty arises that ion cluster solvation energies and surface activities are often closely correlated. Ions with low ion cluster solvation energies for which high k's are expected are generally also of high surface activity. For example, the solvation energies $-\Delta G^{\circ}_{sol}$ for the tetraalkylammonium ions decrease in the order: Me_4N^+, Et_4N^+, Pr_4N^+, see Table 3-2, leading to expected higher k' in that order, but the surface activities also increase in the same order (27).

The k values for the tetraalkylammonium ions are much higher than those for the alkali cations. The cluster solvation energies for these ions are lower than those for the alkali cations, see Table 3-2. However, the surface activities are also much higher.

Fortunately, the previous discussion of the phenomena involved suggests a solution for this dilemma. It was shown in section (e), that as the initial concentration C is decreased, one reaches the condition where the number of unipolar ions on the surface exceeds the number of charge paired ions in the bulk of the ion emitting droplet. This condition holds for $C < 10^{-5}$ M. At such concentrations, the observed gas phase ions reflect directly the surface population of the droplet. In a solution with [A] = [B], the observed k_A / k_B evaluated with equation 3-10 were found to approach the limit $k_A / k_B \approx 1$, for any expected value of the Iribarne constants, k'_A / k'_B, provided that the surface activity of A and B was expected to be equal, see Figure 3-20. The data given in this figure do not include compounds whose surface activities were expected to be very different.

Measured ion intensities I_A, I_B for pairs with expected large surface activity differences: Bu_4N^+/Cs^+, $C_7H_{15}NH_3^+/Cs^+$ and $C_{11}H_{23}NH_3^+/Cs^+$

were shown in Figure 3-12. In all three cases one finds that the observed intensities I_A, I_B do not come together at low concentrations, i.e. the ratio $I_A/I_B = k_A/k_B$ remains quite large, $k_A/k_B \geq 5$, even at the lowest concentrations.

We can conclude that the k_A/k_B ratios observed in the low concentration range $C < 10^{-5}$ M reflect surface activities while those observed in the high concentration range $C = 10^{-3}$-10^{-2} M reflect the ion evaporation constants k'_A / k'_B and also enrichments due to surface activity.

The enrichment of the droplet surface in the more surface active component probably occurs in the evaporation stages of the parent droplets between the Rayleigh instability explosions. As illustrated in Figure 3-18 these evaporation stages are relatively long $t \geq 50$ μs and this should allow the enrichment of the surface with surface active ions.

h. A possible alternative mechanism for gas phase ion formation

In the preceding discussion it was shown that the experimental results are consistent with the Iribarne ion evaporation theory when the surface ion population is corrected for enrichment with ion species which are surface active. However, possibly due to lack of accurate literature data, Table 3-2, a quantitative proof of the Iribarne equation 3-12 could not be obtained.

We consider the relatively narrow range of coefficients k, 1~16, Table 3-1 surprising from the standpoint of the Iribarne theory. A $\Delta G^{\neq}$ difference of only 5 kcal/mol, leads to a $k'_A / k'_B \approx 500$ at 298° K, see equation 3-11. Similarly, the observed selectivity due to surface activity seems too small, since the enrichments of surface active ions could be expected to be much larger. From the standpoint of electrospray mass spectrometry, the relative lack of selectivity is an advantage. All types of ions are expected to be detectable with ESMS.

It is possible that the relative lack of selectivity is due to a gas phase ions production mechanism that is somewhat different from the Iribarne ion evaporation model as represented by equation 3-12. An alternative is suggested from an examination of the time required for the different processes leading to ion emission. A complex series of solvent evaporation and droplet fissions lasting hundreds of microseconds leads to the Iribarne size droplet. According to the model, ion emission then occurs and requires some 1 μs, see Figure 3-17. However, even if the Iribarne ion emission did not occur, the droplet itself will lose most of its solvent molecules, due to solvent evaporation, in only ~8 μs, see equation 3-17b. This time difference is not very large. Suppose that the Iribarne emission did not occur as predicted, solvent evaporation will then continue until a much more disorderly gas phase ion production occurs which may not follow, equation 3-12, of the model. For this type of ion emission, solvation energy differences, surface effects and the effect of temperature may have a much reduced importance relative to the functionalities predicted by equations 3-11 and 3-12.

One reason why equation 3-12 may not apply is the assumed "late" transition state which occurs after the ion cluster has "broken through" the surface of the droplet. An "early" transition state which occurs just as the cluster disrupts the surface may lead to a higher $\Delta G^{\neq}$. In such a case a higher electric field will be required, i.e. a smaller more highly charged droplet. One would expect a decreased functional dependence on parameters like ΔG°_{sol}. Rayleigh fissions will also remain competitive down to a smaller radius. The small highly charged offsprings of such fissions may also lead to gas phase ions so rapidly that diffusion is not able to maintain a constant bulk to surface concentration ratio even for high, above 5 x 10^{-5} M, initial concentrations. In this case a resupply with bulk ions will not occur and a depletion effect similar to that observed at low concentrations will reduce the observed k_A/k_B ratios.

As far as the mechanism of gas phase ion formation is concerned, an alternative mechanism first proposed by Dole (28), i.e. single ion in droplet theory (SIDT), can also rationalize most experimental facts in ESMS. The SIDT postulates that the Rayleigh fission of charged droplet continues until the offspring droplet contains one excess ion, which leads to gas phase ion. This theory also expects the selectivity which result in different k_A/k_B ratios in ESMS. Since surface active ions will be enriched on the surface and be the favored charged carriers, they will be favored in the final very small offsprings which are close to the single ion in droplet state. Thus, selectivity for the SIDT is due to differential surface activity.

If the SIDT holds, ion depletion can also be expected at low concentration for two species A^+ and B^+ of very different surface activity because the surface increase on droplet formation is so large that there just are not enough A^+ ions to supply all the surface charges. Large increases of surface to volume occur not only in the initial formation of the droplet but also in the fission process.

Although the SIDT appears very attractive due to the recently observed not symmetric fission of the charged droplets (17, 18), the type of fission for droplets of sizes much below 1 μm is not known yet. Therefore, a clear choice between Ion Evaporation mechanism and SIDT can not be made at this time. One advantage of Ion Evaporation mechanism over SIDT is that it provides an approach to the quantitative expectation of experimentally detected ion intensity. This is the reason that the experimental data in my research was mainly rationalized on the basis of ion evaporation mechanism.

3.4 Conclusions

(1) Equation 3-4 provides useful predictions, both in the low: 10^{-8} to 5×10^{-6} M, and in the high: 10^{-5} to 10^{-2} M, concentration range. However, the coefficients k have different significance in the two ranges. At low concentration k_A/k_B express relative surface activities of A^+ and B^+. When A^+ and B^+ have equal surface activity, $k_A/k_B = 1$. In this range the unipolar ions on the surface of the ion evaporating droplet dominate over the charge paired electrolyte ions in the drop. At high concentrations, k_A/k_B express the relative ion evaporation rates and relative surface activities.

(2) The relative values k_A/k_B obtained at high concentrations are consistent with predictions of the Iribarne theory. However, a confirmation of the quantitative predictions of the theory could not be obtained due to lack of required literature data. The observed range: 1-20, for the relative values of the coefficients, is smaller than could be expected on the basis of the Iribarne theory and this suggests that the functional dependence, equation 3-12, is not exact.

(3) Solvent evaporation leads to an estimated volume shrinkage which increases the initial concentration $[A^+]$, $[B^+]$ by a factor of ~1500 for change from ES produced drop to ion evaporating droplet.

(4) The formation of the ion evaporating droplets is preceded by a

long (hundreds of μs) and complex process of shrinkage by solvent evaporation and droplet fission. The ion evaporation stage is short - a few μs. Since the solvent evaporation rate is proportional to the vapor pressure of the solvent, equation 3-16, ES with less volatile solvents like water p° = 24 torr relative to methanol: p° = 125 torr at 25°C may lead to higher intensities I_A, I_B if operated above ambient temperature.

(5) The coefficients in Table 3-1 provide a guide to choice for cations in buffers which will lead to the smallest suppression of the intensity of the analyte ion.

(6) In cases where quantitative information is to be obtained by the addition of an internal standard to the solution, the internal standard B^+ should have the same surface activity and the same ion evaporation coefficient as the analyte A^+, as is the case for K^+/Cs^+, Figure 3-10 and Table 3-1. Only in this case will the signal of A^+ be proportional to B^+ over the full concentration range: 10^{-8}-10^{-2} M. In the low concentration range: 10^{-8} - 5 x 10^{-6}, proportionality is maintained even when this requirement is not met.

3.5 Appendix

Evaluation of depletion effect

The depletion of ions from a charged droplet may happen in the low concentration range when one ion species has higher ion evaporation rate constant k. The depletion effect can be evaluated with equations involved in the ion evaporation model.

Ion evaporation from a charged droplet is a first order reaction as described by equation 3-18

$$-\frac{\Delta N}{\Delta t} = k_I N \qquad (3\text{-}18)$$

Taking a binary system, i.e., two major ions (A and B) in electrospray solution, as the simplest case for the study of depletion effect, one can write a rate law for each ion evaporation process.

$$-\frac{\Delta N_A}{\Delta t_A} = k_A N_A \qquad (3\text{-}30a)$$

$$-\frac{\Delta N_B}{\Delta t_B} = k_B N_B \qquad (3\text{-}30b)$$

where $-\Delta N_A/\Delta t_A$ and $-\Delta N_B/\Delta t_B$: rate of ion evaporation for ion A and ion B, respectively;

k_A and k_B: theoretical rate constant of ion A and ion B, respectively;

N_A and N_B: number of ion A and ion B on the surface of a charged droplet.

In equation 3-30, it is assumed that ion evaporation for each ion species is independent of other ions in the droplet. Since rate constant k_I can be factored into two functions $k(R, N)$ and $k(d, \Delta G_{sol})$, as shown in equation 3-14, equation 3-30a can be rewritten in the following form

$$-\frac{\Delta N_A}{\Delta t_A} = k_A N_A$$

$$= k'_A(d, \Delta G_{sol,A})\, k(N, R)\, N_A \qquad (3\text{-}31)$$

Furthermore, diffusion of an ion from the bulk of the droplet to the surface is fast enough to maintain equilibrium of ion population between surface and bulk solution, see equation 3-20 and relevant discussion. This condition can be expressed with equation 3-32.

$$-\frac{N_A}{N} = \frac{N_A+n_A}{N+n} \tag{3-32}$$

N: total positive ions on the surface of a charged droplet

n: total ions in bulk solution

n_A: number of ion A in bulk solution

Combining equation 3-32 with equation 3-31, one can obtain

$$-\frac{\Delta N_A}{\Delta t_A} = k'_A(d, \Delta G_{sol,A})\ k(N, R)\ N\ \frac{N_A}{N}$$

$$-\frac{\Delta N_A}{\Delta t_A} = k'_A(d, \Delta G_{sol,A})\ k(N, R)\ N\ \frac{N_A+n_A}{N+n} \tag{3-33}$$

Similarly, an equation for ion B is obtained as

$$-\frac{\Delta N_B}{\Delta t_B} = k'_B(d, \Delta G_{sol,B})\ k(N, R)\ N\ \frac{N_B+n_B}{N+n} \tag{3-34}$$

n_B: number of ion B in bulk solution

If $k'_A(d, \Delta G_{sol,\ A})/k'_B(d, \Delta G_{sol,\ B})=u$ (constant), the expected experimentally obtained rate constant ratio k_A/k_B at different concentrations can be estimated with following iterative calculation.

As first step (noted in subscript as 1), $\Delta t_{A,1}$ can be calculated for emitting one ion A, i.e., $\Delta N_{A,1}=-1$. Because $\Delta t_{A,1}=\Delta t_{B,1}$, one can obtain $\Delta N_{B,1}$ which is the number of ion B emitted in time $\Delta t_{B,1}$. That is

$$\Delta t_{A,1} = \frac{-\Delta N_{A,1}\,[N+n]}{k'_A(d, \Delta G_{sol,A})\ k(N, R)\ N\ (N_{A,1}+n_{A,1})}$$

$$= \frac{-\Delta N_{A,1}}{u\, k'_B(d, \Delta G_{sol,B})\, k(N, R)} \times \frac{N+n}{N\,(N_{A,1}+n_{A,1})} \qquad (3\text{-}35)$$

and

$$-\Delta N_{B,1} = \Delta t_{B,1}\, k'_B(d, \Delta G_{sol,B})\, k(N, R)\, N\, \frac{N_{B,1}+n_{B,1}}{N+n}$$

$$= \frac{N_{B,1}+n_{B,1}}{N_{A,1}+n_{A,1}} \times \frac{1}{u} \qquad (3\text{-}36)$$

For the second step (noted in subscript as 2), if $\Delta N_{A,2}$ is taken as -1, one can calculate $\Delta N_{B,2}$. Keeping in mind that $\Delta t_{A,2}=\Delta t_{B,2}$, the following two equations will be obtained.

$$-\Delta t_{A,2} = \frac{N+n-(\Delta N_{A,1}+\Delta N_{B,1})}{\left[N-(\Delta N_{A,1}+\Delta N_{B,1})\right]\left[N_{A,1}+n_{A,1}-\Delta N_{A,1}\right]} \times \frac{-\Delta N_{A,2}}{u\, k'_B(d, \Delta G_{sol,B})\, k(N, R)} \qquad (3\text{-}37)$$

then

$$-\Delta N_{B,2} = \frac{N_{B,1}+n_{B,1}-\Delta N_{B,1}}{N_{A,1}+n_{A,1}-\Delta N_{A,1}} \times \frac{1}{u} \qquad (3\text{-}38)$$

The iteration continues until whole ion evaporation process has to stop:

$$\Sigma(-\Delta N_A)+\Sigma(-\Delta N_B)=N \qquad (3\text{-}39)$$

Thus, the experimental rate constant ratio can be estimated:

$$\frac{k_A}{k_B} = \frac{\Sigma(-\Delta N_A)}{\Sigma(-\Delta N_B)} \qquad (3\text{-}40)$$

The condition set in equation 3-39 reveals the possibility of ion depletion. When [A]=[B] and both are at low concentration range, one ion species would be used up early if it has larger rate constant. If it is supposed

$k'_A(d, \Delta G_{sol, A}) / k'_B(d, \Delta G_{sol, B}) = u >> 1$, B ions can still evaporate after most A ions have evaporated. Therefore, the observed rate constant ratio k_A/k_B will be smaller than the value u. This rationalization would be more visual if the ion evaporation process is calculated with above equation in a typical Iribarne droplet. The results of calculation are shown in Table 3-3. In Table 3-3, it is obvious that depletion effect will exist when the analyte concentration is low such as below 10^{-4} M, which is the range widely used in the ESMS practice. Finally, a mention should be made that ion depletion alleviates the difficulty in ion emission of polar compounds and makes the mass analysis of polar compounds possible in ESMS.

Table 3-3. Deviation of the Observed k_A/k_B from Real Ratio $k'_A(d, \Delta G_{sol, A})/k'_B(d, \Delta G_{sol, B})$ due to Ion Depletion

[C] (M) [a]	n_A [b] (or n_B)	N_A+n_A [c] (or N_B+n_B)	Observed k_A/k_B			
			$u=\infty$	u=5	u=2	u=1
5×10^{-6}	9	44	1.69	1.69	1.33	1.0
1×10^{-5}	18	53	3.12	2.33	1.50	1.0
2×10^{-5}	36	71	∞	3.12	1.59	1.0
4×10^{-5}	72	107	∞	3.67	1.69	1.0
1×10^{-4}	180	215	∞	4.00	1.80	1.0

a. [C] is the concentration of analyte A (or B) in the bulk solution, [A]=[B];

b. the number of ions in the bulk solution of a typical Iribarne droplet, R=80 Å, N=70;

c. the total available ions of A (or B) in the charged droplet.

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Chapter 4. Complexation of Alkali Cation M^+ to 18-Crown-6. Comparison of Expected Concentrations of M^+ and $M^+\cdot$18-Crown-6 in Solution with Observed Ion Intensities of M^+ and $M^+\cdot$18-Crown-6 in ESMS

4.1 Introduction

The investigation of the ESMS mechanism has revealed that a charge separation process in electrospray happens at the electrospray tip. This charge separation process is discussed in chapter 2 of this thesis on the basis of the Hendricks model (1). After the charged droplets form, they drift in the atmosphere under the influence of the electric field. The study of the ES mechanism has also revealed that gas phase ions might form via an ion evaporation process, which is the concept first put forward by Iribarne (2). The process of gas phase ion formation was discussed in chapter 3 of this thesis, where it was concluded that gas phase ions are produced by the charged droplets which have already evaporated a large amount of solvent. The work by Gomez and Tang (3) provided experimental data for the droplet shrinkage process, but no direct observation has been made to confirm that the gas phase ions originate from shrunken charged droplets.

To test the assumption that ions in the liquid phase begin to transfer to the gas phase after the charged droplet has evaporated a large amount of solvent, an experiment which takes advantage of reactivity of metal ions with cyclic ligands was devised. The reactions between alkali metal ions and crown ethers have been extensively investigated in both liquid and gas phases (4-18). For instance, equilibrium constants and reaction rate constants for the reaction: $M^+ + L = M^+L$ in methanol has been determined independently by different researchers (5, 6, 16).

In the present work, crown ethers, mainly 18-crown-6 and 12-crown-4 (Figure 4-1), were used as cyclic ligands to the alkali metal cations. The equilibrium constants for the formation of the metal ligand complex M^+L in methanol have been determined (5-7) and therefore the expected concentrations of M^+, L and M^+L at equilibrium can be evaluated if the initial $[M^+]$ and [L] in the solution are known.

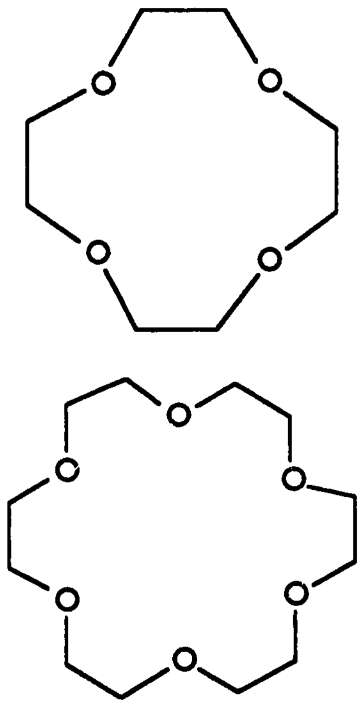
The main purpose of the present work is to attempt to determine the shift of the equilibrium: $M^+ + L = M^+L$ towards the product side caused by the increase of solute concentration due to solvent evaporation from the droplets. The solvent evaporation was discussed in Chapter 3.

4.2 Experimental

a. Mass-dependent discrimination and ion intensity calibration

Because the SCIEX TAGA 6000E used in the work described in chapter 3 was not available at the time of the study described here, my initial experiments were conducted on the quadrupole mass spectrometer SCIEX TAGA 6000, an earlier version of the TAGA 6000E. Some of the later experiments were performed on the TAGA 6000E. Modifications needed to fit ES to the mass spectrometer were discussed in Chapter 3 and reference 19.

In order to compare the ion intensities, a correction must be applied for the mass discrimination introduced by a quadrupole mass spectrometer. The measurement of the mass dependent transmission of the TAGA 6000



(1) 12-crown-4

(2) 18-crown-6

Figure 4-1 Structures of crown ethers used in the complexation with metal ions. (1) 12-crown-4, MW=176; (2) 18-crown-6, MW=264.

was obtained with the same procedure as described in Chapter 3 for the TAGA 6000E. The mass dependent transmission plot is shown in Figure 4-2.

b. Gas phase reactions between ion M^+ and crown ethers.

For the reasons explained in Results and Discussion, it was necessary to examine whether a gas phase ion molecule reaction involving alkali metal ion (M^+) and crown ether (L): $M^+ + L = M^+L$, occurs in the electrospray plenum chamber. A special device shown in Figure 4-3 was designed for this purpose. A stainless steel electrospray tip was installed coaxially within a glass tube. The glass tube was mounted in the plenum chamber as shown in the figure. Reactant crown ether dissolved in methanol was injected at a known flow rate into a vaporizer, where it evaporated. The electrospray tip protruded about 1 cm past the glass tube of the vaporizer in order to avoid any electrostatic influence by the glass. The air flow rate through the vaporizer was the same as in the conventional ES experiment, i.e. 0.5 L/sec. The pressure of crown ether can be controlled by either varying the concentration in methanol or the injection flow rate. The solution used for ES contained only the metal halide, M^+X^- salt, and methanol. Under these conditions, gas phase metal ions are produced by ES. The ions can then react with the vaporized crown ether in the gas phase. The reaction products can be detected with the mass spectrometer.

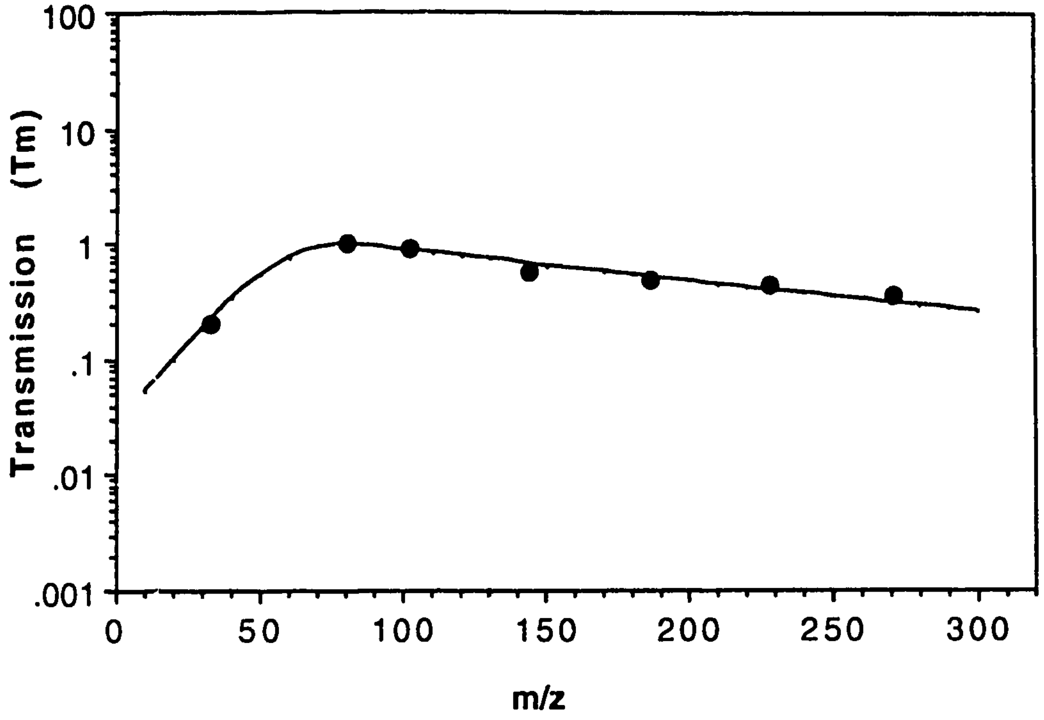


Figure 4-2 Transmission correction curve for ion intensity measurement on TAGA 6000. The seven protonated amine ions are: $CH_3NH_3^+$ (m/z=33), PyH^+ (m/z=80), $Et_3NH_2^+$ (m/z=102), $Pr_3NH_2^+$ (m/z=144), $Bu_3NH_2^+$ (m/z=186), $Pe_3NH_2^+$ (m/z=228), and $Hx_3NH_2^+$ (m/z=271)

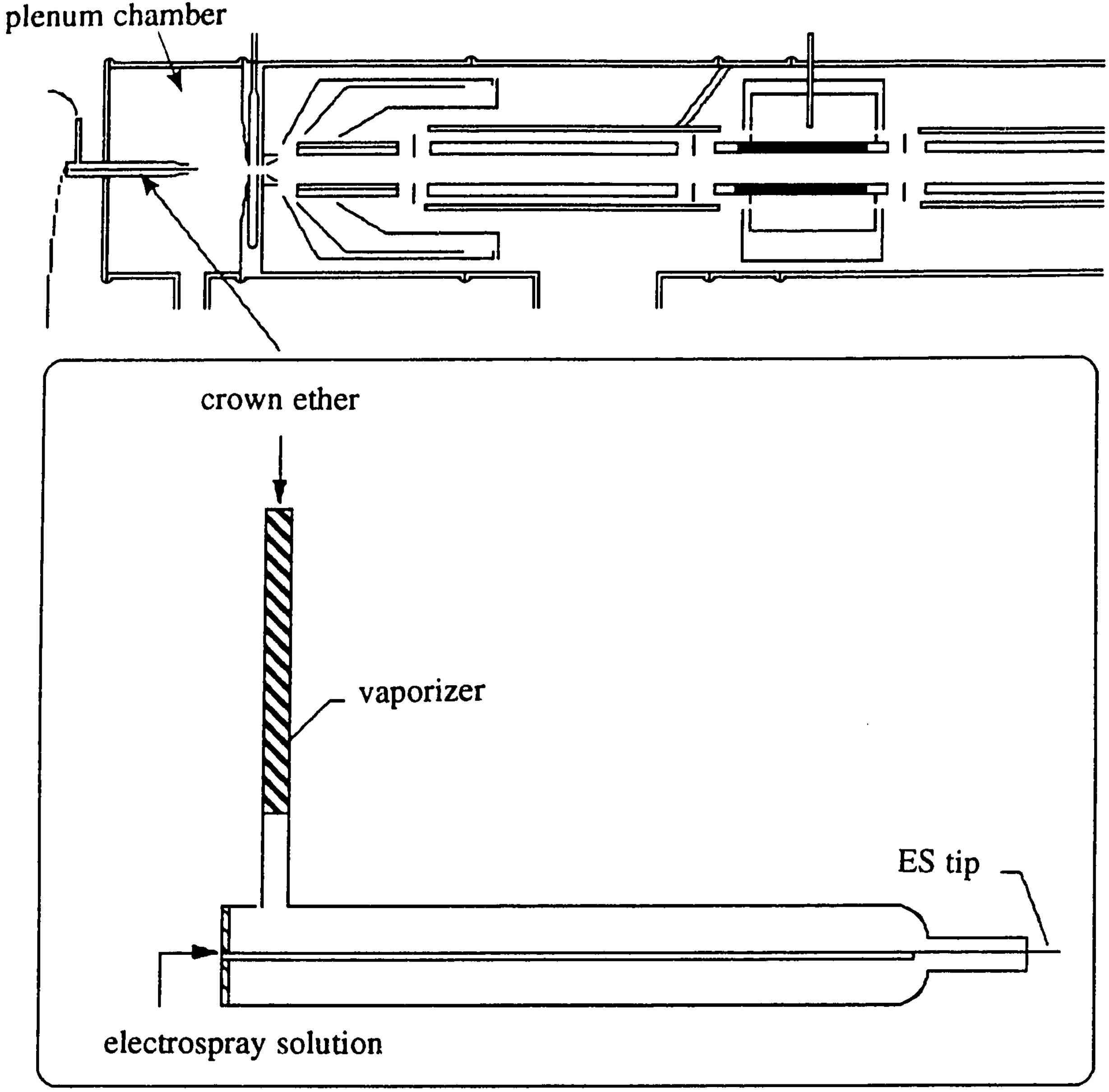


Figure 4-3. Device for the study of gas phase ion molecule reactions. Volatile crown ether is evaporated by vaporizer and transported by air flow to TAGA plenum chamber where it can undergo an exchange reaction with the crown ether-ion from electrospray. ES tip protrudes ca. 1 cm past glass tube. Diameter of glass tube near ES tip is ca. 1 cm (i.d.).

4.3 Results and Discussion

a. Complexation of metal ions and cyclic ligands in solution

The stability constants, K_S, for the complexation of alkali ions with crown ether 18C6 are known (6, 7). Therefore the concentrations of the complex and the free metal ion at equilibrium can be evaluated

$$M^+ + L = M^+L \tag{4-1}$$

$$K_s = \frac{[M^+L]}{[M^+]\,[L]}$$

where $[M^+L]$: concentration of complex (mole/L)

$[M^+]$: concentration of free metal ion (or solvated ion) (mole/L)

$[L]$: concentration of free crown ether (mole/L)

As mentioned in the Introduction, the very small charged droplets that produce the gas phase ions are expected to have lost a large amount of solvent due to solvent molecule evaporation. It was shown in Chapter 3 that the volume ratio, $V_0/V_f = F$, where V_0 is the initial volume at the ES tip and V_f is the volume at the point where gas phase ion emission occurs, can be estimated on the basis of certain assumptions. The factor F could be very high $F \approx 4000$ if the fission of the droplets was symmetric or quite low $F \approx 140$ if the ion emitting droplets were due to non-symmetric fission, see Chapter 3. Furthermore, the assumed size of the ion emitting droplets affected the calculation of F. The concentration of solutes in the ion emitting droplets relative to the initial concentration in the solution is expected to increase by the factor F.

The rationale of the present experiments is to use the equilibrium (4-1) and the measured gas phase ion intensity ratio, I_{ML+}/I_{M+}, in order to obtain an independent experimental estimate of the factor F. Obviously, a large concentration increase due to solvent evaporation will shift the equilibrium (4-1) towards the product side and thus lead to an increase of the ion ratio ML^+/M^+ in the droplet solution. This increase will be reflected in the gas phase ion ratio.

The equilibrium in the ion emitting droplet will be given by:

$$K_s = \frac{C_{M^+L}}{C_{M^+}C_L} \qquad (4\text{-}2)$$

where C_{M+L}: the concentration of M^+L in the ion emitting droplet,

C_{M+}: the concentration of M^+ in the ion emitting droplet,

C_L:the concentration of L in the ion emitting droplet.

In the present experiments the initial concentrations in the solution to be electrosprayed were chosen as: $[M^+] = 10^{-4}$ M = a, $[L] = 10^{-4}$ M. Because the initial concentrations were equal, the equilibrium in the initial solution can be expressed as:

$$K_s = \frac{x}{(a - x)^2} \qquad (4\text{-}3)$$

where x: the equilibrium concentration of ML^+;

(a-x): the equilibrium concentration of M^+ or L.

For the ion emitting droplets the concentrations will have increased by a factor F. Thus the initial concentration before equilibrium would be: $Fa = C_{0M+} = C_{0L}$. Calling the concentration at equilibrium $C_{ML+} = Fy$ then

$$C_{M+} = Fa - Fy = F(a - y)$$

$$C_L = Fa - Fy = F(a - y)$$

substituting in equation 4-2 one obtains:

$$K_s F = \frac{y}{(a - y)^2} \tag{4-4}$$

Equations 4-3 and 4-4 are of the same form.

The gas phase ion ratio I_{M^+L}/I_L can be related to the concentration ratio in the ion emitting droplet by the equation:

$$\frac{I_{M^+L}}{I_{M^+}} = \frac{k_{M^+L}\,C_{M^+L}}{k_{M^+}C_{M^+}} \tag{4-5}$$

as shown in Chapter 3 (see equation 3-10) provided that the ion with the higher coefficient k is in the "high" concentration range, so that no depletion occurs. This condition is met in the present experiments because M^+L is the ion with the higher coefficient, and the concentration of M^+L is in the high concentration range, i.e. $[M^+L] > 5 \times 10^{-5}$ M. The ratio k_{M^+L}/k_{M^+} was determined in experiments where k_{M^+} was obtained with solutions containing only M^+ and k_{M^+L} with solutions of M^+ and L at concentrations such that the dominant ion was M^+L, see Figures 4-4, 4-5. The k_{M^+L}/k_{M^+} values are summarized in Table 4-1. Equation 4-5 can be rewritten as,

$$\frac{I_{M^+L}}{I_{M^+}} = \frac{k_{M^+L}\,C_{M^+L}}{k_{M^+}C_{M^+}} = \frac{k_{M^+L}\,y}{k_{M^+}(a - y)} \tag{4-6}$$

and since y is the only unknown it can be evaluated. Once y has been obtained the product $K_S F$ can be obtained from equation 4-4. Since K_S is known, F can be determined.

