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THE UNIVERSITY OF ALBERTA

NUCLEAR MAGNETIC RESONANCE AND INFRARED SPECTROSCOPIC STUDIES OF ANION-MOLECULE ASSOCIATION IN SOLUTION

by

Ⓒ Robert D. Green

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
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EDMONTON, ALBERTA

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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Nuclear Magnetic Resonance and Infrared Spectroscopic Studies of Anion-Molecule Association in Solution", submitted by Robert D. Green in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

A technique involving the study of 1:1 association to form anion-molecule complexes has been applied to the study of interactions with halide ions of molecules of trihalomethane (haloform, CHX_3) and of alcohol ($R_1R_2R_3COH$). The molecules involved have been examined at low concentrations in relatively inert solvents. The hydrogen bonded and/or polarization complexes were studied by monitoring the N.M.R. signal of the electrophilic hydrogen(s) involved as the concentration of halide ion was increased.

The N.M.R. shifts in the complexes have been found to be in accord with the Buckingham model of electrostatic field-induced shifts. The magnitudes of these shifts show a good correlation with the polarizability of the A--H bond.

In the case of the trihalomethane--anion association, the energy of interaction is calculated to depend primarily on the polarizability of the molecule as a whole. In the case of triiodomethane, the ion actually approaches the molecule from the "wrong", or CI_3, end, the polarizability energy of attraction

completely swamping the polarity energy of repulsion.

In the case of alcohol--anion association, the energy of interaction depends on the inductive effects of the substituents on the α-carbon atom, tending to decrease in the order: nullary > primary > secondary > tertiary, particularly for alkyl substituents.

It is suggested that this approach to ion--molecule interactions may be a useful one in establishing orders of single-molecule solvation energies of ions; these may then be compared with various tests of bulk solvating abilities, and may be comparable for weak solvents. On the other hand, in the case of solvents like water, this may provide a means of separating the effects of polarization interactions from structural effects in the hydration of ions.

GLOSSARY OF TERMS

σ	nuclear screening constant
δ	chemical shift (usually with respect to TMS)
Δ	difference in chemical shifts
Δ_c	difference in shift between "free" and "complexed" molecules
ν	infrared frequency, in cm^{-1}
R	C_nH_{2n+1}
Bu	C_4H_9
Hp	C_7H_{15}
Q	equilibrium quotient: for $A + B \rightleftharpoons AB$, $Q = [AB]/[A][B]$.
X	an unspecified atom or group of atoms
H bond	hydrogen bond
M	moles $litre^{-1}$
D	Debye units
TMS	tetramethylsilane
ppm	parts per million

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Last, and certainly not least, to my dear wife Lois, who showed me that there is so much more to life than mere science.

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CHAPTER 1 INTRODUCTION

1.1 Hydrogen Bonding

Since the present work is largely concerned with hydrogen bonding processes, it is perhaps best to begin with a definition of a hydrogen bond. Pimentel and McClellan, in their excellent text on the subject (1), point out, on page 6, that there is no universally accepted definition, but nonetheless offer the following as an operational one:

"A hydrogen bond exists between a functional group A--H and an atom or a group of atoms B in the same or a different molecule when

(a) there is evidence of bond formation (association or chelation),

(b) there is evidence that this new bond linking A--H and B specifically involves the hydrogen atom already bonded to A."

As these authors go on to mention, "...there are many physical measurements that provide information relative to (a) but only a few substantiating (b). It is specifically criterion (b) that differentiates the hydrogen bond from other types of associative interaction."

The non-spectroscopic methods of detection of hydrogen bonds, such as melting and boiling points, pressure-volume-temperature measurements, cryoscopy, viscosity, etc., provide tests of varying sensitivity for criterion (a) of hydrogen bonding. By their very nature, however, they seldom provide any evidence concerning criterion (b) and hence are useful but not conclusive.

Evidence for criterion (b) is really available only from forms of spectroscopy which are sensitive to changes in structure or environment of different parts within a molecule, rather than merely properties of the molecule as a whole.

It is claimed, with considerable justification, on page 67 of reference 1, that infrared (and Raman) spectroscopy provide the most sensitive, characteristic, and informative manifestations of the hydrogen bond. There are several effects of the hydrogen bond on vibrational spectra:

(a) the A-H stretching mode is shifted to lower frequency by about 10%; as well, this mode is broadened by hydrogen bond formation;

(b) the R-A-H bending mode is shifted to higher frequency, but with no appreciable broadening;

(c) new vibrational modes are associated with the hydrogen bond itself.

A more recent, and in many ways complementary, spectroscopic method of detection is nuclear magnetic resonance (N.M.R.) spectroscopy. This technique is usually less sensitive and less characteristic than I.R. spectroscopy, but can be much more convenient and equally informative.

Characteristically, formation of a hydrogen bond is accompanied by a deshielding of the nucleus, which results in the resonance signal of the proton appearing at lower field than would otherwise be the case. This is neatly illustrated on page 146 of reference 1; the N.M.R. spectrum of ethanol at high dilution exhibits a proton resonance for the hydroxyl proton at a field strength greater than that for the methyl protons, whereas, in the (H bonded) pure substance, the hydroxyl proton resonates at considerably lower field than that for the methylene protons. In addition, the hydrogen bond shifts of a number of substances on passing from the gas phase to the liquid (associated) phase have been determined(2), and vary from zero to 4.6 ppm, always downfield.

When the exchange of a hydrogen between two distinct environments is very slow, then two separate signals are observed, with areas proportional to the relative times spent in the two environments. When the exchange, however, is rapid (i.e. the rate of exchange $\gg$ the frequency interval separating the resonance positions), only a single signal is observed, its position being a population-weighted average of the two extremes. In cases of intermediate exchange rates, the observed resonance is broadened and the analysis is complex.

In spite of the enormous amount of effort expended, there has as yet been no concensus reached on the nature of the hydrogen bond. The electrostatic model due to Pauling(3) and others is based on the Pauli exclusion principle; with a single available orbital, the hydrogen atom is considered incapable of forming more than one pure covalent bond.

The arguments which Pimentel and McClellan(1) advance against the electrostatic model, and hence in favour of covalency in the hydrogen bond, are interesting but by no means convincing. They say that in view of the well-documented enhancement of the stretch mode on hydrogen bond formation, it is impossible electrostatically to account for the decreased intensity of the bending mode; however, the same authors say elsewhere in the text that this latter effect is very small and poorly documented.

The major argument is based on the lack of correlation between $\Delta \underline{H}$ of hydrogen bond formation and dipole moment of the base involved. The fallacy in this argument is immediately obvious. There is no reason why a property of a molecule as a whole should bear any relation to a property of one atom or group of atoms in it. If the presence of excess negative charge at a particular location in a base molecule is regarded as giving the molecule its basic properties, then the matter of whether the balancing positive charge is nearby or more remote in the molecule is of little importance. Since molecular dipole moment is a function of the distance of charge separation as well as the magnitude of the separated charges, it is small wonder that the dipole moment has never correlated well with measures of base strength.

All this is not to rule out the possibility of some covalent character in the hydrogen bond, but there is every reason to regard it as primarily electrostatic until shown otherwise.

1.2 Solvation

The field of solvation of electrolytes is an enormous one, and I shall not pretend to deal with more than very limited parts of it here. Some treatment here is necessary and desirable since it will be shown that the results obtained in this work may be applied to problems of ion solvation.

The basic principle in the solvation of ions is that "like dissolves like" and, while this does not give the entire picture, it serves as a useful guide. Thus, the chemist is spared the indignity of attempting to dissolve sodium chloride in hexane, or tetrabromomethane in water; polar solutes must, in general, be dissolved in polar solvents, and similarly for non-polar materials.

However, this principle does not begin to account for many aspects of solution chemistry. Everybody realises the necessity of allowing for the effects of hydrogen bonding in the cases of solvents with known propensities along that line. It is also recognised that the polarizability of the solvent molecule may play a large, even dominant, role in its solvation processes, particularly of highly dipolar and ionic solutes. A case in point is the very appreciable solubility of tetrabutylammonium halide salts in tetrachloromethane; salt concentrations as high as 1-2 M have been readily achieved. A curiosity noticed in the course of work in this laboratory is that solubility in CCl_4 seems to be favoured by increasing cation size and by decreasing anion size.

For solvents which are strongly self-associated, such as formamide, water, etc., it has proven difficult (4) if not impossible to separate in a meaningful way the effects of "solvent structure" from those of individual ion--molecule interactions in the question of what happens on a molecular scale. A great deal of information has been inferred from changes in behaviour with changes of ionic size, or charge, particularly with respect to the solvent water, but few efforts have as yet been directed at separating the various effects in a systematic manner.

1.3 Scope of the Present Work

The work reported in this thesis had its genesis in the desire to find and study a number of compounds which would serve as models for C--H hydrogen bonding to halide ions. Such hydrogen bonding had been found in a number of glucopyranoside molecules(5) by Dr J. S. Martin, and Dr R. U. Lemieux's group at the University of Alberta.

The techniques are not new(6,7), having been used many times in the study of molecular complexes. The extension of the idea to ion--molecule complexes in these laboratories seems to be unprecedented, and is now described.

The system consists of three components. The solvent is ordinarily chosen to be as "inert" as possible, meaning that it must not contain any strongly electrophilic hydrogens, nor may it contain any strongly electron-donating (basic) sites. The solvents used almost exclusively were ethanenitrile, CH_3CN, which seems to satisfy the necessary criteria, and tetrachloromethane, CCl_4, a non-polar but highly polarizable solvent affording adequate solubility for the materials used.

The solute "acceptor" molecule, the material containing the electrophilic (hydrogen bonding) hydrogen(s), was kept at very low concentrations, usually 0.1 M, in order to minimize self-association effects.

The solute "donor" species is the anion of a tetraalkylammonium halide salt (R_4NX); its concentration varies from ca. 0.1 M to over 1 M. It has been shown(8) that even in ethanenitrile solvent, these salts exist in solution almost entirely as ion pairs. In fact, some of their dipole moments are known(9) and are invariably very large (15-20 D); hence, there is little transfer of charge within the ion pair.

The great advantage of studying hydrogen bonding when the donor species may be regarded as a single ion lies in the fact that the perturbing electrostatic field is exactly known, both in location and in magnitude. One of the major difficulties in calculating the magnitude of the electrostatic effect in hydrogen bonding is in assigning a magnitude and location to the effective dipole moment of the donor base involved(10), **in the case of dipolar bases.**

This method, then, allows an absolute determination of the validity of the expression first derived by Buckingham(11) which relates the extent of deshielding of a proton to the magnitude and direction of an electrostatic field acting upon it. This model is based on the consideration of an X--H bond as a hydrogen atom perturbed by a (positive) charge of magnitude λ at a distance R, this latter being the X atom. The parameter λ, then, represents the polarity of the molecule excluding the hydrogen under consideration, or at least part of the molecule nearest the hydrogen. The expression derived contains terms in the first and second powers of the electrostatic field at the proton. The coefficient of the first-power term contains an angular factor which must be taken into account.

The systems described herein have been set up so as to favour a 1:1 association process only. If it is valid to assume that this is the only process occurring, then it should be possible to make quantitative comparisons of proton shielding and strength of electrostatic field, always on the assumption of certain geometric restraints.

Some considerable support for the idea of electrostatic interactions between anions and molecules *via* electrophilic hydrogen is provided by several observations which were made in the course of this study.

For example, it was found that when the anion size was increased sufficiently, the weaker electrostatic field associated with it was not adequate to cause formation of hydrogen bonded complexes. When a solution in CH_3CN or CH_2Cl_2 of trichloromethane was made up to about 0.5 *M* in tetrabutylammonium perchlorate, Bu_4NClO_4, the downfield shift of the Cl_3CH

proton was an order of magnitude smaller than it was in similar systems with halide (Cl^-, Br^-, I^-) ions. Hence, a change in anion radius from ca. 2 A to ca. 3 A reduces the observed proton shift to the range expected for a host of weaker effects such as solute-solvent interactions, magnetic anisotropy of the solvent, self-association, etc.(12,13).

In order to ensure that the observations could not be explained by a mere replacing of some solvent molcules by foreign bodies, an inert material of comparable molar volume, cyclohexane, was added to an ethanenitrile solution of $CHCl_3$. Successive additions caused absolutely no measurable change in the position of the $Cl_3C\underline{H}$ resonance. Hence, it is fair to conclude that the molecule undergoes a specific interaction with the anion of the added salt.

A check on the catholicity of this field-induced shift effect is provided by the alcohol--anion systems. In, for example, ethanol, the hydroxyl hydrogen is the most electrophilic one in the molecule, the methyl and methylene hydrogens being much less so. When salt is added to a dilute solution of ethanol, the hydroxyl proton is the only one which exhibits a significant deshielding as a result of interaction with the ion. This is again consistent with a description of the interaction as electrostatic in nature.

The effect of competitive solvation by the solvent itself was determined by adding Bu_4NBr to a solution of $CHBr_3$ in ethanol. The $Br_3C\underline{H}$ resonance was not at all affected, demonstrating that the stronger solvent will solvate the anion preferentially.

CHAPTER 2 EXPERIMENTAL

2.1 Materials

Ethanenitrile, CH_3CN (Baker Reagent Grade) was distilled two to five times under nitrogen, from P_2O_5 and Na_2CO_3 initially, and straight the final time. The middle fraction finally collected had a boiling range of less than 0.5 C^o.

Tetrachloromethane, CCl_4 (Shawinigan reagent grade) was passed through a column of alumina (Activity GradeI) before use.

Tetramethylsilane, $(CH_3)_4Si$ (N.M.R. Specialties) was refrigerated over 4A Molecular Sieves (M.S.) until used.

Trichloromethane, $CHCl_3$ (Shawinigan reagent grade) was washed with distilled water to extract the ethanol preservative. The water and residual ethanol were then removed on an alumina column in the dry-box. The effluent was stored in an opaque bottle.

Tribromomethane, $CHBr_3$ (Matheson, Coleman & Bell) as received was stabilised with diphenylamine. It was shaken with acetic acid, and washed with distilled water; it was then put through a column of activated charcoal and into an opaque bottle, which was placed in the dry-box. There, it was passed through an alumina column and stored in an opaque bottle.

Triiodomethane, CHI_3 (BDH reagent grade) was dissolved in acetone; the solution was mixed with activated charcoal, then filtered. Distilled water was added to precipitate the triiodomethane. The precipitate was filtered off, and dried in a vacuum desiccator over P_2O_5.

2-Propanol, $(CH_3)_2CHOH$ (Fisher Certified ACS), Phenylmethanol, $C_6H_5CH_2OH$, 1-Phenylethanol, $C_6H_5CH(CH_3)OH$, 2-Phenylethanol, $C_6H_5CH_2CH_2OH$, and 4-Methoxyphenylmethanol, $CH_3OC_6H_4CH_2OH$ (all Eastman 'white label'), were dried by allowing to stand over M.S. for several days; no impurities could then be detected in the N.M.R.

4-Nitrophenylmethanol, $O_2NC_6H_4CH_2OH$ (Eastman 'white label') was used as received, since it showed no impurities in the N.M.R.

2-Phenyl-2-propanol, $C_6H_5C(CH_3)_2OH$ (donated by L. B. Green) was stored over M.S.

2-Methyl-2-propanol, $(CH_3)_3COH$ (BDH reagent grade) as received was a colourless liquid. This was dried by allowing to stand over M.S., with occasional agitation. As the material became drier, it began to crystallise (mp 25.5°); when about half of the alcohol had crystallised, the remaining liquid was discarded.

Dimethylsulphoxide, $(CH_3)_2SO$ (Fisher Certified Reagent) was dried over M.S.

Ethanol, CH_3CH_2OH. The N.M.R. spectrum of 98% ethanol, as received, showed no trace of benzene and, at most, trace quantities of water. This material was distilled, the middle 75% (b 76.0-77.5°) being collected on M.S. This fraction was then refluxed over the Sieves for one hour, then redistilled; the first 10% was rejected and the next 40% (boiling range 0.4 C°) collected. The tightly-stoppered flask was immediately transferred to the dry-box, where the ethanol was placed in a storage vial over M.S.
A Karl Fischer titration of 20 ml. of this material by L.B.Green showed no more than than 0.01% water, by volume.

Methanol, CH_3OH (Shawinigan reagent grade), as received, is stated to contain less than 0.2% water.

This material was dried by storing over M.S. for several days. The initial vigourous effervescence ceased after about one day.

Formamide-^{15}N, $HCONH_2$ (Isomet Corporation) was used as received (98% ^{15}N).

4A Molecular Sieves (Union Carbide) were used from a freshly opened container.

All solvents were made up to ca. 2 to 5% in TMS before being used.

2.2 Procedures

All samples were prepared inside a sealed dry-box which was kept under a slight positive pressure of dry nitrogen. An open, shallow dish containing P_2O_5 was kept in the box at all times.

Proton N.M.R. samples were prepared as follows. Volumetric tubes (2 ml.) were weighed before and after solid materials (e.g. salts) were placed in them. Enough solvent was added to dissolve the solids; then the liquids were added using a 10- or 50-μl syringe (typical quantities were 5-25 μl.). The solutions were then made up to the mark with solvent, thoroughly mixed, and approximately 0.5 ml. transferred to N.M.R. sample tubes fitted with auxiliary stopcocks to exclude air, connected to a vacuum rack, degassed by freezing and pumping, and sealed.

The N.M.R. spectra were obtained, for the most part, on a Varian HA-60 I spectrometer, and a few on a Varian HA-100. The internal reference used for the lock signal was either TMS or solvent, although all measurements are ultimately referred to internal TMS; the line positions were measured by setting the sweep oscillator at the resonance, and measuring the difference between its frequency and that of the lock-in oscillator.

The HA-100 was used in conjunction with a C-1024 computer to accumulate scans on a few very dilute samples; the recorder of the HA-100 was modified slightly by installing movable microswitches; this permitted operation over only a fraction of the whole recorder range. Hence, multiple scans of a single resonance could be made using only 1/5 or less of the sweep times usually necessary. Since the signal so obtained could not be calibrated directly, the scan limits were calibrated vs. TMS, and the signal position interpolated from these.

Fluorine-19 N.M.R. spectra were obtained by Messrs R. Swindlehurst and J. Hoyle on a Varian A-56/60 spectrometer operating at 56.4 MHz.

Samples for infrared spectra were prepared as for N.M.R., but were placed in matched infrared cells of path length 0.5-1 mm. Cells had windows of NaCl, KBr, or CsCl.

Most I.R. spectra were obtained on a Perkin-Elmer Model 337 spectrometer; some further spectra were run on a Perkin-Elmer Model 421, particularly in the range 625-200 cm^{-1}.

2.3 Analysis of N.M.R. Shielding vs Concentration

Assuming only 1:1 complexes of donor (ion) and acceptor (X-H), and ideal equilibrium behaviour:

$$[1] \qquad D + A \rightleftharpoons C$$

$$[2] \qquad \frac{[C]}{[D][A]} = \underline{Q}$$

N.M.R. spectra of all systems showed only one set of sharp proton signals, whose position varied monotonically with the halide ion concentration. This indicates that the equilibrium is extremely rapid; the observed shielding, σ, is a concentration-weighted average of its value in the free acceptor, σ_A, and in the complex, σ_C.

$$[3] \qquad \frac{(\sigma - \sigma_A)}{(\sigma_C - \sigma_A)} = \frac{\Delta}{\Delta_c} = \frac{[C]}{[C] + [A]}$$

In most cases, the complex is fairly weak

($K < 50$), so it is impossible to obtain pure complex and thus to observe Δ_c directly. To deduce values of $\underline{Q}$ and Δ_c, Scott's modification(14) of the Benesi-Hildebrand method was used. Equations 2 and 3 may readily be combined to yield Scott's equation:

[4] $$\frac{[D]}{\Delta} = \frac{1}{\underline{Q}\Delta_c} + \frac{[D]}{\Delta_c}$$

A least squares fit of

[5] $$y = c_1 + c_2 x$$

where $y = [D]/\Delta$, and $x = [D]$, yields

[6] $$\Delta_c = 1/c_2$$

[7] $$\text{and} \quad \underline{Q} = c_2/c_1$$

with standard deviations

[8] $$(\delta\Delta_c)^2 = (\delta c_2)^2/c_2^{\,4}$$

[9] $$(\delta\underline{Q})^2 = (\delta c_2)^2/c_1^{\,2} + c_2^{\,2}(\delta c_1)^2/c_1^{\,4} .$$

δc_1 and δc_2 include an evaluation of contributions from the experimental uncertainty in Δ and $[D]$. This evaluation is described in Appendix A.

