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THE UNIVERSITY OF ALBERTA

Thermodynamics of Non-Electrolyte Solutions

John F. Smith

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled **Thermodynamics of Non-Electrolyte Solutions** submitted by John F. Smith in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY.

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To my Mum and Dad

Abstract

Results of measurements of excess heat capacities, partial molar enthalpies, and excess volumes for chloroform + benzene have been combined with published data and the ideal associated solution model to obtain an estimate of the minimum stability of the complex necessary for the model to give reliable information about the thermodynamics of reactions of the type A + B = AB in this system. Enthalpies of mixing cyclohexane with solutions of chloroform + triethylamine in cyclohexane have been measured and used to provide evidence that the ideal associated solution model may be applied successfully to analyse the thermodynamic properties of an associated system in an inert solvent.

The ideal associated solution model has been extended to treat the solubility of a gas in a solvent with which it forms a complex, with specific application to new measurements of the solubility of ammonia in chloroform.

A method for estimating the physical contributions to non-ideality (activity coefficients) has been developed by combining the ideal associated solution model with solubility parameter theory and has been applied to the chloroform + triethylamine system. The general method is applicable to other A + B = AB systems.

In another application of the ideal associated solution model we have interpreted excess volumes, excess enthalpies, and vapour pressures of chloroform + n-hexane mixtures in terms of self-association of chloroform.

Using a dilatometer built here, we have measured the partial molar volumes of sulphur dioxide in several organic solvents. Differences between the partial molar volumes of sulphur dioxide in electron donating and non-electron donating solvents have been interpreted in terms of charge-transfer complexes.

Apparent molar volumes of carbon dioxide, ethane, propane, and sulphur dioxide in liquids and liquid mixtures that have some of the same solvent properties as bitumen have led to the partial molar volumes of these gases in bitumen. The relationship of these volumes to the solubilities of gases in bitumen has been investigated.

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In connection with the study of partial molar volumes of dissolved gases I extend my sincere appreciation to Professor G. A. Bottomley for providing inspiration and a great deal of encouragement. I also thank R. P. Schutte his for help with the experimental measurements.

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Introduction

In this work two aspects of non-electrolyte solution thermodynamics are discussed. One of these concerns application of the ideal associated solution model as an approximation to solutions in which chemical association occurs; the other concerns partial molar volumes of gases in organic solvents.

A comprehensive study of the ideal associated solution model is necessary because the model is commonly applied to chemical systems for which the validity of the model is unknown. Chapter 1 describes the model and sets out the important problems and unanswered questions connected with it. Chapters 2 - 6 present the results of measurements and calculations showing that the model is a useful approximation to a variety of associated systems. These results also provide insight into many of the questions concerning the model that are posed in Chapter 1.

The partial molar volumes of gases are of interest primarily because they allow the prediction of gas solubility at pressures above the Henry's law region. We have built a new dilatometer that allows quick and precise measurement of the apparent molar volumes of gases in liquids. Results obtained with this dilatometer have led to the partial molar volume of sulphur dioxide in a range of organic solvents. The results of this investigation and a description of the dilatometer are given in Chapter 7.

The dilatometer has also been used to measure the apparent molar volumes of several gases in solvents which have properties similar to the properties of bitumen. From the results of these measurements, the partial molar volumes of the gases in pure bitumen have been estimated. This work is discussed in Chapter 8.

CHAPTER 1

The Ideal Associated Solution Model

Analyses of the thermodynamic properties of non-electrolyte solutions are generally made by comparing the measured properties with the properties the solution would have if it were ideal. Attempts are then made to explain the observed deviations in terms of some model (or theory) of solutions. As a first step in the development of such a model it is often convenient to separate the deviations from ideality into "physical" and "chemical" contributions, with the latter being due to the formation of distinct, new chemical species in the solution. This separation is an artificial one since there is no sharp dividing line between interactions which may be regarded as physical and those which may be regarded as chemical. Nevertheless, the distinction between the two contributions is useful if one of the contributions can be considered as negligible with respect to the other.

It has recently been shown (Baker, Watson, and Williamson, 1971; Hepler and Fenby, 1973; Matsui, Hepler, and Fenby, 1973; Fenby and Hepler, 1974 a,b; Pasco, Hepler, and Fenby, 1974; Handa, Fenby, and Jones, 1975; Hepler, Kooner, Roux-Desgranges, and Grolier, 1985) that for some non-electrolyte solutions in which chemical reactions are expected (or known) to occur all of the observed deviations from ideality may appropriately be attributed to the formation of new chemical species. That is to say, it is assumed that the physical contributions to the deviations from ideality are negligible with respect to the chemical contributions. Since the physical contributions (usually accounted for by activity coefficients) are assumed to be unimportant, the activity coefficients of all species are set equal to unity at all compositions and temperatures. The solution is, therefore, considered to be an ideal solution of all the species present at equilibrium. This is known as the ideal associated solution model (Prigogine and Defay, 1954; McGlashan, 1979; Acree, 1984).

The ideal associated solution model has been extensively used by investigators of a wide range of systems in which complex formation is expected. For example, many spectroscopic studies are conducted on a dilute solution of the associated system in some "inert" solvent. Studies have also been made of systems in which more than one associated species is expected and of systems in which some degree of self-association is anticipated. Yet, despite the widely varying nature of the systems, most users of the ideal associated solution model provide no evidence that the model is indeed a valid approximation to the system they are investigating.