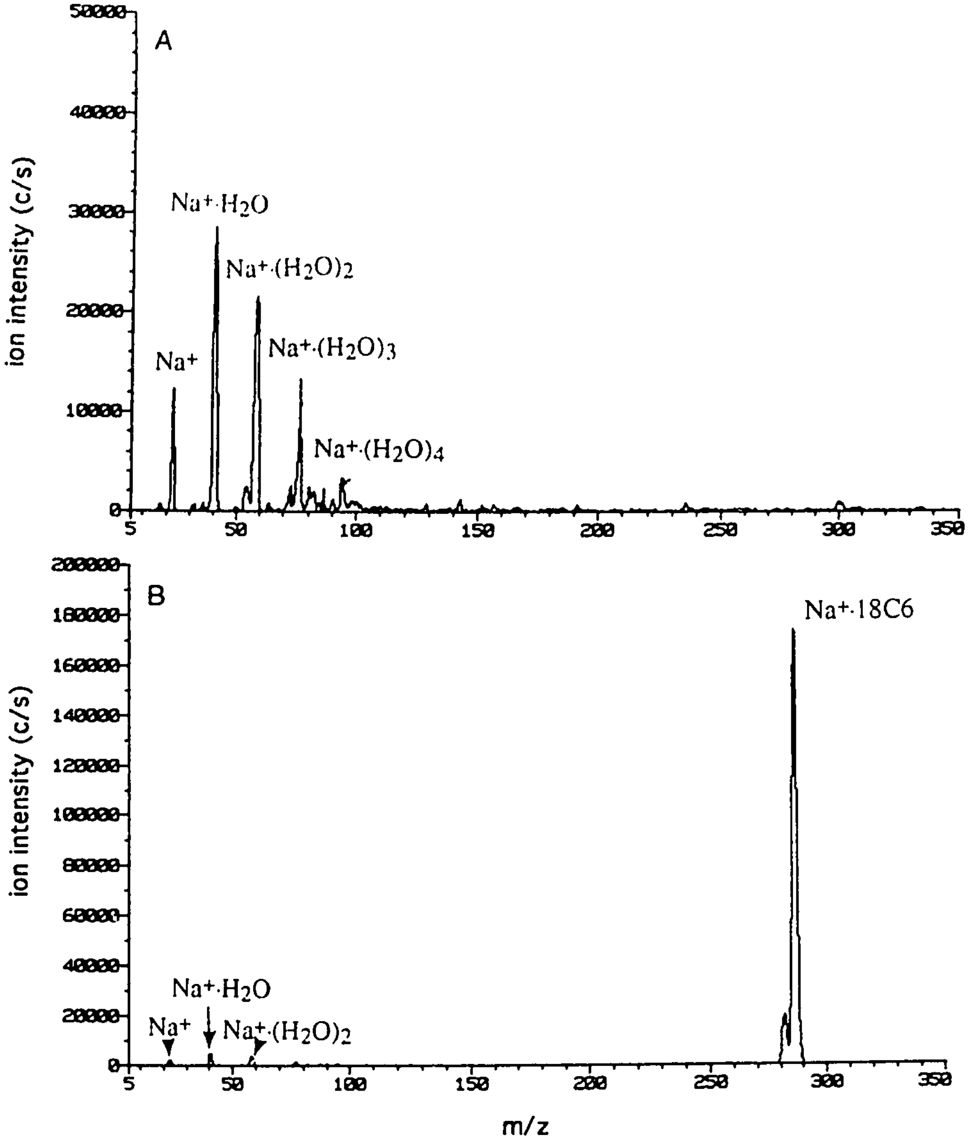


Figure 4-4 Electrospray mass spectra of (A) sodium ion and its solvated clusters from a 10^{-4} M NaCl methanol solution; (B) sodium and crown ether complex ions from a 10^{-4} M NaCl and 10^{-4} M 18C6 methanol solution. Flow rate=20 µL/min.

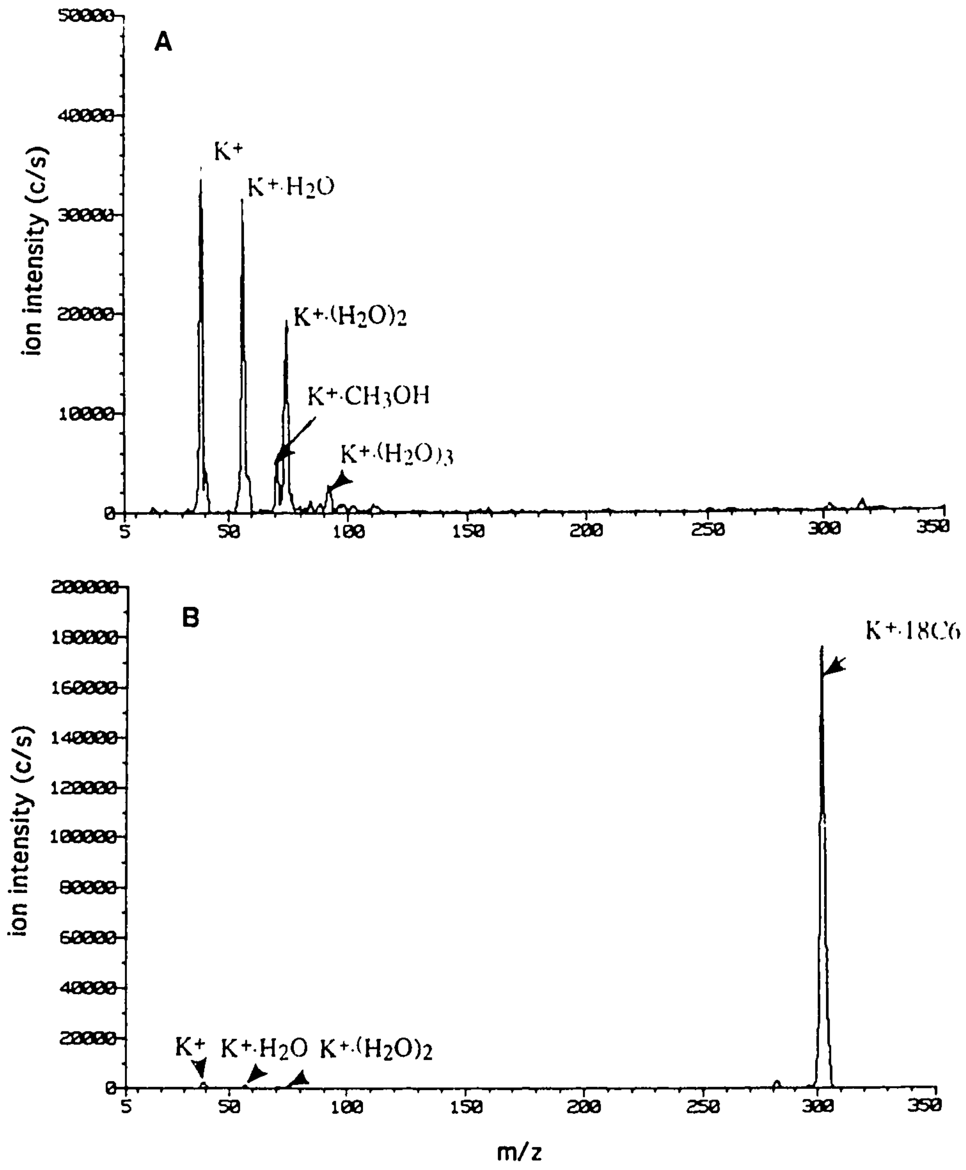


Figure 4-5 Electrospray mass spectra of (A) potassium ion and its solvated clusters from a 10^{-4} M KCl methanol solution; (B) potassium and crown ether complex ions from a 10^{-4} M KCl and 10^{-4} M 18C6 methanol solution. Flow rate=20 μL/min.

Table 4-1. Sensitivity Comparison between Gas Phase Alkali Ion and Complex Ion [a]

M	Li	Na	K	Rb	Cs
$\Sigma M^+(H_2O)_n$ [b] (c/s)	2.0×10^5	2.2×10^5	1.7×10^5	1.7×10^5	1.3×10^5
S.F[c].(18C6)[d]	2.0	2.9	4.1	3.9	2.6

a. Both the metal ion and ligand initial concentrations were 10^{-4} M; Metal ion (or solvated cluster) and crown ether complex were measured using two different solutions.

b. transmission efficiency corrected $\Sigma M^+(H_2O)_n$ in absence of crown ether.

c. sensitivity factor:

$$S.F. = \frac{ML^+}{\Sigma M^+(H_2O)_n} \approx \frac{k_{M^+L}}{k_{M^+}}$$

where L=18C6

d. ratio of total ion currents in presence and absence of crown; total ion current in the presence of crown is mainly of $I(M^+L)$.

Table 4-2. Concentration of Alkali Ion and Crown Ether Complex at Equilibrium in Methanol Solution [a]

M^+	Li	Na	K	Rb	Cs
log K_s[b]	~0	4.32	6.29	5.82	4.44
$[M^+]$[c] (mole/L)		4.93×10^{-5}	6.91×10^{-6}	1.16×10^{-5}	4.48×10^{-5}
$[ML^+]$[c] (mole/L)		5.07×10^{-5}	9.31×10^{-5}	8.84×10^{-5}	5.52×10^{-5}
$\frac{[ML^+]}{[M^+]}$[d]		1.03	13.5	7.64	1.23
$\frac{I_{ML^+}}{I_{M^+}}$[e]		13	48	40	16
$\frac{y}{(a - y)} = \frac{C_{M^+L}}{C_{M^+}}$		4.5	12	10	6.2
y		8.2×10^{-5}	9.2×10^{-5}	9.1×10^{-5}	8.6×10^{-5}
K_sF		2.5×10^{5}	1.5×10^{6}	1.1×10^{6}	4.5×10^{5}
K_s		2.1×10^{4}	1.9×10^{6}	6.6×10^{5}	2.7×10^{4}
F		12	0.8	1.7	16

a. Crown ether (L) is 18C6.

b. K_s (moles/L) values in CH_3OH solution are from references 5 and 6.

c. Calculated concentrations of M^+ and ML^+ in CH_3OH at equilibrium, for initial $[M^+] = [L] = 10^{-4}$ M.

d. Calculated ratio at equilibrium.

e. Ion intensity ratio observed in experiment are corrected for transmission, but not corrected for surface activity and ion emission coefficient differences, see Chapter 3.

Mass spectra obtained with a 10^{-4} M NaCl solution in methanol and with 10^{-4} M NaCl and 10^{-4} M L, when L is the crown ether 18C6, are shown in Figure 4-4. It is evident that the equilibrium is shifted very much to the M^+L complex. The transmission corrected ratio, I_{M^+L}/I_{M^+}, obtained from this experiment where $M^+ = \Sigma M^+(H_2O)_n$ is given in Table 4-2. Similar data obtained for K^+ and 18C6 are given in Figure 4-5, which lead to the ratio I_{K+L}/I_{K+} given in Table 4-2. Results for Rb^+ and Cs^+ obtained in analogous experiments are also included in Table 4-2.

The gradual increase of I_{M+L} and decrease of I_{M+} observed with a series of solutions where $[M^+] = 10^{-4}$ M was kept constant and [L] was increased from 1×10^{-5} M to 2×10^{-4} M is shown for $M^+ = K^+$ and L = 18C6 in Figure 4-6. The changes are consistent with a shift of the equilibrium towards the product M^+L which is expected to occur with an increase of the initial concentration of L. A small decrease of I_{K+L} at $[L] > 10^{-4}$ M is observed. This can be attributed to the formation of a M^+L_2 complex:

$$M^+L + L = M^+L_2$$

The formation of such a complex was detected in the mass spectrum (see Figure 4-7). Such sandwich complexes are known to form both by reactions both in solution (4) and in the gas phase (12). Also included in Table 4-2 are the calculated ratios, C_{M+L}/C_{M+} (see equation 4-6). The evaluated $y = C_{ML+}$ and the factor F relate to the concentration increase in the droplet due to volume shrinkage by solvent evaporation.

The value F obtained is not constant as might be expected but varies from ~1 to 16. It should be noted that the experimental conditions, particularly for K^+ and Rb^+, were not well suited for a determination of the constant, K_sF, because the equilibrium is shifted almost entirely towards the complex side. To obtain a good value for K_sF, the

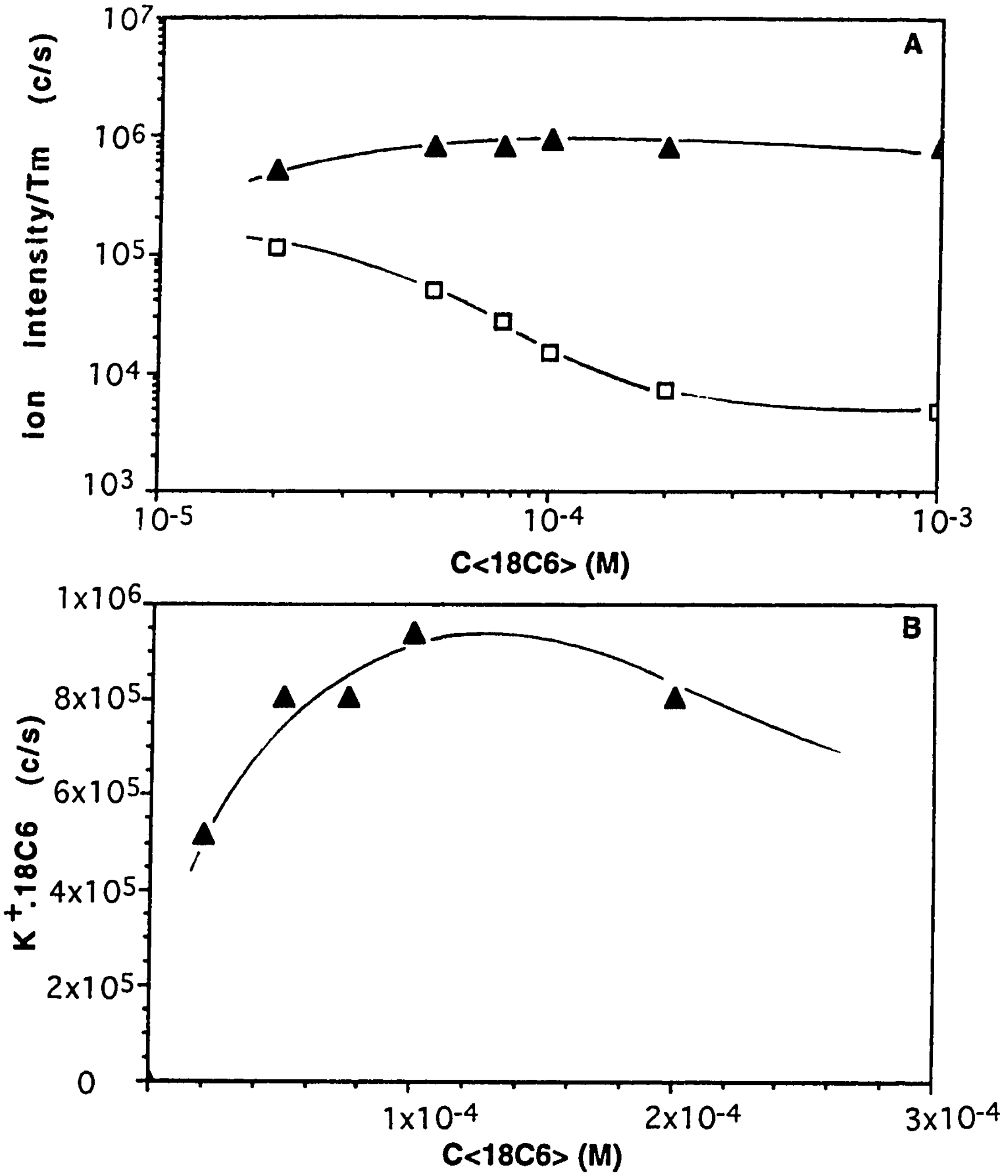


Figure 4-6 Dependence of ion intensities of $K^+ \cdot (Sol)_n$ and $K^+ \cdot 18C6$ on 18C6 concentration: (A) K^+ is transferred to $K^+ \cdot 18C6$ with increase of 18C6 concentration; (B) Change of $K^+ \cdot 18C6$ intensity on a linear scale illustrates that intensity will no longer increase with excess 18C6 in solution. Initial [KCl]=10^{-4} M. □ $\Sigma K^+ \cdot (Sol)_n$; ▲ $K^+ \cdot 18C6$.

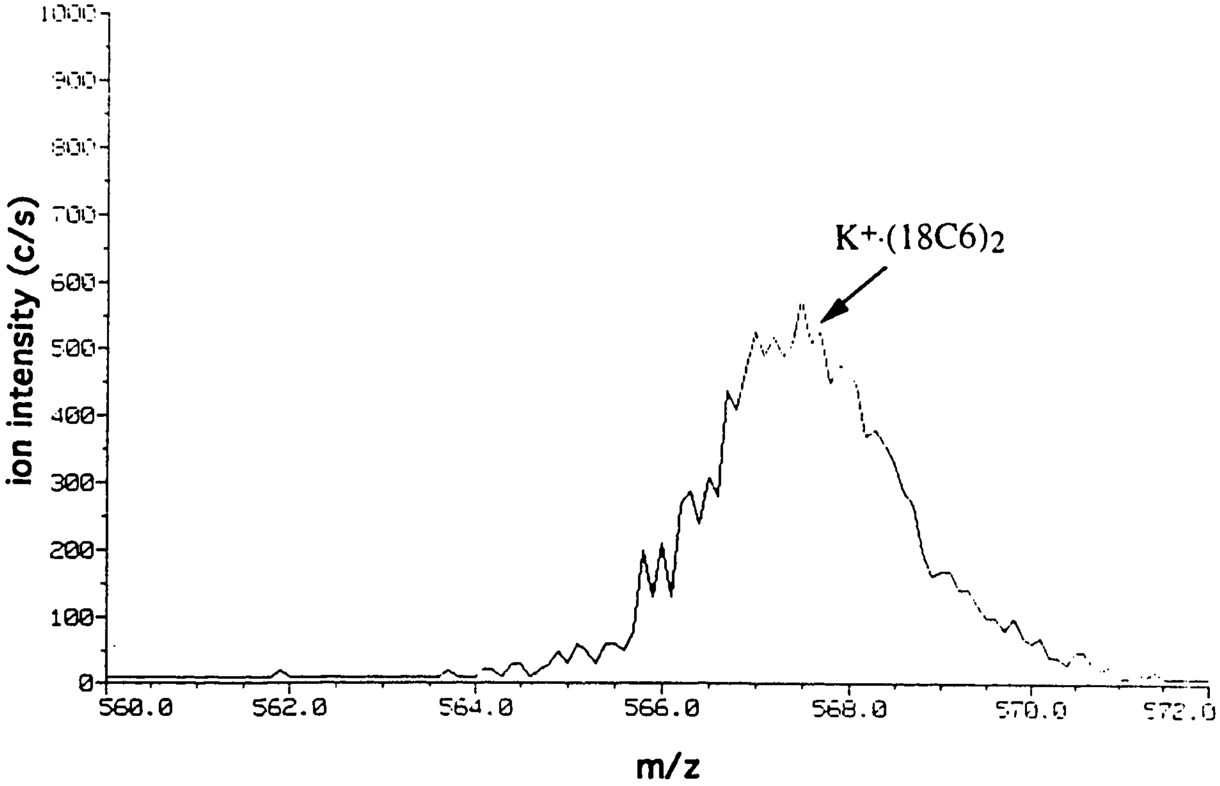


Figure 4-7 Mass spectrum contains a peak due to "sandwich" style complex [$K^+ \cdot (18C6)_2$] (m/z=567) formed when excess crown ether is present in solution; 10^{-4} M KCl and 10^{-3} M 18C6 in methanol solution.

experimental value for I_{M+L}/I_{M+} must be very accurate. But, because I_{M+} is very small, any nonequilibrium source of M^+ ion intensity will have a large effect on the ratio. Sources of nonequilibrium M^+ intensity may be collisional dissociation of the complex in the ion sampling region of the mass spectrometer or slow kinetics for complex formation. An analysis of the kinetics given below indicates that equilibrium may not be attained when K_s is very large as in the case for K^+ and Rb^+. Therefore, we consider the results in Table 4-2 for these two ions unreliable.

Accurate determination of F can be obtained only for cases where C_{M^+L}/C_{M^+} is closer to unity and this requirement is met at least to a certain extent for Na^+ and Cs^+. The F values for these ions are 12 and 16 and thus more in line with the expected concentration increase (see Chapter 3).

The question whether the rate for complex formation is fast enough to allow equilibrium to be attained as the droplets shrink by evaporation, needs to be addressed. Liesegang et al. (16) determined the rate constant for complex formation, $k = 10^9\,(L/mol)s^{-1}$. For an initial concentration of $[M^+] = [L] = a$ of 10^{-4} mol/L, this rate constant leads to an initial half-life for the reaction

$$t_{1/2} = \frac{1}{k_2 a}$$

$$\approx \frac{1}{10^9 \times 10^{-4}} = 10^{-5}\ \text{sec} \qquad (4\text{-}7)$$

It was shown in chapter 3 that the time between droplet fissions are in the 10 to 100 µs time scale. The largest relative volume changes occur for the small droplets. For example (see Figure 3-19 in Chapter 3), offspring droplets of $R = 0.076$ µm shrink to $R_s = 0.029$ µm in 40 µs. The volume decreases by a factor of 20, which means that the concentration of electrolytes should increase by the same factor. It is clear that an adequate answer requires an accurate analysis involving a solution of the appropriate differential equation which includes the time dependence of the concentration due to droplet evaporation in the reaction rate equation. Here we offer only some qualitative considerations. It is clear that the forward rate will increase as the concentration is increased since the rate depends on the square of the concentration, i.e. the product of C_{M+} and C_L. An increase of the concentration will require a shift of the equilibrium to the product side but this shift will be facilitated due to the increased rate of the reaction with concentration.

The time required for a droplet of radius R_0 to decrease its volume by a factor of 2 can be evaluated with equation 3-17. It is given by equation 4-8a, while 4-8b provides the time for a $R_0 = 0.076$ µm droplet.

$$t_{\text{volume halflife}} = R_o \times 1.72 \times 10^2 \text{ ses} \qquad (4\text{-}8a)$$

$$= 0.076 \times 10^{-6} \times 1.72 \times 10^2$$

$$= 1.3 \times 10^{-5} \text{ sec} = 13\ \mu\text{s} \qquad (4\text{-}8b)$$

The time is approximately the same as the reaction halflife, see equation 4-7. However the equilibrium needs to shift less than the concentration shift by a factor of 2 calculated in equation 4-7.

This can be illustrated by the following model calculation for Cs^+. Assume that the concentration before the volume reduction corresponds to $a = 1 \times 10^{-4}$ M, see equation 4-3. The concentrations at equilibrium are shown below on the left most side written as an equilibrium quotient:

$$\frac{C_{M^+L}}{C_{M^+}C_L} = \frac{0.55 \times 10^{-4}}{0.45 \times 10^{-4} \times 0.45 \times 10^{-4}} \xrightarrow{I} \frac{1.1 \times 10^{-4}}{0.9 \times 10^{-4} \times 0.9 \times 10^{-4}}$$

$$\xrightarrow[\Delta t = 3\ \mu s]{II} \frac{1.3 \times 10^{-4}}{0.7 \times 10^{-4} \times 0.7 \times 10^{-4}} \qquad (4\text{-}9)$$

Process I corresponds to an instant volume reduction by a factor of two corresponding to an instant concentration increase by the same factor. Process II is the reactive relaxation towards the new equilibrium concentrations which are shown at the right of equation 4-9. It is seen that the reactive change of concentrations $C_{M+} = C_L$ is only from 0.9×10^{-4} to 0.7×10^{-4} mol/L. The time t required for this concentration change, calculated with the rate equation:

$$\frac{1}{C} - \frac{1}{C_o} = kt \qquad k = 10^{9}\ LM^{-1}s^{-1} \qquad (4\text{-}10)$$

is t=3.2 µs, i.e. considerably smaller than the 13 µs required for the droplet shrinkage. Therefore, for these conditions near equilibrium concentrations will be maintained closing the droplet shrinkage.

It is important to note that the rate of reactive relaxation to equilibrium may not be fast enough when K_s is vary large or when K_sF is very large, such that the equilibrium is shifted far to the right and the concentration of $C_{M+} = C_L$ is very low. Shown below are the equilibrium quotients for K^+ and 18C6, calculated for a = 10^{-4} M and $K_s = 1.9 \times 10^6$.

$$\frac{C_{M^+L}}{C_{M^+}C_L} = \frac{0.93 \times 10^{-4}}{0.07 \times 10^{-4} \times 0.07 \times 10^{-4}} \xrightarrow{I} \frac{1.86 \times 10^{-4}}{0.14 \times 10^{-4} \times 0.14 \times 10^{-4}}$$

$$\xrightarrow{\text{II}} \frac{1.9 \times 10^{-4}}{0.1 \times 10^{-4} \times 0.1 \times 10^{-4}} \qquad (4\text{-}11)$$

Processes I and II have the same meaning as in the example for Cs^+ above. The time evaluated with equation 4-10 for change II is $t = 29\ \mu s$. The time is much longer because the initial concentration $C_0 = C_{K+} = C_L$ for K^+, which has a much higher K_s, is much smaller. In this case the reaction time is longer than the droplet shrinkage time. Furthermore, the scheme of process I-II leads to shorter reaction times than actually expected since it is assumed in process I that the concentration increases instantaneously. These results show that the complex equilibrium will not be established for K^+ and Rb^+, when the droplet becomes very small and the rate of volume changes is very rapid. Of course, these are tentative conclusions since the rate of solvent evaporation predicted by equation 3-17 and 4-8 is only an estimate (see Chapter 3). Nevertheless it is possible that the disagreement with the expected volume shrinkage factors F for the high K_s ions K^+ and Rb^+ is due to slow kinetics, as illustrated above.

Unfortunately, the experimental results for I_{ML+}/I_{M+} may be affected also by another process which has not been considered so far. The electrospray process is a nebulizing process and neutral solutes present in the solution can be efficiently transferred to the gas phase. For example, the crown ether may be sufficiently volatile that the uncomplexed molecule may enter the gas phase and react with gas phase M^+ ions produced by the electrospray in gas phase ion-molecule reactions: $M^+ + L = M^+L$. The possible effect of such a reaction on the results summarized in Table 4-2 is considered in the next section.

b. Gas phase reactions of metal ions and macrocyclic ligands

It is well known that crown ethers have high proton affinities in the gas phase (8, 9) and that they also have strong tendency to form gas phase ion complexes (10-13). In electrospray, formation of the M^+L complex could occur also in the gas phase from gas phase M^+ ions produced by ES and gas phase L evaporated from the small droplets produced by the ES nebulization process. Therefore, it is necessary to investigate the relative importance of gas phase complexation.

The possibility of gas phase reactions of metal ions (and their solvates) with a crown ether was examined by the method illustrated in Figure 4-3. The spectra in Figure 4-8 show that sodium ion-crown ether complexes do form in the gas phase. However, after the intensities have been corrected for transmission efficiency, only about 10% of the sodium ions do react. In the case where both sodium chloride and crown ether are present in the solution, the solution concentration of Na+ is much smaller. Thus, very much less free Na^+ will result in free Na^+ ions in the gas phase and, equally, less free crown ether is available to contribute to gas phase ion-molecule reactions. The contribution of gas phase complexation to the total gas phase ion Na^+L intensity will be much less than 10%.

Similar considerations should hold also for the potassium, rubidium and cesium complexes. For the Lithium ion, with a much smaller complex formation constant, K_S, the Li^+ and crown ether concentration in the gas phase are higher and the observed I_{Li+L} in Table 4-1 might include a substantial contribution from gas phase ion molecule reaction.

Some additional gas phase reaction related experiments, not directly connected with the interpretation of the data in Table 4-2 will be presented below because they are of some general interest.

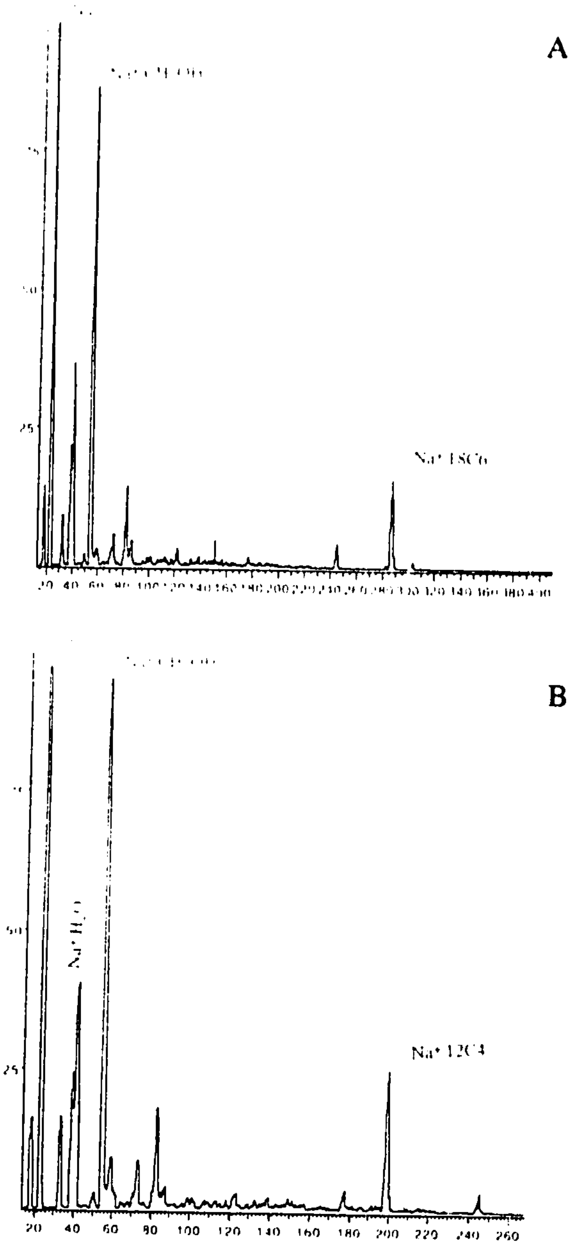


Figure 4-8 Mass spectra obtained from experiment where M^+ is produced by ES and a given crown ether is vaporized as shown in Figure 4-3: (A) Crown ether 18C6, (B) Crown ether 12C4. 10^{-4} M NaCl and 10^{-4} M crown ether are used in (A) and (B). The flow rates of the solution of the ligand L and the solution of NaCl were the same, 20 µl/min.