In practice, the free donor concentration, $[D]$, is unknown; it differs from the total ion concentration by the complex concentration. Since the acceptor concentration has been kept small, the total initial salt concentration is a good first approximation to

[D]. At each concentration, the derived values of Δ_c and Q may be used to compute [C], and thus a better value of [D]. This may be used for a second Scott analysis, yielding better values of Δ_c and Q, and so on to self-consistency. A FORTRAN IV computer programme, SHEBA*, was written to do this.

---

*SHEBA = $P_{34}.P_{13}$.BHSEA (Benesi-Hildebrand-Scott Equilibrium Analysis).

2.4 What Units to Use?

Some concern has been expressed(15) that the results from this type of analysis are not consistent from one scale of concentrations to another. This is undoubtedly true and caution must be used in deriving thermodynamic parameters for a system, since these will be different when derived from different concentration scales.

For example, it has recently been shown(12) that, for a given equilibrium

$$A + B \overset{K}{\rightleftharpoons} AB \,, \qquad [10]$$

the equilibrium constant on a molar scale, K_C, and that on a mole fraction scale, K_X, are related by the expression

[11] $$K_X = K_C/[v_S + X_B(v_B - v_S)],$$

where v_B and v_S are the molar volumes of pure B and pure solvent, respectively. Thus, only on the off chance that $v_B = v_S$ can both equilibrium constants be independent of concentration.

The authors of reference 12. show that, for an admittedly limited range of experiments, K_C is independent of molar concentration in two solvents of very similar properties but very different molar volumes, whereas K_X is quite dependent on mole fraction concentration for the same equilibrium. These experiments may be taken as provisional confirmation that molar concentrations lead to meaningful equilibrium constants.

In addition, the present work involved determinations of several equilibria in two solvents, CCl_4 and CH_3CN. The Benesi-Hildebrand-Scott analyses of these systems consistently yielded the same complex shift in both solvents, as would be expected for formation of the same 1:1 complex. Presumably, then, this computation is separating the values of Δ_c and $\underline{Q}$ properly, since if $\underline{Q}$ depends on the concentration units in a particular solvent, then Δ_c will change from one solvent to another, since their molar volumes differ by a factor of 2.

CHAPTER 3 TRIHALOMETHANE—HALIDE ION COMPLEXES

This chapter deals with the results of N.M.R. and I.R. spectroscopic studies of trihalomethane (haloform) association with monovalent anions of Group VII elements in solution. It is shown that the ions interact more strongly with the induced molecular dipole than with the permanent one.

3.1 N.M.R. Shift in the Complex

In Table I are the ambient-temperature (ca. 27°C) values of the limiting shifts, Δ_c, for complexes of the four trihalomethanes with three halide ions (Cl^-, Br^-, and I^-) in the solvents ethanenitrile and tetrachloromethane. There are no entries for triiodomethane in CCl_4, since it is sparingly soluble in this solvent. While complexes of trifluoromethane

TABLE I. Limiting Chemical Shifts for Trihalomethane--Base Complexes.[a]

ACCEPTOR (Trihalomethane)	DONOR (Base)	LIMITING SHIFT, Δ_c (ppm)	
		in CH_3CN	in CCl_4
CHF_3	Cl^-		−2.15 ± 0.06
	Br^-		−2.17 ± 0.21
	I^-		−3.1 ± 1.7[b]
$CHCl_3$	Cl^-	−3.08 ± 0.11	−2.92 ± 0.12
	Br^-	−2.76 ± 0.33	−2.51 ± 0.08
	I^-	−2.18 ± 0.22	−2.30 ± 0.90[b]
$CHBr_3$	Cl^-	−2.34 ± 0.11	−2.29 ± 0.10
	Br^-	−1.57 ± 0.24	−1.82 ± 0.04
	I^-	−0.83 ± 0.05	−1.06 ± 0.22[b]
CHI_3	Cl^-	+0.31 ± 0.01	
	Br^-	+0.32 ± 0.01	
	I^-	+0.36 ± 0.01	
$CHCl_3$	pyridine		−1.07 ± 0.19
$CHBr_3$	pyridine		−1.16 ± 0.17
CHI_3	pyridine		−0.38 ± 0.06[b]

a: Salts were tetrabutylammonium salts, except as noted

b: Donor anion provided by tetraheptylammonium iodide do form in ethanenitrile, the variation of shift with ion concentration in these systems was so slight that a meaningful analysis of the data was not possible. It appears likely that the complex shifts are about the same as in tetrachloromethane, but that the equilibrium quotients are extremely small. Except where otherwise noted, tetrabutylammonium halide salts were used. It was necessary to use a larger cation in the iodide salt when in CCl_4, since tetrabutylammonium iodide is virtually insoluble in that solvent. Table I also contains data for complexes of a nitrogen base, pyridine, with the trihalomethanes.

The analysis was verified by observation of the infrared spectra of deuterated trihalomethanes in the same solvents (the ^{2}H isomers were used since the C--^{1}H bands of interest are obscured by absorptions due to cation). On addition of a tetraalkylammonium halide to a $CDCl_3$ or $CDBr_3$ solution, the characteristic C—D H-bonded stretch(1) band appeared at about 2170 to 2200 cm^{-1}. In every case, the intensity of this band was proportional to the concentration of complex as computed using the equilibrium quotient deduced from N.M.R. measurements. Figure 1 is a plot of some H bond band intensities (I.R.) against computed complex concentration (N.M.R.).

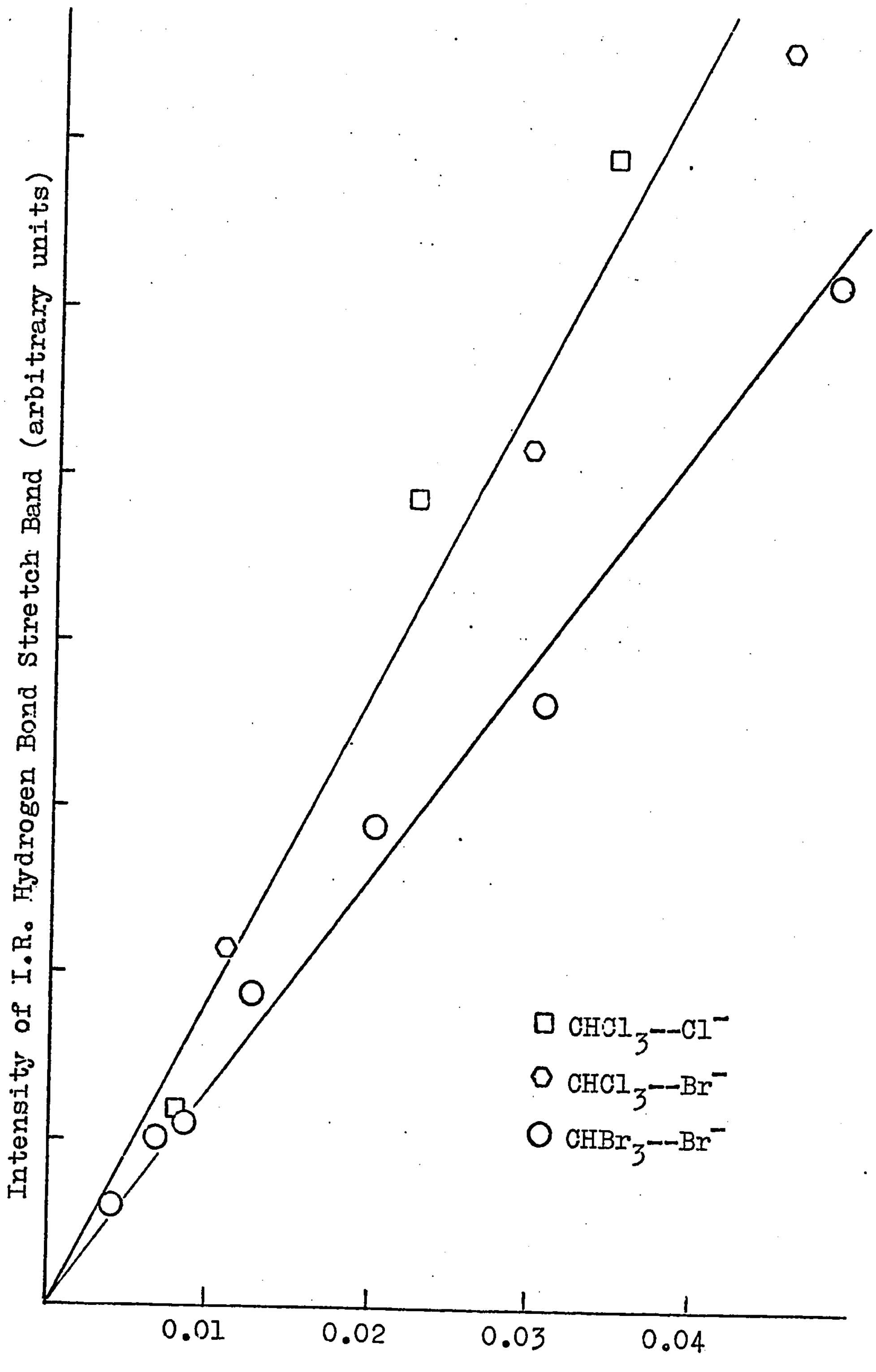

Figure 1

Complex Concentrations as Determined by N.M.R. and I.R.

CDI_3, at concentrations comparable to those for the N.M.R. work, showed no evidence in the infrared of H bond formation. Inspection of Table I reveals that the N.M.R. results for anion complexes of this compound are anomalous. This behaviour will be discussed later.

3.1.1 Effect of Temperature

Table II shows Δ_c as a function of temperature for complexes of trichloromethane and tribromomethane with the three halide ions studied.

Muller and Reiter(16) have estimated the temperature dependence of the chemical shift of H bonded complexes *via* excitation of the H bonded stretch vibrational mode, for various assumed potential-well depths, and corresponding enthalpies of H bond formation. They predict that for weak hydrogen bonds, and thus shallow wells, many excited vibrational states are thermally accessible, and $\delta\Delta/\delta T$ is large.

Fitting the values of Δ_c over a range of temperatures for each complex (see Table II), a least-squares straight line was obtained and its slope taken as a measure of $\delta\Delta_c/\delta T$ (see Table III); the standard errors for these lines are in general larger than the

TABLE II. Temperature Dependence of Δ_c for Trihalomethane--Anion Complexes.[a]

ACCEPTOR	DONOR	TEMPERATURE (^oK)	LIMITING SHIFT, Δ_c (ppm)
$CHCl_3$	Cl^-	248	-2.91 ± 0.08
		268	-2.99 ± 0.09
		288	-3.04 ± 0.10
		313	-3.12 ± 0.13
		333	-3.08 ± 0.19
$CHCl_3$	Br^-	248	-2.92 ± 0.28
		273	-2.92 ± 0.31
		298	-2.81 ± 0.33
		318	-2.81 ± 0.44
		338	-2.72 ± 0.43
$CHCl_3$	I^-	248	-2.32 ± 0.18
		273	-2.34 ± 0.20
		323	-2.19 ± 0.31
$CHBr_3$	Cl^-	248	-2.27 ± 0.11
		273	-2.34 ± 0.11
		298	-2.38 ± 0.11
		323	-2.34 ± 0.11
		348	-2.38 ± 0.22

$CHBr_3$	Br^-	248	-1.58 ± 0.12
		273	-1.63 ± 0.16
		298	-1.62 ± 0.18
		323	-1.63 ± 0.19
		348	-1.56 ± 0.19
$CHBr_3$	I^-	248	-0.89 ± 0.05
		273	-0.92 ± 0.06
		298	-0.93 ± 0.07
		323	-0.80 ± 0.06
		348	-0.76 ± 0.06

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a: Solvent -- ethanenitrile.

TABLE III. Temperature Variation of Limiting Shifts, by Least Squares.

COMPLEX	$\delta\Delta_c/\delta T$ (ppm deg.$^{-1}$)
$CHCl_3 + Cl^-$	$(+0.24 \pm 0.23) \times 10^{-2}$
$CHCl_3 + Br^-$	$(-0.22 \pm 0.64) \times 10^{-2}$
$CHCl_3 + I^-$	$(-0.18 \pm 0.78) \times 10^{-2}$
$CHBr_3 + Cl^-$	$(+0.09 \pm 0.23) \times 10^{-2}$
$CHBr_3 + Br^-$	$(-0.01 \pm 0.27) \times 10^{-2}$
$CHBr_3 + I^-$	$(-0.15 \pm 0.11) \times 10^{-2}$

slopes themselves, indicating that the uncertainties in the values of Δ_c are of at least the same magnitude as any systematic variation could possibly be. Furthermore, four of the six lines so obtained give a slope in the wrong sense to fit the analysis of Muller and Reiter. Thus, it seems reasonable to say that $\delta\Delta_c/\delta T$ is no greater than 0.25×10^{-2} ppm deg.$^{-1}$, and thus the complex represents the minimum of a potential well of depth $\gg$ RT. Lines 6, 7, and 8 of Table I in reference 16 are reproduced here as Table IV; comparison of this estimate with their calculated values indicates an energy of interaction of perhaps -10 kcal. mole^{-1}.

Such a value is fairly consistent with the observed enthalpies of formation of X--H...B bonds in the gas phase, where B is a dipolar base. These are generally in the range -3 to -8 kcal. mole^{-1}(1). It seems reasonable to expect that the enthalpies of hydrogen bonds to monopolar bases (anions) would be at least as large. For example, the enthalpy of hydration of chloride ion is -80.3 kcal. mole^{-1}; dividing this among four or five solvating water molecules yields an O--H...Cl^- energy of 15-20 kcal. mole^{-1}. This may be regarded as establishing a range for enthalpies of formation of hydrogen bonds to anions from isolated constituents.

TABLE IV. Calculated Temperature Dependence of O--H...
..O Shift as a Function of H Bond Energy.[a]

H BOND DISSOCIATION ENERGY (kcal. mole^{-1})	$\frac{\delta\Delta}{\delta T}$ (ppm deg.$^{-1}$)
4.0	0.78×10^{-2}
6.0	0.44×10^{-2}
7.5	0.30×10^{-2}

a: Lines 6, 7, and 8 of Table I in reference 16.

A recent study of Cl_3CH--X^- interactions by means of pressure--composition measurements(17) has yielded the enthalpies of trichloromethane hydrogen bond formation to the halide ion of tetrabutylammonium halide salts in the solid phase. The values found were:

Complex	ΔH (kcal mole^{-1})
Cl_3CH--Cl^-	-14.0
Cl_3CH--Br^-	-12.6
Cl_3CH--I^-	-9.6.

These compare favourably with the estimate made here of approximately -10 kcal. mole^{-1}.

3.1.2 Discussion of Shifts in the Complex

Buckingham, Schaefer, and Schneider(18) divided the extra-molecular effects on the shielding in solution of a proton into four terms; a bulk susceptibility term, which in this case will be constant since all chemical shifts are referred to an internal reference signal (TMS); a solvent anisotropy term, which for this system turns out to be small even for ethanenitrile, the shift of $CHCl_3$ from TMS being 7.22 ppm in CCl_4 and 7.57 ppm in CH_3CN; a van der Waals term and an electrostatic field term, both of which will be discussed in greater detail.

Buckingham(11) has shown that the shielding, σ, of a proton in X--H subjected to an electric field will be proportional to the first power of the component of the field along the bond, and to the second power of the field.

$$[12] \qquad \Delta_c = \underline{A}\, E_z - \underline{B}\, E^2 .$$

He considers a model of the X--H bond in which a hydrogen <u>atom</u> is at a distance R from a point charge λ, which represents the X atom. Thus, the X--H bond is treated as essentially a perturbed hydrogen atom. Since this perturbation is in the X--H direction only, the coefficient of the term in the second power of E ($\underline{B}$) should be nearly the same as for a hydrogen atom; this is exactly calculable and has been evaluated as 0.738×10^{-18} esu. While the range of values found for $\underline{B}$ for all bond types is at least $0.4\text{-}44 \times 10^{-18}$ (19), the values for the C--H bond for hydrocarbons and for CHF_3 appear to fall close to the calculated one, having been assigned the values 1.0×10^{-18} and 0.84×10^{-18} respectively(19).

On the other hand, the coefficient of the term in the first power of E ($\underline{A}$) contains the term λ/R^2; hence, λ becomes, in effect, an adjustable parameter, although it is a measure of the polarity of the X--H bond. "In most X--H bonds, it is reasonable to assume that there is an increased electronic charge between the nuclei (as for a positive λ), so that an electric field in the X--H direction will tend to draw this excess charge further away from the proton, thereby decreasing its shielding constant."(11). That is, for

$$X \longleftarrow\!\!\!\!+ H$$

a field in the sense ⟶ will cause deshielding of the hydrogen nucleus.

In the present case, a collinear X--H...Y^- complex is postulated, and the electrostatic field may be regarded as originating in a point charge at the centre of the ion. If the distance from the ion centre to the hydrogen nucleus is $\underline{r}$ Angstrom units, and the angle between the X--H and H--ion vectors is θ the complex shift, in parts per million, is predicted to be:

$$[13] \qquad \Delta_c = -4.803\,\underline{A}\,(1/\underline{r}^2)\cos\theta - 23.07\,\underline{B}\,(1/\underline{r}^4).$$

If the anion is assumed to be collinear with the X--H bond, this equation expresses the complex shift as a quadratic in $1/\underline{r}^2$.

The analysis of the shieldings, and related infrared evidence, suggests that trifluoromethane and trichloromethane interact with halide ions via hydrogen, while triiodomethane interacts by a charge-transfer, or polarization mechanism. Tribromomethane appears to be an intermediate case. The four molecules will be discussed in an order which emphasises this interpretation.

3.1.2.1 Trichloromethane

Throughout this thesis, unless stated otherwise, the analysis of shift--field dependence assumes that the anion is collinear with the X--H bond to which it is hydrogen bonded. This has been done for two reasons: (a) a substantial body of opinion and evidence favours near-linear hydrogen bonds in the absence of other restraints(1); (b) the effect of the anion field drops off very rapidly as θ increases, and the observed shifts are of magnitude such that the maximum field effect is necessary to account for them.

Table V compares the observed Cl_3C--H...X^- shifts with those calculated using equation 13, and taking from the literature, values for the coefficients <u>A</u> (3.0×10^{-12}) and <u>B</u> (0.738×10^{-18}); van der Waals contact has been assumed. It is seen that this calculation does reproduce the trend in shifts,

TABLE V. Experimental and Calculated Complex Shifts For Trichloromethane with Halide Ions.

DONOR ION	Δ_c (experimental) in CCl_4	Δ_c (experimental) in CH_3CN	Δ_c (calculated)
Cl^-	-2.92	-3.08	-1.80
Br^-	-2.51	-2.76	-1.61
I^-	-2.30	-2.18	-1.37

although the absolute values are low*. The term in $\underline{B}/r^4$ contributes only about 15% of the total shielding.

3.1.2.2 Trifluoromethane

The complex shifts of this molecule are imprecisely determined, and their variation is not significant. They appear to be of about the same magnitude as those in trichloromethane.

3.1.2.3 Triiodomethane

The paradox of positive complex shifts is resolved if one postulates a complex involving the anion and the iodine atoms, rather than the hydrogen. E_z now is directed in the reverse sense, and $\delta\sigma$ is positive.

To test this postulate, the entire infrared spectrum, from 4000 to 200 cm^{-1} was examined for each trihalomethane, alone in solution and in the presence of tetraalkylammonium salts at concentrations comparable to those used in the N.M.R. study (0.1 - 1 $\underline{M}$). As

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* for further discussion of this point, as well as the magnitude of the van der Waals deshielding, see p 117

described previously, C--D H bonded absorptions at 2170-2200 cm^{-1} were observed for CHF_3, $CHCl_3$ and $CHBr_3$ in the presence of the halide ions studied.

C--D H bond absorptions have been reported for complexes of triiodomethane with several strong dipolar bases(20). I was able to observe the H bond band of CDI_3 in CCl_4 solution in the presence of excess dimethylsulphoxide or pyridine, but not in the presence of tetraalkylammonium halide salts up to about 1 M. (A weak H bond band was observable in a Nujol mull of equimolar CDI_3 and any tetrabutylammonium halide).

The triiodomethane spectrum does, however, show evidence of perturbation in the low-frequency region on addition of anions. The absorption at 420 cm^{-1}, a symmetric CI_3 stretch designated ν_2 in Herzberg's notation(21), is extremely weak in ethanenitrile solution. On addition of a halide ion at concentrations in the range 0.1-1 M, the intensity of this band was enhanced by a factor of about 100 (see Figure 2) and became comparable to that of the e-stretch ν_5, at 580 cm^{-1}.