In order to provide some guidelines as to when the ideal associated solution model should (and should not) be used, we have undertaken a study of the model as an approximation to a variety of chemical systems. In doing so we have also extended the model so that it can be applied to complex formation in a dissolved gas + solvent system and to complex formation between molecules of the same component (self-association). The results of these investigations are presented in Chapters 2 - 6 of this thesis. Chapter 2 examines the question of how stable the complex must be for the model to be a good approximation. Chapter 3 discusses the use of the model as an approximation to associated systems that are dissolved in an "inert" solvent. Chapter 4 treats complex formation between a dissolved gas and its solvent. In Chapter 5 the model is extended by combination with solubility parameter theory to obtain a value for the thermodynamic equilibrium constant for the association (1:1 complex formation). By comparing the thermodynamic equilibrium constant with the equilibrium constant calculated from the model the error introduced by the neglect of physical contributions to the deviations from ideality can be estimated. Chapter 6 demonstrates the ability of the model to deal with the problem of self-association.

CHAPTER 2

Thermal and Volumetric Properties of Chloroform + Benzene Mixtures and the Ideal Associated Solution Model of Complex Formation

Introduction

Recently the ideal associated solution model has been extended and applied to thermodynamic properties (K, ΔH^{θ}, $\Delta C_p{}^{\theta}$, and ΔV^{θ}) of chloroform + triethylamine mixtures (Hepler, Kooner, Roux-Desgranges, and Grolier, 1985). It was shown that this relatively simple model is consistent with many accurate experimental results so that there is no compelling empirical justification for introducing more complicated theoretical treatments. The chloroform + triethylamine system was chosen as the focus of that earlier work for two principal reasons. First, there is strong evidence that the 1:1 complex exists in the solid state (Stapleton, Bellay, Wulff, and Hepler, 1966) and good spectroscopic evidence for the existence of the 1:1 complex in the liquid state (Howard, Jumper, and Emerson, 1963; Wiley and Miller, 1971). Second, it was recognised that the ideal associated solution model was most likely to provide an accurate and useful representation of properties of mixtures in which the observed non-ideal thermodynamic properties are due to the formation of a reasonably stable complex, as in this system. The desirability of testing the adequacy of this model on other systems containing less stable complexes was also recognised.

The underlying assumption of the model is valid only when the chemical interactions are large with respect to the physical interactions. Therefore, we expect that the ideal associated solution model will be a better approximation for systems in which a stable complex is formed than for systems in which the complex is less stable (weak). The question then arises: how weak can the complex be before the neglect of the physical contributions introduces too much error for the ideal associated solution model to be a useful approximation? This question is addressed in the current Chapter by applying the model to the chloroform + benzene system, in which the existence of weak 1:1 complexes has been proposed.

As discussed in Chapter 1, in the ideal associated solution model it is postulated that all deviations of thermodynamic properties from those of the ideal solution can be accounted for in terms of one or more chemical equilibria, with activity coefficients of all species taken to be unity at all compositions and temperatures. It is therefore necessary to begin by identifying the pertinent chemical equilibrium as

[2-1] $A + B = AB$

in which A and B represent chloroform and benzene, respectively, and AB represents the 1:1 complex. We will later cite and use results of thermodynamic investigations that provide supporting evidence for the existence of the 1:1 complex; here we cite five spectroscopic investigations (Reeves and

Schneider, 1957; Cresswell and Allred, 1962; Huntress, 1969; Lin and Tsay, 1970; Homer, Everdell, Jackson, and Whitney, 1972) and one investigation of dielectric properties (Boule, 1972), all of which provide evidence in support of the idea that the equilibrium represented by equation [2-1] is the most important non-ideal interaction in mixtures of chloroform + benzene.

Experimental

All enthalpies of solution were measured with an LKB 8700 Precision Calorimetry System, using the ampoule method. Ampoules containing about 10^{-3} mole of a pure liquid were broken in the calorimetric vessel that contained 100 cm^3 of the other pure liquid. Thus, the observed enthalpies (after small corrections for vapour spaces in ampoules) are very close to the desired differential or partial molar enthalpies of solution at infinite dilution. All such enthalpies refer to the stated temperatures ± 0.05 K.

Heat capacities and densities at 298.15 ± 0.05 K were measured using a Picker flow calorimeter and densimeter as described by previous workers (Picker, Leduc, Philip, and Desnoyers, 1971; Picker, Tremblay, and Jolicoeur, 1974).

Benzene (Caledon) was distilled and then dried by prolonged contact with molecular sieve. Chloroform (Caledon) was washed five times with doubly distilled water, dried over anhydrous calcium chloride, and fractionally distilled twice. The middle fraction from each distillation was retained. At all stages of the process the chloroform was protected from light. The purified chloroform was stored under nitrogen in the dark and was used within three days of purification.

Calorimetric and Volumetric Results

As stated in the preceding section, our enthalpies of solution are taken to be differential or partial molar enthalpies of solution at infinite dilution, which we represent by L_A^o and L_B^o, with the subscripts A and B indicating chloroform and benzene, respectively, as the dilute components. Results are summarised in Table 2-1, where each L^o is the average of enthalpies from four measurements.