It is believed that maximum complex stability is obtained when a crown ether has a cavity size similar to that of ion (4). Even though there is still uncertainty as to the solvation contribution in solution (15), it is certain that macrocyclic effects and size-selective reactivity dominate in gas phase (14). Lithium was chosen as an example. Lithium, with the smallest ion radius of all alkali ions, has a large stability constant in lithium 12-crown-4 complex, while 12-crown-4 (12C4) is relative volatile among crown ethers. In the experiment lithium chloride and 18C6 methanol solutions were electrosprayed. At the same time, a pure 12C4 methanol solution was introduced by a vaporizer connected to the glass tubing. It was found that lithium 12C4 complex ion was formed in gas phase. The gas phase reaction can be written as

$$\mathrm{Li^{+}\cdot 18C6_{(g)} + 12C4_{(g)} = Li^{+}\cdot 12C4_{(g)} + 18C6_{(g)}} \qquad (4\text{-}12)$$

This discovery also supports that the ligand (L) and ion reaction can happen in the gas phase as well as in the liquid phase. The ion intensity of $\mathrm{Li^{+}\cdot 12C4}$ is weaker than the ion intensity of $\mathrm{Li^{+}\cdot 18C6}$ by a factor of 100 although the former is favored because of size-selectivity (14) (see Figure 4-9). Maleknia and Brodbelt found that the selectivity of complexation of crown ether and metal ions in the gas phase is different from that in the liquid phase (10). The best selectivity of a crown ether in solution is for the metal ion whose ionic radius fits best the cavity size of the crown ether. But, the selectivity of crown ether in gas phase will be for a slightly smaller ion due to the achievement of a higher electric field-dipole interaction within the cavity for a given conformation of the ether. This concept is referred as "maximum contact point" (10).

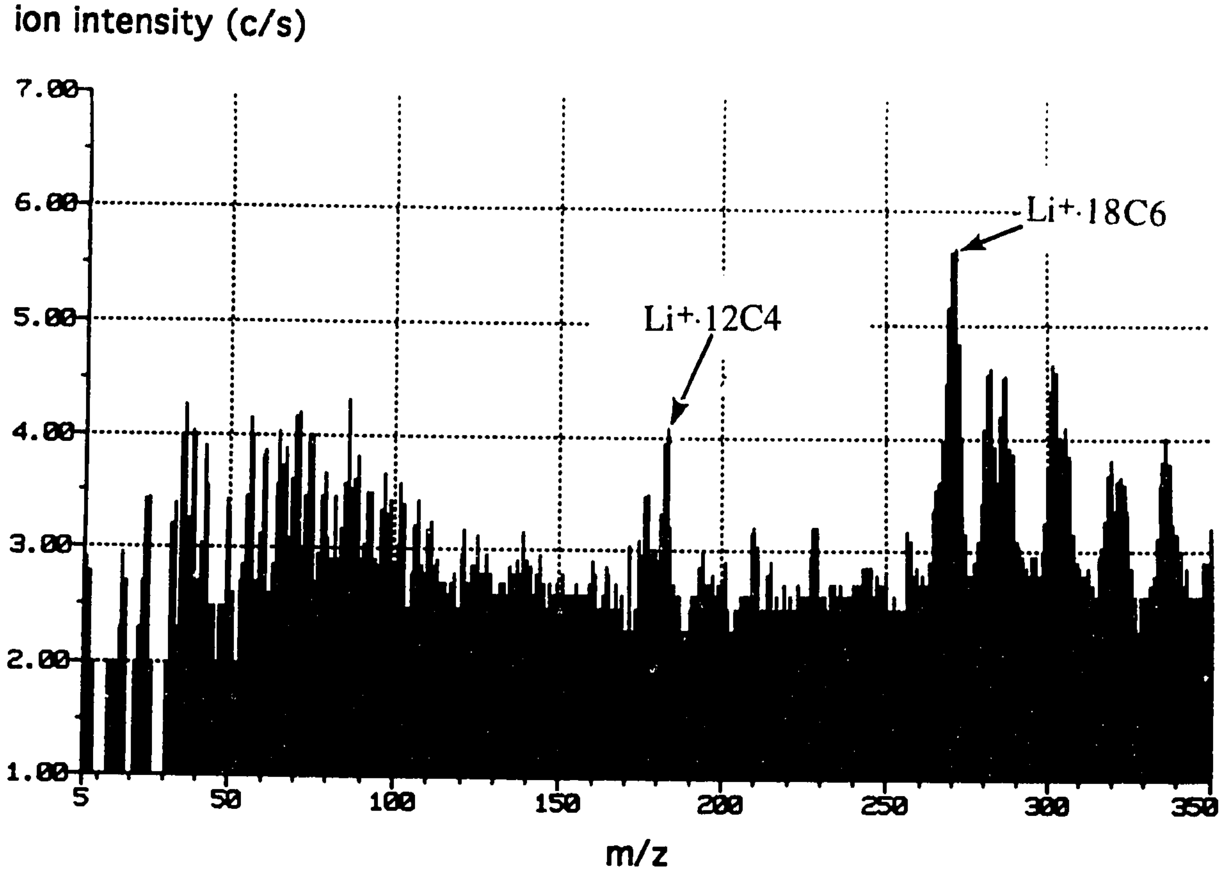


Figure 4-9 Crown ethers 12C4 and 18C6 undergo gas phase ion-molecule exchange reaction: $M^{+}\cdot 18C6 + 12C4 = M^{+}\cdot 12C4 + 18C6$. Gaseous $M^{+}\cdot 18C6$ is produced by electrospray and 12C4 by a vaporizer.

Due to the ion evaporation mechanism, the gas phase metal ions produced by electrospray are actually solvated clusters, see Figure 4-10. If "maximum contact point" dominates the gas phase complexation process of crown ether and metal ion, the formation of the host-guest complex is not favored because most solvated clusters have a larger size than the cavity of 18C6. Thus, most of M^+L complex ions should be formed in solution instead of in gas phase. However, the contribution of gas phase complexation should also be considered when the sensitivity enhancement by complexation is going to be assessed.

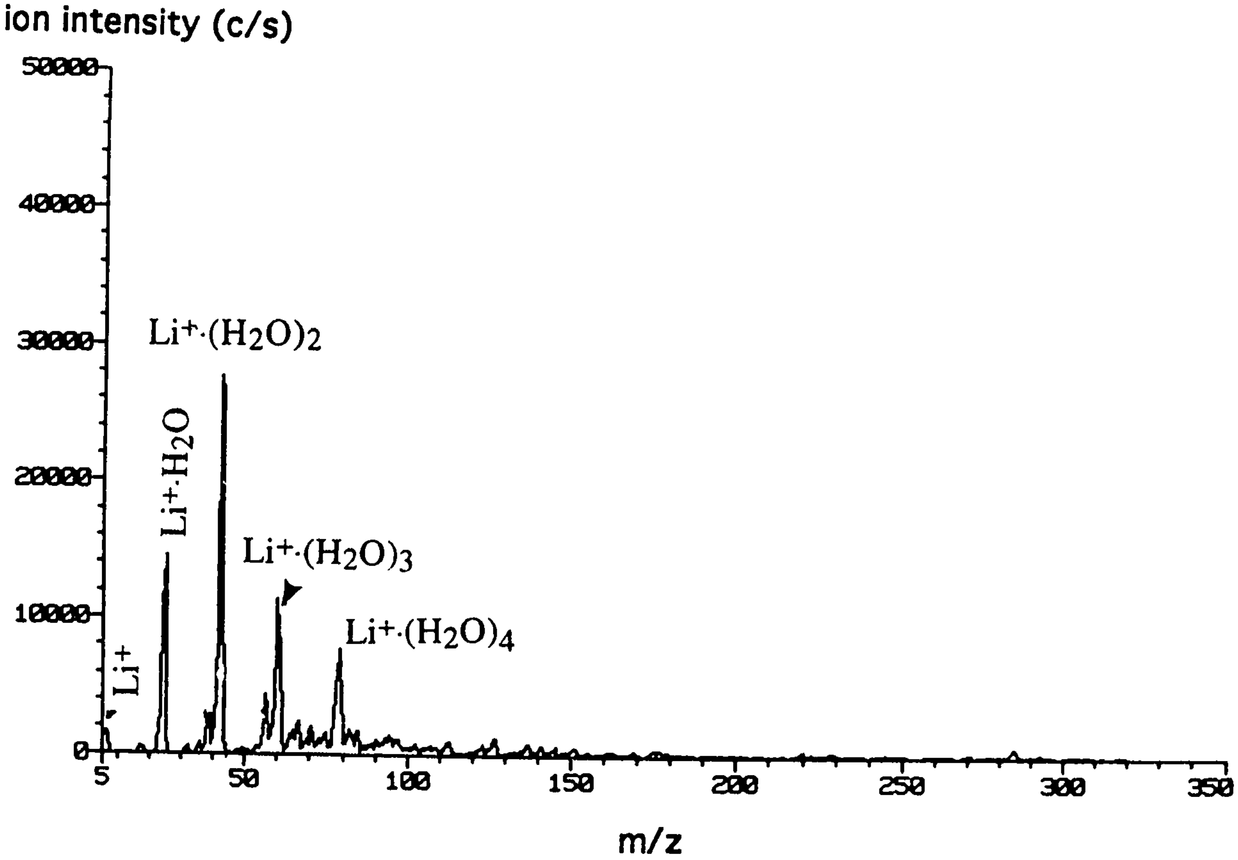


Figure 4-10 Electrospray mass spectra of lithium chloride in methanol solution; gas phase lithium ions are mainly in the form of solvated clusters; [LiCl]=10^{-4} M in methanol.

4.4 Conclusions

Measured ion intensity ratios: I_{ML+}/I_{M+} of electrosprayed solutions of M^+ and L in methanol where $M^+ = Na^+, K^+, Rb^+, Cs^+$ and L = 18C6, are compared to the expected ion ratios due to the solution equilibria and due to an increase of solute concentrations because of solvent evaporation from the droplet prior to gas phase [illegible]on from the droplets. K^+ and Rb^+ have very high stability consta[illegible]nd the equilibria are shifted too far to the product (M^+L) side. The [illegible]$/I_{M+}$ for these systems do not provide a confirmation for a large evaporative solvent loss. The position of the equilibria for Na^+ and Cs^+ which have lower K_s values are more suitable for the measurements and these systems indicate a decrease of solvent volume by a factor of ~15. This factor is smaller than expected in chapter 3 but still of sufficient of magnitude to indicate that there is a large loss of solvent which will lead to important changes of the solute concentration in the droplets.

4.5 References

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Chapter 5 Sampling Efficiency in ESMS

5.1 Introduction

In electrospray, the solution sprayed from the electrospray tip consists of unipolarly charged droplets. For the positive-ion mode of ESMS, the droplets have excess positive ions and a positive electrical current, resulting from the positively charged droplets, flows from the electrospray tip towards the counter electrode on the mass spectrometer. Because this cloud of droplets is charged, it gives rise to a radial electrostatic field E which increases with distance from the axis of the cloud, where it is zero, to a maximum value at the outer edge of the cloud. This field acts upon the charged droplets and drives them radially outwards.

The field strength due to the space charge can be assessed with the Poisson equation (1). Since a cross section of the charged-droplet cloud may be considered to have cylindrical symmetry, the Poisson equation in cylindrical coordinates can be applied:

$$\frac{1}{r}\frac{d}{dr}\left[r\frac{dV}{dr}\right] = -\frac{\rho}{\varepsilon_o}, \qquad \text{where} \qquad (5\text{-}1)$$

r: radial distance from the axis of the cloud to the edge of the cloud

V: potential of charged-droplet cloud

ρ: space charge density

ε_0: permittivity of vacuum.

Substituting the field, E = dV/dr, into equation 5-1 and integrating one obtains

$$E = -\frac{\rho r}{2\varepsilon_0} \qquad (5\text{-}2)$$

If the number density of charged droplets in the cloud is n and each droplet is assumed to carry the same quantity of charge q, the charge density ρ is

$$\rho = nq \qquad (5\text{-}3)$$

The radial, coulombic force F on the droplets within the cloud is given by

$$\begin{aligned} F &= qE \\ &= nq^2r/(2\varepsilon_0) \qquad (5\text{-}4) \end{aligned}$$

The effect of the radial field due to the space charge is very noticeable in photographs of the electrospray jet (2) which show that the droplet cloud expands radially very rapidly. Sunner et al. (3) were among the first to propose that the space charge will have an important influence on the observed ion intensities in ESMS. The presence of the radial space charge induced electrical field suggests that it is desirable to sample the ions as close to the ES capillary tip as possible, in order to achieve maximum MS sensitivity. On the other hand it is not desirable to sample too close to the ES tip because gas phase ions may not yet have been formed from the droplets. Also, at close distance, the average droplet size is relatively large and evaporation of the droplet in the sampling region will lead to undesirable high solvent vapor pressure and ion-solvent cluster formation. In practice (4) a compromise between the conflicting requirements is chosen which depends also on the details of the ion sampling arrangement. For example, when the interface to the vacuum is via a capillary (5), heating of the capillary causes solvent evaporation from the droplet and ion declustering, and in such a case the distance between the ES capillary tip and the sampling orifice can be shorter.

From the above discussion, it is evident that the space-charge effect may influences the mechanism of gas phase ions produced from the charged droplets (see Chapters 3 and 4). For example, one can question whether the space-charge causes relative ion-detection sensitivities to change. In our work, Chapter 3 and 4, we assumed that the relative sensitivity coefficients, k_A/k_B, for various ion species A^+ and B^+ depend only on Iribarne-type ion evaporation differences or differential surface enrichment effects, i.e. the tacit assumption was made that species-selective space charge effects are unimportant.

The effect of the radial field on the ions will change relative intensities if the gas phase ion mobilities of A^+ and B^+ are significantly different. Ion mobilities are approximately proportional to $(\mu/\alpha)^{1/2}$ where α is the polarizability of the ambient gas (N_2, O_2, CH_3OH, etc) and μ is the reduced mass of the ion and ambient gas molecule. For ions whose mass is considerably higher than the mass of the ambient gas (~30) the reduced mass becomes equal to that mass (6). Such ions, which include the majority of ES ions of interest, will have very similar mobilities. On this basis selectivity affecting k_A/k_B due to space charge is not expected. However, the situation may be more complicated.

Hiraoka (7) recently published measurements of relative intensities of ESMS ions as a function of the axial and radial positions of the ion sampling orifice relative to the ES capillary tip. In the measurements, the author changed the position of the ES capillary, leaving the sampling orifice position constant. The solution used was 10^{-3} M acetic acid and 5×10^{-6} M $(CH_3)_4NBr$ in methanol. The author observed large changes in the positive ion intensities with axial and radial distance. The results for axial distance are given in Figure 5-5 in the Discussion section. The observed major ions were $CH_3OH_2^+$, NH_4^+ and $(CH_3)_4N^+$. The $(CH_3)_4N^+$ ion is expected, as is $CH_3OH_2^+$ due to the protonation of CH_3OH by acetic acid in the solution. However the presence of NH_4^+ is unexpected since this cation was not added to the solution. The NH_4^+ could be formed by the gas phase ion-molecule reaction:

$$CH_3OH_2^+(g) + NH_3(g) = CH_3OH(g) + NH_4^+(g) \quad (5\text{-}5)$$

where $NH_3(g)$ is due to the presence of ammonia in the ambient air. This reaction is routinely observed in our laboratory whenever NH_3 at concentrations equal to greater than ~10 ppb is present in the laboratory air. Therefore, the presence of NH_4^+ in Hiraoka's results represents a complication and is essentially a flaw in his experiments. In our opinion, he should not have used a precursor ion like $CH_3OH_2^+$ which is due to a base (CH_3OH) of low proton affinity, and is therefore easily deprotonated by gaseous impurities. Also, all the observed $CH_3OH_2^+$ in Hiraoka's experiment may not be due to ion desorption from solution. Corona discharge produces this ion in abundance in the gas phase when a methanol solution is electrosprayed (8). Hiraoka did add CCl_4, as a discharge suppressant, to the methanol solution. However, he provides no specific evidence that the CCl_4 is able to suppress the discharge at small axial distances.

Hiraoka's results interpreted his results on the basis of differential ion-evaporation efficiencies, i.e. k_A/k_B ratios in our nomenclature. It was suggested that $(CH_3)_4N^+$, which is expected to have a high k_A, evaporates from the droplet before the other ions and its ion profile is interpreted on that basis (7).

While the intent and interpretation of Hiraoka's experiment are interesting, they are not concordant with the models of gas phase ion formation considered in Chapter 3, where it was concluded that gas phase ions are formed from very small droplets whose lifetime (several µs) is very much shorter than the total lifetime of the droplets emitted from the ES capillary (~100 µs). The interpretation used Hiraoka implies a rather long duration of the ion emission stage of a droplet, i.e. a duration comparable to the total transit time of a droplet from the ES capillary tip to the sampling orifice (~100-1000 µs).

In an attempt to resolve this contradiction, we decided to perform experiments of the same kind as those of Hiraoka's. We did not use $CH_3OH_2^+$ as one of the ions, but a species that must be produced by the ES process and is not reactive in the gas phase. Therefore, the solution that we used contained equimolar KCl and $(C_2H_5)_4NBr$ at concentrations of 5×10^{-5} M in methanol. It should be recalled (Chapter 3) that Et_4N^+ is an ion with a higher sensitivity coefficient than K^+. Therefore, this pair of ions has different ion sensitivity coefficients as was the case in Hiraoka's experiment, but is not affected by gas-phase ion-molecule reactions.

5.2 Experimental

The experiments were performed with the TAGA 6000E which was described in Chapter 3. In the present experiments, the position of the electrospray tip relative to the aperture of the mass spectrometer was changed in three dimensions. The axial distance (L) between the ES tip and the aperture was varied by moving the supporting rod of the ES tip in an axial direction, z, while the radial distance (r) between the ES tip and the aperture was varied by adjusting the position of the x-y manipulator as shown in Figure 5-1. The flow rate of the spray solution was controlled by changing the selector positions on the syringe pump (syringe pump model 341B, Sage Instrument).

When the effect of axial distance on the detected ion intensity was investigated, the experiments were conducted in two modes. One is the constant voltage mode, which keeps the voltage on the capillary tip constant, the other is the constant current mode, which changes the voltage on the capillary tip to maintain constant ES current. It should be recalled that the ES current is a function of the electrical field on the capillary tip as stated in Chapter 2, while this electrical field depends on both voltage and axial distance (9). The object of the constant voltage mode was to examine the ion intensity dependence on the axial distance. However, the electrical discharge at short distance results in severe interferences. It was found that this problem could be obviated with the constant current mode.

5.3 Results and Discussion

a. Ion intensity dependence on axial distance between ES tip and ion sampling orifice

When a solution of Et_4N^+ and K^+ in methanol was used, the ion intensities changed with axial distance as shown in Figure 5-2 and 5-3. The K^+ ion species were K^+, $K^+{\cdot}H_2O$ and $K^+{\cdot}CH_3OH$. The intensity ratios for these three species change somewhat with distance. Thus, the $K^+{\cdot}CH_3OH$ intensity increased as the distance is decreased. We attribute this effect to penetration of methanol droplets into the interface chamber at short

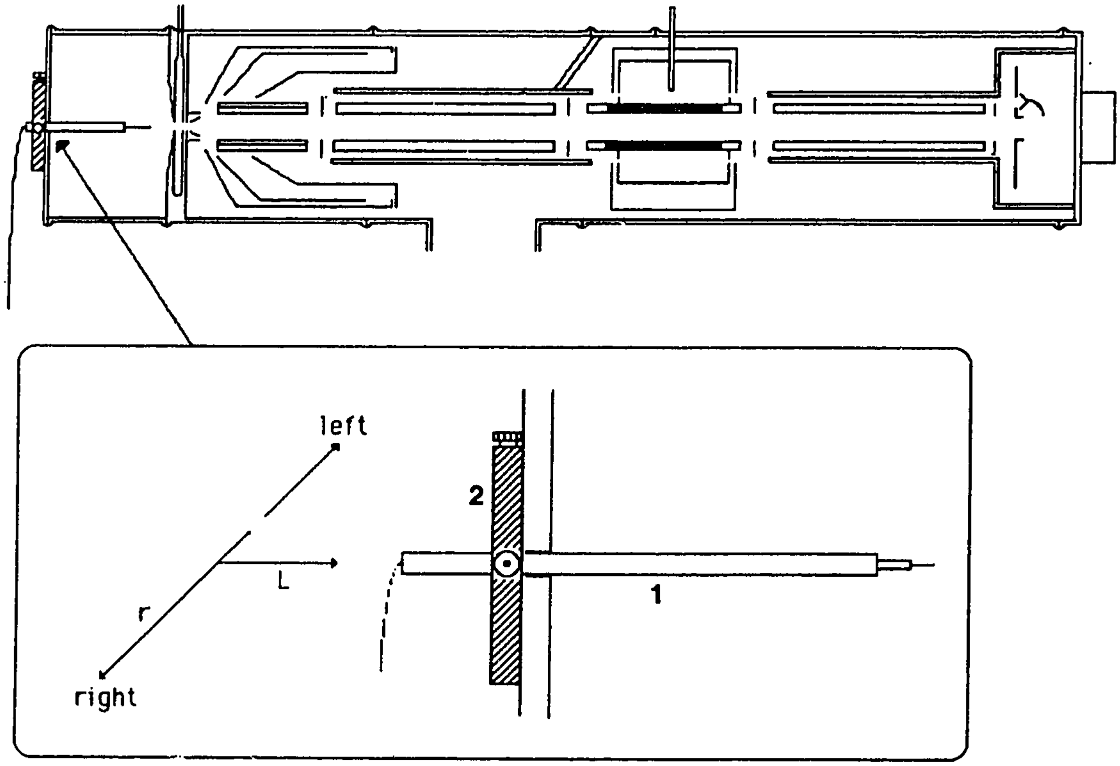

Figure 5-1 The position of electrospray tip is controlled by moving either supporting rod or x-y manipulator. 1. supporting rod; 2. x-y manipulator.

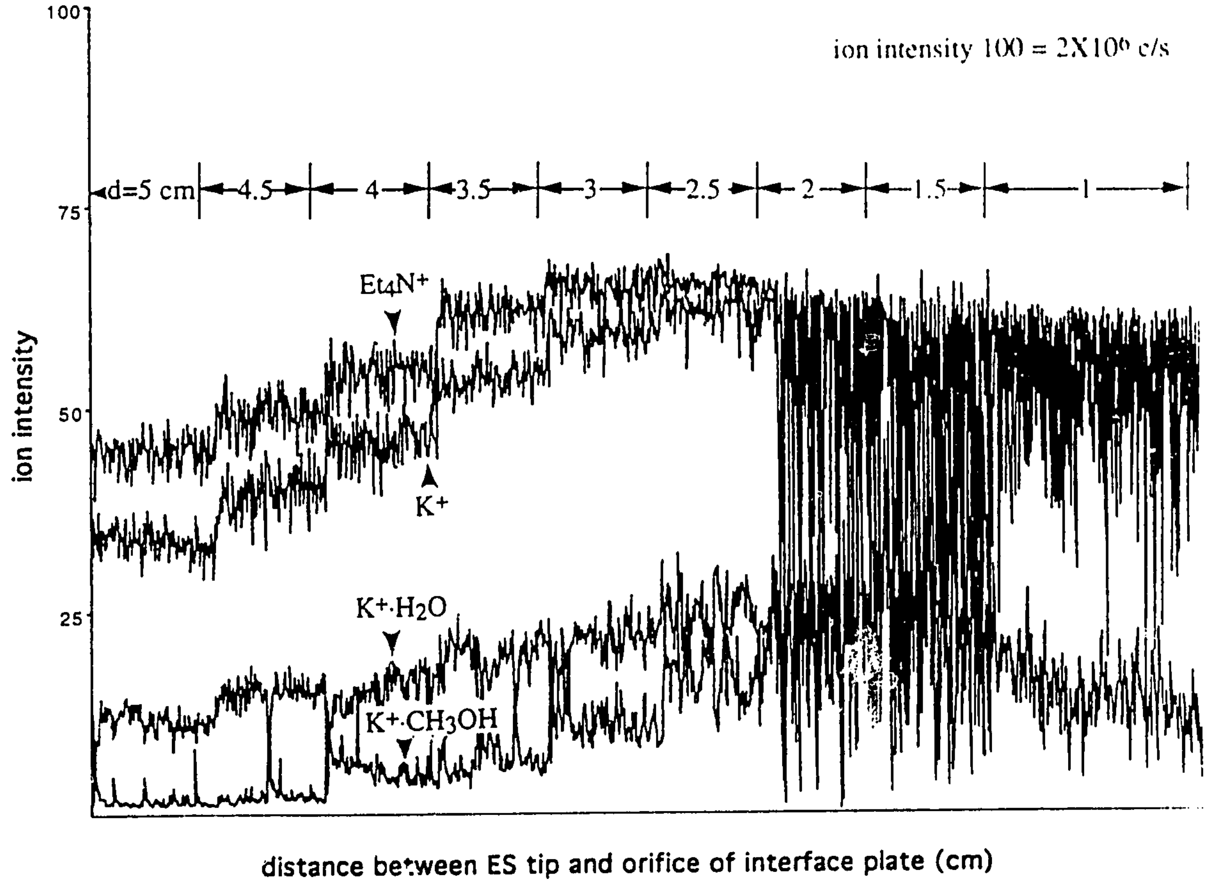

Figure 5-2 The axial distance dependence of ion intensities of Et_4N^+ and $K^+{\cdot}(Sol)_n$ at constant ES voltage. Methanol solution contained $5x10^{-5}$ M Et_4NBr and $5x10^{-5}$ M KCl. Experimental conditions were with r=0 mm, F=20 µL/min and constant capillary voltage V=5 kV.

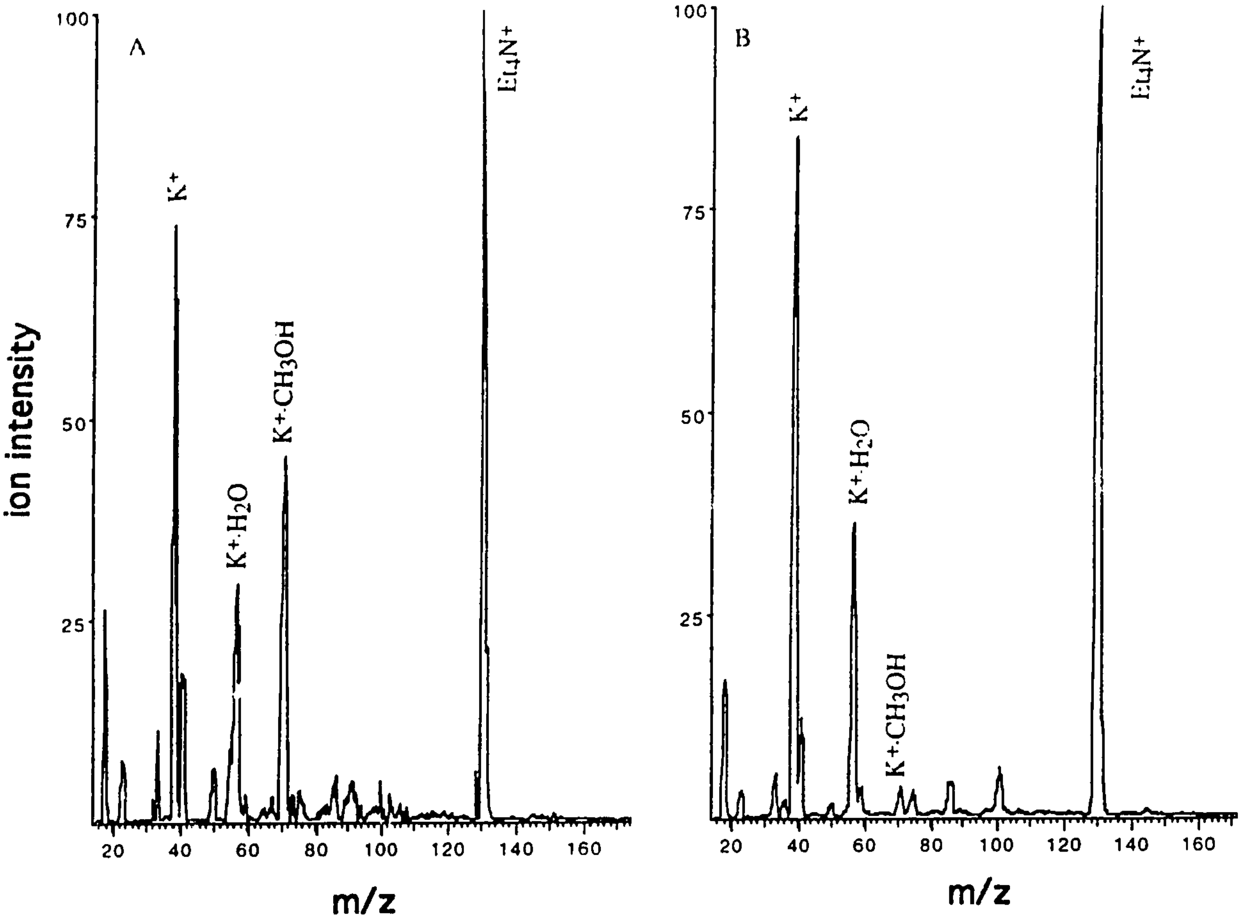

Figure 5-3 The distance (L) change of ES tip from opposite electrode on the mass spectrometer shifts the relative ion intensities of $K^+ \cdot H_2O$ and $K^+ \cdot CH_3OH$. Both KCl and Et_4NBr concentrations were 5×10^{-5} M. (A) L=2.5 cm; (B) L=4 cm.

distances, see Figure 3-1 of apparatus in Chapter 3. Methanol evaporating from these droplets leads to methanol vapor in the interface region which competes with the 2 ppm water vapor in the N_2 gas present in the interface chamber. This leads to a clustering reaction of CH_3OH with the potassium ion.

The Et_4N^+ ion, which has a much larger radius than K^+ and hydrophobic substituents, has much lower binding affinity for a solvent molecule and is observed only as the naked ion Et_4N^+. To compare the Et_4N^+ with K^+ ion intensities, we summed over all the K^+ ion intensities. These data are given in Table 5-1, for both constant voltage and current modes. For constant voltage mode we included data only down to distances of 2.5 cm because electrical discharges apparently occur at smaller distances. This is indicated by the very noisy ion signals at distances less than 2.5 cm in Figure 5-2 in constant voltage mode. As the distance (L) is decreased, the electric field near the capillary tip increases as indicated by equation 2-8 in Chapter 2. Evidently, the field becomes large enough to initiate an electric discharge for d<2.5 cm. The ratio between the ion intensities, Et_4N^+/K^+, at constant V in Table 5-1 is seen to change little, i.e. from 2 at d = 5 cm to 1.4 at d = 3 cm, after correction for mass discrimination. The increase of ES capillary current with the decrease of axial distance is expected, see Hendricks equation

$I = \left(\frac{4\pi}{\varepsilon}\right)^{3/7} (9\gamma)^{2/7} \varepsilon_0^{\ 5/7} Q^{4/7} (\sigma E_c)^{3/7}$ in Chapter 2.