This enhancement may be taken as evidence for polarization of the C--I valence electrons by a nearby ion, which causes enhancement of the bond dipole transition moment. No such enhancement is

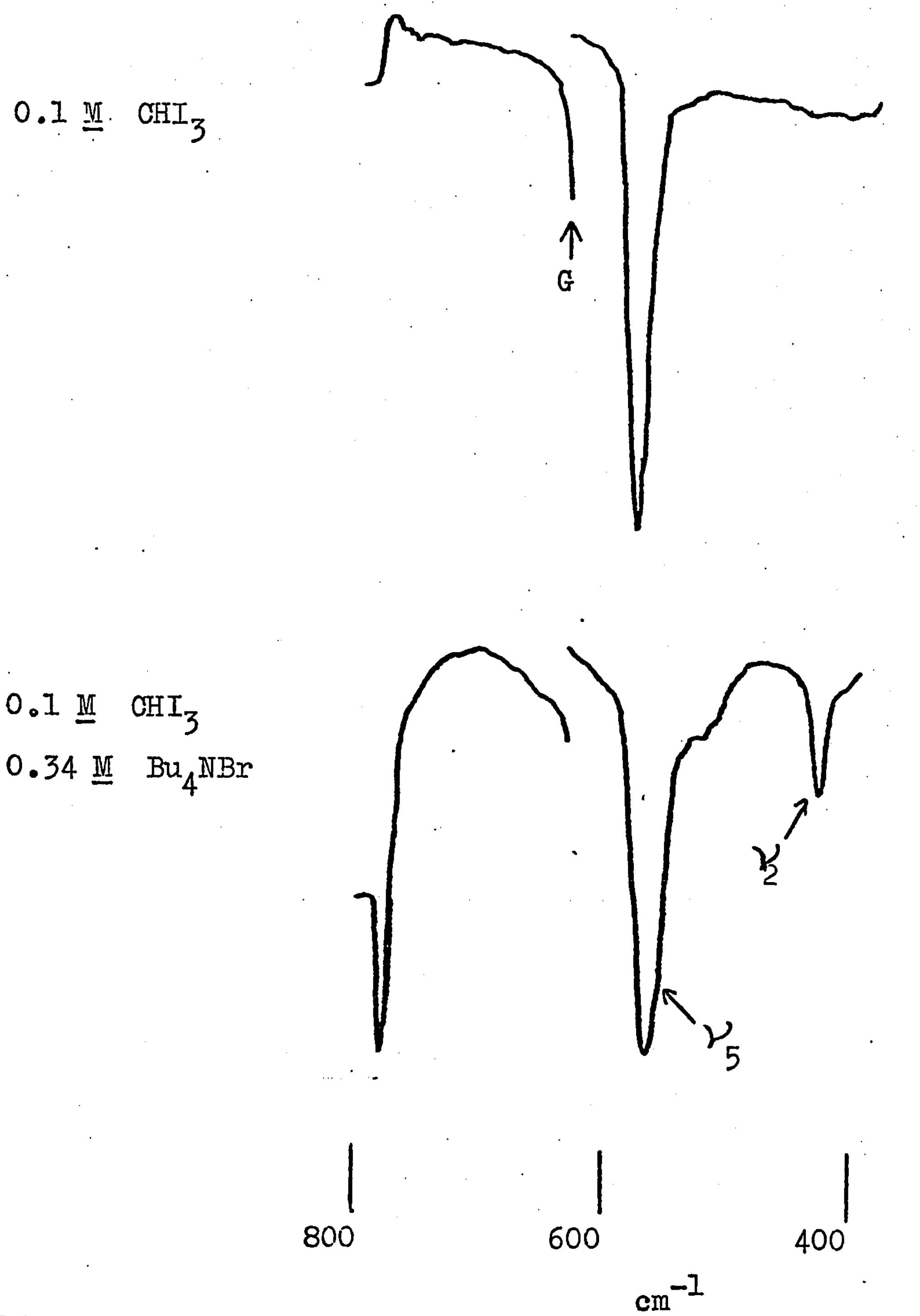

Figure 2

Infrared Spectrum in the Carbon--Halogen Region of a Polarization Complex. (G = grating change) observed for the corresponding absorptions in the other trihalomethanes on the addition of salts. In $CHCl_3$ and $CHBr_3$, a satellite of ν_2 appears and grows in intensity as the proportion of complex increases, with the new peak 5-10 cm^{-1} to low frequency of, of width and intensity comparable to, and growing at the expense of, the parent (see Figure 3). This presumably reflects a slight change in carbon--halogen force constant on formation of the hydrogen bonded complex. In a very recent paper(22), Devaure et al have made a thorough study of the I.R. spectra of $CHCl_3$ and $CDCl_3$ in a variety of solvents. They, too, find a second ν_2 peak appearing when Bu_4NBr is added to a CCl_4 solution of $CHCl_3$ or $CDCl_3$, at 12 cm^{-1} to low frequency of the parent. They conclude that this second band cannot be due to dipole-dipole interactions, and must be due to a perturbation of the C-Cl force constant upon formation of a hydrogen bond by C-H or C-D.

The C--H and C--D bend absorptions at ca. 1065 and 790 cm^{-1}, respectively, are masked by solvent absorption in solution. However, these regions are relatively transparent in Nujol, and in several cases the complexes are sufficiently soluble to show an infrared spectrum in the mull. A normal H bond shift of 25 cm^{-1} to high frequency was observed for the $CHCl_3$--Br^- complex; however, the complex band of

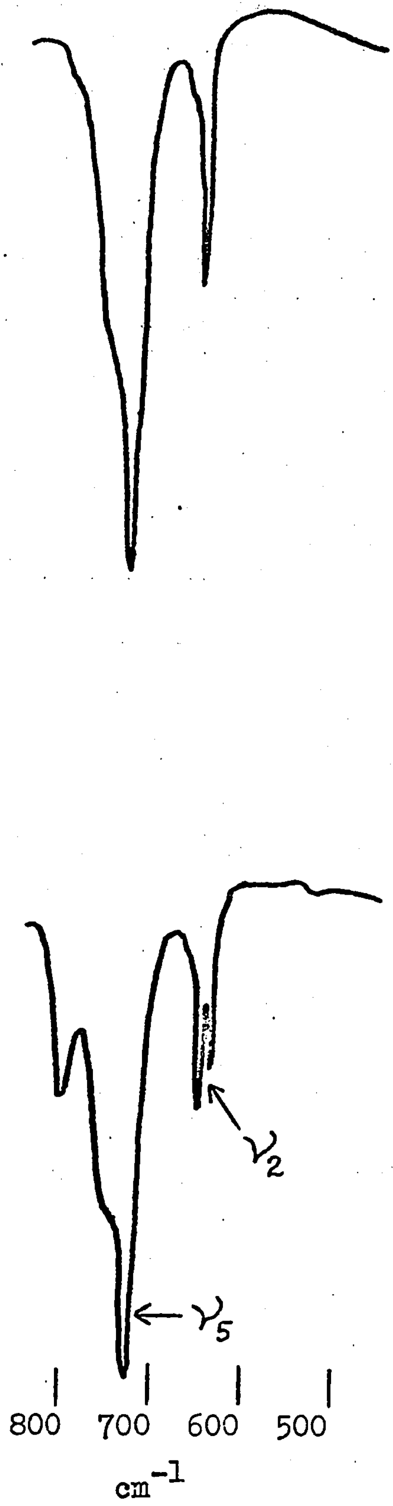

Figure 3

Infrared Spectrum in the Carbon--Halogen Region of a Hydrogen Bonded Complex.

CHI_3--Br^- in this region is 22 cm^{-1} lower than the parent CHI_3 bend at 1065 cm^{-1}. A similar shift to lower frequency was observed for the CDI_3--Br^- complex. This is further evidence that the interaction of anions with triiodomethane is substantially different from the "normal" hydrogen bonding of trichloromethane.

I consider the sum of this evidence to be adequate to justify the postulate that the triiodomethane complexes involve interaction of the iodine, rather than the hydrogen, with the anion (see also reference 23).

Two configurations of such complexes suggest themselves: (a) an asymmetric structure, the ion collinear with the C--I bond; (b) a trigonally symmetric complex, the ion collinear with the C--H bond, and equidistant from the three iodine atoms. The asymmetric structure involves strong interaction with a single iodine atom and is analogous to that of the linear I_3^- ion, whereas the symmetric structure preserves the symmetry of the molecule and involves relatively weaker interactions with all three iodine atoms. The latter model would be more consistent with the observation that the most significant change in the infrared spectrum on complex formation is the enhancement without frequency shift, of a symmetric

CI_3 stretch mode absorption.

N.M.R. complex shifts, Δ_c, computed using equation 13, are: +0.11 ppm in the asymmetric model, and +0.54 ppm in the symmetric one. The observed values are all in the range +0.30 to +0.36 ppm. It is not easy to rationalize the observed values' being more positive than the predicted ones in the unsymmetric complex. On the other hand, three mechanisms could reduce the shielding from +0.5 to +0.3 ppm in the symmetric complex. (a) A small fraction, f_H, of the triiodomethane complex may be hydrogen bonded; this would decrease the shift by <u>ca.</u> 2.5 f_H ppm. Thus, less than 10% of hydrogen bonding, which would be virtually undetectable by other means, could account for the discrepancy. (b) The pyridine shifts suggest that <u>A</u> may be smaller in CHI_3 than in $CHCl_3$. (c) The field at the proton is transmitted from the ion primarily through space occupied by highly polarizable iodine atoms. Using an estimated molar polarization of iodine of 14.5 cm^3 $mole^{-1}$, I compute an effective dielectric constant of 3.4 for space filled by covalent iodine; this is in excess of the value of 2-2.5 for hydrocarbon structures, which is contained implicitly in the coefficients of equation 13. It is reasonable to expect that the field at the proton, arising from an ion beyond the CI_3 structure, would be reduced by about 40%.

The N.M.R. and I.R. spectra of solutions of 2-iodopropane and halide salts showed no evidence of complexing with a single iodine atom, as would be expected for linear C--I...X^- bonding.

3.1.2.4 Tribromomethane

The complex shifts for tribromomethane are intermediate between those of $CHCl_3$ and of CHI_3. This compound probably interacts with halide ions *via* hydrogen bonding and *via* its halogen atoms in roughly equal proportions. The infrared evidence gives no indication of other than hydrogen bonding. On the other hand, ν_2 is already fairly intense in the uncomplexed species, possibly making enhancement difficult to detect. As mentioned before, normal H bond absorption is observed. Possibly of greater significance is the fact that the constant of proportionality between H bond absorption intensity and complex concentration as computed from N.M.R. data is smaller for $CHBr_3$ than for $CHCl_3$ (see Figure 1). This suggests that only a constant fraction of the $CHBr_3$ complex involves hydrogen bonding.

3.2 Equilibrium Quotients

In Table VI are the ambient-temperature values of Q (=[C]/[A][D]) for the complexes studied. The significant trends may be summarized as follows:

(a) In a given solvent, for a given trihalomethane, the equilibrium quotient increases in the order $I^- < Br^- < Cl^-$ as the anion radius decreases. This is the order expected if the complex energy is controlled by the electrostatic field of the anion.

(b) In a given solvent, with a given anion base, the equilibrium quotients increase in the order $CHF_3 < CHCl_3 < CHBr_3 < CHI_3$. This is the opposite order to that of the molecular dipole moments, which presumably determine the electrophilicity of the hydrogen.

(c) For a given complex, the equilibrium quotient in tetrachloromethane is about twice that in ethanenitrile at ambient temperature.

(d) The equilibrium quotients for association of pyridine with $CHCl_3$, $CHBr_3$, and CHI_3 are essentially equal, in contrast to the large variation relative to any anion base. The interaction of the dipolar base, pyridine, appears to differ essentially from that of the monopolar anions with trihalomethane molecules.

TABLE VI. Equilibrium Quotients for Trihalomethane--Base Complexes.[a]

ACCEPTOR	DONOR	EQUILIBRIUM QUOTIENT, $\underline{M}^{-1}$ in CH_3CN	EQUILIBRIUM QUOTIENT, $\underline{M}^{-1}$ in CCl_4
CHF_3	Cl^-		2.43 ± 0.13
	Br^-		1.38 ± 0.16
	I^-		0.55[b] ± 0.30
$CHCl_3$	Cl^-	1.18 ± 0.05	2.51 ± 0.17
	Br^-	0.73 ± 0.09	1.78 ± 0.08
	I^-	0.48 ± 0.05	1.07[b] ± 0.43
$CHBr_3$	Cl^-	1.10 ± 0.06	2.45 ± 0.16
	Br^-	1.11 ± 0.20	1.86 ± 0.09
	I^-	1.17 ± 0.09	1.95[b] ± 0.45
CHI_3	Cl^-	3.30 ± 0.25	
	Br^-	3.76 ± 0.22	
	I^-	3.56 ± 0.18	
$CHCl_3$	pyridine		0.38 ± 0.07
$CHBr_3$	pyridine		0.34 ± 0.05
CHI_3	pyridine		0.39[b] ± 0.07

[a]: Salts were tetrabutylammonium salts, except as noted

[b]: Donor anion provided by tetraheptylammonium iodide.

In view of the difficulty of obtaining precise values of $\Delta \underline{H}$ and $\Delta \underline{S}$ for all the complexes studied (those given in the next section are experimentally the most favourable cases), I shall assume that the relative magnitudes of the ambient-temperature equilibrium quotients generally reflect corresponding changes in $\Delta \underline{H}$. This requires that $\Delta \underline{S}$ either be substantially constant, or at least vary in the same way as $\Delta \underline{H}$ (ref. 1, p220).

3.3 Energetics

3.3.1 Experimental

Table VII shows the equilibrium quotient as a function of temperature for complexes of trichloromethane and tribromomethane with the three halide ions studied. A least-squares fit of log $\underline{Q}$ to 1/T yields the enthalpy and entropy changes on complex formation; these are given in Table VIII. As one might expect, $\Delta \underline{H}$ becomes increasingly negative with decreasing ionic radius. No trend in $\Delta \underline{S}$ relative to ionic radius is apparent beyond the limits of experimental error.

The discrepancy between these values for $\Delta \underline{H}$ (ca. -1 kcal. mole^{-1}) and the lower limit established from the temperature dependence of the complex shifts

TABLE VII. Temperature Dependence of the Equilibrium Quotient for Trihalomethane--Halide Ion Complexes.[a]

ACCEPTOR	DONOR	TEMPERATURE °K	EQUILIBRIUM QUOTIENT $\underline{M}^{-1}$
$CHCl_3$	Cl^-	248	1.98 ± 0.09
		268	1.61 ± 0.07
		288	1.34 ± 0.06
		313	1.08 ± 0.06
		333	0.98 ± 0.07
$CHCl_3$	Br^-	248	0.99 ± 0.10
		273	0.83 ± 0.09
		298	0.74 ± 0.09
		318	0.65 ± 0.10
		338	0.60 ± 0.10
$CHCl_3$	I^-	248	0.64 ± 0.05
		273	0.55 ± 0.05
		323	0.43 ± 0.06
$CHBr_3$	Cl^-	248	1.64 ± 0.11
		273	1.32 ± 0.08
		298	1.09 + 0.06
		323	0.99 ± 0.05
		348	0.85 ± 0.09

$CHBr_3$	Br^-	248	1.63 ± 0.16
		273	1.27 ± 0.15
		298	1.10 ± 0.14
		323	0.95 ± 0.12
		348	0.87 ± 0.12
$CHBr_3$	I^-	248	1.58 ± 0.11
		273	1.29 ± 0.10
		298	1.06 ± 0.09
		323	1.13 ± 0.09
		348	1.01 ± 0.09

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a: Solvent -- ethanenitrile

TABLE VIII. Thermodynamic Quantities for Trihalomethane--Halide Ion Complexes.[a]

COMPLEX	ΔH kcal. mole^{-1}	ΔS e.u.
$CHCl_3 + Cl^-$	-1.38 ± 0.04	-4.2 ± 0.1
$CHCl_3 + Br^-$	-0.93 ± 0.04	-3.7 ± 0.1
$CHCl_3 + I^-$	-0.84 ± 0.01	-4.3 ± 0.1
$CHBr_3 + Cl^-$	-1.10 ± 0.04	-3.5 ± 0.2
$CHBr_3 + Br^-$	-1.07 ± 0.05	-3.4 ± 0.2
$CHBr_3 + I^-$	-0.71 ± 0.09	-2.0 ± 0.3

a: Solvent -- ethanenitrile

(ca. -10 kcal. mole^{-1}) may be removed by considering the process of complex formation as differential solvation of the ion, where the trihalomethane molecule displaces n solvent molecules

[14] $$XS_m^- + CHY_3 \rightleftharpoons XS_{m-n}CHY_3^- + nS .$$

If the trihalomethane molecule displaces a single solvent molecule, the observed value of ΔH (ca. -1 kcal. mole^{-1}) is the difference between the "solvation" energies of the two molecules for the ion.

If the difference of 9.23 in pK_{SP} values of thallous chloride, TlCl, in water and ethanenitrile(24) is regarded as arising from the difference in solvation enthalpy of the chloride ion between the two solvents, then the solvation enthalpy of Cl^- in ethanenitrile is $-80.3 + RT \ln 9.23$, or -66 kcal. mole^{-1}. This implies single-molecule solvation enthalpy of -12 to -15 kcal. mole^{-1}.

3.3.2 Theoretical. An Electrostatic Model of Anion-Molecule Interaction

The anion complexes studied appear to be of two distinct types: hydrogen-bonded (CHF_3, $CHCl_3$, $CHBr_3$) and halogen-bonded or charge-transfer ($CHBr_3$, CHI_3). All the complexes with pyridine appear to be

H bonded.

Both H bonding and charge-transfer bonding have been evaluated by quantum-mechanical models(10,25). Quantitative application of such models is restricted by the need for such parameters as intermolecular overlap integrals and excited-state configuration data.

Simple electrostatic models, involving parameters such as dipole moments and polarizabilities which are accessible to independent determination, have been used successfully to evaluate hydrogen bond energies(26). I shall adapt, for the present, a model of this sort which has been useful in predicting ion hydration energies(27,28).

The computation involves evaluation of the electrostatic potential energy of interaction of the ion, regarded as a point charge Ze, with the permanent and induced dipole moments of the molecule. The details of the computational procedure are given on pages 3665-6 of reference 29.

Among the more important terms omitted from this computation are the dipole-dipole repulsion of the molecules solvating the ion, and the molecular dipole--ion polarizability interaction. Both of these can be estimated, and are found to be about an order of magnitude smaller than the primary interaction energies.

They will also tend to cancel out in the complex vs. the homogeneously solvated ion.

I believe that it is fair to expect the electrostatic interaction energy, U_e, computed using this conceptually simple model to reflect the large-scale trends in ΔH and thus the equilibrium quotients. It is probably not fair to expect valid comparison of the energies of structurally different complexes; such cases, in addition to being exceptionally severe tests of the consistency of the two terms in the energy (ion--permanent dipole, and ion--induced dipole), are also those in which there may be significant differences in the entropy contribution to Q. Nevertheless, if the model is a reasonable one, it should predict energies of the same order for complexes of comparable stability.

The computations, using bond moments derived from experimental dipole moments (and assuming $\mu_{CH}=0$) and polarizabilities from Groves and Sugden(30) and Denbigh(31), with the geometric parameters given in the Handbook of Chemistry and Physics, were programmed in FORTRAN IV for the IBM 360-65/67 computer*; the

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* I am indebted to Dr J. S. Martin for this programming

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programme is named IONPOT.

Table IX gives the minimum computed values of U_e for all the complexes treated in this chapter. As might be expected, for a particular complex U_e is computed to be more negative as the ionic radius decreases; this simply reflects the increase in electrostatic field strength.

If the experimental variation of equilibrium quotients in the trihalomethane family is determined by electrostatic energy, then the monotonic increase in energy from CHF_3 to CHI_3 indicates that the induced, rather than the permanent, dipole of the molecule dominates in its interaction with the anions (of course, the permanent dipole term in the energy <u>decreases</u> from CHF_3 through CHI_3). The computed energies are in accord with this conclusion, since for the series $CHCl_3$, $CHBr_3$, CHI_3, they become increasingly negative as the polarizability of the halogen increases. An increase in the estimate of the polarization energy contribution in the model would tend to put CHF_3 into the observed sequence.