Molar excess heat capacities, C_p^E, are defined by

[2-2] $$C_p^E = C_p - x_A C^{\bullet}_{p,A} - x_B C^{\bullet}_{p,B}$$

in which C_p represents the heat capacity of a mixture containing a total of 1.0 mole of stoichiometric A + B, x_A and x_B are stoichiometric mole fractions, and $C^{\bullet}_{p,A}$ and $C^{\bullet}_{p,B}$ are the molar heat capacities of the pure liquids A and B. The molar excess volume is defined similarly in terms of the volume of a mixture and the molar volumes of pure liquids. Results of our measurements of excess heat capacities and densities are summarised in the form of these C_p^E and V^E values in Table 2-2. Our heat capacities for pure chloroform and pure benzene are $C^{\bullet}_{p,A} = 113.85$ J K^{-1} mol^{-1} and $C^{\bullet}_{p,B} = 135.75$ J K^{-1} mol^{-1}, respectively. Densities are 1.47835 g cm^{-3} for chloroform and 0.87370 g cm^{-3} for benzene.

Table 2-1. Infinite dilution partial molar enthalpies of solution of chloroform in benzene and of benzene in chloroform[a]

Temperature/K	L_A^o /kJ mol^{-1}	L_B^o /kJ mol^{-1}
288.15	-1.15	-1.89
298.15	-1.17	-1.81
308.15	-1.21	-1.76

---

[a] Subscript A indicates dilute chloroform (A) in benzene (B) while subscript B indicates dilute benzene in chloroform

Table 2-2. Molar excess heat capacities and volumes of mixtures of chloroform + benzene at mole fractions x_A of chloroform at 298.15 K.

x_A	C_p^E/J K^{-1} mol^{-1}	V^E/cm^3 mol^{-1}
0.00000	0.0000	0.0000
0.05241	-0.00[illegible]	0.0477
0.08062	-0.0163	0.0665
0.14451	-0.0306	0.1067
0.20312	0.0319	0.1348
0.25975	0.1080	0.1466
0.41618	0.4378	0.1690
0.52199	0.6590	0.1710
0.61445	0.7643	0.1516
0.69814	0.7984	0.1243
0.79493	0.6698	0.0707
0.85978	0.5365	0.0644
0.92281	0.3904	0.0402
1.00000	0.0000	0.0000

Thermodynamic Analysis

The equilibrium speciation of a mixture of N_A moles of A and N_B moles of B can be obtained by consideration of the mass balance shown in Table 2-3. The symbol r in Table 2-3 represents the amount of complex at equilibrium relative to the stoichiometric amount of mixture and is equivalent to the extent of reaction, ξ, introduced by De Donder (Prigogine and Defay, 1954).

In the ideal associated solution model the activity coefficients of the various species are taken to be unity at all compositions; therefore the thermodynamic equilibrium constant, K, for reaction [2-1] can be expressed in terms of the equilibrium mole fractions, z_i, of these species:

[2-3] $K = z_{AB}/z_A z_B$

Substituting the expressions for the equilibrium mole fractions from the last column of Table 2-3 into equation [2-3] (noting that $x_A = 1 - x_B$) we obtain an expression for the equilibrium constant in terms of the extent of reaction (r) and the stoichiometric mole fractions, x_i:

[2-4] $K = r(1 - r)/[x_B(1 - x_B) - r + r^2]$

Rearrangement of equation [2-4] yields

[2-5] $r = (1 - [1 - (4x_A x_B K)/(K + 1)]^{0.5})/2$

Therefore, the value of r can be calculated for any given mixture of A and B for which the equilibrium constant of association is known.

The equilibrium constant of an association reaction such as that

Table 2-3. Mass balance in the liquid phase for reaction [2-1].

Species	Stoichiometric Amount/mol	Stoichiometric Mole fraction	Equilibrium[a] Amount/mol	Equilibrium[b] Mole Fraction
A	N_A	x_A	$N_A - n_{AB}$	$(x_A - r)/(1 - r) = z_A$
B	N_B	x_B	$N_B - n_{AB}$	$(x_B - r)/(1 - r) = z_B$
AB	-	-	n_{AB}	$r/(1-r) = z_{AB}$

[a] Total number of moles at equilibrium is $(N_A + N_B - n_{AB})$

[b] $r = n_{AB}/(N_A + N_B)$

represented by equation [2-1] may be calculated from vapour pressure data by the method described in Appendix A. Applying this method to critically analysed and selected vapour pressure - composition data for the chloroform + benzene system at 323.15 K (Gmehling, Onken, and Arlt, 1980), we obtained a K value for each of 19 different compositions. The average value is K_{323} = 0.378 with standard deviation 0.054. Because there is a distinct trend for the calculated values of K_{323} to increase with increasing mole fraction of chloroform, the K_{323} values can be summarised by

[2-6] $K_{323} = 0.2928 + 0.1753x_A$

for which the correlation coefficient is 0.992. In the subsequent calculations we havs used the average value of K_{323} calculated from equation [2-6] at $x_A = 0.5$ ($K_{323} = 0.380$).