The ion intensities shown in Figure 5-4 were obtained in the constant capillary current mode with I = 0.2 μA. In this case an electric discharge at low distance does not occur and undisturbed ion intensities

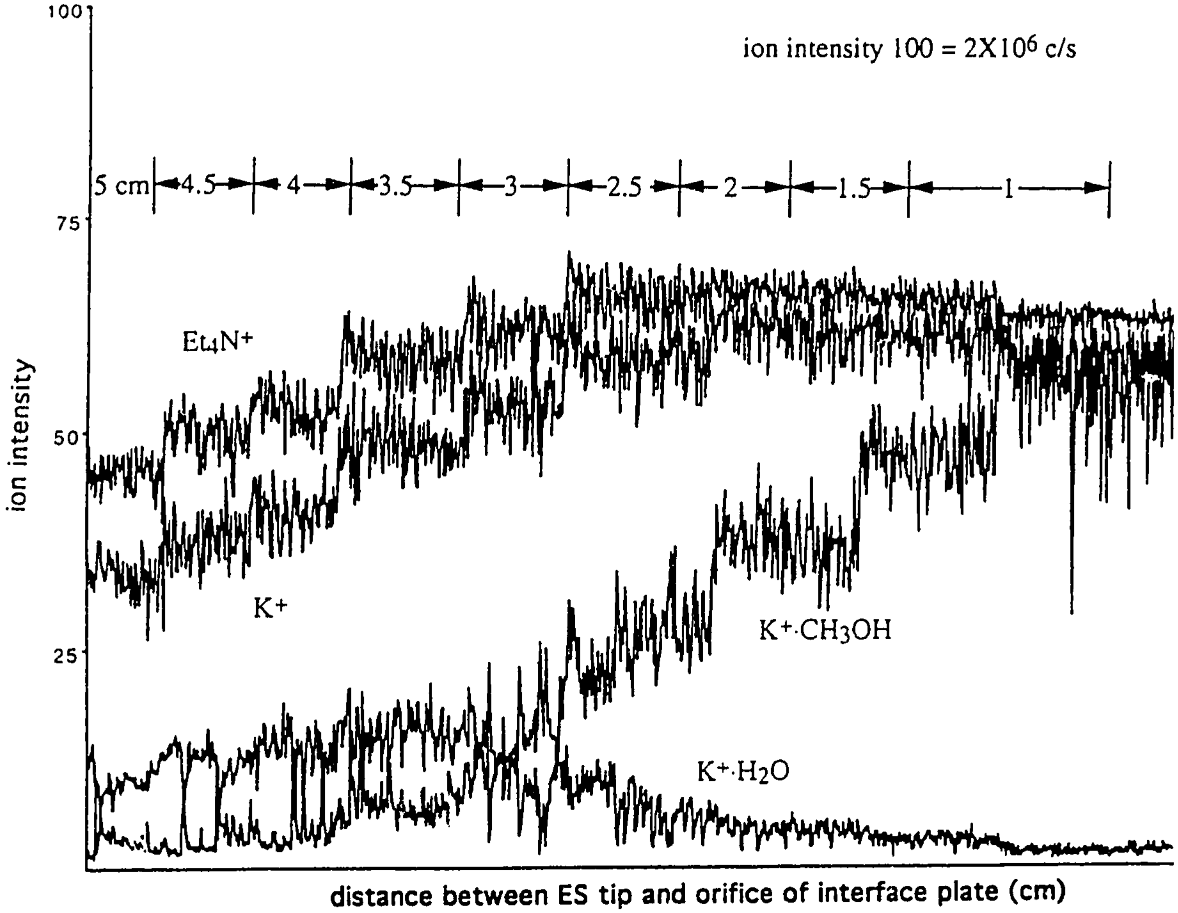

Figure 5-4 The axial distance dependence of ion intensities of Et_4N^+ and $K^+\cdot(Sol)_n$ at constant ES current. Methanol solution contained 5×10^{-5} M Et_4NBr and 5×10^{-5} M KCl. Experimental conditions were with r=0 mm and constant ES current 0.2 μA.

Table 5-1. Ion Intensity Changes with Axial Distance between ES Capillary and Sampling Orifice

d (cm)	Constant V [a]			Constant I [b]			Ref. 5[c]
	K^+ (c/s)	Et_4N^+ (c/s)	$\frac{Et_4N^+}{K^+}$	K^+ (c/s)	Et_4N^+ (c/s)	$\frac{Et_4N^+}{K^+}$	$\frac{Me_4N^+}{MeOH_2^+}$
5	6.6×10^5	1.3×10^6	2.0	6.7×10^5	1.3x106	2.0	~10
4	1.0×10^6	1.6×10^6	1.6	8.8×10^5	1.5x106	1.7	~3.5
3	1.4×10^6	1.9×10^6	1.4	1.2×10^6	1.8x106	1.5	~0.5
2	-	-	-	1.6×10^6	1.9x106	1.2	~0.16
1	-	-	-	1.9×10^6	1.9x106	1.0	~0.1

a. Present work. Distance was changed at constant ES voltage. For $d<3$ cm, electrical discharges were observed, see Figure 5-2. K^+ ion intensities are summed over K^+, $K^+ \cdot H_2O$ and $K^+ \cdot CH_3OH$.

b. Present work. Distance was changed at constant ES current I, i.e. capillary voltage was decreased with decrease of distance. Data from Figure 5-4.

c. From Hiroaka's work, see Figure 5-5. Intensities of $CH_3OH_2^+$ include intensity of NH_4^+ because NH_4^+ is probably an ion-molecule reaction product of CH_3OH, see text.

could be observed down to a distance of L = 1 cm. The $Et_4N^+/\Sigma K^+$ ratios, Table 5-1, observed at large L are similar to those obtained with constant capillary voltage. This is to be expected since the conditions for the two sets of experiments are very similar. The ratio $Et_4N^+/K^+ = 1.0$ observed for the smaller distance L = 1 cm is roughly half that for the largest distance. Thus, changes occur but they are not drastic. Hiraoka's data are difficult to interpret because of the presence of the extraneous NH_4^+ ions. If one assumes that NH_4^+ was formed by the ion-molecule reaction (equation 5-5) from $CH_3OH_2^+$, the sum of intensities for $CH_3OH_2^+$ and NH_4^+ should be representative of the $CH_3OH_2^+$ intensity produced by the ES process in the absence of an electric discharge. The ratio $Me_4N^+/CH_3OH_2^+$ given in Table 5-1 was calculated from Figure 5-5 with this assumption. The ratio changes drastically with distance from 10 at L = 5 cm to 0.1 at L = 1 cm, i.e. by a factor of 100! The presence of a weak electric discharge in Hiraoka's experiments at short distance would give high protonated-ion densities and provide an explanation for the low ratio of intensities. The high ratio at L = 5 cm is more difficult to explain. The solution contained 5×10^{-6} M of Me_4N^+ and about 3×10^{-5} M of $CH_3OH_2^+$ calculated for a 10^{-3} M CH_3COOH solution (assuming a $pK_a = 6$ in methanol-water solvent (10, 11)), i.e. the protonated species dominate the Me_4N^+ six-fold. Since the solution concentrations are low, the $k_{Me_4N^+}/k_{CH_3OH_2^+}$ effectively observed due to depletion will not be larger than 3 one expects an ion intensity ratio: $Me_4N^+/CH_3OH_2^+ = 1/2 = 0.5$ in the absence of distance effects. Therefore, it appears that the large value, 10, at large distance is the unexpected value, although we don't know the mass dependent discrimination present in his quadrupole. For the present, we are unable to rationalize the large difference between Hiraoka's

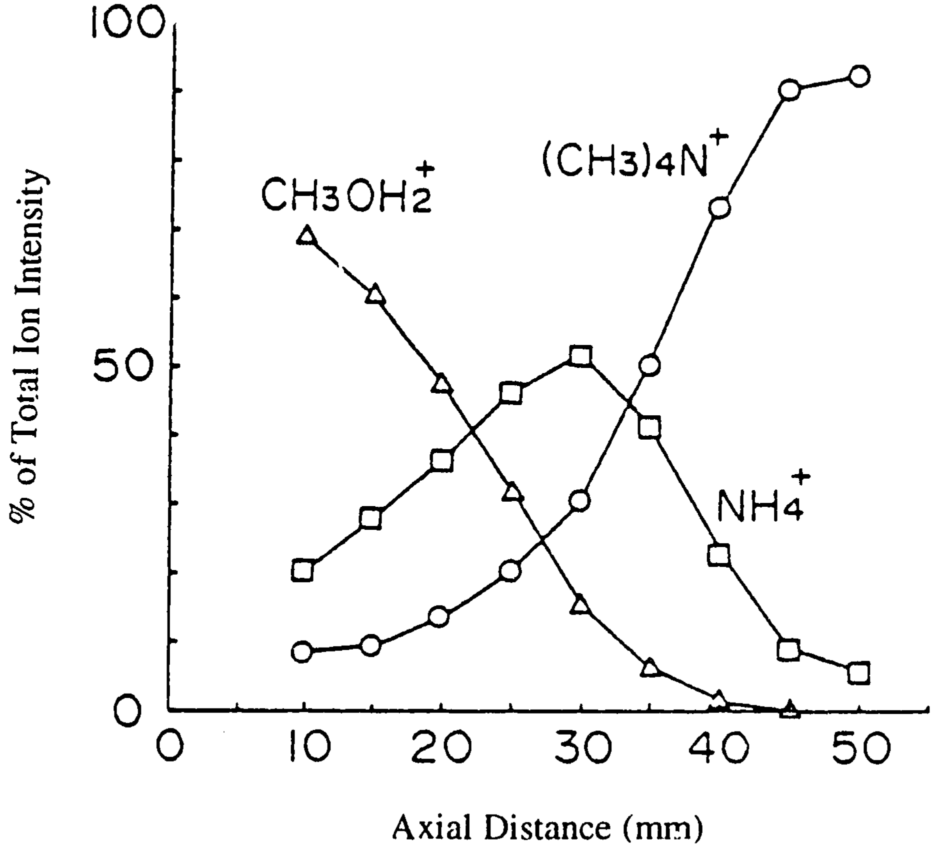

Figure 5-5 Ion intensities change with axial distance observed by Hiraoka (7). ES solution is 5x10^{-6} M $(CH_3)_4NBr$ and 1x10^{-3} M CH_3COOH in $CH_3OH+H_2O+CCl_4$ (8/2/0.5 v/v/v); Flow rate=10 μL/min; Capillary voltage V=3.1 kV.

data and our own.

b. Ion intensity dependence on radial distance between the ES tip and ion sampling orifice

The study of the effect of radial distance on the relative ion intensities was carried out with Et_4N^+ and K^+ as analyte ions since Hiraoka's work demonstrated that radial distance between ES tip and sampling orifice can cause a large difference in analyte ion intensity. He investigated the effect of radial distance on the detected ion intensities with $5x10^{-6}$ M $(CH_3)_4NBr$ and $1x10^{-3}$ M CH_3COOH as analytes in ESMS solution. His findings, shown in Figure 5-6, suggest that careful consideration of radial distance is necessary when analyzing the detected ions. For example, all $(CH_3OH)_n{\cdot}H^+$ ($n = 1{\sim}3$) ion intensities are sensitive to radial distance. The intensities are at a maximum at the axis of the droplet cloud and decreases rapidly with the distance from the axis. On the contrary, NH_4^+ from ambient air has its lowest ion intensity in the center of droplet cloud and reaches its highest intensity near the edge of the cloud. The ion intensity of $(CH_3)_4N^+$ is relatively insensitive to the change of radial distance if compared to $(CH_3OH)_n{\cdot}H^+$, even though it eventually decreases at a large radial distance (of about 10 mm). Thses results can be rationalized in terms of gas phase ion-molecule reactions. The ions near the edge of charged droplet cloud are subject to reactions with air-born molecules more than the ions in the center of the cloud. In Figure 5-6, the molecule NH_3 in the ambient air can penetrate the charged droplet cloud and, since NH_3 is a stronger base than CH_3OH, it will remove the protonated analyte ion produced by electrospray. The ions in the central

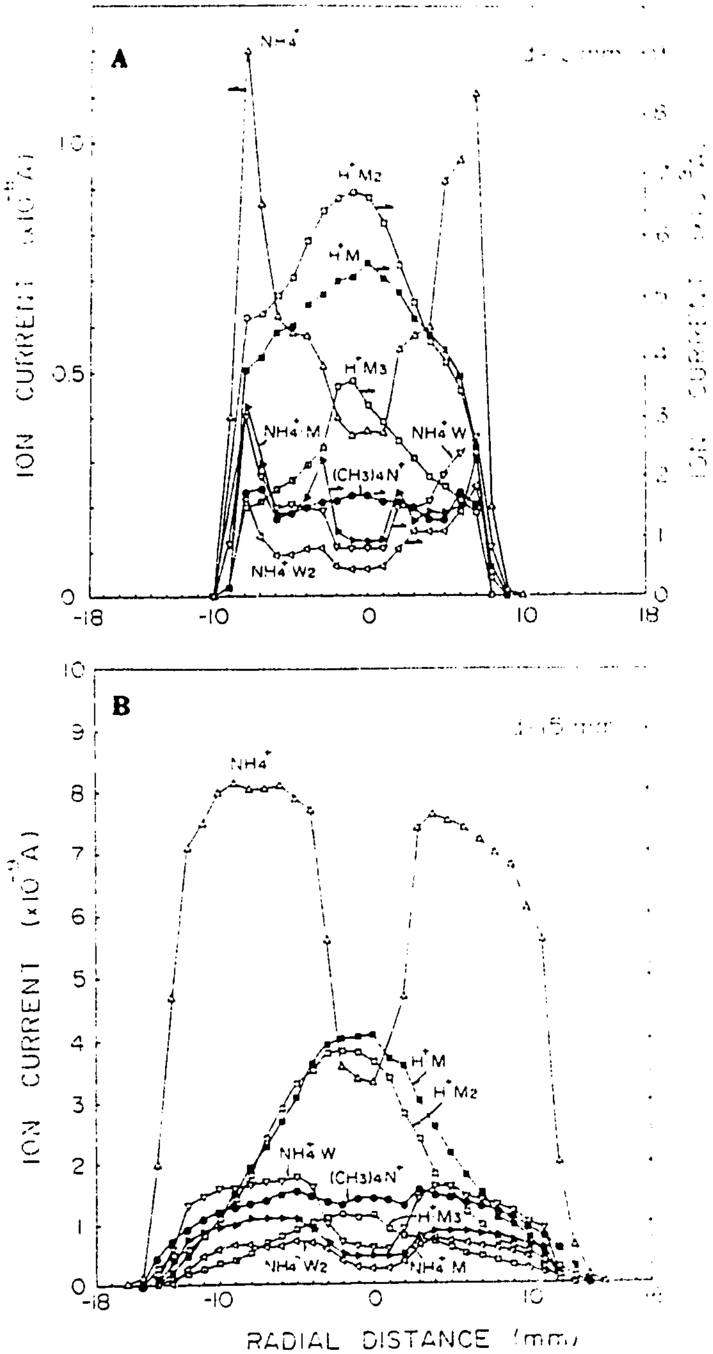

Figure 5-6 Ion intensities change with radial distance observed by Hiraoka. ES solution was $5\mathrm{x}10^{-6}$ M $(CH_3)_4NBr$ and $1\mathrm{x}10^{-3}$ M CH_3COOH in $CH_3OH+H_2O+CCl_4$ (8/2/0.5 v/v/v); Flow rate=10 μl/min; Capillary voltage V=3.1 kV. (A) L=1 cm; (B) L=1.5 cm.

region of the cloud are less affected by the reaction, since the NH_3 concentration is relatively low. In this sense, sampling at the center of the charged droplet cloud will provide optimum conditions for the detection of ES produced ions. The interference from impurity gases in ESMS is also alleviated if the analyte ion, such as $(CH_3)_4N^+$, is unable to transfer its charge to other gaseous molecules. Proton transfer from NH_4^+ to analyte was not a problem in our research on the ES mechanism as all the experiments in Chapter 3 used analytes which either had a high proton affinity or can not transfer charge to neutral molecules.

The radial distance effect was evaluated again with the consideration of gas phase reaction. Figure 5-7 shows that ion intensities of both Et_4N^+ and K^+ essentially remain constant in the whole range of radial distance change which is available on the modified TAGA 6000E. From equation 5-3, we know that the charge density ρ is proportional to the number density n. According to Hendricks equation, the capillary current is determined by distance and voltage. We found that charge density ρ in electrospray is constant everywhere in the cloud at a specific distance with our experimental conditions, which maintain total ES ion current constant. The ion intensity might eventually decrease if the distance could be adjusted further away from the aperture on TAGA 6000E. However, our concern is with the ion intensity which arises from electrospray. The constant ion intensity relative to the radial distance indicates that the ion intensity detected in the experiments reflects the gas phase ion density.

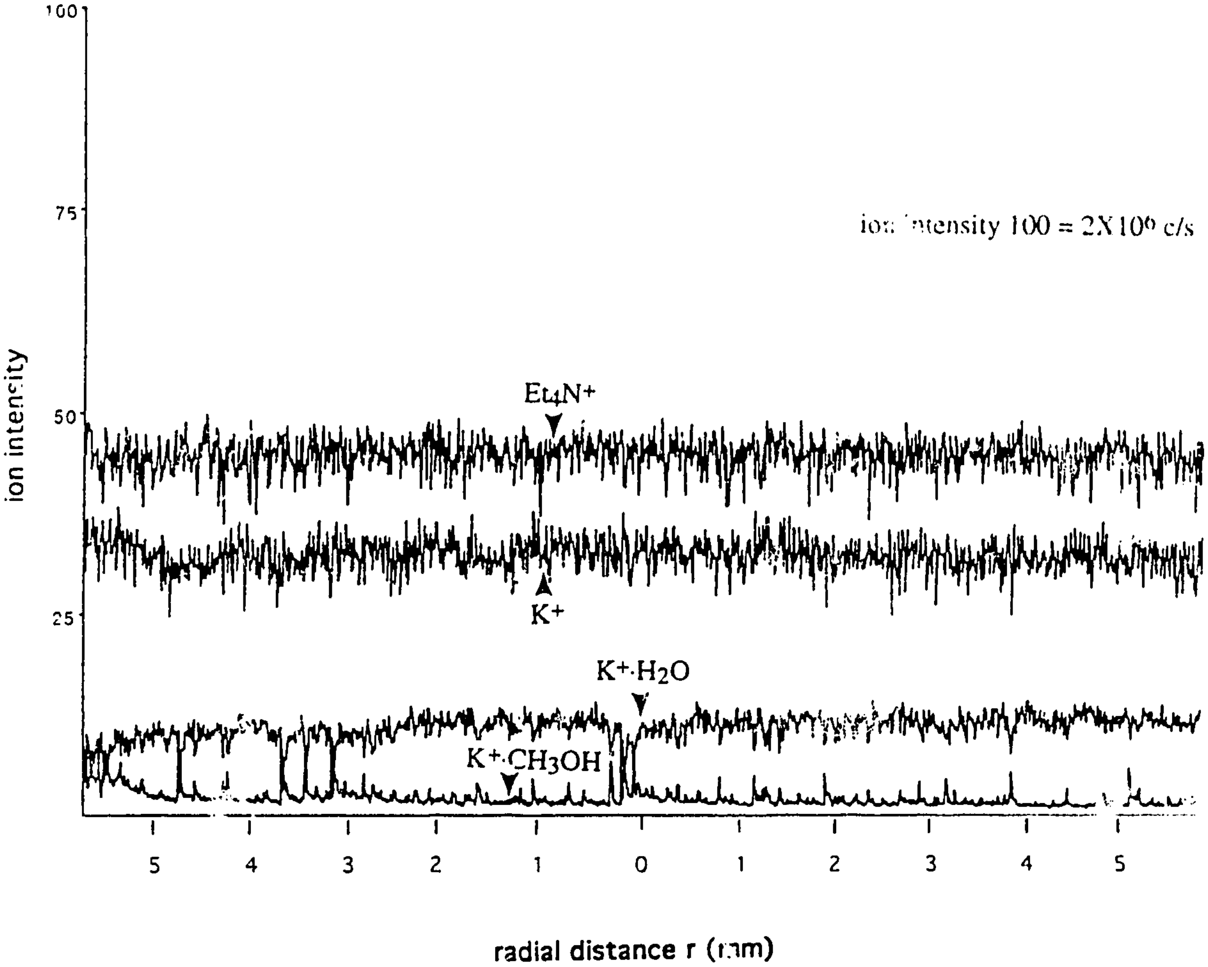

Figure 5-7 The radial distance dependence of ion intensities of Et_4N^+ and $K^+ \cdot (Sol)_n$. Methanol solution contains 5×10^{-5} M Et_4NBr and 5×10^{-5} M KCl with L=5 cm, F=20 μL/min and V=5 kV.

c. Influence of flow rate on relative ion intensities

In Chapter 3, the flow rate used in the experiments was unchanged. Although 20 µL/min is a reasonable flow rate in the ESMS experiments under the conditions developed in our group, it was subjected to verification of its effect on sampling efficiency. After the flow rate was reduced 50%, the ion intensity changed in a pattern similar to the original flow rate. Figure 5-8 illustrates that both Et_4N^+ and K^+ intensities maintain a similar ratio but increase with the decreasing axial distance. Figure 5-9 shows that radial distance has almost no effect on ion intensity. When L = 1 cm, there is little difference for $K^+\cdot CH_3OH$, which shows a bit higher intensity at r = 0 mm. Therefore, a higher flow rate (20 µL/min) is more suitable in the ESMS mechanism study.

5.4 Conclusions

The space charge in ESMS exerts a force on charged species which moves them radially outwards in the droplet cloud. The detected ion intensities decrease with increase of axial distance due to the expansion of the droplet cloud when the ES current is constant. As ion mobilities at atmospheric pressure are very similar, the relative ion intensities among gas phase ions are relatively stable with change in axial distance. The ion density seems constant in the droplet cloud with our experimental conditions and the ion intensities are independent of the radial distance, although ion intensity will eventually decrease outside the cloud. Gas phase ion-molecule reactions must be taken into account in order to avoid interference from impurity gases of high proton affinity in the ambient air.

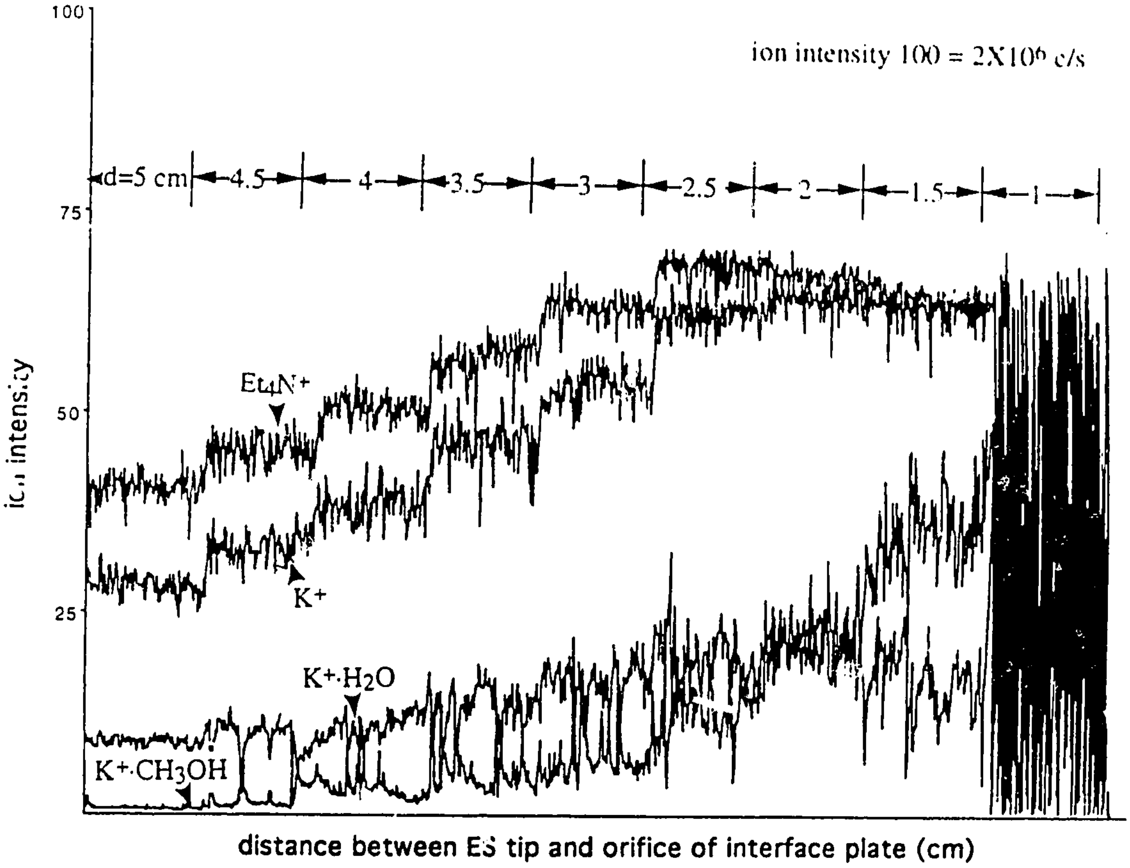

Figure 5-8 The axial distance dependence of ion intensities of Et_4N^+ and $K^+ \cdot (Sol)_n$. Methanol solution contains 5×10^{-5} M Et_4NBr and 5×10^{-5} M KCl with r=0 mm, F=10 µl/min and V=4 kV.

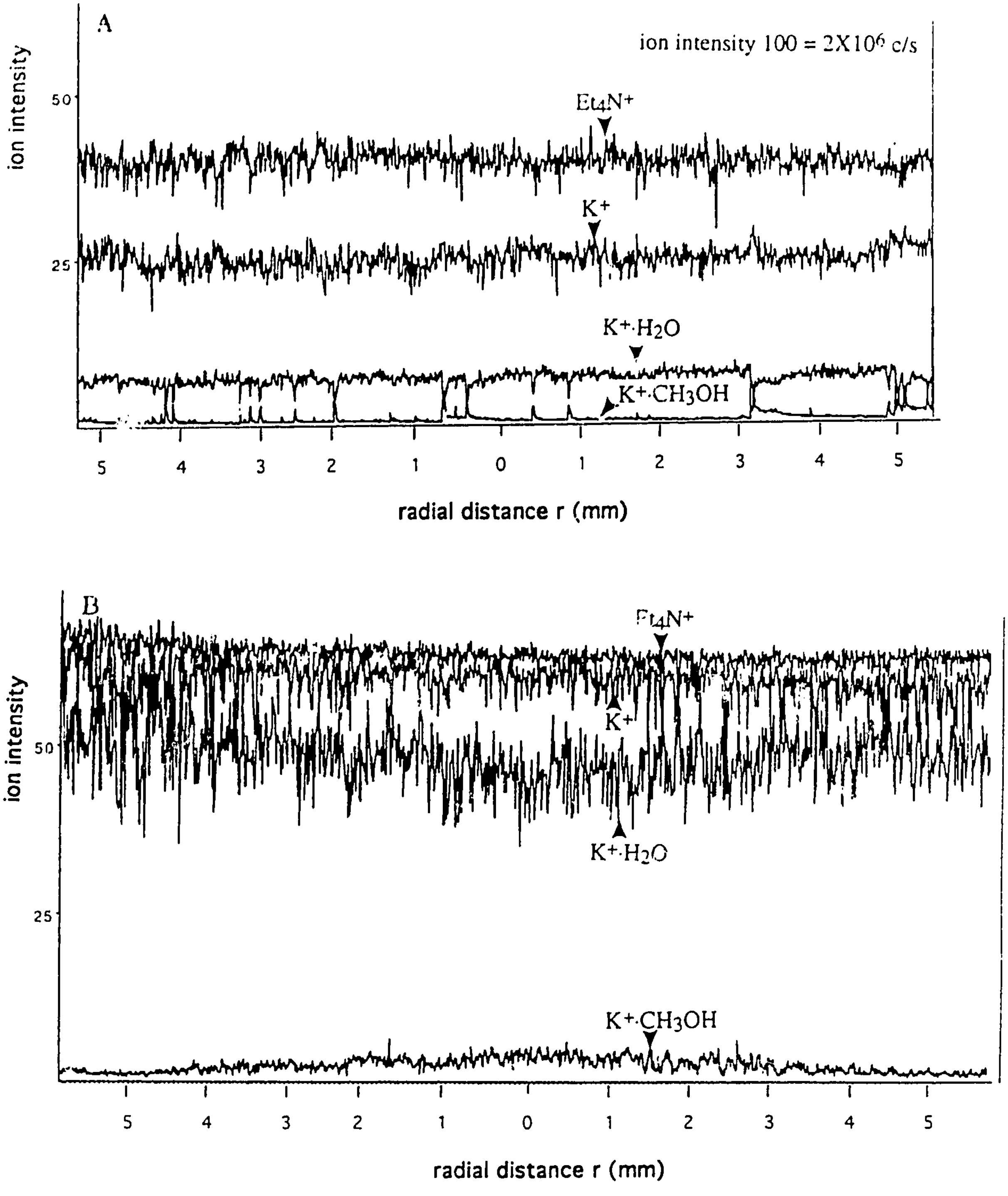

Figure 5-9 The radial distance dependence of ion intensities of Et_4N^+ and $K^+{\cdot}(Sol)_n$. Methanol solution contains $5x10^{-5}$ M Et_4NBr and $5x10^{-5}$ M KCl with (A) L=5 cm, F=10 µl/min and V=4 kV and (B) L=1 cm, F=10 µl/min and V=3.1 kV.

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UNIVERSITY OF ALBERTA

The State and Sport Development in Alberta: Conflict, Corporatism and Change.

BY

Robert Pitter

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy.

DEPARTMENT OF PHYSICAL EDUCATION AND SPORT STUDIES

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Robert Pitter
10907 81 Avenue
Edmonton, AB
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October 7, 1993.

Democracy

Democracy will not come
Today, this year
        Nor ever
Through compromise and fear.

I have as much right
As the other fellow has
        To stand
On my own two feet
And own the land.

I tire so of hearing people say,
Let things take their course.
Tomorrow is another day.
I do not need my freedom when I'm dead.
I cannot live on tomorrow's bread.

Freedom is a strong seed
Planted
In a great need.
I live here too.
I want freedom
Just as you.

Langston Hughes

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled The State and Sport Development in Alberta: Conflict, Corporatism and Change submitted by Robert Pitter in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

~~Dr.~~ Trevor ~~Slack~~ (Supervisor)

Thomas L. Burton

for Dr. Rob Beamish

Dr. Robert P. Gephart

Dr. M. Ann Hall

Dr. Raymond Morrow

David J. Whitson

Dr. David Whitson

October 4, 1993

DEDICATION

To my mother Norma Elaine Pitter
and her belief in the value of higher education.

ABSTRACT

This case study examines the factors that led the Alberta government to create the Alberta Sport Council and discusses some of the council's impact on sport development in Alberta. The analysis of these factors draws primarily from Claus Offe's discussions of corporatism and welfare state development The data used in this study were collected from interviews, government documents, annual reports, minutes, press releases, newspaper articles, committee reports, letters, government legislation and scholarly publications dealing with politics and/or sport development in Alberta.

The results of this study indicate that key individuals, organizational factors and Alberta's social and political characteristics influenced the events that led to the creation of the Alberta Sport Council. Individuals interested in promoting sport in Alberta sought to create an institution that would, with the assistance of the provincial government, foster the development of sport in Alberta. Beginning in 1967 the Alberta government, in which the Social Credit Party held a majority, sponsored numerous discussions that led to the creation of Sport Alberta in 1970. Sport Alberta was the first organization with the mandate of supporting the interests of sports groups throughout the province. During the 1970s the Progressive Conservatives were elected to government. This party implemented an approach to government that transformed the way in which sport interests were represented in Alberta. Interpersonal and intra-organizational conflict, the corporatist ideology of the Progressive Conservatives and a rapid downturn in the economic growth of Alberta combined together to foster the creation of the Alberta Sport Council.

Further observations made in this study indicate that the Alberta Sport Council's approach to sport development mirrors that of other governments which have directly intervened in sport development. This has occurred in three ways. First there has been a rapid growth in the bureaucratization and related professionalization of sport delivery, second there has been an increase in the emphasis on high-performance sport, and third there has been movement towards recommodifying sport delivery.

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I would like to thank my supervisory and examination committee. I am thankful for Dr. Trevor Slack's patience and for the effort he made to convince the student awards office that a nine-point-zero grade-point average at the master's level was worthy of a PhD. scholarship. Dr. Ann Hall's careful attention to detail and protocol contributed to the overall quality and coherence of this project. Dr. David Whitson provided endless hours of moral support during our many runs through the campus area as we discussed state theory and its relevance to my data. The many hours of employment I received as a research assistant to Dr. Bob Gephart not only provided necessary financial resources but also exposed me to both the potential and the pitfalls of microcomputer-assisted research methods. Dr. Ray Morrow's interest and passion for critical theory intensified my own interest and kindled my motivation to complete this project.