One of the most striking features of the computed set of U_e's is the rapid decrease (negative increase) in energy in all series of symmetric halogen-bonded complexes, in the order $CHF_3 > CHCl_3 > CHBr_3 > CHI_3$. As the polarizability increases, such structures

TABLE IX. Computed Ion—Molecule Electrostatic Potential Energy.[a]

Type of Complex[b]	Molecule	Ion		
		Cl^-	Br^-	I^-
(h)	CHF_3	-9.8	-8.9	-7.9
	$CHCl_3$	-8.5	-7.7	-6.6
	$CHBr_3$	-9.1	-8.3	-7.1
	CHI_3	-9.5	-8.6	-7.4
(s)	CHF_3	+1.3	+1.6	+2.0
	$CHCl_3$	-5.2	-4.1	-2.8
	$CHBr_3$	-6.7	-5.4	-3.9
	CHI_3	-9.4	-7.8	-6.0
(a)	$CHCl_3$	-1.3	-1.1	-0.8
	$CHBr_3$	-2.1	-1.8	-1.3
	CHI_3	-3.9	-3.4	-2.7
(f)	CCl_4	-9.1	-7.7	-6.0
	CH_3CN	-13.4	-12.4	-10.9

a: kcal. mole^{-1}

b: (h) — hydrogen bonded complex

(s) — symmetric halogen bonded complex

(a) — asymmetric halogen bonded complex

(f) — most favourable configuration

become increasingly stable. This model predicts that CHI_3 halogen bonded complexes will have stabilities comparable to those of the corresponding hydrogen bonded complexes. The experimental evidence strongly suggests that the two complex types are of comparable stability in the case of $CHBr_3$, and that, in the case of CHI_3, the halogen bonded complex is significantly more stable. Again, the model would appear to be somewhat underestimating the polarization contribution to the energy.

In the absence of reliable values of the carbon-hydrogen bond moments, μ_{CH} was assigned the value zero in all cases. Denariez and Lecayer(32) have estimated, from absolute infrared intensities, that the value of μ_{CH} in $CHCl_3$ is 0.69 D, hydrogen positive. It is reasonable to suppose, then, that μ_{CH} increases in the series $CHI_3 < CHBr_3 < CHCl_3$. Such a trend strengthens the argument that the complex type changes between $CHCl_3$ and CHI_3.

The model predicts unambiguously that the symmetric halogen bonded complex will in every case be of considerably lower energy than the asymmetric complex containing a linear $C{-}{-}I\ldots X^-$ structure. Computation of U_e at various points on the halogen van der Waals surface reveals a strong potential minimum in the region of symmetric interaction with all three halogens.

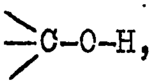
Consistent with the previously mentioned concept of complex formation as differential solvation, the model predicts solvation energies of tetrachloromethane which are slightly smaller, on the average, than the energies of those trihalomethane complexes which are observed to be stable. It correctly predicts a more negative solvation energy for ethanenitrile; indeed, one much larger than those of the trihalomethanes. The latter condition is patently untrue and may be rationalised by considering the model as too simpleminded an approximation to the structure of ethanenitrile, since it treats the very large molecular dipole as arising from two charged atoms, as $C^+—N^-$.

Interaction energies with anions were also computed at distances of approach 0.5 A closer than the sum of radii, as would be consistent with the shielding computations. These energies were consistently about 30% greater in magnitude but showed exactly the same trends as the values in Table IX.

3.4 Monopolar vs. Dipolar Bases

The failure of the dipolar base, pyridine, to form halogen bonds to CHI_3 could be explained, within a charge-transfer formalism, as a consequence of its very high ionisation energy, 213 kcal. mole^{-1}, relative to those of the halide ions, 74-96 kcal. mole^{-1}. However, the U.V. spectrum from 190 to 390 mµ of CHI_3 with added salt showed no charge-transfer bands. The electrostatic model affords an explanation, provided that the stable complex is the symmetric one. A monopolar ion has a spherically symmetric potential and can interact strongly with three polarizable halogens simultaneously. Dipolar pyridine, on the other hand, can interact strongly only in one specific direction, as in hydrogen bonding; its interaction over a large solid angle, as in the halogen polarization complex, will be relatively weaker than that of a monopole.

CHAPTER 4 ALCOHOLS AND BROMIDE ION

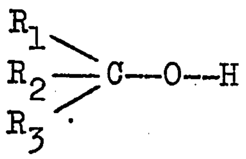
This chapter deals with the association by hydrogen bonding of a number of compounds containing the moiety , where the α-carbon is nominally sp^3 hybridized. The principal substituents dealt with are hydrogen, methyl, and phenyl, although a few others have been used for limited, specific purposes. This work was done in collaboration with Dr J. B. Hyne at the University of Calgary, who, with Mr W. B. McG. Cassie, initiated the study in 1964. These workers obtained data for the alcohols phenylmethanol, 1-phenylethanol, 2-phenylethanol, and 2-phenyl-2-propanol at 0.1 M with added tetrabutylammonium bromide in tetrachloromethane solvent. Because of significant differences in their experimental techniques from ours, in both sample preparation and spectral measurements, it was decided to repeat a portion of their work; the results were in agreement to well within experimental uncertainty. Hence, the remainder of their results were accepted, and, when quoted herein, are designated (C*H). Also, These workers first observed the perturbation of the N.M.R. spectrum of the phenyl groups in the α-phenyl substituents on the addition of salt.

4.1 Obtaining Complex Shifts of Alcohols with Br^-

The N.M.R. shielding of the hydroxyl protons of the various alcohols as a function of salt concentration was analysed by an iterative B-H-S method in the same way as for the trihalomethanes. In the present cases, the equilibrium quotient, Q, falls into a wider range of 10-125 $\underline{M}^{-1}$. Consequently, in some cases, at salt concentrations of about 1 M, essentially all of the alcohol was complexed. In these cases, the complex shift was observed directly, and verified the value derived from the B-H-S analysis.

Tables X and XI give the ambient-temperature (ca. 27°C) limiting complex shifts for a number of alkyl-, aryl-, and arene-substituted carbinols with halide ion in tetrachloromethane. The values so

TABLE X. Limiting Complex Shifts for Alcohol--Bromide Ion Complex Formation in CCl_4 at 27°C.[a]



R_1	R_2	R_3	Δ_c(raw) ppm	$\Delta_{\mathrm{dil}\underline{n}}$ ppm	Δ_c(corrected) ppm
H	H	H	-3.40 ±0.07	0.30 (0.35)	-3.70
CH_3	H	H	-3.32 ±0.13	0.38 (0.48)	-3.70
CH_3	CH_3	H	-3.42 ±0.20	0.36	-3.78
CH_3	CH_3	CH_3	-3.24 ±0.17	0.58 (0.45)	-3.82
C_6H_5	H	H	-3.92 ±0.04[b]	0.45	-4.37
C_6H_5	CH_3	H	-3.70 ±0.07	0.30	-4.00
C_6H_5	CH_3	CH_3	-3.76 ±0.09	0.15	-3.91
$C_6H_5CH_2$	H	H	-3.47 ±0.06[b]	0.21	-3.68

a: Donor anion provided by Bu_4NBr

b: (C*H)

TABLE XI. Effect of Anion Size on 1-Phenylethanol--Anion Complex Shifts in CCl_4 at 27°C.[a]

DONOR (Anion)	Δ_c(raw) ppm	Δ_{dil^n} ppm	Δ_c(corrected) ppm
Cl^-	-4.50 ± 0.17	0.30	-4.80
Br^-	-3.70 ± 0.07	0.30	-4.00
I^{-b}	-2.89 ± 0.26	0.30	-3.19

a: Donor anion provided by Bu_4N^+ salt.

b: Donor anion provided by Hp_4NI.

obtained are listed as Δ_c(raw).

Complicating the treatment of these systems as involving simple 1:1 complex formation is the well-known self-association of alcohols(13), even at very low concentration. Figure 4 shows the concentration dependence of the OH proton shielding of phenylmethanol from 0.002 to 0.2 M; the three most dilute points were obtained from spectra accumulated on the C-1024 computer, using as many as 300 scans per spectrum. The region below about 0.1 M is very nearly linear with the possible exception of a small deviation near 0.05 M. It is evident that extrapolation to infinite dilution gives a δ_{OH} for "free" phenylmethanol of -1.05 ppm, whereas at the 0.1 M concentration used in this study, the δ_{OH} is -1.50_5 ppm, 0.45 ppm to low field of the "free" OH resonance.

I have performed a "dummy" calculation on a set of parameters typical of an alcohol in order to arrive at an estimate of the amount of error introduced into the results by the assumption that the measured shifts are not influenced by alcohol self-association.

I take as numbers representative of alcohol--anion complexing

$$\Delta_c = -4 \text{ ppm} \; ; \quad Q_c = 25 \; M^{-1}.$$

Consistent with other results(13), I take a dimer-

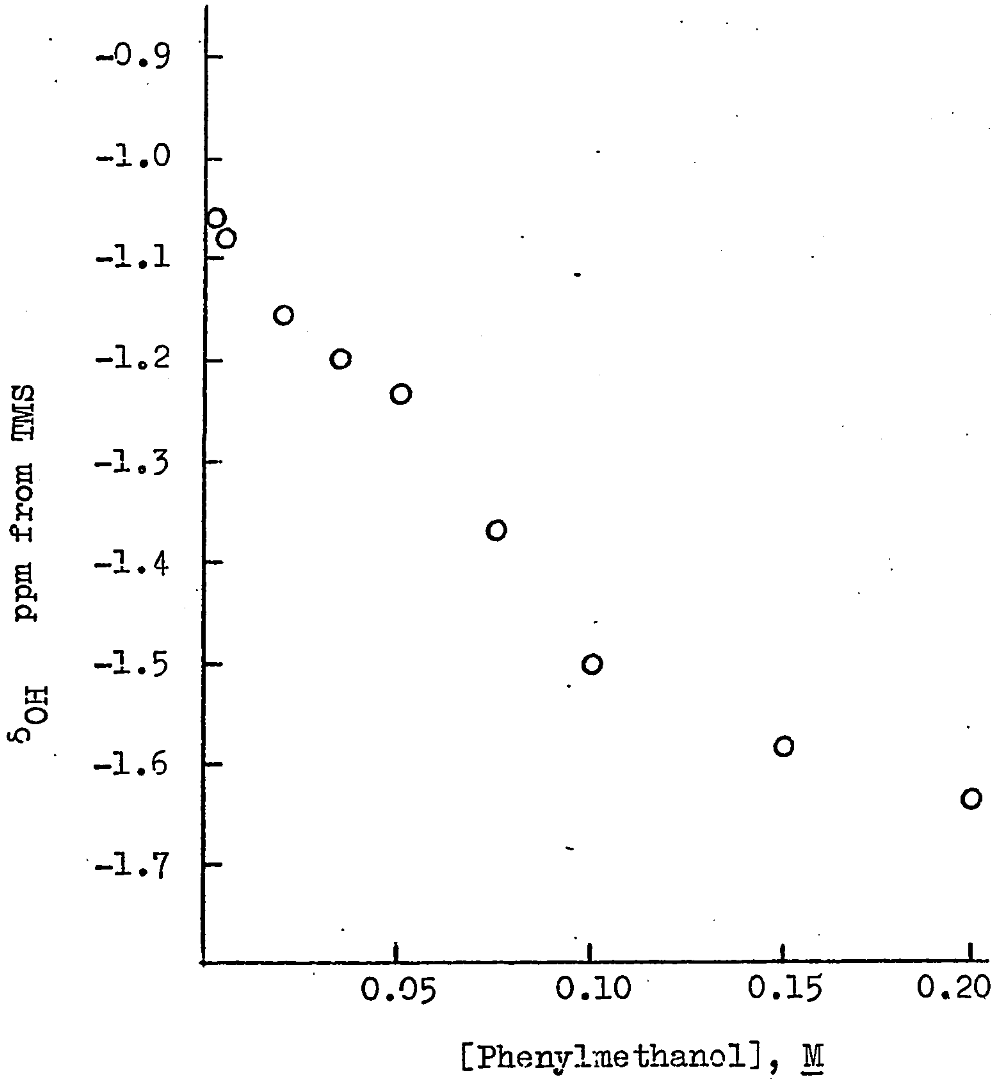


Figure 4

Dilution Curve for Phenylmethanol in CCl_4.

isation equilibrium quotient (ignoring all other polymeric forms) $\underline{Q}_D$, of 0.75. In order to arrive at a reasonable estimate of the dimer shift, I take the slope of a dilution curve (Figure 4) at infinite dilution and use the relationship

$$[15] \qquad \left(\frac{d\Delta}{dC}\right)_{C\rightarrow 0} = 2\,\underline{Q}_D\,\Delta_D$$

the origin of which is given in Appendix B. From this, I obtain $\Delta_D = -3.1$ ppm.

At each of four typical salt concentrations, the concentration of each of the three alcohol species was evaluated by repeated calculations of the two equilibria to self-consistency. These calculations were also performed assuming no self-association. The results are given in Table XII. It is evident that the presence of self-association of the alcohol effects virtually no measurable change in the N.M.R. observations.

As a result, I feel that the treatment of the data as due only to alcohol--anion complexing is reasonable, all the more so in that the high-concentration points are more heavily weighted in the calculation (see the Appendix to reference 29) than are the ones at lower salt concentrations. Hence, by adding the dilution shift to the shift of the

TABLE XII. Results of Dummy Computation of Shift Data, Allowing for Alcohol Self-Association.

[Salt], M	SHIFT ASSUMING DIMERS, ppm			SHIFT ASSUMING NO DIMERS, ppm
	Complex Shift	Dimer Shift	Total Shift	
0.1	2.08	0.06	2.14	2.20
0.2	3.00	0.02	3.02	3.00
0.4	3.54	0.01	3.55	3.54
0.6	3.68	0.00	3.68	3.68

complex obtained in the usual way, the resulting value should be quite a precise measure of the difference in shielding of the hydroxyl proton in an isolated alcohol molecule and in the complex with the anion.

This has been done in the last two columns of Tables X and XI to give Δ_c(corrected). As may be seen, this correction for self-association is typically only about 3 times the experimental uncertainty, the average standard error being 0.11 ppm, and the average dilution shift 0.33 ppm.

Three-point dilution curves (0.03, 0.06, 0.10 M) were obtained for all the other alcohols; these were all linear (Cf. Figure 1 of reference 33) and were used to obtain each dilution shift individually, although all were found to fall within quite a narrow range of values. The dilution shifts in parentheses in Table X are taken from Figure 1 in reference 33, which are in turn based on other works cited therein.

In summary, the alcohol--anion complex shift data have been treated as follows. The alcohol shifts on addition of various amounts of salt have been analysed in the usual way, completely ignoring the alcohol self-association. To the limiting shift obtained in this way has been added the dilution shift of the alcohol alone, from 0.1 <u>M</u> to 0 <u>M</u>. The resulting quantity is regarded as a measure of the difference in shielding of the hydroxyl proton in an isolated alcohol molecule and in an alcohol molecule hydrogen bonded to the anion. This treatment is depicted graphically in Figure 5.

4.2 Alcohol--Anion Complex Shifts

As may be seen from Table X, the complex shifts of this variety of alcohols is, within experimental uncertainty, the same no matter what the degree of substitution by alkyl (methyl, phenylmethyl) groups. On the other hand, an arene substituent consistently accompanies shifts approximately 0.2-0.4 ppm greater.

4.3 Equilibrium Quotients of Alcohol--Anion Complexes

The equilibrium quotients for complexes with bromide ion are given in Table XIII. They show a marked dependence on the degree of alkyl substitution at the α-carbon atom, decreasing by 30-50% with each additional methyl (or phenylmethyl) group; on

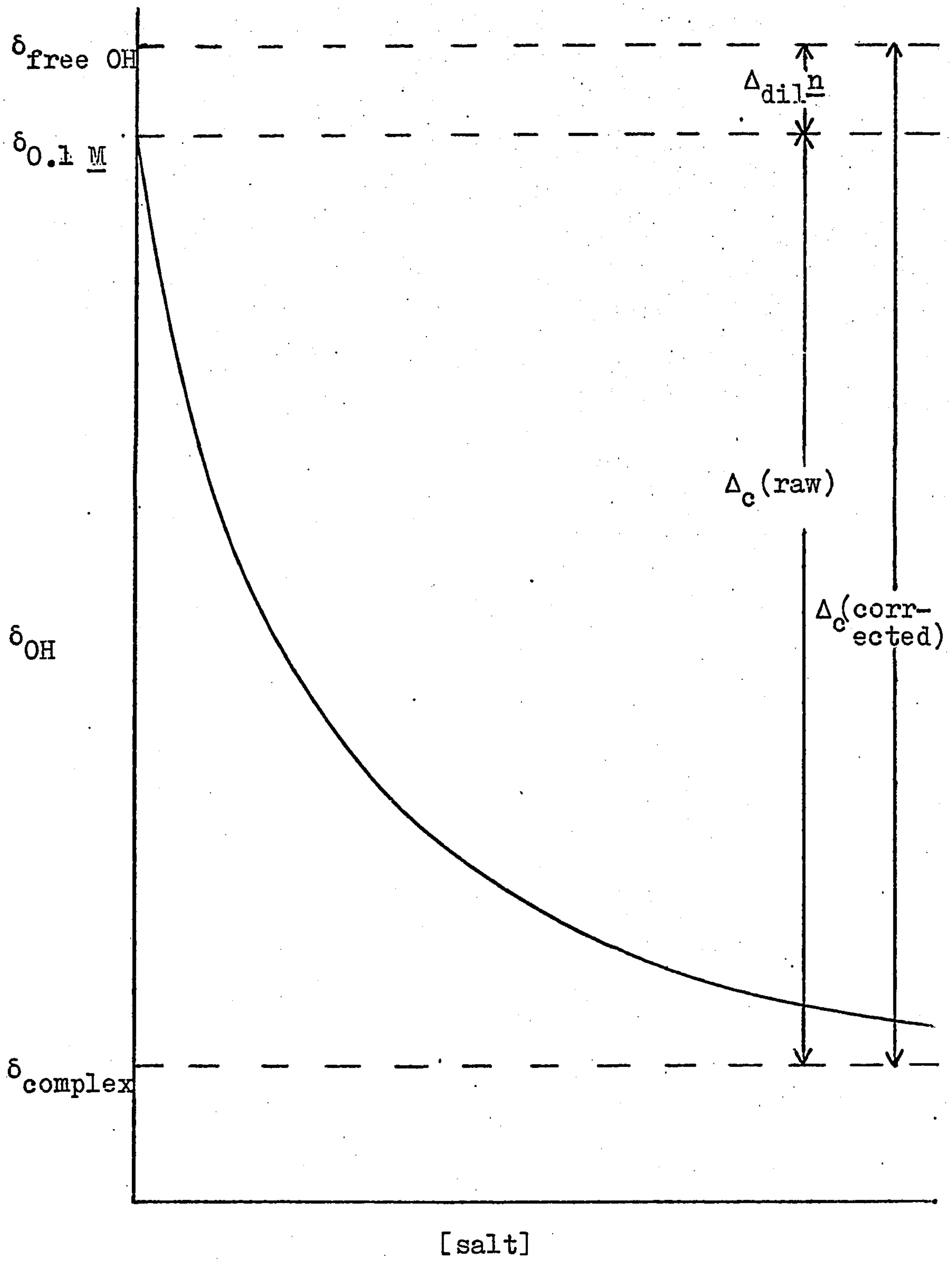
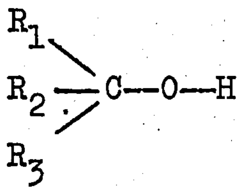


Figure 5

Obtaining of Alcohol Complex Shifts.

TABLE XIII. Equilibrium Quotients for Alcohol--Bromide Ion Complex Formation in CCl_4 at 27°C.[a]



R_1	R_2	R_3	Q, M^{-1}
H	H	H	70 ± 18
CH_3	H	H	40 ± 16
CH_3	CH_3	H	21 ± 6
CH_3	CH_3	CH_3	15 ± 4
C_6H_5	H	H	71 ± 40[b]
C_6H_5	CH_3	H	39 ± 14
C_6H_5	CH_3	CH_3	15 ± 2
$C_6H_5CH_2$	H	H	43 ± 24[b]

a: Donor anion provided by Bu_4NBr

b: (C*H)

the other hand, they appear to be unaffected by substitution of a phenyl group for hydrogen.

These observations may be rationalised on the basis of an inductive effect as follows.

An alkyl group is electron-donating relative to hydrogen; hence, the presence of an alkyl group would be expected to reduce the electrophilicity of the hydroxyl proton relative to methanol, causing a decrease in equilibrium quotient. On the other hand, the phenyl group should exhibit an inductive effect similar to that of hydrogen (replacement of one hydrogen in methane by a phenyl group [i.e. toluene] gives rise to a dipole moment of only 0.4 D), and so should not appreciably affect the acidity of the OH hydrogen.