In the ideal associated solution model all deviations from ideal solution behaviour are said to arise from chemical interactions in the solution. Therefore, the excess enthalpy (molar enthalpy of mixing), H^E, is related to the standard enthalpy of process [2-1] , ΔH^θ, by

[2-7] $H^E = r\Delta H^\theta$

To obtain ΔH^θ_{323} from equation [2-7] we need values of H^E at 323.15 K. These values are calculated by combining our heat capacities (Table 2-2) with 12 selected H^E_{298} values (Nagata, Tamura, and Tokuriki, 1981; Rastogi, Nath, and Misra, 1971). In this way we obtain 12 calculated values of H^E_{323}. Each calculated $H^E{}_{323}$ corresponds to a particular composition of chloroform + benzene and hence to a particular value of r. The value of r corresponding to each $H^E{}_{323}$ value is calculated from equation [2-5] using $K_{323} = 0.380$ (obtained as described above). The $H^E{}_{323}$, r pairs are then combined in equation [2-7] to obtain 12 values of $\Delta H^\theta{}_{323}$. The mole fraction dependence of $\Delta H^\theta{}_{323}$ is given by

$$[2\text{-}8] \qquad \Delta H^\theta{}_{323}\,/\text{kJ mol}^{-1} = -4.599 - 1.604x_A$$

for which the correlation coefficient is -0.994. For $x_A = 0.5$ equation [2-8] leads to $\Delta H^\theta{}_{323} = -5.40$ kJ mol^{-1} which is the value used in subsequent calculations.

If the experimental results that we have used were without error and if the ideal associated solution model were exactly correct for the chloroform + benzene system, the calculated values of K_{323} and $\Delta H^\theta{}_{323}$ would not depend on composition. Because all available evidence suggests that the experimental results we have used are very good, we must attribute most of the observed variation with composition to inadequacies in the model. However, the variations are of such magnitude that it is still appropriate to regard the ideal associated solution model as being worth further testing as follows.

Taking the value of K_{323} (given above) with the value of $\Delta H^\theta{}_{323}$ in $(\partial \ln K/\partial T)_p = \Delta H^\theta/RT^2$ we obtain $K_{298} = 0.45$. Next, we use this K_{298} with calorimetric H^E for 298.15 K (Nagata et al., 1981; Rastogi et al., 1971) in equations [2-5] and [2-7] to obtain 12 values of $\Delta H^\theta{}_{298}$ with an average value of of -4.88 kJ mol^{-1} and standard deviation 0.61 kJ mol^{-1}. We summarise these 12 values with

[2-9] ΔH^{θ}_{298} /kJ mol^{-1} = $-3.988 - 1.912x_A$

for which the correlation coefficient is -0.994. At $x_A = 0.5$ equation [2-9] leads to $\Delta H^{\theta}_{298} = -4.94$ kJ mol^{-1}.

Another approach to evaluating ΔH^{θ} is by way of limiting partial molar enthalpies of solution, L^o, since it has been shown (Matsui, Hepler, and Fenby, 1973) that

[2-10] $\Delta H^{\theta} = L_A{}^o(K + 1)/K = L_B{}^o(K + 1)/K$

Use of $L_A{}^o$ and $L_B{}^o$ at 298.15 K from Table 2-1 and $K_{298} = 0.45$ in equation [2-10] yields $\Delta H^{\theta}_{298} = -3.8$ kJ mol^{-1} from $L_A{}^o$ and $\Delta H^{\theta}_{298} = -5.8$ kJ mol^{-1} from $L_B{}^o$. The average of these two values is in excellent agreement with ΔH^{θ}_{298} = -4.9 kJ mol^{-1} from H^E and K_{298} values. Also, the individual values of ΔH^{θ}_{298} (calculated from $L_A{}^o$, $L_B{}^o$, and $H^E{}_{298}$) agree within our estimates of the relatively large uncertainties in ΔH^{θ}_{298} from L^o and the smaller uncertainty in ΔH^{θ}_{298} from excess enthalpies.

In principle we can use our ΔH^{θ} values at 298 K and 323 K in $\Delta C_p{}^{\theta} = (\partial \Delta H^{\theta}/\partial T)_p$ to obtain $\Delta C_p{}^{\theta} = -18$ J K^{-1} mol^{-1} for reaction [2-1]. Because of the large uncertainty of ±35 J K^{-1} mol^{-1} in this value we turn to our excess heat capacities in Table 2-2 to try to obtain a better value of $\Delta C_p{}^{\theta}$. By differentiating equation [2-7] with respect to temperature and rearranging we obtain

[2-11] $\Delta C_p^\theta = [C_p^E - \Delta H^\theta(\partial r/\partial T)_p]/r$

As shown by Mains, Larson, and Hepler, (1984), differentiation of equation [2-4] in combination with $(\partial \ln K/\partial T)_p = \Delta H^\theta/RT^2$ permits equation [2-11] to be written in the form

[2-12] $\Delta C_p^\theta = [C_p^E - (\Delta H^\theta)^2/(RT^2Q)]/r$

where

[2-13] $Q = [-1/(1 - r)] + [1/r] + [1/(x_A - r)] + [1/(x_B - r)]$

In these calculations we have used $K = 0.45$ and $\Delta H^\theta = -4.94$ kJ mol^{-1} (both for T = 298.15 K) obtained as described earlier in this Chapter. The results of these calculations are 12 different ΔC_p^θ values, each corresponding to the composition of one of the C_p^E values in Table 2-2. The average value is $\Delta C_p^\theta =$ -18 J K^{-1} mol^{-1} with a standard deviation of 6 J K^{-1} mol^{-1}. Because the calculated values of ΔC_p^θ vary with the composition of the solution we also summarise them with

[2-14] $\Delta C_p^\theta /\text{J K}^{-1}\text{ mol}^{-1} = -26.8 + 19.7x_A$

with correlation coefficient 0.979. Equation [2-14] leads to a value of $\Delta C_p^\theta = -17$ J K^{-1} mol^{-1} at $x_A = 0.5$.