I would also like to thank the Sir Izaak Killam Scholarship Committee and the Alberta Sport Council for their financial assistance which enabled this research to be conducted.

This study would not have been possible without the contribution of the many individuals who agreed to be interviewed and/or provided materials that were used. Their cooperation is greatly appreciated.

I would also like to acknowledge the contribution of my many friends in the Political Science Department at the University of Alberta. The informal discussions of politics in Alberta that took place in and around our Friday night ball hockey games and Tuesday evening baseball games introduced me to literature on Alberta politics that proved to be fundamental to the analysis presented in this project. In this regard I am particularly indebted to Dr. Donald Carmichael and Dr. Ian Urquhart.

Finally, I must also note that the greatest contributions came from the ongoing encouragement and assistance I received from my closest friends: Ellen, Laura, Steve and especially Andriel. Most of all I am grateful for the moral and financial support of my mother who has continued to provide more than she could be expected. It is my hope that I will some day be able to repay her.

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Chapter One

Trends, Issues and Themes in the Analysis of the State and Canadian Sport Development

Canada's sport system has grown tremendously since the turn of the century. The growth of sport has been so great that ever increasing numbers of Canadians confront sport, in one form or another, every day of their lives. Some people participate in sport directly, as they aspire to become professional athletes or world champions. Other individuals participate recreationally as a means to maintain or improve their health, for the fun of it and/or for other personal reasons. The greatest number of people participate indirectly either as spectators or as parents supporting aspiring athletes.

Even those who are indifferent towards sport must deal with the consequences of its growth. For example, in several Canadian cities formula-one car racing disrupts the lives of many people who have no interest in this sport. The courses upon which these events take place are built within city limits and pass through residential neighbourhoods. The cars that drive along these courses expose residents to undesirable levels of noise and air pollution. Other consequences of sport's growth include the increased traffic caused by major sports events and even riots[1] that spill out of stadiums into city streets. Less noticed and far more reaching in its effects is the public money spent on, and the public-sector debt incurred in, financing many of these stadiums and sports events. The extent of sport's magnitude is further epitomized by its dominant position in

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[1] The problem of soccer hooliganism in Great Britain is an extreme example of this sort of event which has no direct equivalent in Canada. However, riots that have a direct relation to sporting events have been known to break out in Canadian cities. As recently as the spring of 1993, riots and looting occurred in downtown Montreal immediately following the game in which the Montreal Canadiens won the Stanley Cup.

the mass media. There is considerable talk about sport in the media, government and places of work and leisure.

Canada's sport delivery system has also been transformed significantly during this period of substantial growth. Richard Gruneau's book, *Class, Sports, and Social Development*, exemplifies research that provides a historical account of the ways in which the structures and meanings of Canadian sport have been transformed since the turn of the century. The most recent phase of transformation discussed by Gruneau (1983) is a phase in which:

> the Canadian state, in conjunction with national and internationally established sporting associations, began to broaden its influence in sport to include national and subnational programs in recreation, physical fitness, and provincial, national and international athletics (p. 93).

This phase of transformation goes back to 1961 and the passage of Bill C-131 which led to the creation of Canada's first federal government department responsible for sport development. Since the creation of that department, the Fitness and Amateur Sport Directorate, state intervention in sport development has increased rapidly, bringing about significant changes to Canadian sport.

One of the most important changes in the Canadian sport system has been generated by what Gruneau (1983) identifies as the government's shift away from sport development policies of social control and non-involvement towards policies that focus on "welfare oriented programs ostensibly designed to increase the quality of life in Canada and expand people's opportunities for the pursuit of athletic excellence" (p. 130). This state intervention has brought about the establishment of extensive sport bureaucracies at the federal and provincial levels. Sport policies are now implemented through government departments such as Sport Canada, the Alberta Department of Recreation and Parks[2] and the Ontario

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[2] As this dissertation was being written the name of this department was changed to the Department of Community Development. The former name Alberta Recreation and Parks is used throughout this study because this was the proper name of this agency during the historical period discussed in this study.

Department of Tourism and Recreation. These government departments devote a significant amount of their attention and resources to the purposes of overseeing, facilitating, and, in many cases, directing sport development through national and provincial sport associations. According to Gruneau (1983), explanations of the developments that have led to this and other transformations "can only be speculated upon" due to the lack of research on sport and the state (p. 130). Harvey's paper, "Sport Policy and the Welfare State," represents one of the few efforts to address this lack of research. Harvey (1988), like Gruneau (1982), notes that additional empirical studies are still needed in order to develop a comprehensive understanding of sport and the state. Harvey (1988) states:

> More studies on actors such as voluntary organizations or class-based groups in the development of the welfare state are needed. We also need an in-depth study of the actual interventions of the Canadian state. . . . Finally, any analysis of the Canadian case has to keep in mind that because of the constitutional division of powers the responsibility for the provision of welfare services falls primarily on the provinces and local governments. All interventions of the federal government must deal with this reality. It also means that for a **full** account of the Canadian welfare state one has to look at all levels of government and especially at the municipal and provincial levels (p. 328, emphasis in original).

To date, the response to the needs articulated by Harvey (1988) and Gruneau (1982) has been sparse, particularly with regard to studies of actors and groups, at the municipal and provincial levels of the Canadian state[3]. A review of the literature uncovered only one study, Harvey and Proulx's (1988) examination of Quebec, that has addressed any of these four areas. Harvey and Proulx (1988) reveal many similarities between provincial and federal intervention in sport development as well as a number of phenomena that are particular to Quebec. They also suggest that intervention in sport has been linked to welfare state policy and used as a means of promoting both Canadian and Quebec nationalism.

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[3] The historical importance of the provincial state power has been emphasized by Panitch who also indicates its importance has been growing.

The absence of theoretically informed research on other Canadian provinces has made it difficult if not impossible to compare sport initiatives across the country and to see if the characteristics and explanations of state involvement in sport put forward by Harvey and Proulx (1988) can be generalized to other Canadian provinces. It also leaves us with an incomplete picture of sport development and emphasizes the need for more studies of this type.

As a means of facilitating the development of a more complete picture of sport development in Canada, I have chosen to undertake a case study of the state's role in sport development at the provincial level. Of the nine provinces which have yet to be studied in depth, the province of Alberta represents one of the more interesting choices because its government boasts a unique approach to sport delivery. This unique approach to sport development is embodied in a provincial Crown corporation called the Alberta Sport Council. The Alberta Sport Council is the only Crown corporation in North America that has sport development as its mandate. Initiated in 1984 following the passage of *Bill 21, An Act to Establish The Alberta Sport Council*, this new organization has meant a significant change in sport development policy in Alberta. The Alberta Sport Council is unlike Sport Canada and government departments in other provinces, is a non-profit, publicly owned Crown corporation.

Notwithstanding the Alberta Sport Council's Crown corporation status, preliminary research revealed that other people have argued that the Alberta Sport Council is not unique at all (Pitter, 1984). They have suggested it was merely a unique means of camouflaging the Alberta government's *plot* to control the direction of sport development in Alberta. This preliminary research into this topic revealed a series of events that at first glance appeared to be an indication of just such a plot. In view of this preliminary finding and the call for more research into provincial government intervention into sport I felt that an analysis of the characteristics of this political strategy would make for an interesting case study. This study then came about as a result of the endeavour to investigate the possiblity of such a conspiracy by addressing the following two questions:

1. Why did the Alberta government choose to create the Alberta Sport Council as a Crown corporation instead of using its internal departmental bureaucracy to oversee sport development in a manner similar to the federal and other provincial governments?
2. Has the impact of the Alberta Sport Council been significantly different from the impact of government institutions involved in sport development elsewhere in Canada?

The case analysis of the development of the Alberta Sport Council is presented in the six chapters that follow this introduction. Chapter Two contains a discussion of the theoretical basis of this inquiry. This discussion identifies the theoretical concepts that were used to guide data analysis and data collection by means of a concise review of related literature. This literature review considers writings that have attempted to theorize the state very broadly and within the context of Canada.

Chapter Three includes an overview and discussion of the research methods that were employed in this case study. Chapter Four provides a brief historical background to the study and a historical analysis of a seven-year-period that set the stage for the discussions that would ultimately lead to the creation of the Alberta Sport Council. Chapter Five examines the time period in which the Alberta government developed its first official sport policy. It was these discussions that led to the legislation which created the Alberta Sport Council. Chapter Six examines and assesses the impact of the Alberta Sport Council. This is accomplished through a discussion of some of the issues that were raised by people who were interviewed for this study. Chapter Seven draws the observations presented in the fourth, fifth and sixth chapters together and comments on their implications at the level of theory. This chapter also speculates regarding the future course of state intervention in sport development.

Chapter Two

Basis of the Inquiry

The best investigations of the state's role in sport development have been written carefully to situate their analyses within the context of coherent theory of the state[4]. It would be somewhat remiss to conduct an investigation into sport and the state without, at the very least, placing that analysis within the context of these other investigations. The characteristics of this context have changed over time in conjunction with the changing role of the state and changes in our theoretical understanding of the state.

This chapter summarizes some of the insights that have been provided by scholars who have examined the Canadian state's role in sport development. Attention is drawn to the key assumptions that underlie the insights that these researchers have identified. The work of these researchers indicates the value of combining the data collected about the Canadian sport system with theories of the state politics and organizational administration.

The State, Sports and Social Life

Sport has, like many other elements of social life, been touched in significant ways by the various institutions that comprise the state. This is especially true in Canada. Recent history has provided numerous examples of the growing impact that a variety of state institutions have had on sport. For example, consider the federal government. In the early 1970s the federal government began to introduce programs to supplement the income of top athletes in exchange for their commitment to aspire towards achieving international athletic excellence. In 1980 the federal government of Canada

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[4] This view is shared by Gruneau (1982) who has indicated that early investigations into the state and sport were deficient because they "failed to situate sport in the context of any coherent theory of the state" (p. 2).

prevented Canadian athletes from attending the Summer Olympic Games in an attempt to pressure the U.S.S.R. to withdraw troops from Afghanistan. The federal government has also introduced sport programs designed to manage relations within Canada. One such program is the Canada Games. Originally introduced to promote national unity, the Canada Games has matured to a point where it has become the focus of provincial flag-waving: an arena where many provinces aim to foster solidarity among their citizens and to demonstrate their superiority to other provinces[5].

Soon after the Canada Games was introduced, state involvement in sport at the provincial level began to increase significantly. Like their federal counterpart, provincial governments have developed programs designed to fund athletes and sport development within their respective provincial borders. Many other aspects of provincial involvement in sport development mirror initiatives at the federal level. For example, several provincial governments sponsor their own provincial games. Most provinces have also centralized the headquarters of their provincial sport organizations at a single site analogous to the Canadian Sport and Fitness Administration Centre in Ottawa. Funding for the technical and executive directors who work at the provincial centres is provided by provincial governments in a manner comparable to the funding provided for national sport organizations by the federal government through its agent Sport Canada.

The above examples illustrate that the state and sport are two institutional spheres that have become entwined in Canadian society. They have become so connected that debates over the desirability of state intervention in sport development have become moot. A variety of literature has focused on the impact of increasing state intervention in sport. Some scholars have examined

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[5] The relative success that governments have enjoyed in this context is limited considering the fact that there are many Canadians who have never heard of the Canada Games. Nonetheless, for those Canadians who do participate, the emphasis on winning for the sake of enhancing their province's identity is a significant feature of their participation.

government involvement in sport from a historical and/or descriptive point of view (e.g. Broom & Baka, 1978; Franks & Macintosh, 1984; Macintosh, Bedecki & Franks, 1987). This group of scholars has provided chronological accounts of the events that highlight key features of provincial and federal government involvement in sport. Other scholars have attempted to go beyond historical description and put forward theoretical explanations that account for observed trends in the relationship between the state and sport by approaching their research from within the context of theories of the state (e.g. Kidd, 1981, 1982; Harvey, 1988; Harvey & Proulx, 1988; Macintosh & Whitson 1990). A concise examination of these theoretical explanations will illustrate the way in which theories of the state have contributed to understanding the Canadian state's involvement in sport.

Explaining State Intervention

The beginning of a significant interest in the area of the state and sport in Canada can be traced back to the year 1979. It was during October of that year that Queen's University in Kingston, Ontario hosted a conference dealing specifically with sport, culture and the modern state. Gruneau's paper, "Sport and the Debate on the State," opened the conference. In that paper he argued that current studies that examine the relationship between sport and politics have been deficient in the sense that they failed to "situate sport in the context of any coherent theory of the state" (Gruneau, 1982, p. 2). Since the Queen's conference there has been a steady trickle of research that has focused on explaining state intervention in sport in Canada.

The development of these explanations has followed a pattern that has been consistent with the development of state theory. Explanations of state intervention in Canadian sport have moved from studies inspired by the Marxist state theory of the early 1970s towards those inspired by post-Marxist[6] theories of the state that have gained popularity since the 1980s.

Kidd's (1981) discussion of the dilemma of government intervention in sport development represents one of the earliest endeavours to explain the Canadian state's role in sport development through the use of state theory. His explanation of federal government sport policy initiatives relies heavily upon Panitch's (1977) Marxist discussion of the role and nature of the Canadian state. Panitch (1977) argues that the Canadian state has three specific functions: capital accumulation, legitimation and social control. According to Kidd (1981), it is these functions that explain the federal government's choice of sport development initiatives. Kidd (1981) suggests that any model of sport development that fails to contribute to the Canadian state's functions of capital accumulation, legitimation and social control is likely to be ignored. To support this claim he provides numerous examples of initiatives that have facilitated capital accumulation at the expense of alternative approaches to sport development that provide long-term benefits for amateur sport.

Because Kidd (1981) situates his analysis within the context of a coherent theory of the state and sport, he is able to emphasize two important ideas. First of all, he links the accessibility of sport to the larger social context within which sport is practised, arguing that unequal access to sport "reflects general inequality in Canada" (Kidd, 1981, p. 244). Second, he indicates that the state has the capacity to address these inequalities by implementing programs that encourage progressive change. He notes, however, that this capacity is circumscribed by the present stage of capitalism in which states are facing crises of accumulation and legitimation.

Kidd's (1981) focus on the writings of Panitch (1977) is emulated by Harvey and Proulx's (1988) comparison of the federal and Quebec governments'

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[6] For a full discussion of this theoretical trend and its implications, see Pierson (1984).

sport policy. In agreement with Kidd (1981), Harvey and Proulx (1988) argue that the three functions of the Canadian state delineated by Panitch (1977) are important structural constraints that have influenced state intervention in sport. Harvey and Proulx (1988) extend the context of their analysis and move beyond the ideas put forward by Kidd (1981). They introduce the notion of the welfare state into their analysis and they compare the federal government's role in sport development with that of the Quebec government. Harvey and Proulx (1988) suggest there is a link between the development of the welfare state and the nature of federal and Quebec government intervention in sport: "In Canada, the initiatives of the state at the federal and provincial levels in the area of sport have been primarily linked to the development of policies of the so-called welfare state and to measures promoting nationalism (Harvey and Proulx, 1998, p. 95)." The bulk of Harvey and Proulx's (1988) discussion focuses on the ways in which the Quebec and federal governments have taken over control of sport and physical fitness in their bids to promote their own versions of nationalism. The significance of the development of the welfare state is left undeveloped apart from the authors' concern that the crisis of the welfare state might lead the state to retreat from intervening in sport while at the same time encouraging private enterprise to help fund sport.

The significant role that the development of the welfare state plays in the explanation of state intervention in sport is emphasized by Harvey (1988) in a later paper. Harvey's (1988) analysis of the development of the welfare state and its impact on state intervention in sport is influenced by a set of five theoretical assumptions he develops by considering ideas put forward by Clarke and Critcher (1985), Djao (1983) and Offe (1984). These five assumptions can be summarized as follows:

1. The welfare state is made up of a set of multi-functional institutions designed to manage the structures of socialization and the capitalist economy and as such exhibits contradictory tendencies due to the countervailing nature of socialization and the capitalist economy.

2. The welfare state is a historical phenomenon that develops according to periods delineated by crises of development.

3. The welfare state is continually shifting between commodified or decommodified production of value because each crisis of development it faces involves a redefinition of what part of social life should be commodified or recommodified.

4. The welfare state's actions regarding the form of state intervention with respect to commodification/decommodification are partially governed by pressures exerted on the state by organized groups or social movements and partially by the necessity of furthering capitalist development.

5. Welfare state measures are defined as citizen rights, which are to be guaranteed by the state.

With the aid of the analytical context provided by these assumptions, Harvey (1988) is able to link changes in the federal government's approach to the delivery of welfare state initiatives to changes in the form and content of sport policy. In accordance with the second assumption that the welfare state develops according to periods marked by development crises, Harvey (1988) divides the Canadian case into three periods: the emergence of the welfare state (1930-1940), the consolidation of the welfare state (1940-1975) and the present period of contestation (1975-1988). Harvey's (1988) discussion of each of these periods indicates that the form of state intervention in sport during each of these periods reflected the state's concern with fostering capitalist development and/or the state's desire to respond to pressure exerted by organized groups.

For example, Harvey (1988) suggests that the economic depression of the 1930s created a set of events that led to the creation of the Canadian welfare state. In 1935 the Canadian government implemented an unemployment insurance scheme in order to cope with the problems associated with high unemployment[7]. At that time the Canadian government's first interventions into sport also began to take shape. These interventions were primarily concerned with using sport and recreation as a means of training and conditioning Canadian youth in order to raise their physical and mental fitness and concomitantly raise their level of employability.

Welfare state services grew and became firmly entrenched in the time period between 1940 and 1975. Harvey (1988) shows how the Canadian government's concern for the social and economic consequences of the Second World War influenced the welfare policies that were introduced at the beginning of this period of consolidation:

> State intervention in sport in this period was less characterized by the kind of labour related measures of the previous period. Indeed, a new image of health and fitness emerged. During the war years, state policy focused on the production of men fit for war and for the industrial war effort. After the war this objective was replaced by a preoccupation with the total fitness of the body (p. 323).

According to Harvey (1988), by 1960 the Canadian government was firmly committed to the welfare state logic of promoting social equality. This commitment influenced the scope and form of Bill C-131, *An Act to Encourage Fitness and Amateur Sport*. Harvey (1988) maintains that "given the hegemony of the social democratic role of the state to equalize opportunities, the bill had to give the image of equality of opportunity in order to gain legitimacy" (324). Initially, this image of promoting equality of opportunity was sustained through transfer payments to the provinces and study and research grants to universities. Later on during the 1970s and 1980s, welfare programs in the area of high-performance sport were initiated. These programs were aimed at providing financial assistance

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[7] Harvey (1988) indicates that this first unemployment insurance scheme was declared unconstitutional in 1936. However, in 1940 an unemployment insurance program was successfully implemented. This event marked the beginning of the period of the consolidation of the welfare state.

to athletes, increasing the participation and the status of women in all aspects of sport and assisting people with disabilities.

This period of consolidation of the welfare state and increasing government intervention in sport resulted in a significant decommodification of sport whereby the provision of sport-related services and opportunities was undertaken and determined by government rather than by market forces[8]. The consolidation of the welfare state and the decommodification of sport have, however, been interrupted by the consequences associated with the fiscal crises of the state. These crises have made it difficult for governments around the world to finance their welfare initiatives. Harvey (1988) notes that a resurgence of neo-conservative ideology has developed in conjunction with these difficulties. Proponents of this neo-conservative ideology question the state's ability to overcome social inequality through welfare programs and the appropriateness of this type of state intervention. The solution offered by neo-conservatives involves cutting back spending on social programs and government services—including sports programs—in order to encourage the growth of the private-sector economy.

Harvey (1988) suggests that the Canadian government has responded to this neo-conservative ideology by cutting its spending on sports programs devoted to the equalization of opportunity while simultaneously increasing its spending on elite sport. Neo-conservatism has also, says Harvey, promoted a re-commodification of sport and leisure services that were once provided directly or indirectly by the government. Harvey provides several examples of this movement including the state's recent programs that encourage national sports associations to find private sponsors for their sports.

Several ideas that inform Harvey's (1988) discussion are also cultivated in Macintosh and Whitson's (1990) analysis of the administration of national sport organizations. Macintosh and Whitson focus their analysis on the state's role in

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[8] For an in-depth discussion of commodification and decommodification see Offe (1984).

sport development during the time period that Harvey describes as the period of contestation. Guided by work on the contemporary contradictions of the welfare state Macintosh and Whitson (1990) argue that,

> There are structural pressures that have moved many governments to redirect welfare or equity-oriented expenditures into programs that articulate more easily with the public relations goals of government and the corporate sector, as well as with the ideological premises of a market society and material pressures to expand the sphere of commodity production (p. 92).

In the area of federal sport policy this has meant that the federal government has shifted its support of sport towards "forms of sport that offer significant opportunities for the corporate sector" (Macintosh & Whitson, 1990, p. 103).

The evidence indicates that the development of the Canadian welfare state and its policies is continually being shaped and reshaped by a combination of forces related to the pressures exerted by the structure of Canadian capitalist society and the social/interest groups that comprise it. These pressures have revolved around the issue of defining the nature and purpose of state intervention in civil society and the issue of determining what is a public good and what is essential to human life[9]. As the state confronts these pressures people are becoming increasingly aware that the welfare state has its limitations with regard to its ability to provide more and improved social services without undermining economic growth or placing a significant strain on the public purse.

The analyses of the federal government's role in sport development presented by Harvey (1988) and by Macintosh and Whitson (1990) suggests that a *laissez-faire* strategy, promoted by the new right, has been largely responsible for current trends in the development of Canadian sport. This strategy is one of the three forms of strategic responses to the crisis of the welfare state that have been

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[9] Further discussion of these debates as they relate specifically to Canada can be found in Macintosh and Whitson (1990). More general discussions of the ways in which social rights have been contested can be found in Giddens (1982) and Macpherson (1985).

identified by Offe (1984). Keane summarizes Offe's description of this strategy in his introduction to Offe's *Contradictions of the Modern Welfare State* as follows:

> Supported by sections of large capital and the traditional middle classes, the goal of this *laissez-faire* coalition is the recommodification of social life. It seeks to *decrease* the scope and importance of decommodified political and administrative power by resuscitating 'market forces'. Those forces that are unable to survive within the commodity form, it is argued, should also be allowed to fall victim to 'market pressures' and, at the same time, urged to 'modernize' by transforming themselves into marketable commodities (Offe, 1984, p. 26).

These insights into the state's role in sport development have, however, focused exclusively on the federal government. The extent to which these ideas can be extended to the provincial government is relatively unknown. Has the way in which provincial governments dealt with the limitations of the welfare state influenced provincial sport policy? Has provincial sport policy also moved towards supporting forms of sport that offer significant opportunities for the corporate sector in the same way as federal sport policy? If it were possible to assume that provincial governments faced the same structural pressures from capital and interest groups as faced by the federal government, one could expect sport policy at both levels to be identical. However, Canada's regional diversity in terms of economics and geography coupled with the high degree of autonomy possessed by provincial governments makes such an assumption untenable.

The unique character of each province has not made any of the provinces immune to the fiscal crises that confront welfare states throughout the world. Like their federal counterparts, provinces have had to manage these crises and respond to pressures from the political right and left. The diverse nature of the ten Canadian provinces makes it presumptuous to assert, without the appropriate empirical evidence, that provincial governments have applied the same strategies as the federal government in their efforts to deal with economic development and/or the fiscal crisis. Furthermore, one would expect to discover that the implementation of different strategies would produce different consequences for sport policy and subsequent sport development. Consequently, the study of the province of Alberta that is pursued in this thesis attempts to identify the strategy or strategies for dealing with the fiscal crisis and economic development that have influenced the Alberta government's actions in the area of sport policy. A particular approach to dealing with the fiscal crisis and the contradictions of capitalism may, very likely, account for the development of the Alberta Sport Council and its distinctive characteristics.

Richards and Pratt (1979) have described the Alberta government's approach as corporatist. As Jessop (1990) notes, the most often cited definition of corporatism is the one contained in the work of Phillippe Schmitter:

> Corporatism can be defined as a system of interest representation in which the constituent units are organized into a limited number of singular, compulsory, noncompetitive, hierarchical, ordered and functionally differentiated categories, recognized or licensed (if not created) by the state and granted deliberate representational monopoly within their respective categories in exchange for observing certain controls on their selection of leaders and articulation of demand supports. (Schmitter qtd. in Jessop, 1990, p. 111).

Corporatism is a second strategy that Offe (1984, 1985) suggests has been pursued by governments in order to deal with the problems of fiscal crisis and the contradictions of capitalism. Keane summarizes Offe's (1984) account of this strategy as follows:

> Given the probable failure of strategies of *large-scale* recommodification, a greater reliance upon state-supervised, 'corporatist' forms of policy-making and administration cannot be excluded as a second, and possibly complementary, response to the present contradictions of the welfare state. This strategy of corporatism, Offe contends, is concerned with reviving the commodification process and alleviating the fiscal and planning problems of the welfare state. It seeks to exclude 'excessively political' demands and to institute state-supervised and informal modes of bargaining between representatives of key interest groups such as labour and capital. Corporatist policies are designed to develop a consensus among power elites in order to readjust welfare state policy making and administration to the requirements of the economic subsystem. Corporatist mechanisms rely upon arcane and highly inaccessible elite negotiations and increased political representation and surveillance, rather than autonomous public discussion and accountability (Offe, 1984, p. 27-28).

There has been some debate about the extent of corporatism in Canada. Panitch (1979) has been critical of scholars who have suggested that corporatist forms exist in Canada. Panitch maintains that although it is possible to argue that there has been an ideological basis for corporatism in Canada, "these ideological strains have not given rise to corporatist political forms" (Panitch, 1979, p. 51). "Only by the most simplistic of reasoning can it [the Canadian state] be considered as corporatist," writes Panitch (1979, p. 49). According to Panitch (1979) truly corporatist political forms have not been developed in Canada mainly because of the absence of strong centralized associations of business and labour. "The most popular ideology with affinities to corporatism was that of western Canadian wheat farmers' organizations and leaders in the second and third decades of this century as expressed in their doctrine of 'group government'" (Panitch, 1979. p. 53). However, once Albertans elected William Aberhart and the Social Credit party to power, corporatist ideology faded. Yet, in a more recent account of politics in Alberta, Richards and Pratt (1979) suggest corporatist strategy and ideology saw a resurgence after Peter Lougheed's Progressive Conservatives replaced the Social Credit as the governing party of Alberta. The result of this corporatist strategy was the establishment of a number of what Richards and Pratt term *quasi-corporatist* alliances between the Alberta government and a rising urban bourgeoisie.

There is a discrepancy between the viewpoint of Panitch (1979) and that of Richards and Pratt (1979). This may be due to the fact that Panitch's (1979) view and definition of corporatism is only one amid many that have been used by scholars (see Offe 1985). Recognizing this, Offe (1985) maintains that:

> Corporatism is a concept that does not describe a situation but rather an 'axis' of development. In other words, political systems can be more or less corporatist, more or less advanced in the process of corporatization, depending upon the extent to which public status is attributed to organized interest groups. The process is relatively advanced when many interest groups have publicly attributed status in all or most of the relevant dimensions of institutionalization, and is relatively undeveloped where none

> or only a few groups are institutionally defined in a few of the dimensions (p. 236-37).

The label, "quasi-corporatist," that Richards and Pratt (1979) use to describe the Alberta government's approach to managing its economy is consistent with Offe's (1985) contention that corporatism is best used to describe an axis of development. The very use of the prefix "quasi" implies that a less advanced form of corporatism exists in Alberta.

It should also be noted that the corporatism literature contains a debate over the groups that should be included in the corporatist framework. This debate is over the necessity of distinguishing interest-based organizations that are class-based (such as labour unions) from organized interest groups (such as a sport advocacy organization) representing other collectives that are specifically affected by state policies. Panitch's (1979) reluctance to recognize the existence of corporatism in Canada because of the absence of strong labour and capital-based collectives, places him on the side of the debate that insists only class-based organizations are relevant. Richards and Pratt's (1979) position is less restrictive and places them on the side of the debate which is open to including interests that are not class-based.

Offe (1985) maintains that neither point of view needs to be sacrificed when considering the phenomenon of corporatist developments. He writes:

> The phenomenon of corporatist developments thus seems . . . to require a *dual* or *combined* explanation that exclusively relies neither on the social class nor the group paradigm. In such an explanation, the state would pursue quite different objectives when granting the right to functional representation to unions, on the one hand, and to any 'pluralist' interest group (e.g. doctors) on the other (Offe, 1985, p. 240).

Offe's (1985) arguments and the analysis of politics in Alberta provided by Richards and Pratt (1979) suggest that it is advisable to consider the role that corporatist ideology may have played in the Alberta government's approach to sport development.

Considered collectively, the above arguments comprise a framework for understanding the role that the Canadian state has played in sport development. The framework provided by theories of the welfare state suggests that it may be possible to explain the development of the Alberta Sport Council by drawing attention to the ideology and strategies employed by the Alberta government in response to the demands of capitalism during the time period in which the Alberta Sport Council was conceived and implemented. It is from within this context that this investigation is undertaken. It should, however, also be noted that within this context, the explanation of government intervention in sport "cannot be reduced to a description of 'system needs,' whether these refer to the needs of capitalism or the needs of sport" (Macintosh & Whitson p. 107). In addition to focusing attention on the structure of the social system this study also examines the role played by individual actors and the organizations of which they are a part.

Chapter Three

Research Methods and Procedures

A variety of research methods and procedures were considered for use in this investigation. Qualitative methods were judged to be the most compatible with the focus of this study due to its historical nature, its focus on chronological events, its focus on human experience and its emphasis on explanation. As Miles and Huberman (1984) note, qualitative data "are a source of well-grounded, rich descriptions and explanations of processes occurring in local contexts. With qualitative data one can preserve chronological flow, assess local causality, and derive fruitful explanations" (p. 15).

Focused interviews and document analysis were the two qualitative data gathering techniques most appropriate for this case study. Other techniques, such as those associated with participant observation, were inappropriate because of this study's historical nature. This chapter contains a summary discussion of the ways in which these techniques were implemented and a detailed description of the ways in which a microcomputer was used to assist with the analysis of the data.

Focused Interviews

A significant amount of the data upon which this study was based was collected through focused interviews with a variety of individuals. This section outlines the various steps that were involved in the collection of interview data. The steps involved in the actual analysis of the interviews are discussed later under the heading 'Analysis and Treatment of Data'.

Selection of the Interviewees

Several steps were involved in the identification and selection of interviewees. The first step entailed generating a list of potential interviewees. A preliminary list of interview candidates was generated through a literature and document review and discussions with knowledgeable individuals. An extensive review of the literature on sport development in Alberta was conducted and a chronology of events was developed. This chronology listed the names of individuals who served in various leadership roles in several organizations or who had been associated with significant events. These organizations included, for example, Sport Alberta, the Alberta Sport Council, the Alberta Games Council, the government of Alberta and other relevant organizations. Significant events included, for example, sport conferences such as Operation Giant Stride and the annual Intersport conferences. A preliminary list of one hundred and seven key actors was compiled initially. This list excluded any key actors who were deceased.

This preliminary list was then shown to several of the people named on it. These individuals were people who were known to have had extensive involvement and influence within the sport community. Each of these people was asked to place a mark next to the names of any people they felt had played a significant role in sport development in Alberta since 1970. If they desired, they could indicate the significance and/or degree of each person's involvement as high, medium or low. They were also asked to add any names they felt were missing from the list.

The second step in the interview process involved determining a manageable number of interviewees. The number of interviews conducted had to be limited to an amount that was appropriate to the time available for the study and to the researcher's capacity to manage the volume of data generated by the interviews. After reviewing these limitations it was determined that between twenty-five and thirty interviewees would be a reasonable target for this investigation.