Putting this argument on a more quantitative basis, it is possible, by regarding resonance and steric effects as negligeable, to relate the equilibrium quotients to the appropriate Taft polar substituent constants, σ^*(34); the latter have been shown to be very closely additive. By regarding the C-O-H moiety as the basis of all the alcohols, only four values of σ^* are required, and have been normalised to H rather than CH_3: H, 0.0; CH_3, -0.49; C_6H_5, +0.11; $C_6H_5CH_2$, -0.27.

Figure 6 shows ln Q as a function of $\sum \sigma^*$; the relationship is quite linear, consistent with the postulate that the variations in Q are indeed due to inductive effects of the substituents. The only point falling appreciably off the line is the one for $C_6H_5C(CH_3)_2OH$, the compound most likely to be subject to steric effects.

If the increase in molecular polarizability with phenyl substitution were a significant factor in the energy of the complex species, one would expect, in Figure 6, that the point for 2-phenyl-2-propanol would lie near the line, with points for 1-phenylethanol and phenylmethanol lying successively greater distances above the line (i.e. larger Q). In fact, the points for the latter two fall near the line, and that for 2-phenyl-2-propanol substantially below the line.

4.4 Other Topics

4.4.1 Effect of Anion Size

It may be seen from Table XIV that for a typical alcohol, 1-phenylethanol, the equilibrium quotient increases in the order $I^- < Br^- < Cl^-$, as expected if the complex energy is controlled by the electrostatic field of the anion.

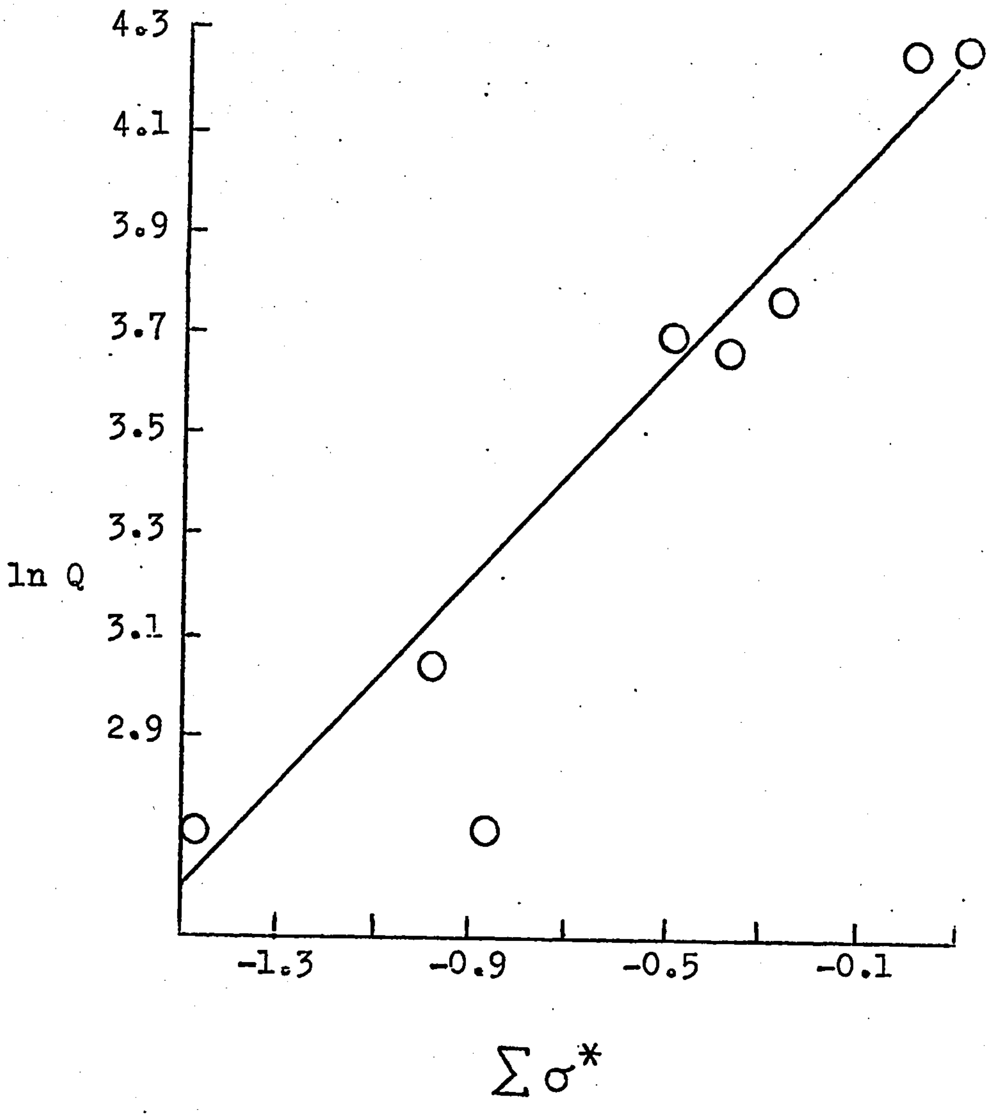


Figure 6

Alcohol Equilibrium Quotients as a Function of Inductive Effects of Substituents on the COH Group.

TABLE XIV. Effect of Anion Size on 1-Phenylethanol--Anion Complex Formation in CCl_4 at 27°C.[a]

DONOR (Anion)	EQUILIBRIUM QUOTIENT, Q M^{-1}
Cl^-	130 ± 110
Br^-	39 ± 14
I^{-b}	12 ± 3

a: Donor anion provided by Bu_4N salt.

b: Donor anion provided by Hp_4NI.

Table XI also shows the effect of changing the size of the anion on the complex shift with this alcohol, (because tetrabutylammonium iodide is insoluble in CCl_4, the tetraheptylammonium salt was used.). Consistent with the model of purely electrostatic interactions, as developed in reference 29, the complex shifts are largest for the smallest anion.

In the case of the OH bond, there is not a body of theoretical or experimental results comparable to that for CH; however, provided that the molecule--anion interaction may be treated as being entirely electrostatic, the Buckingham equation [12] may be expected to apply. Assuming, still, that the B coefficient has the hydrogen atom value, the contribution from the E^2 term is about 10% of the total observed shift.

Treating the data in a manner exactly analogous to the method in Chapter 6, , the A coefficient may be evaluated using the experimentally obtained complex shifts, Δ_c. The resulting plot in Figure 7 is analogous to that in Figure 13; the slope of the resulting line gives a value of $\underline{A} = 5.5 \pm 0.3$. For essentially the same reasons as presented in Chapter 6, this value should be regarded as a lower limit for A, and not a definitive value of the coefficient.

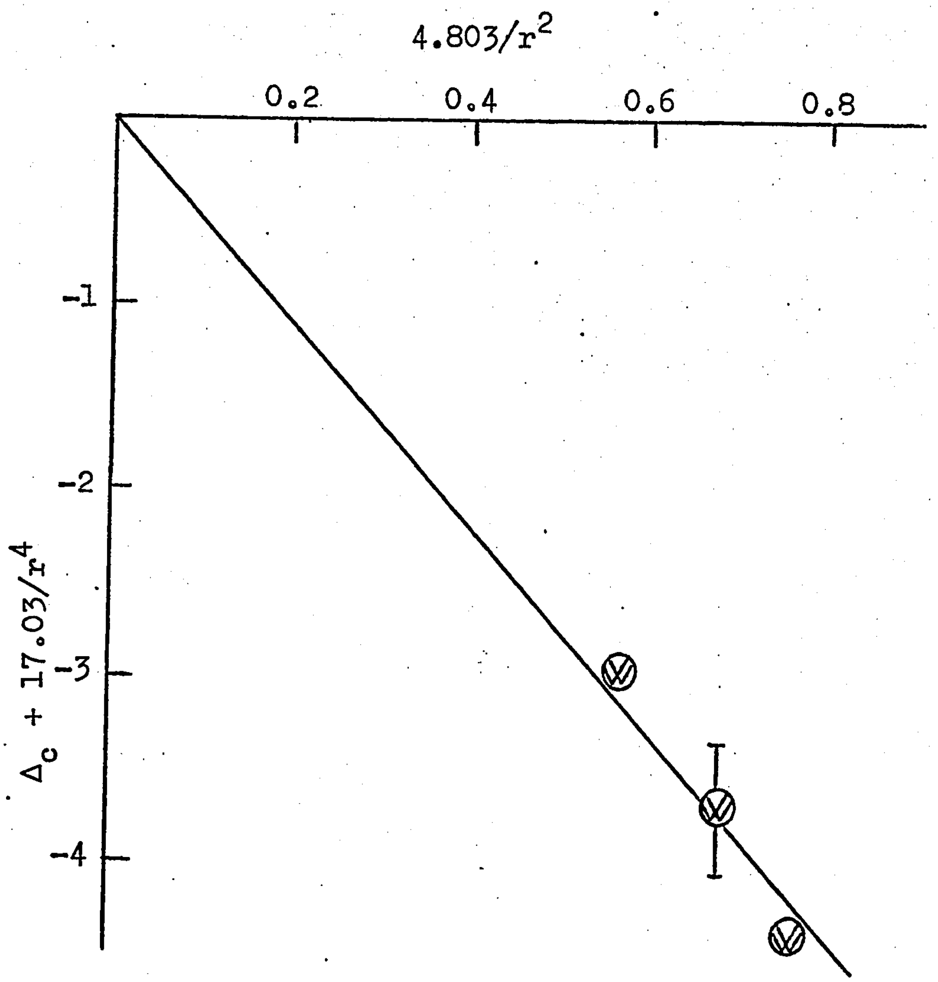


Figure 7

Determination of Buckingham's A Coefficient for Alcohols.

Within the framework of this model, it is difficult to explain the systematic trend of the points, tending to give a positive intercept. The van der Waals shifts, which, as discussed Chapter 6, are likely to be very nearly constant for the three anions, would tend to give a negative intercept.

One possible explanation would involve a variable degree of hydrogen bond shortening, depending on the size of the anion; a smaller anion can get closer to the O $\leftarrow\!\!+$ H dipole and presumably is more strongly attracted by it. In fact, if the bond shortenings are taken as Cl^-, 0.6 A; Br^-, 0.5 A; I^-, 0.4 A; instead of a uniform 0.5 A for all anions, then the three points in Figure 7 all fall on the line shown. These suggested values for hydrogen bond shortenings are probably a little excessive in absolute terms, but the trend does seem reasonable.

In view of the fact that the deviations of the points for chloride and iodide ions from the line are less than the range found for bromide ion, concern over these deviations would presently appear to be unwarranted.

4.4.2 Anion Interaction with the Aromatic Ring

It was observed during the course of this investigation that the addition of Bu_4NBr to a CCl_4 solution of an arene alcohol resulted in a change in the N.M.R. spectrum of the phenyl protons. Whereas, in the absence of salt, these were all essentially equivalent and gave rise to a single narrow band, the spectrum broadened into a very complex multiplet having, at the highest salt concentrations, a total width of about 20-25 Hz.

In an endeavour to find out what part or parts of the ring were being affected, and to simplify the spectral analysis involved, the complexing behaviour of 4-nitrophenylmethanol and 4-methoxyphenylmethanol with bromide ion was studied. It was found that, in both cases, the ring protons meta to the CH_2OH group were unaffected by the addition of salt, while those ortho to the group shifted downfield monotonically with salt concentration. The N.M.R.-derived parameters are given in Table XV for the ortho and OH protons in these two compounds. Since, for reasons of solubility, the 4-nitro compound was run in ethanenitrile as solvent, its results are not directly comparable to the other systems. Nonetheless, for both compounds, the equilibrium quotient is found to be a factor of three smaller for "complexing" of the ortho protons than for the OH

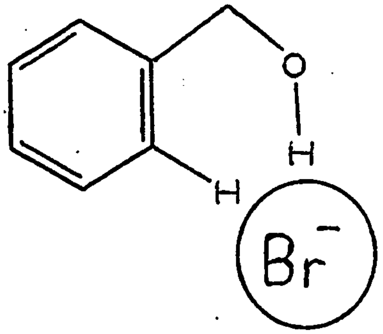
TABLE XV. Comparison of Hydroxyl- and *ortho*-Proton Behaviour in 4-Substituted Phenylmethanols on Addition of Bromide Ion.

4-Substituent	Δ_c(OH) ppm	Δ_c(*ortho*) ppm	*Q*(OH) $\underline{M}^{-1}$	*Q*(*ortho*) $\underline{M}^{-1}$
OCH_3 [a]	-3.82	-0.13	49	19
NO_2 [b]	-2.50	-0.16	10	4

a: Solvent — CCl_4

b: Solvent — CH_3CN

protons. Figure 8, which is a plot of OH shift *vs.* *ortho* proton shift for each of the 4-methoxy- and 4-nitrophenylmethanol, shows clearly that the salt-concentration dependence of these proton resonances is not the same; hence, they are not measures of the same equilibrium. This rules out the possibility that the *ortho* shift observed is directly related to the OH--anion interaction, either by a possible inductive effect, or by formation of a chelated complex



as had been originally suspected. Instead, the *ortho* protons would seem to be complexing with bromide ion independently of the OH--Br$^-$ interaction, and to quite an appreciable extent. However, owing to the small magnitude of the effect (limiting shift of *ca.* 10 Hz) and the present lack of supporting evidence, this interpretation must remain subject to revision. It may be noted that in 2-phenylethanol, where the phenyl ring is one more bond removed from the OH group, no

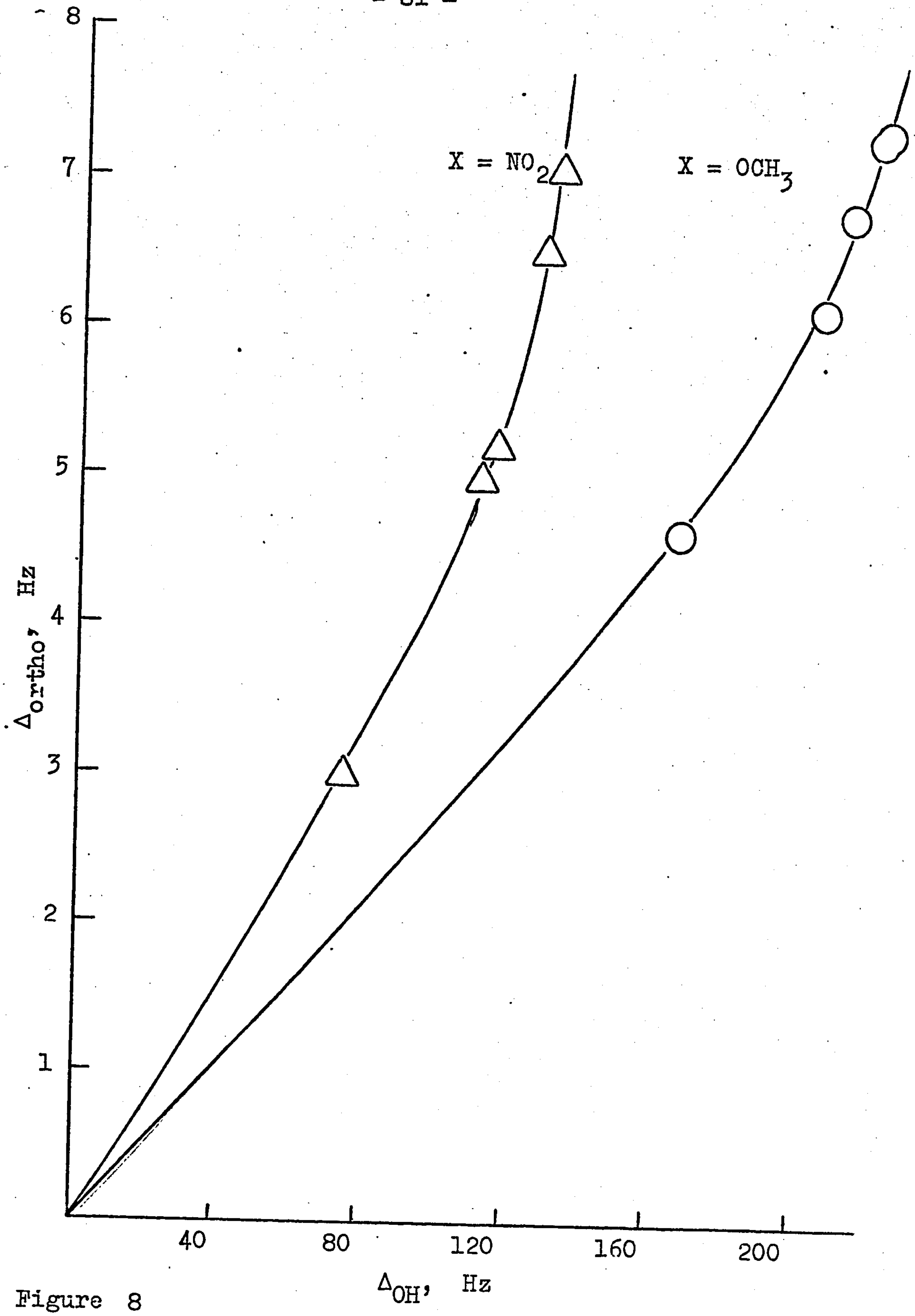


Figure 8

Extent of Aromatic Ring Participation in Alcohol Complexes such effect is observed.

This is not the first time that such a phenomenon has been observed. In reference 5, a similar effect was found for the ortho protons on the phenyl substituent at the aglucon oxygen of β-D-glucopyranose tetraacetate, involving shifts of 0.4 to 0.6 ppm; unfortunately, insufficient data were obtained with those systems to allow separate determination of the equilibrium quotients for the ortho protons.

4.4.3 I.R. vs. N.M.R.

Several studies have been made on this type of system using infrared spectroscopy(35). These have of necessity assumed that the new band at about 3300 cm^{-1} is due to O-H hydrogen bonded to the anion; however, it has also been suggested(35) that this band may be due to aggregations of polymeric alcohol, with the anion serving as a centre of nucleation.

The N.M.R. results strongly support a 1:1 alcohol--anion complex over alcohol aggregates, under the conditions employed. I have very nearly duplicated these conditions for one of the systems studied (1-phenylethanol and tetrabutylammonium bromide) in an attempt to see whether the assumption that the band at 3300 cm^{-1} is due to 1:1 complexes alone, is valid. If it is, then the equilibrium quotient obtained should agree with that derived from N.M.R.

In Table XVI are given the absorbances of five sample solutions at 3610 and 3300 cm^{-1}, as measured by reading from the chart the absorbance at the band maximum relative to the baseline at this frequency. The baseline was estimated as a straight line connecting the two minima closest to the band being measured.

The spectrum of the sample containing no salt exhibited two maxima, at approximately 3470 and 3390 cm^{-1}, which have been assigned(35,36) to associated forms of alcohol; these maxima either are not present, or are obscured by the 3300 cm^{-1} band, when salt is present (see Figure 9).

Table XVI also contains values for Q obtained at each salt concentration by two methods: 1) by taking the decrease in absorbance of the 3610 cm^{-1} band as a measure of the decrease in uncomplexed alcohol concentration; and 2) by taking the result for one sample (the third in the Table) as exact, and comparing the complex concentration with the absorbance at 3300 cm^{-1}, using this to obtain complex concentrations for the other samples from A_{3300}.