We can also obtain $\Delta C_p^\theta = -23$ J K^{-1} mol^{-1} for reaction [2-1] at $x_A = 0$ by way of the L^o results in Table 2-1, using

[2-15] $\Delta C_p^\theta = [(\partial L^o/\partial T)_p - (L^o)^2/(RT^2K)](K + 1)/K$

that was derived by Hepler et al. (1985). Similarly, our values of L_B^o lead to $\Delta C_p^\theta = -11$ J K^{-1} mol^{-1} at $x_A = 1.0$ and thence to an average (from L^o results) $\Delta C_p^\theta = -17$ J K^{-1} mol^{-1} for reaction [2-1]. Although there is a non-trivial dependence of the calculated values of ΔC_p^θ on composition of solution, it should be noted that the composition dependence of these ΔC_p^θ values based on L^o values is the same as that for our earlier ΔC_p^θ values based on the C_p^E values that were used in equation [2-11] (as summarised by equation [2-14]). This latter agreement shows that our experimental results (L^o and C_p^E) are consistent with each other, so that the observed dependence of calculated values of ΔC_p^θ on composition of the solution must be attributed mostly to cumulative inadequacies in the ideal associated solution model.

Although the above ΔC_p^θ values are not very accurate, the average value can be combined with our ΔH^θ_{323} in $(\partial \Delta H^\theta/\partial T)_p = \Delta C_p^\theta$ to obtain a usefully accurate equation for the temperature dependence of ΔH^θ:

[2-16] ΔH^θ /J mol^{-1} = 94 - 17T

Combination of equation [2-16] with $(\partial \ln K/\partial T)_p = \Delta H^\theta/RT^2$ and our $K_{323} = 0.380$ yields an expression for the association equilibrium constant as a function of temperature

[2-17] $\ln K = -(11.31/T) + 10.86 - 2.04 \ln T$

The volume change for reaction [2-1] at 298.15 K, ΔV^{θ}, can be calculated from our excess volumes (Table 2-2) from

[2-18] $V^E = r\Delta V^{\theta}$

in just the same way that we have obtained ΔH^{θ} from excess enthalpies and equation [2-7]. The average of the 12 values obtained in this way is $\Delta V^{\theta} = 2.2$ cm^3 mol^{-1} with a standard deviation of 0.5 cm^3 mol^{-1}. Because the calculated values of ΔV^{θ} vary with composition of the solution, we also summarise these results by

[2-19] $\Delta V^{\theta}/\mathrm{cm^3\ mol^{-1}} = 2.87 - 1.55x_A$

for which the correlation coefficient is -0.94. The value of ΔV^{θ} at $x_A = 0.5$ is 2.1 cm^3 mol^{-1}.

We have also used the excess volumes reported by Rastogi et al. (1971) for 20, 30, and 40°C for similar calculations. Because of the scatter in their values of V^E, we note only that the derived values for ΔV^{θ} are all small and positive.

Discussion

The results presented here show that there is good consistency between vapour pressure data, calorimetric data, volumetric data, and the ideal associated solution model for reaction [2-1]. This consistency, together with the modest dependences of the calculated thermodynamic quantities (K, ΔH^{θ}, ΔC_p^{θ}, and ΔV^{θ}) on composition of solution, indicates that the ideal associated solution model is a useful approximation for assessing the stability and related thermodynamic properties of 1:1 complexes in the chloroform + benzene system.

The dependences of the calculated thermodynamic properties on composition of solution are larger (relatively) than those observed for the chloroform + triethylamine system. This was expected since the chemical interactions between chloroform and benzene are weaker than the chemical interactions between chloroform and triethylamine; thus the ideal associated solution model is not as good an approximation for the chloroform + benzene system as it is for the chloroform + triethylamine system.

The degree of composition dependence of the thermodynamic properties of the chloroform + benzene system indicates that the ideal associated solution model will not be a useful approximation for associated systems in which the complex is markedly less stable than the chloroform-benzene complex. On this basis we suggest that the model should not be applied to associated systems for which the association equilibrium constant (expressed in terms of mole fractions) is less than about 0.1.

It is also noteworthy that all of the values of V^E and hence all of the values of ΔV^{θ} for the chloroform + benzene system are positive, while all of the values of V^E and ΔV^{θ} for the chloroform + triethylamine system are negative. It follows from $(\partial \ln K/\partial p)_T = -\Delta V^{\theta}/RT$ that the stability of the chloroform-triethylamine complex increases with increasing pressure while the stability of the chloroform-benzene complex decreases with increasing pressure. Spectroscopic measurements offer the best method for testing this prediction.

CHAPTER 3

Examination of the Inert Solvent Assumption in the Ideal Associated Solution Model. Enthalpy of Chloroform-Triethylamine Complex Dissociation.

Introduction

As noted in Chapter 1, associated non-electrolyte systems (A + B = AB) are often studied as dilute solutions in some more or less inert solvent. For such investigations there are two ways of choosing standard states and evaluating activity coefficients. First, we may choose standard states for A, B, and AB based on Henry's law, which means that activity coefficients for all species that are sufficiently dilute are taken to be unity. An advantage of this choice is that it avoids the need to specify any particular model or theory of activity coefficients, but there are important difficulties. The first difficulty arises from the practical necessity of working with solutions that contain a reasonable concentration of complex. Many complexes are not formed in an appreciable amount in very dilute solution. Therefore, investigators are forced to work with reasonably concentrated solutions for which activity coefficients based on Henry's law may not be equal to unity, which then leads to the need for some further model or theory of activity coefficients. A second difficulty is that there is no straightforward way to compare K, ΔG^{θ}, and ΔS^{θ} values based on a Henry's law standard state with K, ΔG^θ, and ΔS^θ values based on Raoult's law, which is the usual standard state for binary mixtures of A + B (no solvent).