The results of the survey were used to compile a final list of thirty interview candidates. The thirty interview candidates were a collective representation of a number of groups involved in sport development in Alberta.

Ten of the interview candidates had been primarily involved with the Alberta Games Council and/or the Alberta Sport Council. Eight of the interview candidates had been primarily involved with Sport Alberta. Eight other interview candidates had been primarily involved with the provincial government (this included four ministers, two deputy ministers and two senior civil servants). Four interview candidates were involved with the sport community as administrators in provincial sport associations.

Interviewing began in April 1990 and continued through to the end of the fall of 1992. Over this time period the list of interview candidates was modified slightly because some of the individuals originally identified were found to be inaccessible since they had left Alberta and/or could not be contacted. A few other interview candidates declined to be involved. In a few instances these individuals were replaced with others whose names were mentioned repeatedly in the interviews already conducted. By the conclusion of the interviews twenty of the thirty people originally identified had been interviewed. Two additional people, who were identified while the study was in progress, brought the total number of completed interviews to twenty-two.

Most of the eight people who were not interviewed played a lesser role during the time period studied. Their exclusion was inconsequential inasmuch as they were representatives of the groups already represented and/or the information they were expected to provide was obtained from other data sources. Although it was not possible to interview all the original interview candidates, all senior decision-makers in office in the Alberta Sport Council, Sport Alberta and Alberta Recreation and Parks between 1981-1984, with the exception of the chair of the Alberta Sport Council, were interviewed.

The collection of interview data and data analysis was an ongoing recursive process. Consequently, information gathered in early interviews influenced the focus of later ones. For this reason the scheduling of interviews was organized to ensure that individuals involved in senior positions within the organizations studied were interviewed towards the end of the data collection. This made it possible to ask senior organzational actors specific questions related to events and issues raised by lower level actors and other sources of data.

Interviews were conducted throughout Alberta in a variety of locations. These locations were: the homes of respondents, respondents' places of work and the researcher's office at the University. One interview was conducted over the phone. Interviews lasted anywhere from a minimum of 45 minutes to a maximum of 90 minutes. Of the 22 interviews, 14 were recorded. Eight interviews were not recorded because the equipment necessary to record the interview was not available or because the researcher felt the interviewee might be more candid if the interview was not recorded.

Of the 14 recorded interviews, 13 were transcribed verbatim directly onto computer disks using the program Wordperfect. All transcripts were reviewed by the researcher to ensure their accuracy. There were a few occasions when the transcriber misinterpreted or excluded words. These inaccuracies and omissions were corrected. It was impossible to transcribe one of the recorded interviews because the recording was inaudible due to audio interference generated by mechanical noises in the tape recorder that was used. Extensive field notes were taken during and following the other eight interviews. These notes were later typed into computer files.

Topics Addressed in the Interviews

Prior to the administration of the interviews a list of general research topics was developed. These research topics were derived by considering the theoretical ideas discussed in Chapter Two. A master list of potential interview questions was developed next. These questions were designed to elicit responses that would provide data relevant to the research questions. Prior to each interview the master list was customized to suit the context of each candidate's involvement as it was felt that too many irrelevant questions might hamper the flow of the interviews and respondents would be more at ease and forthcoming with responses if the majority of questions addressed the context of their involvement. For example, questions about the day-to-day operation of the Alberta Sport Council were omitted from the set of questions that was administered to persons whos sport involvement ended prior to the creation of the council.

Below is an outline of the research topics. This list is followed by the master list of interview questions.

Research Topics

I. Demographic information

A. Characteristics of key leaders

1. What demographic features (i.e. race, gender, class, ethnicity) are representative of key individuals involved in the creation and implementation of the Alberta Sport Council?

II. Historical Background and Events.

A. Chronology of Events.

1. What is the chronology of events that led up to the creation of the Alberta Sport Council?

III. Scope of Authority

A. *Pre-Council Period (Pre-1983)*

1. Patterns of participation and authority of politicians in power.

2. Patterns of participation and authority of government institutions and civil servants.
3. Patterns of participation and authority of the legislative assembly.
4. Patterns of participation and authority of collectives representing the sport community.
5. Patterns of participation and authority of any other key interest groups or individuals (i.e. the federal government or the Recreation, Parks and Wildlife Foundation).
6. Individual's own involvement.

B. *Post-Council Period (1983-1988)*

1. Patterns of participation and authority of the Alberta Sport Council.
2. Patterns of participation and authority of politicians in power.
3. Patterns of participation and authority of government institutions and civil servants.
4. Patterns of participation and authority of the legislative assembly.
5. Patterns of participation and authority of collectives representing the sport community.
6. Patterns of participation and authority of any other key interest groups or individuals (i.e. the federal government or the Recreation, Parks and Wildlife Foundation).
7. Individual's own involvement.

C. Comparative Issues

1. Have any changes taken place in the power and/or authority of any groups over the delivery of sport in Alberta?

IV. Contradictions

A. Sport's role in the economy.

B. Unresolved dilemmas in sport pre- and post-Alberta Sport Council.

Potential Interview Questions

I. Demographic information

A. Characteristics of key leaders

1. Please tell me a little about your general background with sport and how you became involved with this (these) particular sport organization(s).
2. What type of person is likely to be appointed to the council's board of directors? Why?

II. Historical Background and Events.

1. In your opinion what were some of the major events that resulted in the idea for the Alberta Sport Council?
2. In your opinion, who do you believe were the most influential people as far as bringing the Sport Council into being is concerned?

III. Scope of Authority

A. *Pre-Council Period (Pre-1983)*

1. What is your opinion of the process that led to the creation of the Sport Council?
2. At one point in time, Sport Alberta was responsible for a number of the services now provided by the Alberta Sport Council. Why in your opinion has its role in sport changed so dramatically? Why in your opinion did the provincial government change the nature of its endorsement of Sport Alberta?

B. *Post-Council Period (1983-1988)*

1. Describe your opinion of the relationship between the council and government departments that are responsible for sport. What is your opinion of this relationship? Has (have) this (these) department(s) attempted to exercise control over the council? How is this accomplished?
2. Describe your opinion of the relationship between the Alberta Sport Council and the many provincial associations with which it must deal. What if anything do you think these groups would like to change? How likely are such changes to occur?
3. Has the creation of the Alberta Sport Council changed the role of government in the delivery of sport? On what grounds is your opinion based?
4. To whom, in your opinion, is the council responsible?
5. What is your opinion of the Alberta Sport Council's structure and function? Is it appropriate to the demands it must meet? Are there changes that you believe are necessary? Why?

6. Who are the key decision makers within the Alberta Sport Council?
7. Is the Alberta Sport Council a collective voice for sport? If yes, how does it accomplish this? If no, is there a need for an alternative voice for sport?
8. Has the council as it exists now lived up to the expectations people (i.e. the Ad Hoc Committee) had for it when it was being conceived?
9. After several years of operation, what have proven to be some of the more concrete/substantive advantages of the Crown corporation approach to sport delivery and funding? What have been some of the most obvious disadvantages? Which of these results were anticipated? Which of these results were unanticipated?

IV. Contradictions

1. Does sport play a role in the economy of Alberta?
2. What are some of the major issues/dilemmas that face the Alberta Sport Council today? What makes these such major issues? Will they be difficult to solve?
3. What are some of the major issues faced by other sports groups? (Follow-up as per # 2.)
4. What in your opinion have been the major criticisms, just and unjust, of the council? What reasons explain the unjust criticisms?

Collection of Organizational and Archival Documents

Organizational and archival documents were collected as a means of supplementing and confirming the accuracy of the information collected in the interviews. In this study several types of organizational and archival documents were considered:

1. Alberta government publications related to sport policy
2. Annual reports of the Alberta Sport Council, the Alberta Games Council, Alberta Department of Recreation and Parks
3. Minutes of Sport Alberta meetings
4. Letters (e.g. government correspondence, letters to the Minister of Alberta Recreation and Parks)
5. Press releases
6. Committee reports (e.g. Ad Hoc Committee on Sport Coordination in Alberta, Intersport Task Force Committee)
7. Legislation
8. Newspaper and magazine articles
9. Scholarly publications dealing with politics and/or sport development in Alberta and elsewhere.

These documents were retrieved from a variety of sources that included public and university libraries, private collections, the Queen's Printer, the Glenbow Museum and Archives and the Provincial Archives.

Analysis and Treatment of the Data

Data analysis was an ongoing process throughout the administration of this study. Several techniques were used to analyze the interviews and documents as they were being collected. This approach to data collection and analysis was very helpful because as Miles and Huberman (1984) have suggested:

> Analysis during data collection lets the fieldworker cycle back and forth between thinking about existing data and generating strategies for collecting new—often better quality—data; it can be a healthy corrective for

> built-in blind spots; and it makes analysis an ongoing, lively enterprise that is linked to the energizing effects of fieldwork (p. 49).

In the early stages of data collection, document forms similar to those suggested by Miles and Huberman were developed and filled out for the majority of organizational documents collected (see Appendix A). These forms included space for a document's name, events associated with the document, significance of the document, a summary of the document's contents and questions or issues that needed to be investigated as a result of the document's content. This procedure enabled the researcher to fine-tune future data collection and also facilitated information retrieval during the analysis process that continued after all data had been collected.

Interview data were handled in a manner very similar to that of the documentary evidence. Interview summary forms were developed and filled out at the conclusion of each interview. These forms summarized the interview's main themes and salient points as well as new target questions that might be asked of future interviewees. Interviews and documents were also subjected to a rigorous and intensive analytical process that combined aspects of latent content analysis with aspects of grounded theory development (cf. Strauss, 1987; Turner, 1981). Data were coded into categories and sub-categories relevant to the study's focus on the development and impact of the Alberta Sport Council. These categories (e.g. inter-organizational relationships, decline of Sport Alberta, consequences of Sport Alberta, etc.) and sub-categories (e.g. Sport Alberta relationship with Alberta Sport Council, expertise of Sport Alberta Board and bureaucratization of sport, etc.) were used to develop a number of topic areas. As the results for each section of this study were compiled, the information associated with each topic area was consulted and evaluated in conjunction with other documentary evidence and field notes to form the basis of the observations and conclusions of this study.

A number of microcomputer-assisted techniques were used to aid the data analysis. These techniques were developed independently as they have not appeared in other research. The use of a microcomputer did not play a significant role in the data analysis due to the small sample of interviews to which these techniques were applied and to the fact that the microcomputer did not by itself actually analayse the data. Nonetheless, several valuable lessons about the advantages and disadvantages of using microcomputers to assist in the organization of qualitative data were learned as this study progressed. A personal account of these lessons is provided in Appendix B.

Chapter Four

Sports Interests and the Struggle for Public Status, Part One: Sport Alberta, the Progressive Conservatives and Corporatist Ideology

The events leading up to the enactment of *Bill 21, An Act to Establish the Alberta Sport Council* are presented in this and the following chapter. Enacted in 1984, this legislation officially marked the beginning of the Alberta Sport Council, a Crown corporation assigned the responsibility of overseeing sport development in Alberta. This legislation emerged from an effort to create an institution that would act as a unified voice, speaking on behalf of all Albertans interested in the development of sport in Alberta. The events culminate in an ironic situation: although the initiative to create this institution came from individuals who were detached from the provincial government and leery of government intervention, the organization that was born as a result of their struggle would be one over which they would have little authority in comparison to that of the provincial government.

The results of the study are organized chronologically, beginning in 1963, continuing through the enactment of *Bill 21, An Act to Establish the Alberta Sport Council* in 1984, until the present. Much of the sport development activity that took place during this time period focused on developing a means through which sport development in Alberta could be effectively and efficiently co-ordinated. The first organization created for this purpose was called Sport Alberta. Sport Alberta was created in 1972 as an independent association of provincial sport organizations. It struggled for over a decade to represent and co-ordinate the interests of Alberta's amateur sport groups. In 1984, when the Alberta Sport Council was implemented, Sport Alberta subsequently withered into obscurity.

The study begins with a brief discussion of the Alberta government's involvement in sport development prior to 1971. This main part of the study is presented in three sections. Each section is organized to follow the chronology of government intervention in sport development in Alberta. Part One is presented in this chapter and examines the five-year time period between 1972 and 1977. This period is distinguished by the birth of Sport Alberta and its subsequent struggle for legitimacy and official recognition from the government of Alberta and the sport community. It is also characterized by a significant increase in the degree and kind of funding provided to sport organizations by the Alberta government. By 1977 it became clear that Sport Alberta was losing its struggle for legitimacy when the government usurped control of the programs essential to this legitimacy. It was at that time that the Alberta government created the Alberta Games Council, its first sport-related Crown corporation.

Part Two is presented in Chapter Five and examines the time period from 1978 through 1984 and the enactment of the legislation that created the Alberta Sport Council. During this third time period discussion focusing on the co-ordination of sport in Alberta was reopened. An Ad Hoc Committee was formed to ascertain the needs of the sport community and to submit a proposal for action. The government also began to formulate its first official policy on sport and recreation development in Alberta. The idea of creating an Alberta Sport Federation was put forward and after some debate and discussion it was determined that a new Crown corporation, the Alberta Sport Council, would be created. The Alberta Sport Council significantly changed the character of sport development.

Part Three is presented in Chapter Six. It examines the Alberta Sport Council's impact on sport development in three areas. First, concerns regarding the composition of the council's board of directors are discussed to illustrate concern that control over sport development in Alberta has been secured by an alliance between government and Alberta businessmen. Second, concerns associated with the growth of Alberta's sport bureaucracy are discussed and compared with concerns of those raised in other studies. Third, concerns about the focus of the Alberta Sport Council's programs are presented.

Background to the Study: The Social Credit and the Pursuit of an Integrated Sport System, 1963-1971.

While there are few published commentaries that provide a detailed account of the history of the Alberta government's role in sport development, there have been a number of dissertations that have focused on this subject. Two dissertations of particular interest to this study are those written by Richard Baka (1978) and Ernie Nicholls (1982).

Baka's (1978) historical account of the Alberta government's involvement with sport in Alberta begins in 1905 and covers a period through 1977. The period 1905 through 1938 is described as one in which government involvement was very limited, with some very small contributions made to sport organizations. The next period examined by Baka spans 1938 through 1955. It is during this period that the Social Credit Party gained control of the provincial government and joined the federal government's "Dominion-Provincial Youth Training Program". A very small health and recreation branch of the Department of Education was formed and staffed by a single individual until 1945 when staff size increased slightly. As in the previous time period, involvement with sport was minimal apart from agreements made under the National Physical Fitness Act and a small number of grants provided to sport organizations as in the past. A notable feature of the period 1955-1966 was the establishment of the Community Recreation Bureau (CRB) in 1955 which by 1961 was transformed into the Recreation and Cultural Development Branch, the government agency primarily responsible for sport as well as numerous other areas. Baka's review of budgets during that time period indicates a steady increase in government assistance to culture. Baka notes that gradually the CRB began to take on a supportive role in the area of sport. This role was one where assistance was provided to communities and organizations in the administration and operation of recreation programs. In addition, a number of coaching, officials and participant clinics were sponsored or co-sponsored by Alberta's provincial government in conjunction with the federal government through provisions contained in the Fitness and Amateur Sport Act.

It was during this time period when the disinterested Social Credit government agreed to fund a workshop titled "Operation Giant Stride." This workshop, held March 8-10, 1963, brought many leaders from within the Alberta sport community together for the first time to discuss several issues related to the future of sport- and fitness-oriented activities in Alberta. In a letter sent to provincial associations by the workshop's steering committee, the workshop's purpose was described as being "to encourage the various provincial sporting groups of Amateur Athletic and Outdoor Education to make suggestions as to how this division (Athletics and Outdoor Education) may serve the Fitness and Recreation movements in Alberta more effectively." Nicholls (1982) notes that this provincial workshop is significant because it was the first forum in which the notion of a single unified voice for amateur sport was mentioned. It was funded by the provincial government primarily because the government was apprehensive about duplication, overlap and a frequent lack of continuity in the programs offered by the numerous provincial associations and municipalities and by the government. It was successful in bringing a large group of people with very diverse interest and backgrounds together to exchange ideas. However, Nicholls (1982) concludes that aside from the enthusiasm that was generated "little else of a concrete nature developed in the matter of the formation of a provincial sports collective" (p. 102).

Four years later in 1967 the idea for a provincial sports collective would surface once again at a seminar sponsored by the government's Department of Youth. This time the government was interested in discovering a means whereby co-operation might be used to enhance the opportunities for Albertans to participate in a wide variety of sports. The seminar concluded that an advisory council on amateur sport be established. By January 1968 a ten-member committee was established with the task of determining if a single body, speaking on behalf of all sports associations, was in the best interests of the development of amateur sport.

The notion of a single sport body was raised again at a second major seminar of provincial sport governing bodies in March 1969. Once again the seminar was sponsored by the Alberta government's Department of Youth. Nicholls (1982) notes that this was an information-sharing session where discussion focused on facilitating communication between associations and eliciting their views on the feasibility of establishing an Alberta Sports Federation.

Finally, in April 1970 the Department of Youth sponsored a third seminar with some assistance from the Alberta Council on Amateur Sports. This seminar was conducted to review the report of the Alberta Council on Amateur Sports and discuss the feasibility of continuing to pursue the establishment of an Alberta Sports Federation. The report contained 21 recommendations. The first recommendation was that a sports federation be established immediately. The remaining 20 recommendations focused on specifying guidelines for the establishment of the federation. They dealt with administration and composition, financing and initial goals.

As outlined in the recommendations a steering committee was created to implement all accepted recommendations. On November 21, 1970, the steering committee addressed a motion pertaining to the establishment of an Alberta Amateur Sports Federation. The motion was approved and followed by a motion which changed the name to Sport Alberta. On April 10, 1972, Sport Alberta was formally registered under the Societies Act in Alberta.

The objects of Sport Alberta as outlined in its constitution and bylaws were:

a. To promote amateur sport in the province of Alberta.
b. To act as a forum for the exchange of members' views.
c. To act as liaison with government agencies and to bring before the provincial government such recommendations as approved by the society.

d. To correlate the efforts of all amateur sports governing bodies in Alberta in stimulating interest in amateur sport.

e. To assist in the development, organization and execution of the Alberta Summer and Winter Games.

Now formally registered, it appeared that Sport Alberta could focus entirely on the five points of its mandate, but that would not be an easy task. Sport Alberta had to struggle very hard to firmly establish itself as the legitimate voice of the sports community and as a legitimate source of leadership in sport development. The Social Credit government had been supportive of the formation of Sport Alberta without making any explicit demands on the organization. However, in 1971 the Social Credit Party lost its majority in the provincial legislature to the Progressive Conservative Party. The Progressive Conservative approach to government would be entirely different to that of the Social Credit Party.

The Progressive Conservative Party

Although the seeds to create an organization to oversee sport development in Alberta were planted during the tenure of the Social Credit Party, they would germinate in a fundamentally different social and political climate. From the moment of its inception, Sport Alberta would struggle tenaciously with its members and with the provincial government to establish itself as a legitimate institution. In its first five years it would lose several important battles, many of which those interviewed for this study suggest contributed to its eventual demise.

The social, economic and political context within which Sport Alberta was born has been described as one of rapid social and economic change in Alberta (Baka, 1978)[10]. This period of change and growth, which began in the mid-1960s and lasted until the mid-1970s, was partly a consequence of the wealth resulting from Alberta's expanding oil revenues. Richards and Pratt (1979) note that

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[10] See also Richards and Pratt, 1979; Pratt, 1986.

during this time period, marked by the beginning of the 1970s, Alberta's population saw the advent of a new middle class, "urban and secular in its outlook and impatient with the Social Credit's blend of religious fundamentalism and the remnants of its agrarian populist past" (p. 166). It was this new middle class that gave Peter Lougheed the support that eventually enabled the Progressive Conservative Party to rest control of the provincial government out of the hands of the Social Credit Party.

Several political analysts have stressed that the election of the Progressive Conservatives marked a new era in Alberta politics and a distinctive approach to government (cf. Alexander, Clement, Marchak, Pratt, & Percy, 1981; Pratt, 1977, 1986; Richards & Pratt, 1979). In contrast to their Social Credit predecessors the Progressive Conservatives advocated an entrepreneurial approach to government, emphasizing "economic development and the enhancement of Alberta's power position within Confederation" (Shaffer, 1986, p. 119). This approach, spearheaded by Progressive Conservative Party leader Peter Lougheed, has been described as "province building" in which:

> the resources of an interventionist provincial government are being employed to nurture the development and defend the interests of an ascendant regional bourgeoisie. The purposes of this rising class are to strengthen its control over the Alberta economy, foster regional capital accumulation, [and] reduce Alberta's dependence on external political and economic forces (Richards and Pratt, 1979, p. 215).

Richards and Pratt (1979) highlight an assortment of tactics characteristic of a businesslike approach to public affairs that accompanied this new focus on economic development. Two notable tactics from this assortment were intervention through quasi-state corporations and joint ventures, and the relegation of discussion and decision-making to the secrecy of cabinet chambers and federal-provincial conferences. This left the legislature with a minor role (Tupper, 1986). "Lougheed's philosophy could be described as corporatism inspired by the purpose of winning business support for intervention and of giving the public a sense of participation in large scale economic development" (Richards and Pratt, 1979, p. 242).

This section explores the relationship between Sport Alberta and Alberta's Progressive Conservative government during the time period between the years 1971 and 1977. Key events that marked this period of frequent and rapid change in the Alberta government's involvement with sport delivery and development are outlined. These events culminated with the creation of the Alberta Games Council, the Crown corporation that would later be transformed into the Alberta Sport Council. The analysis presented here reveals that the Alberta Games Council emerged as a consequence of the actions of specific individuals and the influence of institutional factors of a structural nature. The institutional factor deemed to be the primary determining ingredient is the Progressive Conservative government's unfolding corporatist ideology. The analysis of the data collected for this study indicates that the Progressive Conservative government's corporatist tactics were not restricted to economic policy in the oil and gas industries or other sectors of the Alberta economy. These tactics also influenced the government's approach to sport development in Alberta in such a way as to recast the role played by the various social groups involved in sport and the scope of government authority over sport development. The implementation of a corporatist ideology is also illustrative of the links between the structure of the economy, economic policy and sport policy.

The shift from a Social Credit to a Conservative government gave rise to a period of transformation in which there was a significant change in the degree and kind of government involvement with sport development. Considering that the Progressive Conservatives were new to governing and Alberta was riding the wave of an economic boom, it is not surprising to discover that during the first five years of Progressive Conservative government rule there was an "almost annual" restructuring in the elements of the government bureaucracy assigned to deal with sport (Baka, 1978). For example, in 1971 a Department of Culture, Recreation and Youth was introduced and replaced the Youth Department and the

Recreation Branch, which had replaced the Recreation and Cultural Development Branch of the early '60s. In 1975 a new Department of Recreation Parks and Wildlife was created which in 1976 was followed by a major restructuring of the Recreation Development Division.

Amidst this constant organizational shuffling the Alberta government expanded and revised the role of its primary agency responsible for sport. The magnitude of this expansion is indicated by the growing size of the government agency responsible for sport and an increase in the amount of money that was being spent on sport. Figures unearthed by Baka (1978) show that in the year 1966 $512,416.91 was spent on sport while in 1976 the budget of the Recreation Development Division was $6,547,676.00, of which 1.2 million was dispersed to the Sport and Fitness Branch. Over this ten-year period spending had increased tenfold.

Government involvement with sport development was not limited to the events that took place within its bureaucratic structure. As noted earlier, the government supported an effort to create a non-government organization to facilitate sport development in Alberta that began in 1967. During the 1970s, government expanded its relationship with Sport Alberta in a manner that had many consequences for sport development. The relationship between Sport Alberta and the provincial government underlies much of the analysis of Sport Alberta contained in Nicholls' (1982) dissertation about the structure and function of three sport collectives in Western Canada. The events that came to pass as a result of this relationship would inadvertently set the stage for the birth of the Alberta Sport Council and the demise of Sport Alberta.

Nicholls (1982) indicates that three of the recommendations for the creation of an Alberta Sports Federation (read Sport Alberta) made by the Alberta Council on Amateur Sport in 1970 were never implemented. The recommendations were:

> 1. That each member association [of Sport Alberta] provide $200 of its governmental special projects grant of $300 to the

> new sports federation for promotion of amateur sport in the province.
>
> 2. That efforts be made in conjunction with the Minister of Youth to set aside a capital sum from the Provincial Treasury for the establishment of a fund for amateur sports and recreation.
> 3. That all budgets and requests for grants of the provincial sports associations be channelled through the new sports federation for submissions as one large request for funding by government (Nicholls, 1982, p. 107).

Nicholls (1982) argues that these three recommendations are noteworthy merely because they were never implemented. Notwithstanding this conclusion, it is possible to argue that had these three recommendations been fulfilled Sport Alberta may have been able to attain a greater degree of legitimacy as a voice for the sport community. These three recommendations could have served to enhance Sport Alberta's legitimacy in two ways. First, Sport Alberta would have received the funds necessary to establish the strong financial base necessary for it to achieve its objectives. Second, by implementing the third recommendation the government would have communicated that it recognized Sport Alberta to be the legitimate and official liaison between government and provincial sport associations. With such a sanction Sport Alberta would have been able to focus on implementing programs to enhance sport development through its member associations. Without this sanction Sport Alberta had to devote a considerable amount of time and energy towards activities aimed at establishing its legitimacy.

The reasons why these recommendations were never implemented are unclear, but they may have something to do with the fact that, midway through the struggle to create a collective voice for sport in Alberta, control of the provincial government changed hands. With the change of the party in power there also came a new approach to politics and government in Alberta which, on the substance of the evidence collected for this study, appears to have worked against the viability of Sport Alberta. The idea for Sport Alberta emerged under a Social Credit government. The Conservative Party did complete what the Social

Credit had begun. However, the commitment to the intent of this initiative was at the very least tenuous.

Following its creation Sport Alberta wasted little time establishing programs to fulfil its objectives as a collective voice for and supporter of the amateur sports community. Initial projects implemented by Sport Alberta included: the development and execution of the Alberta Winter and Summer Games, establishment of a central administrative centre for sport, development of a central computerized sports registry, implementation of fund-raising programs to support sport, enhancement of Sport Alberta's relations with government and the inception of a program to establish an Alberta sports hall of fame. In its efforts to implement each of these projects, Sport Alberta faced many difficulties, which appear to follow from Sport Alberta's relationship with the Progressive Conservative government and its bureaucracy. They would also lead many members of the sports community and government to question Sport Alberta's ability to live up to its mandate.

Considering that Sport Alberta came into being as the result of initiatives sponsored by the Alberta government, it is ironic that government action and disregard played a role in Sport Alberta's failure to overcome these difficulties. For example, consider Sport Alberta's efforts to raise funds. The first of the three recommendations advanced by the Alberta Council on Amateur Sport noted above was never implemented. At the founding meeting of the society, membership fees had been set at $25 per association, the equivalent of 1/8 of the amount recommended by the Alberta Council on Amateur Sport (Nicholls, 1982, p. 123). With a membership of 60 associations, the $1,500 collected in membership fees was far below Sport Alberta's operating expenses of more than $44,000.

In an effort to make up the difference, Sport Alberta turned to the government for support. In January 1970 a brief was submitted to the Minister of Youth and Culture. Before the brief could be acted upon, however, the election that led to the defeat of the Social Credit Party was called. Several months passed before the new and inexperienced Progressive Conservative government got around to dealing with this matter. Nicholls (1982) reports that Sport Alberta revised its brief and re-submitted it to the new government. He also notes, "As a document designed to substantiate a request for significant funding from the public purse, the brief was sadly lacking . . ." (Nicholls, 1982, p. 127). A letter from the Honourable Minister dated November 15, 1971 advised Sport Alberta that extra funds were not presently available, but $34,000 would be given to Sport Alberta for the 1972-73 fiscal year.

According to Nicholls (1982), Sport Alberta also attempted to raise funds through a lottery scheme that would be run in conjunction with a publishing company. The Attorney General's office would not give the organization permission to operate the lottery in Alberta. Nonetheless, the Minister of Culture, Youth and Recreation provided the funds required for Sport Alberta to begin to develop the infrastructure necessary to go ahead with its sports lottery or another similar fund-raising scheme by means of a $20,000 loan. However, the Attorney General's office could not be convinced to approve either of the two lottery schemes the organization had presented. Sport Alberta had plainly failed in its endeavour to obtain government sanction of this very important fund-raising initiative. This, however, was not the only area where the organization failed to get the government to sanction its activities and to recognize it as the legitimate representative of Alberta's sport community.

Sport Alberta was involved with two other more important and more visible initiatives which the government handled in a completely different manner. The first of these initiatives involved the establishment and co-ordination of a central administrative centre for provincial sports associations. The second initiative involved the establishment and co-ordination of the Alberta Games. The government's involvement with these two initiatives would ultimately have a greater impact on Sport Alberta and sport development in Alberta than the government's response to Sport Alberta's fund-raising ideas.

Sport Alberta approached the government in order to receive some financial assistance so it could establish a centralized sport administration centre for its member associations. As Nicholls (1982) points out, in view of the growing trend towards the establishment of centralized sport administrative centres that was characteristic of the early 1970s, it is not surprising that sports associations in Alberta began to request that an amateur sport administration centre similar to those established in Ontario, Quebec and Ottawa be set up in Alberta[11]. The Alberta government responded by acquiring space in an old school located in St. Albert. By 1973 the building was ready for occupancy. According to Nicholls, during a 1972 meeting, Sport Alberta's board of directors discussed its fear that its control of a central administrative support services office that it had already established might be taken away by the provincial government. Nonetheless, Sport Alberta decided to support the centre provided that Sport Alberta would be designated to take on the number one leadership role in administration.

Unfortunately for Sport Alberta, this demand would ultimately be ignored as it became "lost in the excitement of the government's decisions regarding the Alberta Summer Games programme" (Nicholls, 1982, p. 122). The administrative centre was established without Sport Alberta acting as its manager. The government had successfully appropriated the leadership role in the development of the administration of amateur sport in Alberta. The organization was unable to claim status as the legitimate leader in this capacity and this would ultimately hinder its efforts to gain support from the community.

While Sport Alberta's failure to gain recognition as the director of the provincial sport administrative centre was a significant blow to its quest for legitimacy, it was a gentle rebuff in comparison to the fatal impact of the government's decision to remove the administration of the Alberta Games from

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[11] Macintosh et al. (1987) note that the development of provincial sport administration centres occurred partly as a result of the creation of the Canada Games (p. 37).

the hands of Sport Alberta. This decision came about as a means to resolve a conflict between the board of directors of Sport Alberta and its Executive/Managing Director, Mr. Ron Butlin. More than one individual interviewed for this study referred to this decision and time period as "the beginning of the end" for Sport Alberta.

Nicholls' (1982) analysis of Sport Alberta devotes considerable attention to this time period and describes it as the "Butlin years, 1973-1977." During this time period concerns about the closeness between government officials and Alberta Summer Games Officials (including Ron Butlin) were being raised by members of the sport community[12]. The conflict which has made this period of time noteworthy is often referred to as the "Butlin Affair." According to Nicholls (1982), the Butlin Affair entailed a dispute between the board of directors of Sport Alberta and its Executive/Managing Director, regarding the administration of the Alberta Games. At Sport Alberta's 1975 Annual General Meeting the question of Sport Alberta's authority over policy decisions pertaining to the Alberta Winter Games program was raised. In particular, "a member association (the Alberta Basketball Association) was then wanting to enter the Games with competition for age-class (13 and 14) competitors" (Nicholls, 1982, p. 154). This was in direct contrast to the Games Policy Committee's position that competition at the Games be for senior competitors. Butlin advised that such disagreements with member sports would be settled between each sport and the Games Policy Committee (which makes the decisions and regulations pertaining to the Games).