The latter method is somewhat arbitrary,

TABLE XVI. Infrared Data and Results for 1-Phenylethanol and Bromide Ion.[a]

$[Bu_4NBr]$	Absorbance		Q, M^{-1}	
M	A_{3610}	A_{3300}	method 1)	method 2)
0	0.179	0	--	--
0.0248	0.113	0.161	91	44
0.0586	0.077	0.265	44	(44)
0.085	0.068	0.309	30	37
0.171	0.023	0.398	54	46

a: [1-Phenylethanol] = 0.05 M

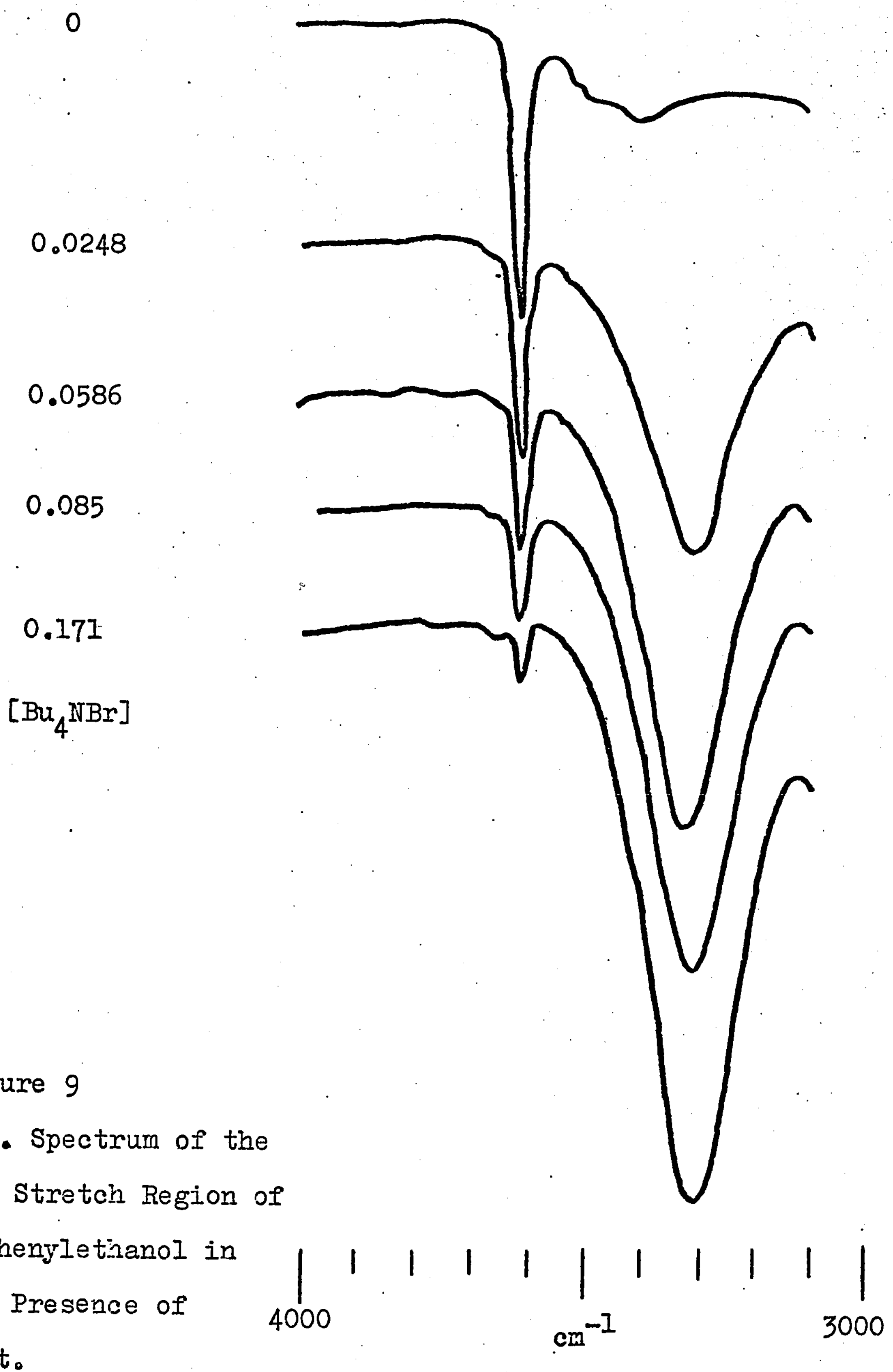


Figure 9

I.R. Spectrum of the O-H Stretch Region of 1-Phenylethanol in the Presence of Salt.

but this appears to matter little. If one assumes $\underline{Q} = 30$, for the fourth sample, instead of $\underline{Q} = 44$ for the third, the average $\underline{Q}$ from method 2) is 39 instead of 43, an insignificant difference.

The average value of $\underline{Q}$ from Table XVI is 54 $\underline{M}^{-1}$, with a maximum deviation of 37, and an average deviation of 15. If the value having the greatest uncertainty, by virtue of being the result of taking a small difference between large numbers, is omitted, the remaining seven values would have an average value of 43 $\underline{M}^{-1}$ (maximum deviation, 13; average deviation, 5). These results agree quite well, considering the crudity of the I.R. measurements, with the N.M.R. result of $\underline{Q} = 39\ \underline{M}^{-1}$ with a standard error of 14. I consider this to be good evidence that the absorption band at 3300 cm^{-1} is entirely due to 1:1 complexes between ROH and bromide ion.

CHAPTER 5 SOLVATION OF GROUP VIIB ANIONS

In this section, I take the results of Chapters 3 and 4, as well as results obtained for several other systems, and attempt to cast them in a form such that they may shed whatever light possible on the problem of competitive solvation of halide ions in non-aqueous solvent systems. It is suggested that the technique exploited herein may, for many systems, yield relative anion solvating abilities for a number of solvents, both on the basis of homogeneous solvation by a bulk solvent, and on the basis of one ion--one molecule interactions.

5.1 Salts in Binary Solvent Systems

The systems treated in Chapters 3 and 4, and those to be added in the present discussion, may be regarded as binary solvents with, normally, the more strongly solvating species present to the extent of about 1% and the weakly solvating material as the bulk solvent. The behaviour of the minor component of the solvent mixture is then monitored by N.M.R. as successive amounts of salt are added.

By making certain assumptions, such as 1:1 association of ions with acceptor molecules, and replacement of one (bulk) solvent molecule by one acceptor moecule, it is possible to draw tentative conclusions regarding relative "single-molecule energies of solvation" toward various anions. These are obtainable directly, where the bulk solvent is suitable for variable temperature work, via determinations of ΔH and ΔS from the temperature dependence of the equilibrium quotients.

It should also be possible to obtain some idea of relative solvation energies from the relative magnitudes of the equilibrium quotients for structurally similar acceptor molecules with a common ion and solvent, as in the series of trihalomethanes or of alcohols.

In addition, if it is possible to make the assumption that one solvent molecule is displaced from the anion when one acceptor molecule enters its "solvation sphere",

[16] $$YS_n^- + A \rightleftharpoons YS_{n-1}A^- + S \ ,$$

it becomes possible to obtain single-molecule solvation energy differences from the differences in $\Delta \underline{H}$'s or log $\underline{Q}$'s of a single acceptor molecule and ion in two different bulk solvents.

Unfortunately, this situation need not universally obtain. Unless the stoichiometries of the solvation spheres of the homogeneously and heterogeneously solvated ions are the same, the technique obviously fails. This may occur where (a) the molar volumes of solvent and acceptor are much different, (b) the molecular dipole-dipole repulsion energies in the solvation sphere differ substantially, (c) any structure in the solvent itself is significantly altered, or (d) other factors, such as chelation, etc., appear.

Perhaps related to the subjects in the previous paragraph, it is necessary to be aware that $\Delta \underline{G}$ and $\Delta \underline{H}$ will be comparable only in the event that $\Delta \underline{S}$ remains constant or shows the same variation as $\Delta \underline{H}$. This point was discussed in Section 3.2 with respect to the trihalomethane complexes. It was found that for

$CHCl_3$ and $CHBr_3$, $\Delta\underline{S}$ remained essentially constant with changing ion, and that, for a particular ion, $\Delta\underline{H}$ and $\Delta\underline{S}$ both increased on going from $CHBr_3$ to $CHCl_3$.

5.2 Relative Solvation Energies

Table XVII gives the equilibrium quotients for the complexing of bromide ion with certain acceptor molecules in the bulk solvents shown. Although the entries are far from complete, it is apparent that one or more scales of relative solvating abilities towards anions may be set up.

Considering the weakest solvent so far used, tetrachloromethane, the equilibrium quotients for 1:1 association with Br^- are arranged in decreasing order from the top in the column, with the minor exception of ethanenitrile which is so placed for reasons given below. This ordering, then, is based on the free energy of displacement by one acceptor molecule of one or more solvent molecules from a solvated bromide ion. In other words, of these compounds, ethanol displaces CCl_4 from a bromide ion most readily, piperidine displaces CCl_4 somewhat less readily, DMSO still less readily, and so on down the series to dichloromethane which is seen to interact least strongly.

TABLE XVII. Equilibrium Quotients for:

Acceptor + Br^- $\rightleftharpoons$ Complex.

Acceptor	As Solute in CCl_4	As Solute in CH_3CN	As Solvent for C_2H_5OH
C_2H_5OH	40	2.1	
piperidine	9.3		
$(CH_3)_2SO$	4.8		0.7
formamide	3.2		
$CHBr_3$	1.9	1.1	
$CHCl_3$	1.8	0.7	1.9
CH_3CN	2.2		2.1
CH_2Cl_2	0.7		3.2
CCl_4			40

From the few data available in ethanenitrile as bulk solvent, the same decreasing progression is observed, with ethanol being a stronger electrophile than the trihalomethanes.

The ordering of bulk solvents for ethanol solute is also presented. The same trend is apparent here; one ethanol molecule displaces CCl_4 more readily than it displaces dichloromethane, which in turn is easier to displace than ethanenitrile, and so on up the column. Ethanenitrile is placed consistently with the trend of Q's in this series.

This series provides a measure of anion solvating ability of the bulk solvents and, of course, need not necessarily follow in the same order as the energies of 1:1 association.

From the rows, the trihalomethanes are also seen to displace CCl_4 more readily than CH_3CN. However, the difference for the trihalomethanes between the two solvents is only about a factor of 2 (see also entries in Table VI), whereas the ratio in the case of ethanol is about 20.

This difference in ratios, together with the uncertain placing of ethanenitrile, makes it desirable to have a more complete tabulation of values; it seems possible that such might reveal some information about solvent structures and their relation to the solvation of anions.

Ideally, of course, comparisons of this sort should be based on the quantities $\underline{\Delta H}$ and $\underline{\Delta S}$, rather than $\underline{Q}$, since the structures of various solvation complexes will by no means be the same.

5.2.1 Comparison with "Classical" Solvation Energies

Alexander and Parker [A*P](37) have brought together what they term 'distribution coefficients', based on K_{SP}, for a large number of ions. The actual meaning of their numbers is not of interest here, but their relative magnitudes are. They have referred each ion to methanol, and assigned this the value 0.0. The other values they give have this significance: a more positive value indicates a smaller solvation energy for that ion in this particular solvent; a more negative value means the opposite.

Table XVIII gives the values of $\underline{Q}$ for the 1:1 association of an acceptor molecule with bromide ion in CCl_4, and the corresponding A*P 'distribution coefficients' for bromide ion in the solvent. The same trend appears in both sets of values with the exception of formamide, although the set of comparisons

TABLE XVIII. Relative Solvation Energies of Bromide Ion as Determined by N.M.R. and from Solubility Products.

Solvent	$\underline{Q}$, $\underline{M}^{-1}$ present work	"Distribution Coefficient", (A*P)
CH_3OH	70	0.0
$(CH_3)_2SO$	4.8	+3.4
$HCONH_2$	3.2	+0.2
CH_3CN	2.2	+4.3

is too small for anything resembling quantitative deductions. It is nonetheless encouraging to find the results of the present method agreeing moderately well with other methods such as simple solubility product determination.

5.3 Structure of Solvation Complexes

One of the problems remaining unresolved in the realm of ions in solution is the geometrical nature of the "solvation sheath" of a particular ion. Even for the most intensively studied solvent, water, there appears to be no general agreement concerning the orientation of neighbouring water molecules with respect to dissolved ions(38). Presumably the orientation could be dominated either by the direction of the net molecular dipole moment, or by the local "positively-charged hot spots" (usually hydrogens) and "negatively-charged hot spots" (lone pairs), although, according to the results of Mohr, Wilk, and Barrow(39), as well as Alexander and Parker(37), anions are good hydrogen-bond hydrogen acceptors.

As far as the Group VIIB anions are concerned, the present work has provided some indications as to anion--solvent molecule orientations, primarily from the Buckingham model of field-induced shifts, for a 1:1 complex, regarding the bulk solvent as an inert space filler.

5.3.1 Trihalomethanes

For the trihalomethanes likely to be considered as solvents under ordinary atmospheric conditions, $CHCl_3$ and $CHBr_3$, the evidence is as follows.

The a priori calculations by Buckingham(11) yielded an A coefficient of 2×10^{-12}. Subsequent work(40) established that a value closer to 3×10^{-12} was in order. Applying the larger value to calculations of the trichloromethane shifts determined herein yields calculated shifts which are just large enough to account for the experimentally observed ones.

This calculation assumed a collinear $C{-}{-}H\ldots X^-$ configuration. If it were assumed that the configuration were angular, the calculated shifts obtained would be reduced by a factor of $\cos\theta$. It is difficult to imagine how the deficiency in shift so created could be replaced. Hence, in the case of trichloromethane, the collinear anion--molecule configuration may be taken as reasonably well established.

As was mentioned in Chapter 3, the case of tribromomethane is not so clear-cut. If the complexes had the same structure as those of $CHCl_3$, one would expect that the complex shifts would be much the same and exhibit a similar trend with increasing anion radius. In fact, the shifts are substantially smaller than those observed with $CHCl_3$, and show a greater dependence on anion size.

It is possible that these effects are due to a progressively greater deviation from linearity, Br_3C--H...X^-, in the series $Cl^- < Br^- < I^-$. This would account for the observed shifts, but nonetheless is not a happy explanation. It leaves unanswered a nagging doubt about why this should occur for $CHBr_3$ and not for $CHCl_3$.

The other apparent explanation, as suggested in Chapter 3, is that a fraction of the $CHBr_3$ molecules interact with X^- in the usual, collinear manner, and the remainder from the CBr_3 end of the molecule, in a manner analogous to the CHI_3...X^- interaction.

A curiosity which may be noted is that this explanation of $CHBr_3$'s shifts implies that I^- forms a higher percentage of "backside" complexes than does Cl^-. This phenomenon would have the double virtue of having the larger ion, and hence more remote charge, at the "wrong" end of the molecular dipole moment, and of having the larger ionic polarizability close to the source of the dipole moment; both these factors should tend to favour "backside" complex formation, at least on a relative basis.

5.3.2 Alcohols

The evidence available from the present work, as it pertains to the present discussion, is somewhat more tenuous with regard to alcohols, but is nevertheless of some interest.

As was pointed out in Chapter 4, the complex shifts for all the alcohols with bromide ion fall into quite a narrow range, lying between -3.7 and -4.4 ppm. The only detectable influence of alcohol structure on these shifts lay in the observation that a phenyl ring on the α-carbon atom generally accompanied a slightly larger shift (0.2-0.5 ppm).

If one is able to rely on the Buckingham model of field-induced shifts as describing the predominant mechanism of shielding change, it becomes possible to infer some information concerning the geometry of the ion--molecule complex. It is unfortunate in this regard, that the literature contains no reliable determination of the Buckingham $\underline{A}$, since this would have provided a basis from which to work.

The most likely conclusion to be drawn from the constancy of Δ_c with various alcohols is that the O--H...Br$^-$ geometry is the same in all the complex species. This involves the assumption that the bond parameter, λ, be essentially the same for all the alcohols; this was shown in Chapter 4 to be reasonable. Hence, one concludes that <u>cos θ</u> is essentially constant; from here, it is sheer guesswork to say that $\theta = 0^{\circ}$, but probably as good a guess as any. This was the guess that yielded $\underline{A} = 5.5$; in fact, it would be truer to write $\underline{A} = 5.5(\cos\theta)^{-1}$, since there is little independent evidence of an unambiguous nature to verify that $\cos\theta = 1$.

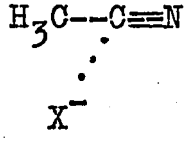
It would be difficult to explain the increase in Δ_c with phenyl substitution as due to a change in complex geometry. This would imply that the O--H...Br$^-$ angle was closer to 0° when the α-carbon bore a phenyl substituent than when it was merely alkyl substituted. On steric grounds, the opposite effect would be expected as the OH group would be slightly less freely accessible. A similar result would ensue if the observed perturbation of the <u>ortho</u> ring protons (page 78) does indeed imply the presence of more anion in the vicinity of the molecule, thus aggravating the crowding near the OH group. The near-constancy is more plausibly explained by a constant $O{-}{-}H\ldots X^-$ structure, most reasonably a geometry with the same symmetry as the O-H bond, that is, linear.

5.3.3 Ethanenitrile

The calculations of anion--molecule interaction energies, as described in Chapter 3, predict quite unambiguously that the ethanenitrile--anion complex has the structure

$$X^- \ldots H_3C{-}{-}C{\equiv}N$$

in which the halide ion is situated on the symmetry axis of the molecule. Coetzee and Campion(24) have suggested that this complex should take the form



$$\begin{array}{c} H_3C{-}{-}C{\equiv}N \\ \vdots \\ X^- \end{array}$$

so that the anion is as physically close as possible to the main centre of positive charge in the molecule. As these authors go on to point out: "...solvation of a [small] anion by more than one acetonitrile molecule then becomes improbable".

The non-linear structure has two obvious deficiencies: 1) the present calculations indicate that this configuration is about 5-10 kcal. mole^{-1} less energetically favourable than the linear form; this is presumable due to the fact that the anion, although slightly closer to the centre of positive charge, is much closer to the centre of negative charge; and 2) only one molecule may interact with any one anion and so the total energy of the anion solvation is <u>much</u> less than the sum of interactions with several molecules is likely to be.

A series of experiments was performed with ethanenitrile in tracer amounts in tetrachloromethane, with added chloride ion and bromide ion. In both these cases, the $\underline{H}$ signal of $C\underline{H}_3CN$ shifted monotonically downfield, giving a limiting complex shift of about -0.5 ppm; in view of the unfavourable angular factor (the ion is not collinear with any one C--H bond and so $\cos\theta \approx 0.2$-0.3), this is good evidence of the end-on configuration. If the side-on complex formed, one would expect an upfield proton shift since the anion field is now directed in the opposite sense.

5.3.4 Formamide

In the interactions of unsubstituted and monosubstituted amides with bases, both dipolar and monopolar, there has been some evidence that an amide hydrogen atom in the position trans to the carbonyl oxygen is more electrophilic than an amide hydrogen cis to oxygen. For example, N-monosubstituted amides tend to have the amide hydrogen trans to oxygen, encouraging the formation of long, hydrogen bonded chains of molecules(41).

In the fundamentally more interesting case of the simplest of all amides, formamide, there are several pieces of evidence available which indicate that the trans hydrogen is more electrophilic than the cis one. Perhaps the most cogent argument derives from the X-ray-determined crystal structure of formamide(42). According to the evidence gathered by Pimentel and McClellan(1) and summarised on page 83 of their text, there is every reason to believe that hydrogen-bond strength is a function of the distances A--H and A--B in the hydrogen bond A--H...B; the shorter the bond length, the stronger is the bond. In the formamide crystal, both amide hydrogen atoms are involved in hydrogen bonds to carbonyl oxygens of other formamide molecules. However, the $N{-}{-}H_{cis}\cdots O$ distance is 2.935 A, whereas the $N{-}{-}H_{trans}\cdots O$ distance is only 2.880 A. The shorter hydrogen bonding distance is presumed to accompany the stronger interaction.

A note of caution should be sounded here. The C--N--O angle is not the same in each case as the C--N--H angle, taking the values 109° and 120.6° on the <u>trans</u> side, and 118.5° and 117.1° on the <u>cis</u> side. In addition, the N--H distance is greater by 0.01 A on the <u>cis</u> side(42,43). Hence, this evidence is not conclusive concerning the relative bonding energies.

It has been found(4) that the enthalpy of solvation of ions by formamide is dependent on the orientation of the formamide molecules with respect to the ions. However, it was not possible to establish the geometry of the formamide--anion solvates.

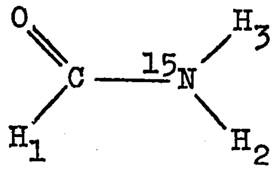
Nevertheless, it was found(44) that the enthalpies of solvation of a series of salts with common cation gave a linear correlation with the inverse of the anion radius. This is taken as evidence that the anion--formamide interaction is essentially electrostatic in nature.

Successive amounts of tetrabutylammonium bromide have been added to a 0.1 <u>M</u> solution of formamide-^{15}N in CCl_4. The three proton N.M.R. signals were monitored at 15°C as a function of salt concentration; the chemical shift and coupling constant data for the various solutions are presented in Table XIX. Several trends are evident. First, all three proton signals show a systematic downfield shift as salt concentration increases. Second, the C-H proton signal shifts very little, and is an insignificant amount virtually constant. Third, the two ^{15}N--H signals shift significantly downfield, but not to the same extent. Figure 10 demonstrates that the H_{trans} signal shifts farther than that of H_{cis}, and its shift-concentration curve is levelling off more quickly.

A Benesi-Hildebrand-Scott analysis of the data yields the complex shifts and equilibrium constants for the association of bromide ion with N--H_{cis} and N--H_{trans}; these are given in Table XX. The indicated uncertainties are the standard errors.