The second approach to solutions of A + B in an "inert" solvent is to choose standard states of all species based on Raoult's law. Compositions are expressed in terms of mole fractions and all activity coefficients are set equal to unity at all temperatures and compositions. This approach is equivalent to extending the ideal associated solution model from binary mixtures of A + B to solutions of A + B in an "inert" solvent and has the advantage that it permits direct comparison of results obtained for binary mixtures of A + B with results obtained for solutions of A + B in a solvent. If this approach is valid, then values of the equilibrium constant (K) and the standard enthalpy (ΔH^θ) for A + B = AB will be the same whether they are determined from the results of investigations of binary A + B (no solvent) or from the results of investigations of solutions of A + B in an inert solvent.

To examine the validity of the extension of the ideal associated solution model to solutions of A + B in an inert solvent we have investigated the chloroform + triethylamine + cyclohexane system. Chloroform + triethylamine was chosen as the complexing pair because the complex formed between chloroform and triethylamine is very stable (K = 2.6 at 25°C) and because the ideal associated solution model has been shown (Hepler, Kooner, Roux-Desgranges, and Grolier, 1985) to work well for this system. Cyclohexane was chosen as the inert solvent in view of its common use as a solvent in spectroscopic and thermodynamic studies of non-electrolyte solutions. In addition, cyclohexane has no obvious chemical reactivity towards either chloroform or triethylamine.

The enthalpies of adding known amounts of cyclohexane to both dilute and concentrated solutions of chloroform + triethylamine in cyclohexane were measured. To the extent that the model is applicable to the binary mixtures of chloroform + triethylamine and also to the solutions in cyclohexane, the results of these measurements will be consistent with the previously reported (Hepler et al., 1985) values of K and ΔH^{θ} that were established on the basis of measurements of vapour pressure and excess enthalpies of binary A + B mixtures.

Treatment of Speciation

The formation of a 1:1 complex, AB, between unlike molecules, A and B, can be represented by

[3-1] $A + B = AB$

When N_A moles of A are mixed with N_B moles of B and N_S moles of inert solvent, S, the equilibrium composition of the solution (expressed in terms of the equilibrium mole fractions, z_i) can be related to the stoichiometric composition (expressed in terms of the stoichiometric mole fractions, x_i). The relationship is derived from the mass balance considerations presented in Table 3-1. In Table 3-1 r represents extent of reaction, as before (Chapter 2).

Table 3-1. Mass balance for A + B = AB mixed with an inert solvent S.

Species	Stoichiometric Amount/mol	Stoichiometric Mole fraction	Equilibrium[a] Amount/mol	Equilibrium[b] Mole Fraction
A	N_A	x_A	$(N_A - n) = n_A$	$(x_A - r)/(1 - r) = z_A$
B	N_B	x_B	$(N_B - n) = n_B$	$(x_B - r)/(1 - r) = z_B$
AB	-	-	n_{AB}	$r/(1 - r) = z_{AB}$
S	N_S	x_S	$N_S = n_S$	$x_S/(1 - r) = z_S$

[a] Total number of moles at equilibrium is $(N_A + N_B + N_S - n_{AB})$.

[b] $r = n_{AB}/(N_A + N_B + N_S)$.

In the ideal associated solution model the activity coefficients of all species are taken to be unity at all compositions. Therefore the equilibrium constant for reaction [3-1] can be expressed in terms of the equilibrium mole fractions, z_i:

[3-2] $K = z_{AB}/z_A z_B$

Substituting the expressions for the equilibrium mole fractions of each species, z_i, from the last column of Table 3-1 into equation [3-2], we obtain an expression for the equilibrium constant in terms of the extent of reaction (r) and the stoichiometric mole fractions, x_i:

[3-3] $K = r(1 - r)/(x_A - r)(x_B - r)$

Rearrangement of equation [3-3] yields

[3-4] $r = [K(x_A + x_B) + 1 - [(K(x_A + x_B) + 1)^2 - 4(K$ [illegible] $)(Kx_Ax_B)]/ (2K + 1)$

Therefore, the value of r can be calculated for any given mixture of A, B, and S for which the equilibrium constant of association is known. The value of r can then be used in the expressions (obtained from Table 3-1)

$$\begin{aligned} z_A &= (x_A - r)/(1 - r) \\ z_B &= (x_B - r)/(1 - r) \\ z_{AB} &= r/(1 - r) \\ z_S &= x_S/(1 - r) \end{aligned} \qquad [3\text{-}5]$$

to evaluate the equilibrium mole fraction of each species in the solution. The equilibrium amount of the complex, n_{AB}, can also be calculated from the extent of reaction using

$$n_{AB} = r(N_A + N_B + N_S) \qquad [3\text{-}6]$$

The equilibrium amounts of A and B, n_A and n_B, can then be calculated from the expressions

$$\begin{aligned} n_A &= N_A - n_{AB} \\ n_B &= N_B - n_{AB} \end{aligned} \qquad [3\text{-}7]$$

which are derived in Table 3-1. The amount of solvent is unchanged by the formation of AB and hence the equilibrium amount of S, n_S, equals the stoichiometric amount of S:

$$n_S = N_S \qquad [3\text{-}8]$$

Thus, for any mixture of A, B, and S for which the stoichiometric amount of each species and the equilibrium constant of association are known, the equilibrium speciation can be calculated.