Nicholls (1982) notes that shortly after this seemingly innocuous meeting of 1975, the board of directors of Sport Alberta had become concerned about Butlin's relationship with government officials. This was indicated by a letter sent from the Director of Sport and Fitness, Dwight Ganske, to Ron Butlin. Nicholls (1982) draws attention to Ganske's comment that Butlin was not really an

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[12] This concern is also discussed in a term paper written by John K. Yardley (1981). This paper was discovered in the Glenbow Museum Archives.

employee of Sport Alberta in the strictest sense since Butlin's salary was paid to him by the government **through** Sport Alberta. Ganske also observed that Butlin had done most of his dealing directly with the Minister and Deputy Minister. Finally, Ganske referred to a need to clarify the role played by the many groups involved with the Alberta Games: Sport Alberta; Alberta Recreation, Parks and Wildlife; the Alberta Games Policy Committee; the Chairman of the policy committee and other government departments (Nicholls, 1982, 154-157). The lack of clearly defined roles allowed Butlin to play many of these groups off against one another.

Approximately one year later Butlin began to pressure Sport Alberta to reorganize. He was particularly eager to see the Alberta Games separated from Sport Alberta. Butlin expressed his opinion in a letter sent to the minister in charge of Recreation, Parks and Wildlife and to other interested parties including Sport Alberta's board of directors. Upset by Butlin's remarks, the board members responded quickly by requesting a meeting with the minister. They also ordered Butlin to present the board with financial statements and the terms of reference of the Alberta Games Policy Committee. Both the minister and Butlin chose to ignore these requests. However, officials with the Sport and Fitness Branch of the government made an effort to bring the minister together with Sport Alberta's board of directors as a means to resolving the problems that were developing.

According to a number of individuals that Nicholls (9182) interviewed, the animosity that was about to erupt between Butlin and the Sport Alberta Board had been brewing for a long time:

Wrangling intensified as Sport Alberta wrote to the minister of Recreation, Parks and Wildlife demanding clarification regarding who was in control of the Alberta Games and the financial affairs of Sport Alberta. At the 1976 annual general meeting of Sport Alberta an unsuccessful effort was made to ameliorate the situation. A further attempt to cool the situation made via the resolutions passed at Intersport II also failed:

> After the raucous Intersport II meeting and the strained annual meeting of 1976, relations between Butlin and Sport Alberta's board broke down almost completely. It seemed, in the ensuing flurry of charges and counter-charges, that almost open warfare had been declared (Nicholls, 1982, p. 170).

Throughout 1976 the situation escalated. Several board members took pleas for the government to intervene to the office of the premier. The government stated that it "would not interfere in the internal affairs of Sport Alberta nor become centrally involved in the dispute between Sport Alberta and its managing director" (Nicholls, 1982, p. 181). Nonetheless, the government did intervene. On February 3, 1977, the minister met with all the parties involved and announced that the Alberta Games would no longer be under the jurisdiction of Sport Alberta. They were, effective April 1, 1977, to be transferred to a newly created Crown corporation, the Alberta Games Council.

Analysis: The Role of Agency and Structure in the Introduction of Corporatism to Sport Development

Insight into each of the theoretical questions that form the basis of this study was gained by treating Sport Alberta's struggle for legitimacy as a struggle to obtain public status[13]. In many instances, interviewees indicated that the friction between Sport Alberta and the Alberta government was tied to issues related to each organization's ability to influence sport development. Without public status, Sport Alberta's power and influence were severely limited.

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[13] Offe (1985) defines public status in terms of the specifically attributed formal status of a group, as opposed to relations of informal co-operation between political and other segments of the elite, and status resulting from ad hoc tactical considerations of various groups or branches of the state. "Formal status is based on legal statute and formally adopted procedural rules that give the interest group some claim on a specific status" (Offe, 1985, p. 238). That is to say interest group-based organizations that have relationships with government that have been formalized through legislation are deemed to have public status.

Offe (1985) has shown that the simultaneous use of three levels of analysis can yield important insights as to why an interest group succeeds or fails in its bid to secure public status. Consequently, the analysis of this time period focuses on the level of the individual social actor, the level of the organization itself and the level of the social system in general. Using these levels of analysis it is possible to illuminate the characteristics of key individuals and their impact on Sport Alberta's struggle. Key traits of the changes in the Alberta government's scope of authority over sport development were also revealed. Furthermore, insight was also gained into key social and structural factors.

(1) The Role of Social Actors

The data most relevant to this level of analysis came from interviews and data contained in Nicholls' thesis. The people interviewed for this study were asked to indicate what they believed were the key reasons that explained why Sport Alberta lost the authority to administer the Alberta Games. Several interviewees raised the issue of Sport Alberta's competence in their accounts of its failure to gain government support, while others praised the efforts of the individuals who were involved at that time. Overall, the overwhelming majority of interviewees praised the contributions made by the individuals involved during that period. For example, Dr. Gerald Glassford, former dean of physical education at the University of Alberta, summed up their contribution by saying,

> I think that Sport Alberta did create a number of programs. They took on the creation of the Sport Museum, Sport Hall of Fame, they retained the concept of let's get together, we can be a voice for sport, and they did do that. There were a number of things that they did and they did well.

People's opinions differed with regard to the administrative competence of Sport Alberta. However, many agreed that conflict between individuals overshadowed the association's contributions to sport development. The conflict between Ron Butlin and the Sport Alberta board of directors was identified as a key factor. The significance of this prominent conflict is described by Nicholls

(1982) who commented on Sport Alberta's situation in 1977 following its loss of jurisdiction over the Alberta Games. He noted, "Sport Alberta's lifetime has been fraught with difficulties. It would seem to be at a precarious point in its existence and must attend to the business of making a fresh start" (Nicholls, 1982, p. 207). This assessment of Sport Alberta's delicate nature at that time is confirmed by the interview data. Gwen Smith, a former President of Sport Alberta, noted that:

> With the Games gone [there was] very little left for them [Sport Alberta] to do because they didn't have enough money. With just Paul Conrad as executive director and the secretary, they didn't have enough personnel to really do good programs and they didn't want to up the membership fees of the sports because they weren't doing that much for the sports. You can't charge membership fees if you're not going to give them something.

While Nicholls (1982) documents many of the events that took place during this conflict, he does not attempt to offer an explanation or rationale for the government's decision to remove the Games from Sport Alberta's jurisdiction. Nicholls' account describes how in April 1974 Butlin signed a nine-clause agreement to become the executive director of Sport Alberta. The agreement gave Butlin considerable powers including: the complete authority over the entire operating budget of Sport Alberta, the authority to hire staff who would be responsible to himself and the assurance that the contract could only be terminated by Sport Alberta in the event of the embezzlement of funds by the executive director (Nicholls, 1982, p. 145). The then-minister of Culture, Youth, and Recreation, Horst Schmid, authorized his Department to provide Sport Alberta with the necessary funds to cover Butlin's salary, emphasizing that Mr. Butlin's responsibility would be the development of the Alberta Games.

The data collected for this study indicate that a close relationship between Ron Butlin and government officials had been developing long before his involvement with the Alberta Games and Sport Alberta. Horst Schmid described the events leading up to Ron Butlin's involvement as follows:

> Anyway, I was at that [hockey] game and a Pastor or a Bishop actually and a Rabbi, both of them from Calgary, introduced me to Ron Butlin. . . . I met him, I talked to him and as I talked to him I felt, my God, that's the

> guy. Because of his attitude, his personality, because of the obvious promoting kind of personality he had. . . . I thought, my God, that's the guy. I needed a promoter, I needed someone who knew some of the ministers, which he did, and someone who could say, 'oh ya, this guy is from that corporation, you Molson's here, and this corporation there' and also, of course, I needed someone who understood sports, who knew what sports is all about and who would be accepted by the sporting community. He had it all in one. . . . Then and there I said, 'You are the one for the Alberta Games.' He said, 'Huh!' I explained to him what it was all about. We set up a contract and that was it. That's how it got started.

Evidence cited by Yardley (1981) further indicates Ron Butlin's rapport with government officials. Yardley (1981) writes that Sport Alberta was forced to sign Butlin's contract under government duress:

> According to Mr [*sic*] Bob Lucas, the then President of Sport Alberta, Mr [*sic*] Butlin arrived one day with a contract he said had been approved by the then Recreation Minister Horst Schmid and implied, 'that if Sport Alberta did not agree, its funding would be cut off completely.' Edmonton Report also reported that it had obtained a copy of an 'inhouse' evaluation of Sport Alberta prepared for Hon. Adair in 1976 in which they report,
>
>> the board members are said to have been thrown off their guard when the government talked to Mr [*sic*] Butlin rather than the Sport Alberta board about the contract. The directors, according the report, were 'manipulated' into signing a contract they would regret (p. 21).

Several individuals described Butlin as a shrewd manipulator who knew how to use the system. One individual used the following words to sum up Butlin's style:

> And Ron would be wise, he'd work with Sport Alberta as it helped him and when it didn't he would run over here and be under the advisory group and if that didn't serve his purposes then he would be under the minister. He was just a manipulator, and again I don't say that negatively, he got things done.

From the accounts of Yardley (1981) and Nicholls (1982) it is evident that government officials never insisted that Ron Butlin make himself accountable to the Sport Alberta board of directors. Nicholls (1982) also indicated that by May 1976 there were complaints:

> . . . that the Games where the be-all and end-all for Sport Alberta's managing director [Ron Butlin] and certain members of the government, and that the board had lost control of the direction of Sport Alberta (St. John's Edmonton Report, February 21, 1977 p. 18 cited in Nicholls, 1982, p. 166).

As noted earlier, the conflict between Butlin and the Sport Alberta board of directors resulted from disagreements over Alberta Games policy. Nicholls indicates that the source of the conflict can be attributed to a clash of personalities between Mr. Butlin and Mr. Alex Romaniuk. However, in focusing exclusively on the individuals involved, he overlooks the significance of the structural conditions he mentions in his own analysis[14].

(2) Organizational Factors

Models of the sources of conflict that have been put forward by organizational theorists illustrate that while conflict is often related to personality and communication differences, several structural antecedents can also facilitate the potential for conflict within an organization (cf. Daft, 1992; Robbins, 1987). The potential for conflict is influenced by an organization's differentiation, shared resources and interdependent activities. These three factors influence the nature of several emergent attributes of interdepartmental relationships which can lead to perceptions of goal incompatibility and opportunities for interference. Uncertainty, ambiguity and goal orientation are examples of attributes of interdepartmental relationships that develop as a result of an organization's structure and can subsequently lead to conflict.

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[14] The significance of "structural antecedents" to organizational conflict is well documented. See Daft (1992) and Robbins (1987) for a detailed discussion of how consideration of these issues can enhance the analysis of conflict.

The data indicates that the ambiguity and uncertainty surrounding the issue of who possessed the ultimate authority over the organization and administration of the Alberta Games were the most important structural issues that promoted the conflict. This ambiguity and uncertainty interacted with the distinct goal orientations that developed within Sport Alberta to produce a conflict. Distinctive goal orientations were evident as far as the administration of the Alberta Games were concerned. There was some disparity between the views of Sport Alberta and its members on the one hand, and the provincial government and Ron Butlin on the other. The board of directors of Sport Alberta viewed the Alberta Games as one of many services it offered to its members. From this point of view Sport Alberta had some responsibility to ensure that this service was administered in a manner that addressed the needs of its member sports associations. Consequently, when the Alberta Basketball Association made its request for some modifications to the way in which basketball would be conducted at the Games, the board of directors of Sport Alberta tried to comply with the request.

However, the data suggest that the Alberta government had a very different goal orientation that it was attempting to implement with the assistance of Ron Butlin. The government was predominately interested in Sport Alberta as a mechanism through which it could ensure that the Alberta Games would be presented to the public. The Alberta Games were developed out of the Southern Alberta Games which had been started in 1970 by Max Gibb, a recreation consultant of the provincial government. Max Gibb developed these games with the hope that they would help to increase the number of athletes from southern Alberta that were on the Alberta Canada Games team. In 1969 only two athletes from southern Alberta were on that team; by 1975 the number had increased to thirty-nine. While Gibb was primarily concerned with the performance of southern Alberta athletes at the Canada Games, Horst Schmid was concerned about the performance of all Alberta athletes. In an interview Schmid recalled,

> Part of the whole idea was . . . how can we in Alberta find in all of Alberta, not just in southern Alberta, the best athletes to compete for

> Canada and internationally . . . . How can we train them? How can we coach them? [We wanted to] find the best athletes possible and not lose them because they happen to be, let's say from Innisfail and not from Edmonton.

According to the data, Horst Schmid initially requested that the government directly fund the proposed Alberta Games. The request was denied, as few members of the legislature believed that government should have such a direct involvement in sport. [illegible] the government agreed it could allocate some funding for the Albe[illegible]rough Sport Alberta. Mr. Schmid accepted this strategy for "it didn't r[illegible]er how I was able to get the money for something as long as I was able to [illegible]t and say okay here to the body and that body will administer the Games."

The discrepancy between the perception of the members of Sport Alberta and Mr. Schmid's perception of Sport Alberta's role is further illustrated by Mr. Schmid's own comments that "Sport Alberta was still a leftover from the Social Credit government. And when I tried to give them pride in their being, I would have to say it just couldn't get its act together the way they were suppose to (sic)."

Statements unearthed by Yardley (1981) provide a further indication that the leadership of Sport Alberta desired a greater role in sport development than that which could be attained by limiting their activities to the administration of the Alberta Games. According to Yardley (1981), in 1975 the President of Sport Alberta stated, "Although one of our major aims is the Alberta Summer and Winter Games, I feel that the Board of Directors need to work towards the expansion of the other aims of Sport Alberta" (p. 23). Yardley reports that other statements made by the president at that time advised Sport Alberta directors to be "conscious of the needs of sports, to not allow government to take over the administration of amateur sports, and to band the Sports [*sic]* Associations [*sic*] together so that they have a strong and powerful voice" (p. 23). Based on these statements, Yardley concludes that there was "a growing concern with the Alberta

Games becoming the only focus of Sport Alberta and that Government had been interfering." (p. 23).

Several people interviewed for this study commented on the negative impact that the dispute over the control of the Games was having on the Games themselves. People also noted that it seemed that the government had become cognizant that the Games had some political value and as a result the government had an interest in doing something to resolve the dispute. The points noted above indicate that the situation was complex. Ron Butlin's ties to government officials hampered his relationship with Sport Alberta, the very organization chosen to be responsible for housing the administration of the Games. Butlin and Sport Alberta's contrasting visions of how the Games should be organized contributed to the dissension. Another component was Sport Alberta's growing aversion to and suspicion of government intervention in their affairs as perceived through the actions of the unwelcome Games administrator.

It had been Ron Butlin's intention to have the Games removed from Sport Alberta's authority. This was accomplished when the act to create the Alberta Games Council was implemented. Yardley (1981) and people interviewed for this study indicated that Ron Butlin was offered the opportunity to be the director of the Alberta Games Council but declined the offer. This suggests that in the end the situation was ultimately resolved in favour of Ron Butlin who must be identified, to some degree, as the government's agent in sport development at the grassroots level.

None of the individuals interviewed for the study suggested that personal relationships had motivated this decision. However, one individual agreed that the decision was indicative of political changes that were in part a consequence of having a Progressive Conservative government:

> I think that it was part of it, yes. But I don't think that was the main reason. I think if there had been a higher level of happiness and harmony within the operation [Sport Alberta] when the Progressive Conservative party came into power that it probably would not have done anything to massively change the system. Bob Clark [of the Social Credit] who was, I

> think, essentially involved when the original things were put together and was at one time the minister and then he went on to become eventually the leader of his party. . . . he was more of a hands-off type. We'll give you support. You people do it.
>
> When Peter Lougheed's group came into power they had an image of some major changes and to get those changes they couldn't be laissez-faire. They had to get in and do some manipulation. They had to rip some pieces apart and put them together the way they wanted them put together. I don't think that Alberta Games was a part of that original vision. However, when it came obvious that this strife was ongoing, and it was primarily interpersonal relationship problems, rather than straight structural problems, when it became evident I think that the people said, 'We've got to get this to a happier environment. The Games are important and that is where we get visibility. And I think that we should take that out. It cost us $400,000 a year,' or whatever they were putting into sport games at that time. 'Let's take that out and make sure we have some control over that. We will put the board of directors in place for that and we will have some control over that.'
>
> They put Don Skagen in place, who was a close friend of Peter Lougheed, and a very good businessman and sharp thinker and a very fine individual. So they said let's separate it, give it to a board of directors, give it some life of its own, let the sport governing bodies go on with their thing in organizing the clubs and organizing the individual sports and so forth. And we will just keep them separate. They don't have to be bedfellows in this environment. So they did. I think it started from internal problems, role relationships, role clarity, interpersonal relationships, egocentrism.

Conflicting personalities and organizational problems related to role ambiguity and divergent goal orientation lay at the root of the problems that confronted Sport Alberta and its relationship with the Alberta government. However, these factors do not entirely explain why the government decided to create a Crown corporation in order to resolve the conflict. This decision can be partly explained by examining Peter Lougheed's rejection of a laissez-faire approach to Alberta politics and Alberta's economy that is noted above. This analysis now turns a discussion of the significance of Lougheed's political ideology and its relationship to the political and economic characteristics of Alberta society.

(3) Social System Factors

In addition to the key role played by the actors and organizational factors, there are features of Alberta's social system that also have some bearing on these events as they developed. Richards and Pratt (1979) describe the philosophy of Peter Lougheed's government as "corporatism inspired by the purpose of winning business support for intervention and of giving the public a sense of participation" in government (p. 242). The displacement of Sport Alberta by a Crown corporation is an example of how those aspects of public policy and political strategy that are directly related to the economy can also infiltrate ancillary sectors. This becomes evident when one considers the outcome of Sport Alberta's struggle to obtain public status in the context of Peter Lougheed's corporatist strategy. It is unlikely that Lougheed's government planned to use the same corporatist strategy it enacted to manage the economy of Alberta. Nonetheless, it is clear that by 1977 its corporatist ideology began to influence its management of sport development and of sport interest groups.

This ideology had a significant impact on the role of the Alberta government in sport development, especially with regard to its scope of authority over sport development. To facilitate the points of this position the argument will begin with a brief discussion of why corporatism has become a popular political strategy. Then an assessment will be made of the degree to which corporatism became characteristic of the Alberta government's involvement in sport development.

According to Offe (1985), corporatism emerged as an outcome of the changing relationship between the system of interest representation and public policy making. In this regard he describes two types of political rationality: *output rationality* and *input rationality*. Output rationality focuses on the satisfying of demands under conditions where: the form and activities of interest groups are not regulated, policy-makers do not have much control over the content and intensity of specific demands that are being made or over the number and identity of political collectives, and at best political parties form a reconciling function.

Input rationality emphasizes the channelling of demand inputs. It may emerge if political parties, in the above circumstances, fail to aggregate and reconcile major segments of the electorate, and/or if policy makers find it difficult or impossible to accommodate significant interests due to the lack of sufficient fiscal and institutional resources at their disposal.

In the first case above, policy-makers strive to meet as many of the demands made by interest groups as possible. As a result, "good" policy makers will focus on rationalizing the effectiveness and efficiency of government outputs. In the second case the measure of good policy shifts from effective and efficient outputs to the shaping and channelling of demands so as to make the demands satisfiable. The conditions that support output rationality closely resemble the liberal pluralist model of politics.

The liberal pluralist model can be seen to underlie the philosophy of the Social Credit government that preceded the Conservatives. Its attitude towards sport development, as outlined in Baka's (1978) thesis and the quote on page 54 that compares the styles of these governments, was clearly one of responding to interests in a political system that frowned upon government intervention in the free market system. This argument is further supported by Finkel (1989) who comments:

> In fact, the Manning regime, true to its word followed a pay-as-you-go policy and resisted calls for government regulation of the oil and gas industry (other than the regulations which the industry wanted itself), for marketing boards, for rent controls, for government housing construction programs, for subsidies to new industries, for free hospitalization and medical care, for public power, and for complete provincial responsibility for relief (p. 139).

The Progressive Conservative Party's successful displacement of the governing Social Credit Party was, in part, a consequence of the Conservative Party's platform of industrialization through government intervention. The ultimate goal of this platform was to increase the provincial government's bargaining power relative to that of the federal government. Unlike the Social

Credit, Lougheed's Conservative government would take the initiative and "consider itself an entrepreneurial actor in provincial economic development" (Richards and Pratt, 1979, p. 170). Towards these ends the Lougheed government would employ a corporatist ideology that would forge a quasi-corporatist alliance of the interests of government and a rising urban bourgeoisie.

> This arriviste bourgeoisie is led by the owners of and managers of the few Alberta-based corporations large enough to compete on a national and international scale—notably such firms such as Alberta Gas Trunk Line, the Mannix-Loram group, ATCO Industries, the Alberta Energy Company—as well as some of the more dynamic oil-related businesses which have their head offices in Calgary. In addition, it includes a large group of well educated upwardly mobile professionals, such as corporate lawyers, economic and financial consultants, engineers, geologists, and other scientists or technical experts providing services of a specialize nature to the petroleum industry and government. A third group, a state-administrative elite, occupies the top bureaucratic posts within the public sector, particularly, though not exclusively, in government departments and boards charged with the tasks of managing the province's resources, negotiating with other governments, investing the huge revenue surpluses of the 1970s and charting future economic directions (Richards and Pratt, 1979, p. 167).

The extent to which this corporatist ideology was being extended to sport becomes evident when one compares the degree of corporatism characteristic of sport delivery before and after the Progressive Conservatives took office. Such a comparison can be made by considering four dimensions of corporatism discussed by Offe (1985). Offe (1985, p. 237) indicates that corporatism increases with the following:

1. *Resource status*: The extent to which the resources of an interest group are supplied by the state.
2. *Representation status:* The extent to which the range of representation is defined through political decision.
3. *Organization status:* The extent to which internal relations between rank-and-file members and executive members of the organization are regulated.

4. *Procedural status:* The extent to which interest organizations are licensed, recognized and invited to assume, together with a specified set of other participants, a role in legislation, the judicial system, policy planning, and implementation, or even are granted the right of self-administration.

Of these four dimensions only the first is characteristic of Sport Alberta which was, until the creation of the Alberta Games Council, the major agency (independent of government) involved with promoting sport and sport development in Alberta. Sport Alberta received funding for some of its activities from both the Social Credit and Progressive Conservative governments. Prior to the rule of the Progressive Conservative Party, Sport Alberta was the singular interest group acting on behalf of the interest of Alberta's amateur sport community. It had no representational status, organizational status, or procedural status as defined by Offe (1985). As noted above, it is possible to interpret the employment of Ron Butlin as an attempt by the provincial government to exert influence at the level of the dimension of representation. However, Butlin's appointment, no matter how coercive it may or may not have been, was not based on any legal statute that gave the government the jurisdiction to appoint representatives. From these facts it can be concluded that Sport Alberta was not, to any degree, an embodiment of a corporatist ideology in the area of sport policy.

Elements of corporatism are characteristic of the Alberta Games Council which displaced Sport Alberta's authority over the Alberta Games. The degree of formal status that can be attributed to each of the dimensions used to define the degree of corporatism was much greater in the Alberta Games Council compared to that of Sport Alberta. Like Sport Alberta, the Alberta Games Council received resources from the state in the form of money. If the degree of resource status is measured in terms of the value of the funding given to an organization, the resource status of the Alberta Games Council was significantly greater than that of Sport Alberta since the former organization received larger sums of money from the government. The degree of representative status was greater with regard to the Alberta Games Council because an act of legislation legally defined the range of representation on the Alberta Games Council to consist "of not more than 15 persons appointed by the Minister" of Recreation and Parks (*Alberta Games Council Act*). The organization status of the Alberta Games Council was greater since legislation gave the minister the authority to determine who would comprise the three-member management committee (executive members) of the Alberta Games Council. Procedure status was also greater since legislation indicated that the Alberta Games Council could be asked to co-ordinate its work "with the programs, policies, and work of the government and public and private institutions in order to avoid duplication and expense (*Alberta Games Council Act*)."

One consequence of this approach was an increase in the Alberta government's scope of authority over sport development. This is to be expected for, as Offe (1985) indicates:

> The attribution of positive political status to, for example, an organization of political refugees, a sports association, or an association of automobilists directly results in an incomplete determination of the organization's behaviour by constituent members (because now the organization has resources to spend that do *not* flow from willingness of members to contribute to a common objective; it has commitments to honour that are the price for political subsidy and hence are irreducible to the membership level); nor can the manifest behaviour be explained by reference to the relative strength of conflicting groups or allies (p. 238).

The new legislation gave the government authority in areas of sport development previously isolated from its jurisdiction. According to the act, it was up to the minister to approve the Alberta Games Council's initiatives in many areas including the appointment of officials and admission of athletes for the Alberta Games, the sports that would form the Alberta Games, the prizes that would be awarded and other matters deemed necessary for carrying out the objectives of the Alberta Games Council. These circumstances were quite different from those that existed prior to the Games or when the Games were being administered by

Sport Alberta. At that time, associations responsible for the delivery of various sports could hope to have some influence over how their sport was administered at the Games through their participation and voting behaviour at general meetings of Sport Alberta. The new legislation meant that this mode of influence was non-existent.

Despite this greater scope of authority, the government's authority was limited to a small area of sport development: the Alberta Games. Areas such as coaching, sport medicine and other aspects of administration and athlete development remained largely detached from government policy.

The Lougheed government's quasi-corporatist approach to sport development also influenced the power that disadvantaged social groups might have over sport development. In the context of the development of oil and other energy industries, Richards and Pratt refer to alliance between politicians, government officials and Alberta's "arriviste" bourgeoisie of corporate lawyers, engineers, scientists and technical experts. These types of individuals comprised the board of directors of the Alberta Games Council. The inaugural Chairman of the Alberta Games Council, Don Skagen, was a close friend of the premier and the chief executive officer of Mohawk Oil, a well-placed Alberta oil company. Other board members were well-placed lawyers and chartered accountants from firms such as Deloitte, Haskins and Sells. Collectively, these individuals were not representative of a cross-section of those individuals who actually participated in sport in Alberta. Being entirely male and mostly upper- and upper-middle class businessmen, their ability to represent the interests of women and other social groups participating in sport is questionable. An alliance between business, government and sport development had been forged in the area of multi-sport games.

Summary

Government interest and intervention in sport development in Alberta increased between the years 1970 and 1977. This increase was manifest in the implementation of a government-sponsored central administrative centre for provincial sport associations and the development of the Alberta Games. Sport Alberta, an independent association of sport organizations, endeavoured to deliver these programs with uncircumscribed financial aid from the government.

A conflict between key individuals in Sport Alberta combined with the corporatist ideology of the newly formed Progressive Conservative government induced the government to become more directly involved in sport development. This was accomplished through legislation that created the Alberta Games Council. The legislation severed Sport Alberta from its role in a very visible and popular aspect of sport development, replacing it with an organization which, by law, would be more sympathetic to government interests. This new approach to sport development also revealed a government predilection to place men from Alberta's upper middle class and business elite in positions on the Alberta Games Council's board of directors. Through these positions these men would have some direct influence over sport development in Alberta through the Alberta Games.

Sport Alberta had lost its leadership role in the Alberta Games and the provincial centre for sport administration and therefore could no longer use these roles as evidence of its value to the sports community. The provincial sport governing bodies that comprised Sport Alberta's membership began to question the value of their membership and soon the role of all organizations involved in sport delivery came under scrutiny. For the next seven years, considerable public and private discussion focused on how to improve the co-ordination of sport delivery in Alberta.

Chapter Five

Sport Interests and the Struggle for Public Status, Part Two: The Decline of Sport Alberta and the Rise of Corporatist Sport Policy

Re-evaluation of Sport Development in Alberta

By the late 1970s Sport Alberta was struggling more than ever to maintain its legitimacy. Nonetheless, the organization still played a leadership role in the sport community through its involvement with the organization of Intersport. Intersport IV, held in June of 1979, examined overlaps and ambiguity among and between the roles played by the various organizations involved in Alberta's sport delivery system. The discussion at this conference focused on building a foundation from which to devise a plan or organizational structure for sport development in Alberta: "At the end of the conference, there was a general agreement that a non-partisan committee be established to examine the need for an improved coordination of sport in Alberta" (Ad Hoc Committee on Amateur Sport, p. 3).

This particular committee was comprised of five members: Barry Mitchelson (chairperson), Doreen Ryan, Gerald Glassford, Don Moore, and Ken Munro. Between April and May 1980[15] the Ad Hoc Committee published its final report entitled *Sport in Alberta: Let's Work Together.* The report considered the strengths and weaknesses of four alternatives for sport co-ordination in Alberta. "Alternative 1" (dubbed "Status Quo") recommended that the provincial government, Sport Alberta and the Alberta Games Council retain their existing functions and that each of their roles be clarified in order to reduce conflicts. "Alternative 2" recommended that a two-player system comprised of the provincial government and a merger of Sport Alberta and the Alberta Games Council be

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[15] The exact date of publication is difficult to pin down. The report itself is dated May 1980; however, comments made in the legislature and recorded in *Alberta Hansard*, 1980 p. 656 suggest it was published in April.

implemented. "Alternative 3" recommended that there be total provincial government co-ordination of sport development. "Alternative 4" recommended that a partnership of public and private sectors should be developed and embodied in a single provincial sport co-ordinating agency called the Alberta Sport Federation.

The committee supported the creation of the Alberta Sport Federation presented in "Alternative 4." This new agency would assume all the functions carried out by Sport Alberta and the Alberta Games Council as well as many of the objectives which at the time were under the jurisdiction of the government's Department of Recreation and Parks. The committee report suggested the following membership policy:

> It is recommended that:
>
> Membership in the Alberta Sport Federation be open to:
>
> - Provincial single sport governing bodies.
> - Multi-sport agencies.
> - Sport related agencies,
>   and
> - Representatives from governments appointed to the Board of Directors.
> - Representatives from the public appointed to the Board of Directors (Ad Hoc Committee on Amateur Sport, 1980, p. 19).

The committee's report also recommended that the board of directors be composed of 23 representatives. Twelve positions would be elected by provincial sport organizations. Seven positions would be filled by appointments from the provincial government. The remaining three would be appointed from the public at large by the board itself. This structure would ensure that Alberta sport associations would continue to play a role in guiding the development of sport and recreation within the province. The government would also be able to give some direction in this system of checks and balances (Ad Hoc Committee on Amateur Sport, 1980, p. 10-21).

As sports groups around the province were discussing these recommendations, the report was also receiving attention in the provincial legislature. On April 29, MLA Sindlinger asked the minister of Alberta Recreation and Parks to make some comments on the report and on his department's position with regard to the report (*Alberta Hansard*, 1980: 656). Mr. Trynchy's response was noncommittal:

> I've looked once at the Sport Alberta report which he [Mr. Sindlinger] had. It's being presented to a conference on May 2, 3, and 4, I believe. That is not the final report; it's a report for discussion. I do not want to comment on whether I accept it. I think the conference will discuss that and come back to us with a final report. I hope that I and other people involved will take a look at it and see where we go from there (*Alberta Hansard*, 1980, p. 660).

As the discussion pertaining to Mr. Trynchy's portfolio continued, a MLA, Mr. R. Clark, asked a question about Mr. Trynchy's commitment to sport for all in Alberta versus an emphasis on Alberta's representation at international games. In response to this issue, Mr. Trynchy said the following:

> I totally agree we should have lifetime sport. I guess that a lifetime sport to me is not a lifetime sport to the Chairman and not a lifetime sport to somebody else, but I understand what he is getting at. . . . But I totally agree that sports should be for all, and that's the kind of programs I try to initiate.
>
> The Sport Alberta report: the member says I have no strong feelings. I want to correct that: I have some pretty strong feelings. As a matter of fact they're pretty darn strong. I want to see that report when it's finished, and I want to take that report and do with it what's best for Albertans, not for myself, not for the department, and not for the sports people out there or anybody else. It has to involve everybody and that's the type of program I'm going to initiate, with the help of my colleagues of course (*Alberta Hansard*, 1980, p. 663).