The difference in equilibrium quotients is sufficiently large to require explanation. It would appear that formamide forms hydrogen bonded complexes with bromide ion at the two N-H sites, by way of independent equilibrium processes. The complex at H_{trans} is evidently considerably favoured over that at H_{cis}, the $\Delta(\Delta G)$ being ca. 0.7 kcal. mole^{-1}. Certainly, the data cannot be explained on the basis

TABLE XIX. N.M.R. Data for 0.1 <u>M</u> Formamide-^{15}N in CCl_4 upon Addition of Bu_4NBr



[Salt]	δ_H, ppm below TMS			J, Hz					
<u>M</u>	H_1	H_2	H_3	1,2	1,3	2,3	1,N	2,N	3,N
0	-8.060	-6.185	-5.888	1.5_5	13.5	2.7	16.3	90.1	87.5
0.228	-8.069	-6.981	-6.161	1.5_4	13.5_5	2.7	16.1	89.7	86.8
0.413	-8.073	-7.322	-6.330	1.6_5	13.5	2.9	16.1	89.6	86.7
0.510	-8.073	-7.418	-6.388	1.6_5	13.8	3.1	15.9	89.0	86.6
0.821	-8.075	-7.673	-6.573	1.7	13.7	2.9	15.9	89.5	87.0

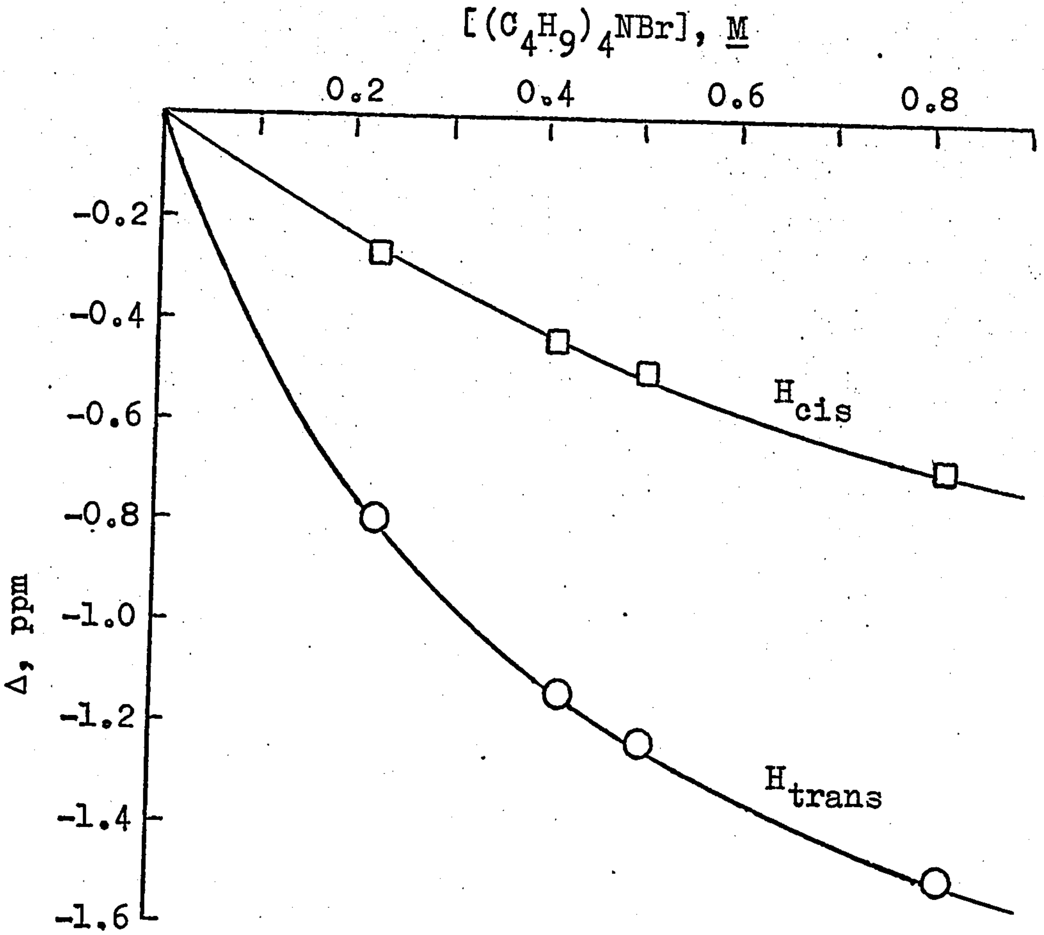


Figure 10

Amide Proton Shifts for 0.1 M Formamide-^{15}N in CCl_4, as a Function of Bromide Ion Concentration.

TABLE XX. Complex Formation Data for Formamide--Bromide Ion Association in CCl_4 at 27°C.

	Equilibrium Quotient, $\underline{Q}$, $\underline{M}^{-1}$	Complex Shift, Δ_c, ppm.
H_{cis}	1.02 ± 0.10	-1.54 ± 0.13
H_{trans}	3.21 ± 0.23	-2.10 ± 0.08

of one bromide ion interacting with both hydrogens simultaneously.

The explanation for the discrepancy in free energy of formation of the two complexes would appear to lie in electrostatic repulsion of the bromide ion by the carbonyl oxygen, when the ion is hydrogen bonded at the cis position. This repulsion should be much smaller at the trans position, resulting in a more stable complex.

I regard the difference in complex shifts of the two protons as not being significant. It probably reflects a slight difference in geometry of the N--H...Br^- complex species due to the repulsion of bromide ion at the cis position by the carbonyl oxygen.

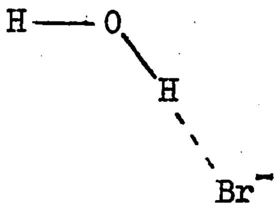
The preference of amides to hydrogen bond trans to oxygen in preference to cis may account for the observations of Bragg and coworkers(45) that some proteins appear to show less than the maximum possible amount of hydrogen bonding. As these authors point out, there would appear to be no reason why there should be less than the maximum possible amount of hydrogen bonding which should tend to minimize the total free energy. It would seem that the explanation for less-than-maximum hydrogen bonding may be that some N-H groups are cis to their adjoining C=O groups, and hence have a very much smaller propensity for hydrogen bonding. Other structural and packing factors may then account for a greater lowering of the total free energy than would a higher degree of hydrogen bond formation.

I regard the variation of each coupling constant with increasing salt concentration (see Table XIX) as being too small to be of any significance. This is in sharp contrast to the marked difference found(46) between formamide-^{15}N solutions in acetone (10 mole %), water (8 mole %), and the neat liquid. In all cases, the present values are within 2% of the ones found in acetone solution; however, changes of up to 50% were found on going to a water solution or the neat liquid, particularly in couplings to the nitrogen nucleus. It would appear that there is some fundamental difference in the nature of the hydrogen bonding interaction of the amide N-H with a dipolar base such as water, and with a monopolar anion base.

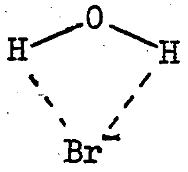
5.3.5 Water

A number of samples of 0.14 M water in CCl_4, containing various concentrations of tetrabutylammonium bromide, have been examined. The water signal remains a single, sharp line, and shifts downfield with added salt. The salt concentration dependence of shift is shown in Figure 11. It is obvious that it is not possible to analyse this curve in terms of a simple 1:1 association; the curve contains at least one break, indicating the presence of multiple equilibria involving water.

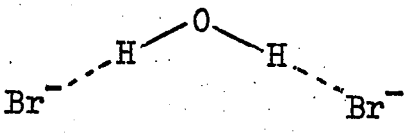
Now there are three plausible "types" of H_2O--Br^- interaction, as shown:



1



2



3

Mohr, Wilk, and Barrow(39), on the basis of infrared spectra of halide ions with water, in CCl_4, conclude that only forms **1** and **3** exist in such systems. Regarding this as established, we would then expect to find the curve containing a single break if the equilibrium quotient for formation of **3** from **1** is substantially smaller than that for formation of **1** from free water.

The dilution shift of water from 0.1 M to infinite dilution was not obtained, so that no correction is made for H_2O self-association.

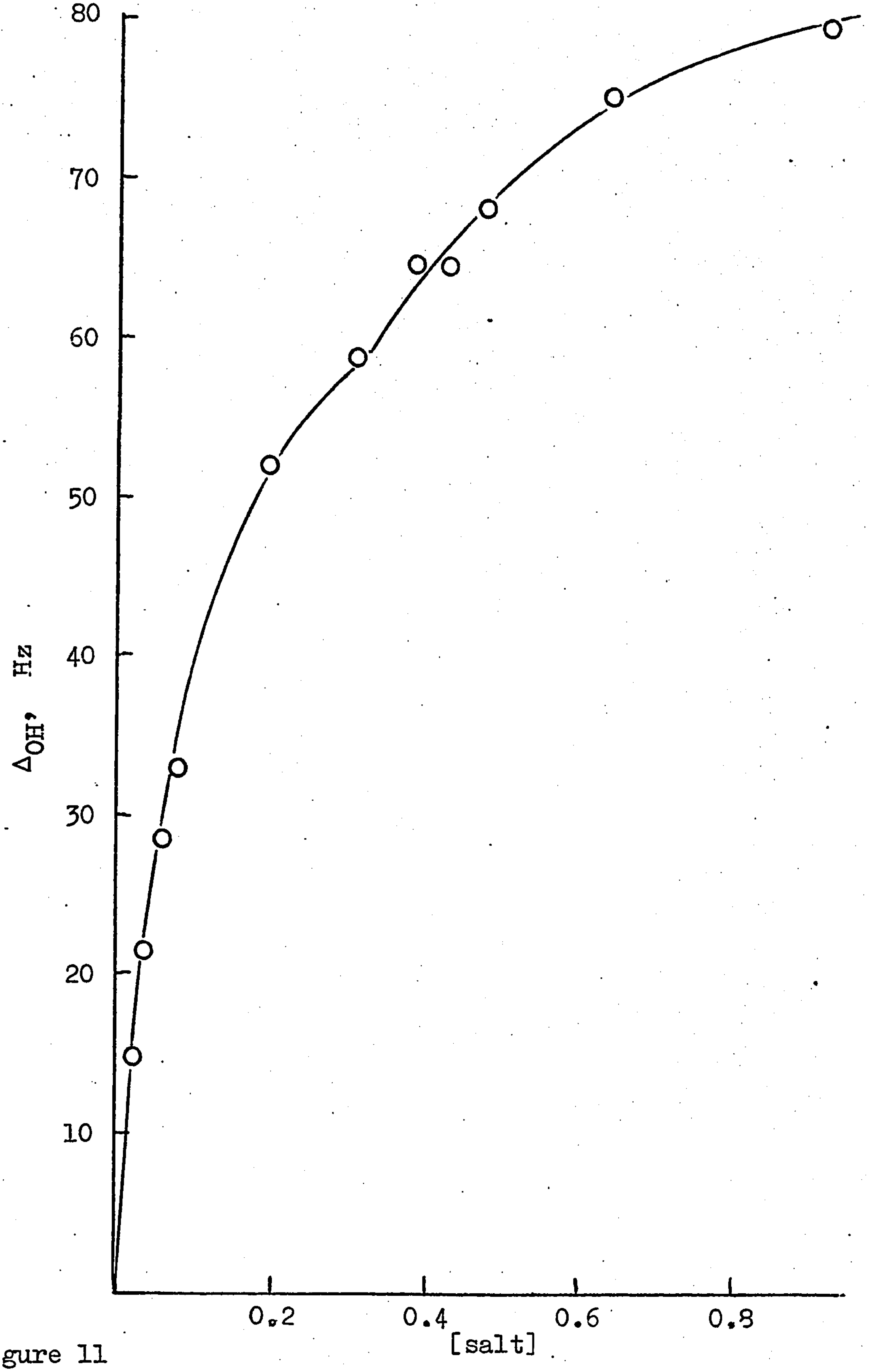


Figure 11

Salt Concentration Dependence of Water P.M.R. Signal.

Figure 11 shows the break in the Δ vs. [salt] curve which presumably indicates the start of formation of significant quantities of doubly-complexed water. Figure 12 is the Benesi-Hildebrand representation showing the break, and the derived parameters for the two presumed processes. The break in the curve appears at about 0.3 M Bu_4NBr, or when the ratio $Br^-:H_2O$ is about 2:1. It seems likely that the first portion of the curve is due primarily to

[17] $$HOH + Br^- \rightleftharpoons HOH...Br^-$$

and the second portion partly due to

[18] $$HOH...Br^- + Br^- \rightleftharpoons Br^-...HOH...Br^- .$$

Since the "observed" complex shift in the 1:1 species is about -1.25 ppm, the complex shift of the hydrogen-bonded hydrogen is 2 x (-1.25), or -2.5 ppm. On the other hand, the shift of hydrogen-bonded hydrogen in the 1:2 complex species is only -1.7 ppm; possibly, the O-H bond polarizability is dramatically reduced when both hydrogens are H bonded.

Comparing the present results for 1:1 association with the results for alcohols presented in Chapter 4, it appears that the complex shift in the

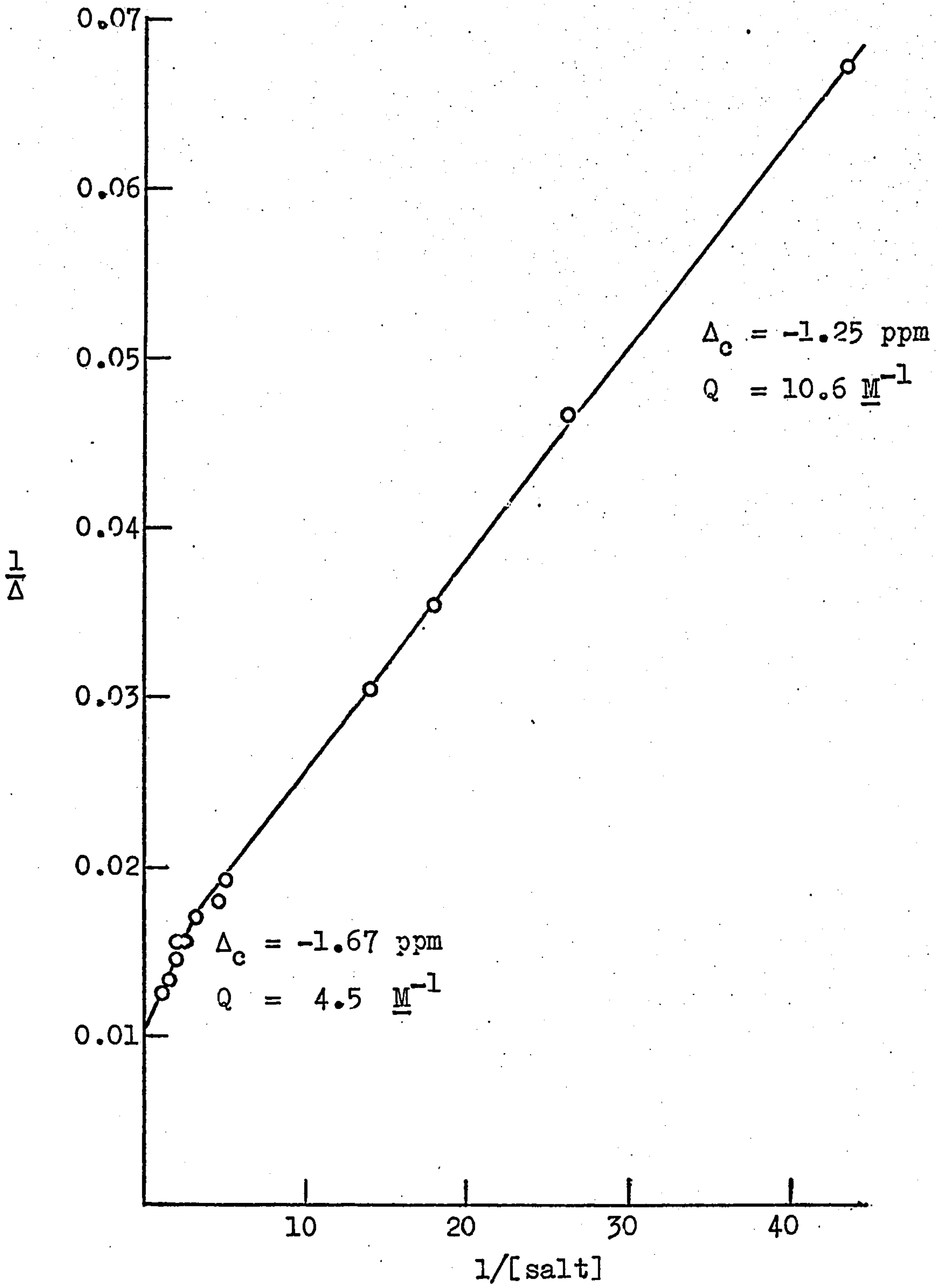


Figure 12

Benesi-Hildebrand Plot for Water--Br^- Complex.

case of water (-2.5 ppm) is a great deal smaller than those for the alcohols (-3.7 to -4.4 ppm). It would be extremely tempting to say that this was a case for non-linear hydrogen bonds in the case of the HOH...Br^- species (structure 2).

If we were to assume the bromide ion to be in the H-O-H plane and in van der Waals contact with both hydrogens, we would find $\cos\theta \approx 0.4$, and would expect, on the basis of Buckingham's A derived from alcohols, to find $\Delta_c = 0.4 \times (-3.8)$, or $\Delta_c = -1.5$ ppm. If, as was established earlier, the ion approaches more closely than this, $\cos\theta$ would be reduced still further. The agreement of this value with the experimentally obtained one of -1.3 ppm may be significant, but may also be simply fortuitous.

The other possibility is that the A coefficient for the OH bond in water is substantially smaller than that in alcohols. Considering the fact that the hydrogen of water is very much different from the $R_1R_2R_3C$ of the alcohols, this is perhaps not too unreasonable a result.

5.4 Reservations

As has been mentioned earlier, the results obtained herein apply only to the 1:1 association processes actually studied. It would be a mistake to try to apply them directly to solutions of ions in a bulk solvent. The purpose of this work is, rather, to help provide an insight into the electrostatic and other interactions between one ion and one molecule. If information, such as molar ionic shifts, is then available concerning solutions of ions, it may be feasible to attribute a certain proportion of the observed results to such interactions. Such a caution is certainly obvious in the case of water, but should be heeded for even the poorest of solvents. Primarily, the effects of molecule-molecule interactions will become important, particularly in the vicinity of ions as contrasted to the bulk medium.

CHAPTER 6 BUCKINGHAM'S A COEFFICIENT

Several attempts have been made at estimating the A coefficient for a number of X--H bonds (see equation 12); the C--H bond has been most vigorously studied, and has regularly yielded values of about 2-3 x 10^{-12} esu.

Taking, for a moment, A = 3 x 10^{-12}, and assuming the anion to be collinear with the C--H bond, and in van der Waals contact with hydrogen, the values of Δ_c obtained for trichloromethane are too low, indicating that the whole of the complex shift cannot be thus accounted for. However, there is evidence that the internuclear distances in hydrogen bonded complexes is typically 0.3 to 0.6 A less than the sum of the appropriate van der Waals radii.

If it is assumed, now, that the C--anion distance is shortened by 0.5 A in the H bonded complex, it is seen from Table XXI that the complex shifts are within about 10% of the experimentally determined values.

At these distances, the term in $\underline{B}/r^4$ in equation 12 will contribute only about 10-15% of the observed shielding change.

A value for $\underline{A}$ may be obtained by plotting ($\Delta_c + 23.07\ \underline{B}/r^4$) vs. ($1/r^2$) (see Figure 13). The trichloromethane data are best fitted by a line through the origin, of slope 16.0, which yields a value of $\underline{A} = 3.3$ esu^{-1}. The broken line on the Figure corresponds to $\underline{A} = 3.0$. The observed values show a consistent deviation of about -0.2 ppm from this line.

Yonemoto(47) predicts a van der Waals deshielding of a hydrogen nucleus at distance $\underline{r}$ from an ion given by:

$$[19] \qquad \Delta_w = 1.8 \times 10^{-53} \frac{\left\langle \sum_i x_i^2 \right\rangle}{a_o^2} \underline{r}^{-6}$$

Using Yonemoto's values for $[\left\langle \sum_i x_i^2 \right\rangle / a_o^2]$, $Cl^- = 12.5$, $Br^- = 18$, and estimating $I^- = 30$ from ratios of ionic radii, the van der Waals shift is the same for all halide ions, -0.9 ppm. The liquid phase van der Waals shifts for hydrocarbons are typically about -0.5 ppm(48), so it is not unreasonable to expect an increae of deshielding by a few tenths of a

TABLE XXI. Experimental and Calculated Shifts for Trichloromethane with Halide Ions, Assuming Hydrogen Bond Shortening.