Experimental

Calorimetric measurements were made using an isoperibol calorimeter. The calorimeter consists of a Dewar flask (capacity 370 cm^3) reaction vessel clamped inside a sealed brass can. The brass can is fitted with an inlet port through which a liquid can be admitted to the reaction vessel by an automatic titrator. Changes in the temperature of the mixture in the reaction vessel are monitored with a thermistor and a resistance bridge. A calibration heater mounted on the inside of the lid of the can is positioned near the bottom of the reaction vessel when the vessel is sealed inside the can. The calorimeter is described in full by Dobrogowska and Hepler (manuscript in preparation).

To begin an experiment the reaction mixture is weighed into the reaction vessel. The reaction vessel is then clamped inside the can and the can is sealed and placed in a contant temperature water bath. The reaction mixture is stirred continuously and the change in resistance of the thermistor with time is recorded. When the resistance of the thermistor reaches a value that has been shown previously to correspond to the temperature of the water bath, a known volume of the liquid in the titrator is admitted to the reaction vessel. The titration leads to a change in temperature of the reaction mixture and a corresponding change in resistance of the thermistor. The change in resistance of the thermistor with time is recorded. When the change in resistance of the thermistor with time has been constant for several minutes the calibration heater is switched on. The current through the heater, I_h, the voltage across the heater, V_h, and the time of the heating, t, are recorded. The heater is then switched off and the change in resistance of the thermistor with time is again recorded.

The resistance changes due to the titration and the electrical calibration are calculated by standard methods (Vanderzee, 1981). The ratio of these resistance changes is equal to the ratio of the energy changes associated with the two processes. Since the electrical energy of the calibration, Q_c, is known (from $Q_c = I_h V_h t$), the energy associated with the titration can be calculated.

When the electrical calibration is finished the mixture in the reaction vessel is heated (or cooled) until the resistance of the thermistor is ~4 Ω above the resistance corresponding to the temperature of the water bath. The calorimetric experimental process (titration followed by calibration) is then repeated. The number of repetitions is limited only by the capacity of the reaction vessel. By this method several calorimetric experiments can be performed without changing the starting mixture in the reaction vessel.

In this work we have measured the heat associated with adding a known volume of cyclohexane to mixtures of chloroform, triethylamine, and cyclohexane. Experiments were performed with two types of mixture in the reaction vessel. The first type of mixture contained concentrated chloroform + triethylamine with a maximum mole fraction of cyclohexane of 0.0971. The second type of mixture contained dilute chloroform + triethylamine with a minimum mole fraction of cyclohexane of 0.7345. For both types of mixture three ratios of chloroform to triethylamine were investigated: 3:1, 1:1, and 1:3. There were, therefore, six different starting mixtures, three concentrated and three dilute.

For each of the concentrated mixtures six additions of approximately 5 cm^3 of cyclohexane were made and the heat associated with each of these additions was measured. For the dilute mixtures the heat associated with each of four additions of 25 cm^3 of cyclohexane was measured.

Chloroform (Caledon) was purified and stored as described in Chapter 2. Triethylamine (Fluka) was refluxed for 2 hours over potassium hydroxide pellets and then distilled from the potassium hydroxide. The middle fraction of this distillation was collected and redistilled. The middle fraction was again collected and was stored under nitrogen. Cyclohexane (Caledon) was dried over molecular sieve (4A), distilled, and stored under nitrogen.

Results and Analysis

The results of the calorimetric measurements described in the preceding section are given in Table 3-2 (concentrated mixtures) and Table 3-3 (dilute mixtures). Both tables list results of three sets of measurements, each set corresponding to a different ratio of chloroform to triethylamine. For each set of measurements the stoichiometric amounts of chloroform and triethylamine are invariant and are given above the results to which they relate. The first two columns of Tables 3-2 and 3-3 list the amount of cyclohexane in the reaction vessel before an experiment and the amount of cyclohexane added during the experiment. The third columns list the heat absorbed when this amount of cyclohexane is introduced to the reaction vessel. The uncertainty in these measured heats is estimated to be less than 2%.

The fourth columns of Tables 3-2 and 3-3 list the heat arising from complex

Table 3-2. Heats measured on addition of a known amount of cyclohexane to concentrated mixtures of (chloroform + triethylamine) in cyclohexane.

$n(C_6H_{12})^a$/mol	$n(C_6H_{12})^b$/mol added	Q_{meas}/J	Q_{diss}/J
	$n(CHCl_3)^c = 2.5048$ mol	$n(TEA)^c = 0.8405$ mol	
0.0000	0.0463	113.472	49.780
0.0463	0.0463	111.203	49.460
0.0926	0.0463	109.213	49.326
0.1389	0.0463	107.199	49.081
0.1852	0.0463	105.151	48.721
0.2314	0.0509	113.403	53.130
	$n(CHCl_3)^c = 1.4192$ mol	$n(TEA)^c = 1.3928$ mol	
0.0000	0.0417	108.485	88.305
0.0417	0.0509	129.165	105.086
0.0926	0.0463	115.064	93.976
0.1389	0.0463	112.105	91.658
0.1852	0.0509	120.895	99.015
0.2361	0.0417	97.633	80.396
	$n(CHCl_3)^c = 0.6468$ mol	$n(TEA)^c = 1.9351$ mol	
0.0000	0.0463	75.715	49.158
0.0463	0.0463	74.313	48.769
0.0926	0.0463	72.459	47.867
0.1389	0.0463	71.120	47.425
0.1852	0.0463	69.747	46.896
0.2314	0.0463	68.601	46.548

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[a] Moles of cyclohexane in reaction vessel before experiment.