The recommendations of the Ad Hoc Committee were reviewed at the meeting of Intersport V during May 1980. The report was endorsed in principle by those in attendance. This endorsement was followed by a resolution for the establishment of a task force to be named the "Advisory Committee on Sport Organization and Development in Alberta." The mission of this task force was to investigate key sport issues and develop an implementation strategy for the proposed Alberta Sport Federation. Headed by Dr. Maury Van Vliet, the task force was to present its findings at Intersport VI. At the same time as this report was being prepared, Peter Trynchy was asked to develop a statement that would spell out the role and priorities of the provincial government in sport development in Alberta.

The implementation strategy proposed in the report of Dr. Van Vliet's "Advisory Committee on Sport Organization and Development in Alberta" had little in common with the Ad Hoc Committee's recommendations. The name Alberta Sports Federation remained intact, so did the idea that "the functions of certain organizations such as Sport Alberta and the Alberta Games Council would be absorbed by the corporation." The similarity between the organization proposed by the Ad Hoc Committee and the one proposed by the task force ended here. The task force proposed a very different organization from that originally proposed by the Ad Hoc Committee. The Alberta Sport Federation was to be a Crown corporation with a board of directors comprised of 11 members appointed by the minister. It was also suggested that "a master plan for sport development in Alberta should be developed by the government in cooperation with the Crown corporation" (Advisory Committee on Sport Organization and Development in Alberta, 1980, p. 5).

The advisory committee's report sparked considerable discussion and concern about the future of sport development in Alberta. Civil servants and members of the sport community were concerned about the recommendations of the advisory committee. Neither group was completely convinced that the creation of a Crown corporation would properly serve the interests of sport development in Alberta. They believed a different approach should be taken, an approach that maintained a role for Sport Alberta.

The Reaction of Civil Servants: Caution

Both the 1980 Ad Hoc Committee and the 1981 Intersport Task Force Committee reports raised concerns among civil servants and the sport community as represented by Sport Alberta. Examples of these concerns were discovered in three pieces of correspondence written by civil servants. The first piece of correspondence is a letter written by Lynn Passey, a Consultant of the Community Recreation Services Branch of Alberta Recreation and Parks and sent to Darwin Park the branch's Section Head. In this letter, Passey took issue with the Ad Hoc Committee's report. Passey's first concern was that "the methodology of this study [was] not statistically sound." Passey also emphasized the need to fully explore the implications of the implementation of "Alternative 4" contained in the Ad Hoc Committee report. Passey was particularly concerned about the structure that was being proposed for the board of directors: "Can we assume that a 23 person Board and an Executive Committee would be more efficient and less bureaucratic than what currently exists?" The letter contains a paragraph which seems to express a fear that Alberta Recreation and Parks would be left without a role to play in sport development in Alberta if this alternative was implemented.

> There are no benefits in Alberta Recreation and Parks controlling the entire development of Sport in the province. However, what are the implications of shedding our current controlls [*sic*] and responsibilities and handing them over to a newly developed Sport Federation? Would a Crown Corporation of the stature proposed in the report really be able to accomplish what it sets out to do? Two organizations working cooperatively may actually be able to accomplish the proposed duties outlined in the report and more (L. Passey, personal communication April 15, 1980).

A second piece of correspondence that reveals some of the concerns held by civil servants is a letter signed by Ed Wilson, assistant Director of Central Recreation Field Services. Wilson's letter is addressed to Jack Monaghan, Director of Recreation Field Services. In this letter Wilson expresses concern about the recommendations to increase the share of lottery funds available to the Alberta Sport Federation, the recommendation to dissolve Sport Alberta and the Alberta Games Council, and the recommendation to establish local and regional sport federations to complement and supplement the functions of the Alberta Sport Federation.

The third and final example of correspondence which raised concern about proposed changes is the most interesting of all. This correspondence was a confidential memorandum sent from Jack Monaghan to Deputy Minister T. A. Drinkwater in March 1981. In the memo, Monaghan focuses on Dr. Van Vliet's draft of the "Minister's Executive Summary." In the seven pages of the memo, Monaghan also draws attention to the report of the Ad Hoc Committee. In reference to recommendations of the Van Vliet Task Force, Monaghan makes the following points:

> 1. Why the urgency in Crown Corporation establishment? . . .
>
> 2. What are the current functions of Sport Alberta? Was not Sport Alberta in its early development responsible for attempting to do what is being recommended in recommendations 1 - 3 of the Ad Hoc report? **If this is the case what caused Sport Alberta to fail? Has it failed or is it a matter of time, encouragement, government direction etc.?** [emphasis added]
>
> 3. This statement is dictatorial and possibly politable [*sic*] to the Government philosophically. Contradicts the concept of self-determination by imposing arbitrary control and mandatory membership (Monaghan, personal communication March 11, 1981)

The letter continues, raising ten more concerns about the recommendations of the Advisory Committee on Sport Development.

The data that were examined gave no indication as to whether or not these concerns were addressed formally or informally. The archival sources which contained the letters described above did not contain any letters or memorandums indicative of the response or actions, if any, that may have been taken in responses to these three letters. Furthermore, although some of the people interviewed for this study mentioned that civil servants were concerned about the impact of the proposed federation, no one provided details that were relevant to these letters. This was not true, however, with regard to the reaction of Sport Alberta and the sports community.

The Reaction of Sport Alberta and the Sports Community: Rejection

Dick White, president of Sport Alberta, was also busy writing letters to government officials. In a letter to Peter Trynchy, White expressed his dismay that the government had been studying the recommendations of the task force prior to their ratification by the Alberta sports community. White wrote:

> We find it totally unacceptable that the mandate of Alberta's sporting community can be ignored and would expect you to disregard any representation made by this Task Force without the sanctioning of their findings by those who were responsible for their establishment (D. White, personal communication March 26, 1981).

Mr. Trynchy responded to White's letter on April 23, indicating:

> once having reviewed the Committee's recommendations, should I feel that I could support them and take them forward to my colleagues for decision, I will take the necessary action to secure the sport community's input and reaction to the recommendations before any decisions are ratified (P. Trynchy, personal communication April 23, 1981).

On September 12, 1981, representatives of 38 sport governing bodies met in Red Deer to discuss the ramifications of "Minister's Draft Number Three: May 28, 1981." The representatives raised concern that the document had been circulated to the province's Recreation and Parks Department. The representatives also observed that "recent 'Position on Policy Papers' solicited by the Recreation & Parks Department to assist them in establishing department policies strongly opposed the Crown Corporation: with 20 of 21 contributors voicing their opposition to this concept" (Sport Alberta, minutes September 26, 1981, p. 3). Nonetheless, the new Deputy Minister for Alberta Recreation and Parks, Barry Mitchelson, was on the record as being very much in favour of the Crown corporation.

The minutes of the meeting indicate the chairman emphasized that it was time for sports groups to take a stand on this issue. Each organization was asked to carefully examine and weigh the proposals outlined by the Intersport task force and then, following some discussion among their members, come to a definite conclusion as to whether or not they would support the creation of a Crown corporation to guide sport development in Alberta. By the end of the meeting, those present made a strong statement of their apprehension regarding the creation of a Crown corporation as proposed in the "Minister's Draft Three."

Sport Alberta's discontent with the minister's response to its previous concerns and his present actions regarding the Task Force report were expressed in a letter dated September 24, 1981 sent from Mr. White to the minister. The letter noted that the 38 sports governing bodies and sport-related organizations had met to discuss the 'ramifications' of the task force report and that as a result of a preliminary review of this document, the following resolution was presented and unanimously carried:

> 'That this meeting, by letter, express concern to the Hon. P. Trynchy that a Crown Corporation may not be the best vehicle to promote amateur sport co-ordination in Alberta, and request time to the end of October, 1981, to allow amateur sport organizations and other interested bodies to react to the proposal and that Sport Alberta be requested to convene a meeting before November 15th to explore the consequences of the proposal and prepare constructive alternatives' (D. White, personal correspondence September 24, 1981, p. 1).

Sport Alberta's concern and disapproval of the way the minister had been handling the affair is restated in the conclusion of White's letter. The tone used by Mr. White to express these feelings is indicative of a growing suspicion:

> Unfortunately the committee chose to ignore its obligation to the sporting community to report back to them prior to making a submission to the Minister. It appears an even more serious breach of trust may have occurred when someone on the committee chose to designate Minister's Draft Number Three as the Committee's Final Draft and to submit the same to the Minister without it ever being reviewed by the committee as a whole . . . (p. 2).

The minister responded to Mr. White's letter promptly, suggesting that Minister's Draft Three was almost identical to Minister's Draft Two which had been ratified by the committee. He went on to state that it was his intention to have an Intersport Conference early in the next year. It is interesting to note that, while this letter gave the impression that the minister had not yet made up his mind as to whether or not he would support the proposal to create a Crown corporation, an earlier draft of the letter suggests that he believed this was the best alternative.

This earlier draft is interesting because several people who were interviewed for this study suggested that it was their belief that by this time the minister and the deputy minister were both committed to the proposal and were committed to eliminating Sport Alberta. An earlier draft of the letter that was sent to Mr. White explicitly expressed the minister's support for the Crown corporation. The sentence quoted below is struck out and the word "omit" appears next to it in the right margin: "After reviewing the information provided to me and considering the current economic climate, it seems that a Crown Corporation may be the best alternative to promote amateur sport co-ordination and development in Alberta."

Further communication between Mr. White and Mr. Trynchy occurred in early November of 1981. Mr. White sent a response to Mr. Trynchy's October 19 letter. The response includes an invitation for Mr. Trynchy or one of his representatives to attend a meeting of provincial sport governing bodies on November 7, 1981. Mr. Trynchy replied that he was unable to attend and would send Jack Monaghan as his representative.

By this time Sport Alberta had completed a position paper outlining its view of the proposed Alberta Sport Federation as summarized in the "Advisory Committee on Sport Development." The thrust of Sport Alberta's (1981) position paper is summarized in the following quotations:

> It is our expressed concern that a crown corporation is not the best tool for the administration and management of sport. A crown corporation means government control, with more bureaucratic processes and red tape than already exist (p. 3).
>
> Sport Alberta, as developed, is already the tool for provincial sports management. It would be far more economical to expand an already existing tool, than to rebuild from the beginning (p. 4).

> It is therefore our recommendation that Sport Alberta continue to be the Alberta Sports Federation, and that necessary constitutional changes be formulated and enacted in order to strengthen relations with the Alberta Department of Recreation and Parks (p. 4).

Put in very succinct terms, the position paper was asking government to stick by Sport Alberta as it was originally conceived under the rule of the Social Credit government. Apart from the recommendation to create a Crown corporation, the paper applauded the initiatives contained in the task force report. It was felt that all these initiatives could be cultivated just as effectively under the auspices of Sport Alberta as they could be under the proposed Crown corporation. In hindsight, the document represented Sport Alberta's final gasp for breath before its demise.

The archival material collected for this study contains a letter dated November 2, 1981 and signed by Dr. M. L. Van Vliet, Chairman of the Advisory Committee. The letter appears to be at the very least an indirect response to the concerns raised by Sport Alberta's position paper. The letter begins by drawing attention to the upcoming Intersport VI conference where the task force recommendations were to be reviewed. The focus of the letter then changes to "a few points" Van Vliet feels "must be emphasized to counteract some of the rather distorted views and incorrect statements which appear to be circulating with no reference to actual facts." Van Vliet's points of clarification include a statement that loss of autonomy for sports associations would not be a consequence of the task force recommendations—"The idea is too preposterous to deserve a comment." Throughout the letter, the word "recommendations" is emphasized (i.e. underlined) wherever it appears and Van Vliet repeatedly tries to discount concerns regarding the potential high cost of a Crown corporation, the potential for autocracy and the fact that the report is anything more than a set of recommendations.

Despite Van Vliet's letter, vocal opposition to the Crown corporation continued and some of that opposition was kindled by concern for the future of

Sport Alberta. A press release written by Lynda Allan and dated February 2, 1982 proclaims "AMATEUR SPORT IN ALBERTA IS REARING ITS HEAD IN RESPONSE TO WHAT THEY CONSIDER GROSSLY INADEQUATE FUNDING BY THE PROVINCIAL GOVERNMENT" (p. 1). Allan expressed outrage at an announcement that "THEY (Sport Alberta) MAY NOT BE ELIGIBLE FOR ANY PROFILE[16] DOLLARS AT ALL THIS YEAR" (p.2). The press release was followed by a letter to the minister. The letter appears to be a rejoinder to a letter from the minister to Lynda Allan. Allan mentions that she attended an information meeting for Intersport VI the evening prior to writing her letter. In her letter, Allan re-emphasizes her concern for Sport Alberta's future given its financial difficulties. She also raises questions about the future of grassroots sport development and the impact of a centralized sport delivery system. Why, asks Allan, doesn't the government "just make Sport Alberta the recipient of the increased funding promised in the policy and let a ten year operation carry on as it stands today?" (L. Allan, personal correspondence November 11, 1982, p. 2).

On February 17, 1982; Sport Alberta's board of directors met and discussed Sport Alberta's future and the role it played with Intersport. The minutes of that meeting indicate that someone suggested "that a committee be formed to prepare a statement from the Board of Directors to the membership, expressing our [the board's] position and suggestions" (Sport Alberta, minutes February 17, 1982, p. 1). The suggestion was acted upon and the following motion was passed:

> This board supports in principle the concept of an umbrella sport organization, but with approximately 50 per cent representatives from the Sport Governing Body or allied groups on the Board, and strongly recommends this position be supported by our member organizations (p. 2).

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[16] "Profile" refers to the provincial government's program for granting funding to amateur sports groups.

By March 8, 1982, Sport Alberta had finished formulating its official position on the proposed sport development policy. The position contained three recommendations which Sport Alberta believed would improve the Alberta government's "Proposed Sport Development Policy." The position paper read as follows:

> Sport Alberta supports the Proposed Sport Development Policy. However, we recommend three major areas which, if amended, would improve the proposal.
>
> **RECOMMENDATION #1**
> Financing is a prime concern. Fundamental to the success of the policy is the concept that the provincial government accept the responsibility of providing funds to sports governing bodies to cover all basic administration costs. . . .
>
> **RECOMMENDATION #2**
> That the Board of Directors of the "Alberta Sport Council/Federation" be made up as follows:
> (a) 50% appointed by the Minister
> (b) 50% selected at an annual forum of the Alberta Sport community in one of the following ways:
> (i) direct election
> (ii) selection of twice as many names as there are Board openings to present to the Minister. The Minister would then appoint the Board from the list.
>
> **RECOMMENDATION #3**
> There must be more than one administration centre to properly serve regions of the province. It is logical that one major operation would exist with smaller satellite offices in several regions of the province (p .1).

Intersport VI finally took place during March 13-14, 1982. Delegates present addressed the report of the task force, a proposed sport development policy, and proposed philosophy and objectives related to sport for Alberta Recreation and Parks. Dr. Van Vliet presented the report of the task force. Mr. Trynchy was also present and accompanied by his senior staff. As expected, the task force recommended that a Crown corporation be created. The corporation would be called the Alberta Sport Council instead of the Alberta Sport

Federation as previously proposed. The Alberta Sport Council would be comprised of a 16 member board of directors that was to be appointed by the minister from a list of nominees from around the province. Lottery dollars would be made available to the Alberta Sport Council for distribution to provincial sports associations in order to assist sport development in Alberta.

Lobbying for Lottery Loot

Numerous people interviewed for this study indicated that many of the people present at Intersport VI spoke against the idea of a Crown corporation as outlined by the Task Force. Although the Alberta Sport Council was deemed by government representatives to be arm's length from the government, many individuals questioned the validity of this claim, especially since the board of directors was to be appointed by the minister. It was indicated by at least two individuals that the minister promised he would make his appointments based upon a fifty-fifty split. That is to say, he would appoint eight of the board members from a slate elected by representatives of the provincial sports associations. The discussion continued covering a wide range of issues and a number of other recommendations were put forward. Despite what some individuals reported to be considerable opposition, at the conclusion of the conference the minister stated it was obvious that everyone at the meeting was overwhelmingly in support of the Alberta Sport Council and the proposed sport policy and he would go forward with its implementation.

Written documentation of the events that occurred in the period between Intersport VI and the approval of the legislation that established the Alberta Sport Council is limited. Several individuals reported that during this time period Mr. Trynchy encouraged members of the sport community to lobby vigorously in order to bring about a change in the percentage of lottery funds that were available to sports groups. For example, Dr. Glassford recalled:

> At that same time, or near that same time, Peter Trynchy charged a group of us [leaders in the sports community] with the responsibility of doing our

> homework with the decision-makers. He said that if you really do want to see more money flow into sport you've got to talk with the members of the legislative assembly. Because they will make the decisions about the redistribution of those lottery dollars. Which up to this time [was]: 35% to Northlands; 35% to the Calgary Stampede Association; and then the other 30% was divided with culture, recreation and sport, and so forth. So we were only getting a small portion of all the lottery dollars. Yet, if you were to have gone back and looked at the advertisements re the lottery at that time, the image was the money was largely going into sport. That is what people were thinking, but it wasn't what was happening.

Further evidence of a campaign to get MLAs to support a redistribution of lottery profits is contained in a letter written by Dr. Mike Apps, president of the Alberta Soaring Association, to his MLA:

> I am writing this letter to you to ask for support in upcoming substantial changes to the manner in which the government of Alberta will aid amateur sport in the province (M. Apps, personal correspondence April 29, 1982, p. 1).

Apps described some of the key items agreed to at Intersport VI and noted that a number of additional recommendations were tabled for the minister's consideration:

> One major change recommended was that
>
> > **fifty percent of the Board of Directors of the proposed Crown corporation be selected from persons nominated from the Sport Governing bodies themselves**
>
> in order that these associations have a direct input to the management of the corporation. This concept was accepted by Mr. Trynchy although the mechanism by which this will be accomplished must yet be devised.
>
> In order to adequately fund this new corporation which would be overseeing lottery disbursements to sport, there was very strong feeling that current division of these lottery funds is grossly inequitable. The Calgary and Edmonton Exhibition Boards now siphon off sixty percent of the total monies generated which is now a considerable sum.
>
> > **Even a relatively small shift in the apportioning of the lottery funds would result in a very large percentage change in the monies available to tens of thousands of Albertans participating directly in sports and recreational activities. Therefore, some reapportioning of the lottery income would very significantly help to place the proposed Alberta Sports Council on a solid financial footing** (p. 2).

The letter continues and Apps personally urges his MLA to support the efforts of Mr. Trynchy.

Mr. Trynchy would be successful in his effort to glean support for the new sport policy and more lottery dollars. A government press release dated March 22, 1984 announced that the method of distributing provincial lottery revenue had been revised: "Based on the 32.5% of lottery profits assigned to sport and recreation, the Alberta Sport Council will receive 66% and the Recreation, Parks and Wildlife Foundation will receive the remaining 34%."

One individual interviewed for this study offered the following explanation for the success of the campaign to redistribute profits from the Western Lottery Corporation:

> Peter Trynchy did the work with the caucus. He talked to these people behind the doors and so forth and he was very good. Without Peter Trynchy, I am not sure that we would have got the act changed the way it was so that now sport/recreation got the larger portion of dollars. For our part, a whole group of us started phone calls and we phoned everybody we knew. We had them talk with their members of the legislative assembly; we talked with the members of the legislative assembly ourselves and explained how important it was to give sport a firmer base, and the funding portion was an essential component. With Peter's help that is the way it evolved. But without Peter Trynchy, I don't think we would have got it.
>
> In my mind, he was absolutely central. He knew how to work the system; he knew how to create the change and maybe he had lots of favours that he could now call in because he supported, you know how governments work: I'll support you on this but something I may need your help, sort of thing. And he called in a lot of the cards that he had out and, with his ability to talk with people who were on caucus and who were on the Treasury Board and who were major decision-making groups of the government and our ability to get to the members of the legislature, they then said, 'hey, we've got all these phone calls. Obviously people are concerned about the monies that go in to support recreation and sport lottery. Not that it is great for us; those are our people we supported.' So It went through with no difficulty at all.

Two other interviewees indicated that Trynchy's ability to get the legislation through easily was also due to the strategy he employed. They noted that Trynchy's position was successful because he was able to point to Intersport and other public meetings as examples of public input. A senior civil servant indicated that:

> He [Trynchy] was able to go forward and say, 'Now I am here with a proposal that was brought to me from the sport community.' And you know there is a lot of legislation that is turned down. There is a lot of legislation that is reacted against. There are a lot of periods where funding decisions are not taken.

Similarly, Gary Tomick, the Ad Hoc Committee's administrative co-ordinator, commented:

> Intersport was in place and the Alberta amateur sport community had a medium to get together and discuss these things. The fact that those things were in place contributed to the overall process, the overall undertaking and the overall acceptance. I think Intersport impacted on the acceptance of it [the redistribution of lottery money]. The other thing definitely is that none of this would have happened without the approval and the support and the workings of the minister in taking it through to Cabinet, and legislation had to be passed and acts had to be passed to formulate the Alberta Sport Council, and that type of thing.

Bill 21, *Alberta Games Council Amendment Act,* was read for the first time on March 14, 1983. It passed through third reading and received royal assent on June 6, 1983, to be effective April 1, 1984. During its journey through the legislature there was little resistance to or discussion of this bill which created the Alberta Sport Council. During the second reading of the bill, Mr. Trynchy remarked:

> We want to amend the legislation so we can involve a number of sporting organizations. We will be asking for nominations from sporting organizations from across the province. They will submit their nominations to the minister, from which the minister will appoint eight members. Eight members will be picked at large from other nominations, to give us a board of some 16 members. This will provide an expansion of their functions. It will involve a great number of volunteers both on the board and in its functions on a day-to-day basis (*Alberta Hansard*, 1983, p. 341)

This method of board selection as outlined in Mr. Trynchy's comments failed to live up to the recommendation made by the people present at Intersport VI. The *Alberta Sport Council Act* section two reads as follows regarding board selection:

> (1.1)The Minister shall designate corporations, educational institutions and organizations involved in sport from which he shall accept nominations for appointments to the Council.
>
> (1.2)From the nominations received by the Minister under subsection (1.1), he may appoint at least 8 persons to the Council.

The other recommendations made by Sport Alberta and those mentioned in the letter of Mike Apps were also absent from the legislation.

Sport Policy Implementation and the Demise of Sport Alberta.

The passage of Bill 21 and the introduction of the Alberta government's official policy on sport development resulted in a realignment of the roles of the institutions involved in managing Alberta's sport development. The government's new policy outlined ten specific goals for sport development. These goals were itemized in the Alberta government's *Sport Development Policy* (pp. 9-11) and can be summarized as follows:

1. To promote health, fitness and a sense of community among Albertans through participation in sport.
2. To encourage a wide, diverse, stable financial base for sport development.
3. To improve the accessibility to sport opportunities for more Albertans for a broader range of activities; to make the practice of sport accessible to all Albertans under the best possible conditions.
4. To encourage greater personal achievements in sport.
5. To move towards diversity of opportunities and to improve the overall quality of sport participation throughout Alberta.
6. To create the environment for a comprehensive and well-developed base of technical knowledge and an improved understanding about the act of sport participation.
7. To have the sport delivery system evolve toward a mature partnership of actors.

8. To strengthen, co-ordinate and maintain an effective sport system in Alberta.

9. To foster a greater commitment to planning throughout the sport system in Alberta.

10. To unify the efforts of the sport community and facilitate the development of a set of directions for sport in Alberta.

In addition to these ten goals, the policy lists eight strategic priorities:

1. To create a stable and diverse financial base for sport by providing operational funds and by generating revenues from the private sector and lotteries.

2. To provide a wider and more advanced base of technical expertise for sport in Alberta.

3. To provide increased opportunities for Albertans to participate in sport.

4. To increase the number of Albertans who are performing at provincial, national and international standards.

5. To improve the communication and co-ordination among sport organizations in Alberta.

6. To improve the organizational development of provincial sports associations.

7. To promote and assist in the effective management and hosting of major games and events.

8. To encourage the maximum use and efficient operation of existing facilities.

Within the framework provided by these goals and priorities, the policy delineates the role to be played by the Alberta Sport Council and by the Recreation Development Division of Alberta Recreation and Parks. The first five strategic priorities were to be addressed by means of the Alberta Sport Council. The remaining three, priorities six through eight, would be addressed through the Recreation Development Division.

Sport Alberta was left completely out of the picture. Reflecting back on the situation that existed just prior to the 1983 policy, a member of the Ad Hoc Committee commented:

> I think that when we finished there was a reasonably good sense that we were moving in the right direction. We still had the problem of the relationship between Alberta Sport[s groups] and the Alberta Sport Council, Sport Alberta and the Alberta Sport Council and government. There was a clearer linkage between government, Alberta Recreation and Parks and the Alberta Sport Council than there was with respect to the role relationship of Sport Alberta and that has haunted us since then.

The most troublesome aspect of the policy was that the new roles given to these government agencies impinged upon the role that Sport Alberta had been struggling to perform as the collective voice for amateur sports groups in Alberta:

> They [the Recreation Development Division] assumed the roles of Sport Alberta. In doing that, the department/division took over all of the administrative support roles that Sport Alberta was doing through the Percy Page Centre and that sort of thing and the Sport Council took the rest. They took a number of programs and grant programs that Sport Alberta was actively involved in. So it was by the time that October, November rolled around of 1984, and I had been into the job for 5-6 months, that it became evident that there was no support in the bureaucracy, and Mitchelson was the DM then, and Peter Trynchy was the minister. There was no support within the government to allow Sport Alberta to maintain any kind of a mandate or role within sport in the province.

Sport Alberta's strained relationship with government continued. The fight against the creation of the Alberta Sport Council had been lost. Now Sport Alberta dug its heels in and made another "final" attempt to secure a role for itself in sport delivery in Alberta.

The two-year period between 1984 and 1986 was fraught with tension in Sport Alberta's relationship with the government's sport delivery institutions. Sport Alberta was dealing with other problems that also threatened its survival. The commitment of its members associations was weakening, its financial situation was weak, and personal friction between certain board members and civil servants obstructed pleas for government assistance. Former Executive Director Paul Conrad reported that:

> When you looked at the membership of Sport Alberta, when you go back into the records and look back to 1983 and 1984, Sport Alberta had 109 provincial sport associations that were paid-up members, that took that $100.00, dropped it down and said, 'We want to be members of Sport Alberta.' But when it came time to put up or shut up and came time to come out to special meetings to determine the future, etc, etc. we would get 15-20 members.
>
> I think the most members that I can ever recall coming out to a general meetings was about 53-54 and that would have been in 1985 that it had happened. So when you looked at it at that point of view [*sic*] provincial sport associations were looking pretty apathetic—they didn't give a shit as to what was going to happen. Sport Alberta had nothing to offer in terms of what Sport Alberta could do to develop athletes, coaches and officials.

Sport Alberta's internal problems and the looming changes to sport delivery left it with few alternatives. However, Conrad was persistent:

> I refused to go away quietly. I knew that Sport Alberta's future was extremely limited and that come 1987-88 Sport Alberta would have gone the way of the dodo bird. It would have just become extinct, gone away quietly. I felt that there needed to be a resolution: it had to be open, it had to be above-board and people had to understand what was going on. Not anything confrontive and we didn't get into any confrontation situations, but what we did do was we presented this to the membership—this is what has happened. You have developed the sport development strategy that identified roles for the department, Sport Council and didn't identify anything for Sport Alberta. Yet the implementation strategy from the Alberta Sport Council that says that is what we are going to do as a Sport Council and everything that was in the Sport Council implementation strategy was a duplicate to Sport Alberta in every area but administrative support because this was a department responsibility.

In recalling the period 1983 through 1986, Conrad emphasized that a large amount of negotiation between Sport Alberta, Alberta Sport Council and Alberta Recreation and Parks was taking place. Much of the negotiation focused on sustaining Sport Alberta's status as an influential component of the sport delivery system in Alberta. The government, however, had become unsympathetic as far as Sport Alberta was concerned. This point is emphasized in the comments made by a former member of Sport Alberta:

> You see the blinders were on by this time and they couldn't see that there was an executive director, Paul Conrad, and a board of directors that was evolving that were positively looking toward or forward to that relationship that we met with roadblocks by Dwight Ganske and Stan Fisher plus Julian Nowicki and to an extent Barry Mitchelson. Those were the roadblocks: they had already decided that Sport Alberta was not going to be allowed to survive, never mind develop. We went through this period of negotiation and meeting and it was very evident that they had the organization by the short hairs by this time. We had no area to negotiate with them; we were negotiating from no string. We were at their mercy and they knew it. They were being very overt in the way they related to us as a result of following that string.

Conrad and Sport Alberta's president, Dick White, believed Sport Alberta could make a valuable contribution to sport delivery as an independent watchdog advocate group. Both Conrad and the Sport Alberta board of directors made an effort to discuss the delineation of a new role for Sport Alberta and a new relationship with the two government institutions responsible for sport development. Conrad recalled:

> We presented this scenario and we met with the senior management staff of Alberta Recreation and Parks and the Sport Council looking to eke out some kind of a niche or role that Sport Alberta could play. Every time the advocacy role came up, it was very negative, negative perception on the part of the department and became very confrontational. As far as they were concerned they didn't want an advocate for amateur sport in Alberta for what in our view was very obvious reasons. They couldn't get beyond that mindset of negativism, confrontation/conflict and again if they had have opened their minds and looked at that situation from an unbiased and objective point of view, there were ample opportunities for Sport Alberta to play out.

As early as July 30, 1984 Paul Conrad had taken steps towards meeting with the Alberta Sport Council to "delineate roles and responsibilities within the sports community as outlined in the Sports Councils [*sic*] implementation strategy" (P. Conrad, personal correspondence July 30, 1984). However, he and others noted that it was difficult to convince government officials to become involved in these meetings. After some discussion had taken place between Sport Alberta, Alberta Sport Council and Alberta Recreation and Parks, the Sport Alberta board of directors and its executive director met with the general membership, Conrad noted:

> We went back to the membership in January 1986 and we presented this to them. What we said to them was that these two organizations, the burgeoning bureaucracy of Alberta Recreation and Parks and the Department, did a restructuring. . . . We went back to the membership and we said that there were tremendous resources that were coming into amateur sport right now. Don't change the administrative and development system that is in place. You have other crossroads and you have a choice. The choice is that you work within the structures that are in place to maximize the benefit to amateur sport or you can try to change those structures. And in our view, Sport Alberta's view, it is fruitless to try to change that structure, so give us the mandate to go back and formally transfer our programs and services to the department and to the Sport Council. This was the board of directors talking to the membership. This is the meeting that we had. We had about 50% of our members out to this one particular meeting. . . . We got the approval from members to go forward with our plan for transfer and by this time our access to government officials was being restricted.

Dick White resigned shortly after the membership approved the transfer. White's suspicion of government and his opposition to the Alberta Sport Council was well known. His resignation was not surprising. Several individuals suggested that White and a few other board members "were in major conflict with some of the key stakeholders in the province." These stakeholders included several civil servants such as the deputy minister. The tension surrounding the relationship between the government and Sport Alberta was reported to have made government officials reluctant to meet with representatives of Sport Alberta to discuss a transfer of power. The following remarks made by an individual who was a member of the Sport Alberta board of directors conveys a sense of the situation during that time:

> He [Dick White] always felt it was government against Sport Alberta. Now he may have had good reason to say this. I never felt that we were agin