DONOR ION	Δ_c(experimental) in CCl_4	Δ_c(experimental) in CH_3CN	Δ_c(calculated)
Cl^-	-2.92	-3.08	-2.72
Br^-	-2.51	-2.76	-2.38
I^-	-2.30	-2.18	-1.95

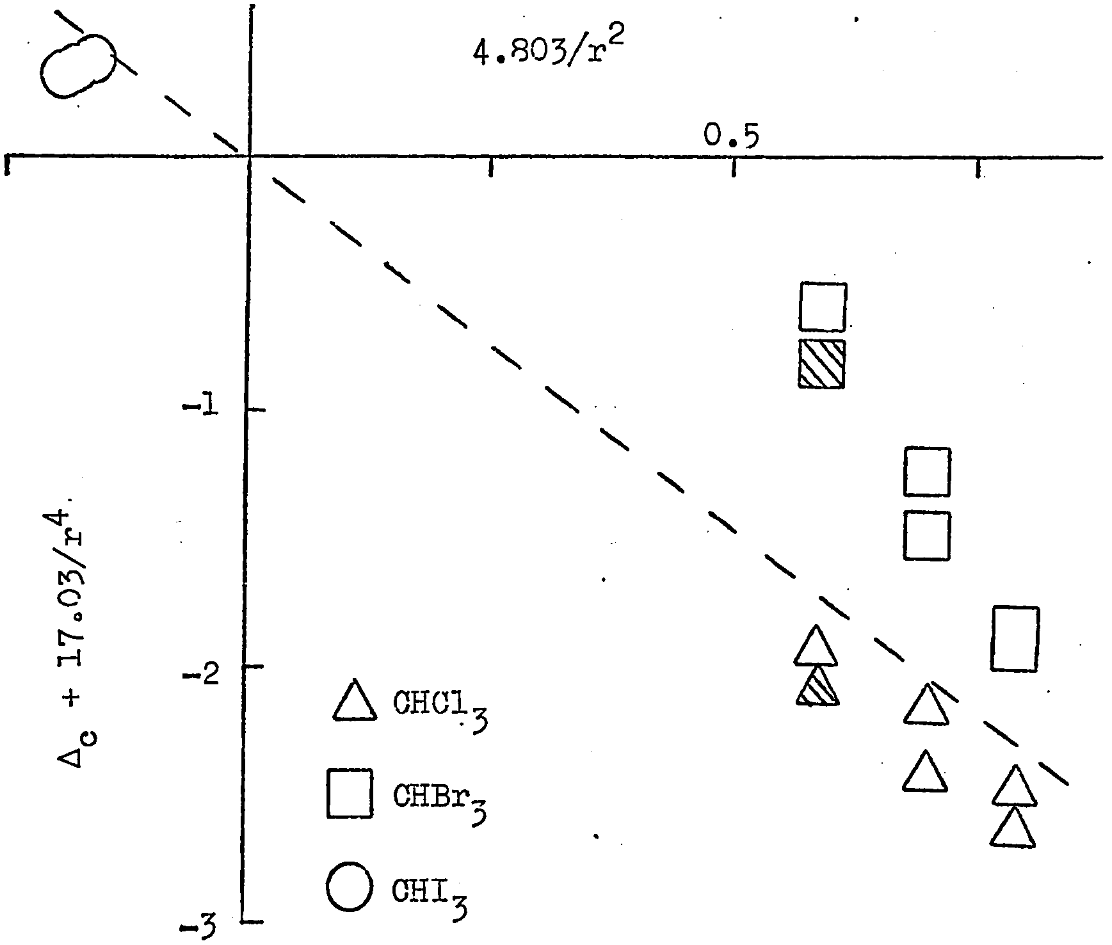


Figure 13

Determination of Buckingham's A Coefficient for Trihalomethanes. (hatched symbols: Hp_4NI)

part per million on formation of the complex.

Several reservations are necessary with regard to the validity of the A coefficient as determined from these experiments. First, since the salts in these solvents are present almost entirely in the form of ion pairs(8) or higher aggregates(49), the counterion (R_4N^+) will have a net effect which will be such as to reduce the field at the hydrogen below the nominal value of Ze/r^2, and to give a value of A which is too low. It had been hoped initially, that the salts used, tetraalkylammonium halides, would be completely dissociated, allowing the "free" anion to interact with the electrophilic hydrogens of the acceptor molecules. In fact, even in ethanenitrile it has been shown(8) that only a small fraction of the salt is present in the form of dissociated ions. Nonetheless, determination of the dipole moments of the ion pairs present(9) has yielded values in the range 10-20 D; there is some reason to believe that the internuclear separation in a Bu_4NX ion pair in solution is on the order 4-5 A, indicating that there is very little transfer of charge within such ion pairs. Hence, it is feasible, to a first approximation, to regard, as has been done herein, the anion as a point electronic charge, and to treat the effect of the accompanying cation as a second-order perturbation. Separate work in this laboratory(50) seems to confirm the validity of this assumption; changing the cation from Bu_4N^+ to Hp_4N^+ results in a change of complex shift of ca. 10%.

Second, I have assumed a shortening of the van der Waals radius of hydrogen from 1.2 to 0.7 A; in fact, the shortening is probably less than 0.5 A rather than more; if the H bond is longer than has been assumed, it becomes necessary to postulate either a larger value of A, or a larger van der Waals term to account for the observed shifts.

Third, I have assumed no dielectric properties of the space intervening between the anion and the proton (i.e. $\epsilon = 1$); this is not necessarily so, and a value of ϵ greater than 1 would decrease the field at the proton. If, indeed, this is a factor, it is probably impossible to say how much, if any, is properly a part of the A coefficient, and how much a breakdown of the point-charge-at-the-nucleus approximation. In any event, any error so caused would make the estimated value of A too low.

All in all, there would appear to be justification for regarding $A = 3 \times 10^{-12}$ as merely a lower limit for the C-H bond, and not necessarily a definitive value of the coefficient.

Another possibility which must be considered is that the A coefficient is likely to be different for the same bond type (e.g. C-H) in different compounds. Indeed, A is estimated as λ/R^2, in which λ is a rather artificial quantity representing the polarity of the remainder of the molecule as a field perturbing the isolated hydrogen atom. Such a term will quite obviously not be the same for all C-H bonds in all molecules(27); in fact, one would expect the compounds studied herein to represent the largest values likely to be encountered (the C-H bond moment in $CHCl_3$ is 0.7 D(32), carbon negative, as compared with the commonly accepted value for C-H of 0.3 D, carbon positive).

Although A has been defined as a polarity term, it is more closely related to the polarizability(51) of the X-H bond and the other bonds to the X atom. It is the ability of the molecule readily to transfer charge internally which determines the extent to which the hydrogen nucleus may be shielded or deshielded by the application of an external electric field. Thus, it matters little if the hydrogen atom be electrophilic; if it cannot readily gain or lose a portion of its electronic screening, there will be little effect on its P.M.R. spectrum by the application of an electric field.

What about the A coefficient of hydrogen bonded to atoms other than carbon? The literature on this subject is scanty(19,52), but experimentally determined values are available for, principally, Cl-H (40×10^{-12} esu). Work is proceeding in this laboratory on the hydrogen halides, and some preliminary results are indicated for HCl, HBr, and HI in Table XXII. Also shown in Table XXII are the A coefficients obtained in this work for C-H and alkyl O-H bonds, the latter actually encompassing a range of about 5 to 6×10^{-12}. Although everal NH-containing molecules were examined, the range of values obtained is very large and seems to depend strongly on the nature of the compound. The value for quaternary $^{+}$N-H is computed from the shift of -4.8 ppm taken from a recent study(53) of "encapsulated" chloride ion in a macrocyclic di-ammonium ion. This value is not strictly speaking comparable to the others since the cation (counterion) is the quaternary nitrogen of the molecule itself; since this "cation" is in the same configuration with respect to hydrogen in the uncomplexed and complexed forms, one would expect virtually no counterion effect, and the derived value of A is probably overstated relative to those obtained

TABLE XXII. Dependence of Buckingham's A on Bond Polarizability.

Bond Type	Buckingham A Coefficient, esu x 10^{-12}	α x 10^{24} cm^{-3}	Reference
C--H	3	0.65	a
$^{+}$N--H	5	0.40	53
O--H	5.5	0.74	a
Cl-H	14 (40)	2.6	a(52)
Br-H	18	3.6	a
I--H	27	5.5	a
N--H	(2.5)	0.72	a

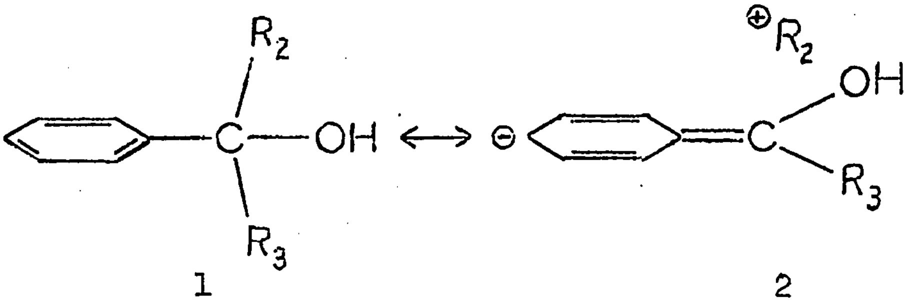
a: this work

by the present work.

The polarizability of the O-H group should not be much affected by alkyl substitution since the bulk of the polarizability will be accounted for by the lone pairs of electrons on the oxygen atom. Therefore, if Buckingham's A coefficient is a function of polarizability rather than of polarity, the constancy of Δ_c(OH) is not surprising.

It may, moreover, be possible to account for the larger shifts in arene substituted alcohols. If the phenyl ring is able, to a very small extent, to conjugate with the oxygen atom, the polarizability of the molecule would be enormously enhanced and a higher A coefficient would be appropriate.

Such interaction may well occur by a hyperconjugative mechanism as shown:



1 2

the remainder of the molecule in structure 2 and its tautomers may conjugate with lone-pair electrons on oxygen, increasing the polarizability of the OH region, thus giving a larger A coefficient and a larger complex shift. It is again emphasised that this mechanism need make only quite a minor contribution to the ground-state energy of the molecule.

It is even possible that this mechanism may account for the regular decrease in Δ_c in the series $C_6H_5CH_2OH > C_6H_5CH(CH_3)OH > C_6H_5C(CH_3)_2OH$, since hyperconjugation would be decreasing in importance in the same series(54). It is seen that Δ_c for 2-phenyl-2-propanol is $<$ 0.1 ppm greater than that for 2-methyl-2-propanol; in other words, when hyperconjugation cannot be a significant factor in the structure of the molecule, the complex shift of an arene-substituted alcohol is indistinguishable from that of an alkyl-substituted one.

From Table XXII, there is an obvious discrepancy between the value for HCl and the literature value of 40×10^{-12}. The latter was obtained from gas-phase measurements of chemical shift <u>vs.</u> pressure, by assuming only dipolar interactions between HCl molecules; if, in fact, hydrogen bonding occurs, any given HCl molecule will spend more time under the influence of other HCl molecules than is allowed for in the computation; hence, the calculated value of <u>A</u> will be too large by a factor of;

$$\frac{\text{actual time in vicinity of other molecules}}{\text{calculated time in vicinity of other molecules}}\ .$$

This factor would then be about 3.

On the other hand, there is no good reason to believe that the model of Buckingham's, which has been moderately successful in explaining the proton shifts in C-H and O-H complexes, is going to be equally valid in these cases. Also, in the present work, it has not yet been possible to identify unambiguously the $X\text{--}H\text{--}Y^-$ species present. In view of these uncertainties, no definite conclusions can be reached as to which value is likely to be more significant.

Some of the bond polarizabilities in Table XXII were taken from Landolt-Børnstein(55); the remainder were obtained from bond refractions as contained in Syrkin and Dyatkina's text(56), and their linear relation to polarizabilities.

The correlation between *A* and α is not a bad one (see Reference 51), although it admittedly depends largely on the preliminary results for the hydrogen halides. Nonetheless, these are expected to be substantially correct and so the relation may be found to be of general applicability.

In reference 19 are given further values for *A* and *B* in different bonds. The C-F bond in CHF_3 is assigned A = -9.9 ± 3.6, and B = 15.1 ± 3.0; these values, when applied to a $F_3CH...Br^-$ complex with linear C--H...Br^-, yields a ^{19}F complex shift of +0.6 ppm. Using the maximum in the range of values for A and the minimum possible B, the shift obtained is +1.4 ppm. Experimentally, trifluoromethane complexes with the bromide ion of Bu_4NBr to give a complex shift of $+1.5 \pm 0.5$, when referred to $CFCl_3$. Considering the uncertainty of the exact complex geometry and the unknown dielectric properties of the space intervening between Br^- and F, the agreement between expected and observed shifts is considered acceptable.

CHAPTER 7 CONCLUSIONS

7.1 Hydrogen Bonding

The results presented in this thesis indicate quite clearly that the technique used herein is a fast, easy, and accurate method for the detection and characterisation of hydrogen bonds between simple molecules and anion bases. It is convenient, in that high resolution N.M.R. in the liquid phase is used. It is direct, in that the hydrogen(s) affected are unambiguously detected and monitored. The range of accessible equilibrium quotients, and hence relative energies of interaction, is very large and readily extended. As far as is known, this is the first time that this technique for studying interactions in solution has been adapted to associations with monopolar, anion bases.

To a good approximation, one knows the magnitude and direction of the perturbing electrostatic field and should be able to make quantitative calculations of its effect on the hydrogens involved. It has been shown that this may be done, and gives reasonable agreement with experimental shift values by using Buckingham's very simple model of field-induced shifts. Also, rough energy calculations involving ion--dipole and ion--induced dipole interactions with trihalomethane molecules predicted energies which are of the correct magnitude, and which exhibit the same trends as those observed.

As the coefficients in Buckingham's equation become well defined for various bond types, it is possible to obtain moderately accurate measures of the structures of hydrogen bonded complexes, employing complex shift magnitudes in conjunction with the angular factor involved.

As has been demonstrated, it is not necessary to observe Δ_c directly in order to obtain its value; when Δ_c is directly observable, the equilibrium quotient is usually difficult to obtain with any precision.

7.2 Do C-H Groups form Hydrogen Bonds?

This question, asked on page 197 of reference 1, is answered there as a probable affirmative, and a sizable body of evidence cited. It is established beyond doubt that a number of molecules interact with bases *via* a C--H bond.

A collection of crystal X-ray data by Sutor(57) purporting to show the existence of C--H...O hydrogen bonds in certain molecules, has been discussed at some length by Donohue(58). He cites work which demonstrates that the minimum H...O distance permitted by Pauling's van der Waals radii, 2.60 A, is not the minimum contact distance, but rather 2.20 A. Taking into account the experimental uncertainties in Sutor's data, none of the H...O distances qualifies to establish unambiguous hydrogen bonding.

The monopolar bases studied herein have been found to interact primarily and most strongly with polarizable groups in the C--H-containing molecule. A simple monopole--dipole electrostatic model, using only independently determined parameters, appears to account adequately for all of the established energetic data, in particular the dependence on ionic size, structure, and molecular polarizability. The interaction energy is dominated by polarization of the molecule by the base. Thus, in every case of C--H hydrogen bonding mentioned in references 1 and 14, the evidence is confined to compounds in which the carbon also bears one or more highly polarizable groups (halogens, nitrile, olefin, etc.).

It is apparent that the anion is "forced" to approach from the more remote, C--H end, only by a strong permanent dipole. The main function of the hydrogen in this "hydrogen bonding" is to be small enough to allow the close approach of the anion to the polarizable groups. Since the bulk of the interaction energy is accounted for by polarization of other groups in the molecule, there would appear to be some doubt as to whether such C--H interactions with anions should properly be called hydrogen bonding, even though criteria (a) and (b) on page 1 are satisfied.

7.3 Ion Solvation

It now appears that the present technique is capable of being applied to the problem of ions in solution, for the process being studied is simply the preferential solvation of an anion by one type of molecule (acceptor) rather than another (bulk solvent). Thus, the energy involved in the displacement of one or more solvent molecules by one acceptor molecule is readily obtained for many solvents from the temperature dependence of equilibrium constants. The free energy differences have been determined in this work, and are consistent with earlier energy measurements. In this way, it should be possible to measure relative single-molecule solvation energies of a given ion by a number of acceptor molecules, relative to a particular weak solvent.. Any large discrepancies in the $\Delta\underline{S}$ so obtained could be taken as an indication that a simple 1 for 1 displacement process was no longer occurring.

In the cases of structured solvents, such as water, amides, etc., this technique may provide a means of actually separating the effects of ion solvation due to polarization of the solvent molecules from those due to ionic effects on the structure of the bulk solvent. Thus, by keeping the acceptor concentration low, it is possible to measure the difference in screening of a proton in the free molecule and in the solvation shell. Then, if the solvation number for an anion by a particular solvent be known, and it may, in principle, be determined, it should be possible from molar ionic shifts to determine the net effect of an anion on the structure of the bulk solvent after making allowance for the solvent molecules in the solvation sphere of the anion.

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APPENDIX A

All of the least-squares fits to straight lines in the Benesi-Hildebrand-Scott (B-H-S) analyses, and the evaluation of $\Delta\underline{H}$ and $\Delta\underline{S}$, and of $\delta\Delta/\delta T$, were done using a weighted polynomial regression subroutine, LSE. In the case of first-order polynomials (linear regression), this is identical to the method described in Worthing and Geffner(59).

In this study, where four to eight points were fitted to a best straight line, fortuitous coincidence of the points to the best line so derived was occasionally observed. In such cases, the resulting extremely small standard deviations of intercept, δc_1, and of slope, δc_2, were not representative of the experiments which yielded the points.

Therefore, the "standard errors" reported in this thesis include estimates of the error contributions arising from evaluable error ranges in the observed quantities, as follows. To each value y_i fitted to an equation such as [5], an error range δy_i was assigned. Now, the standard deviations δc_1 and δc_2 are both proportional to the square root of the sum of squares of residuals:

$$\sum_i w_i \, [r_i^2 + (\delta y_i)^2] \quad . \qquad [20]$$

To allow for skewed error distributions (for example, in the B-H-S analysis, the relative errors in the y_i's became larger at lower concentrations), the points were assigned weights w_i inversely proportional to δy_i. All experimental quantities for which error estimates are given, are reported as best value, plus or minus the standard error computed by this method.

APPENDIX B

Assuming an alcohol to exist as monomers and dimers only, at infinite dilution, I shall define the following quantities:

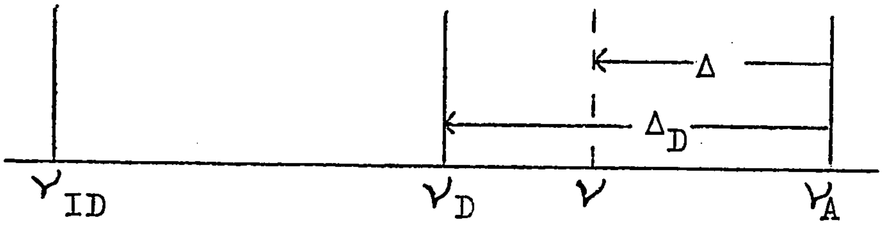
ν_A : shift in the monomer

ν_{ID}: shift of H bonded proton in the dimer

ν_D : averaged shift of the dimer signal

Δ : observed shift of the resonance

Δ_D : total <u>observable</u> dimerisation shift.



C : total alcohol concentration, all forms

[A] : concentration of monomer

[D] : concentration of dimer

K_D : $[D]/[A]^2$

Since one is considering the limit as $C \rightarrow 0$, then it is obvious that $[A] \rightarrow C$. The defining equations are:

[21] $$K_D = [D]/[A]^2 \;\text{---}\; [D]/C^2$$

[22] $$\frac{\Delta}{\Delta_D} = \frac{2[D]}{C}$$

Substituting [22] into [21], one obtains:

[23] $$\Delta = 2\,K_D\,\Delta_D\,C\ .$$

Differentiating with respect to total concentration,

[15] $$\left(\frac{d\Delta}{dC}\right)_{C \rightarrow 0} = 2\,K_D\,\Delta_D$$

which may be alternatively expressed:

[15A] $$\left(\frac{d\Delta}{dC}\right)_{C \rightarrow 0} = K_D\,\Delta_{ID}\ .$$