[b] Moles of cyclohexane added during experiment.

[c] Stoichiometric amount of chloroform ($CHCl_3$) and triethylamine (TEA) in reaction vessel for each set of experiments.

Table 3-3. Heats measured on addition of a known amount of cyclohexane to dilute mixtures of (chloroform + triethylamine) in cyclohexane.

$n(C_6H_{12})^a$/mol	$n(C_6H_{12})^b$/mol added	Q_{meas}/J	Q_{diss}/J
	$n(CHCl_3)^c$ = 0.4261 mol	$n(TEA)^c$ = 0.1566 mol	
1.8953	0.2314	69.103	46.437
2.1268	0.2314	60.877	41.482
2.3582	0.2314	53.808	37.014
2.5896	0.2314	47.857	33.168
	$n(CHCl_3)^c$ = 0.2598 mol	$n(TEA)^c$ = 0.2530 mol	
1.9103	0.2314	64.112	51.529
2.1417	0.2314	55.921	45.129
2.3732	0.2314	48.999	39.636
2.6046	0.2314	43.083	34.879
	$n(CHCl_3)^c$ = 0.1566 mol	$n(TEA)^c$ = 0.4610 mol	
1.7089	0.2314	64.024	49.350
1.9403	0.2314	56.329	43.850
2.1718	0.2314	49.694	38.945
2.4032	0.2314	44.037	34.676

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[a] Amount of cyclohexane in reaction vessel before experiment.

[b] Amount of cyclohexane added during experiment.

[c] Stoichiometric amount of chloroform ($CHCl_3$) and triethylamine (TEA) in reaction vessel for each set of experiments.

dissociation. The heat of complex dissociation was calculated by subtracting the heat due to chloroform + cyclohexane interactions, $Q(CHCl_3/C_6H_{12})$, and the heat due to triethylamine + cyclohexane interactions, $Q(TEA/C_6H_{12})$, from the measured heat:

[3-9] $Q_{diss} = Q_{meas} - Q(CHCl_3/C_6H_{12}) - Q(TEA/C_6H_{12})$

That the interactions of cyclohexane with chloroform and with triethylamine make significant contributions to the measured heat is consistent with treatment of the chloroform + triethylamine system by the ideal associated solution model. Although the model assumes that all physical contributions to the deviations from ideality are negligible, this assumption applies only to those species involved in association. The model contains no requirement that other species (e.g., "inert" solvent) be treated in any particular way. Therefore, we must evaluate the contributions to the measured heat arising from chloroform + cyclohexane and triethylamine + cyclohexane interactions from separate experiments. These contributions can then be subtracted from the measured heat to obtain the heat due to complex dissociation as described by equation [3-9].

The last two terms in equation [3-9] were evaluated for each experiment from equations of the form

[3-10] $Q(J/S) = [2z_J z_S \Delta H^{\theta}(J/S)](n_J + n_S)$ $\quad J = CHCl_3$ or TEA, $S = C_6H_{12}$

where $\Delta H^{\theta}(J/S)$ represents the binary interaction enthalpy of J with cyclohexane. The equilibrium mole fraction (z_i) and equilibrium amount (n_i) of each species was found using the method described in the second section of this Chapter. A value of K = 2.6 for the equilibrium constant of association between chloroform and triethylamine as determined by Hepler et al. (1985) from studies of the binary (no inert solvent) chloroform + triethylamine system was used in the speciation calculations. A value of $\Delta H^{\theta}(CHCl_3/C_6H_{12})$ = 1.40 kJ mol^{-1} was found by fitting an equation of the type represented by equation [3-10] to the data of Findlay, Keniry, Kidman, and Pickles (1967) for the excess heats of the chloroform + cyclohexane system. A similar fit to the data of Murakami and Fujishiro (1966) for excess heats of mixing in the triethylamine + cyclohexane system led to a value of 0.55 kJ mol^{-1} for $\Delta H^{\theta}(TEA/C_6H_{12})$. The maximum residual in the fit to the chloroform + cyclohexane data was 26 J mol^{-1} while the maximum residual in the fit to the triethylamine + cyclohexane data was 33 J mol^{-1}.

The enthalpy of complex dissociation was calculated by dividing the heat of dissociation from an experiment by the amount of complex dissociated, n_{diss}, during that experiment:

[3-11] $\Delta H_{diss} = Q_{diss}/n_{diss}$

The amount of complex dissociated is the difference in amount of complex before and after an experiment:

[3-12] $n_{diss} = n_{AB}(\text{before}) - n_{AB}(\text{after})$

We estimate the uncertainty in our enthalpies of complex dissociation to be around 3%.

For each set of experiments the values of ΔH_{diss} were averaged and these average enthalpies of complex dissociation together with the standard deviations of the averages are given in Table 3-4.

Earlier work (Hepler and Fenby,1973) has shown that it is possible to apply the ideal associated solution model to the results of measurements of excess enthalpies to evaluate simultaneously the equilibrium constant and the standard enthalpy of association reactions. In principle the calorimetric results presented in this Chapter could be treated in a similar way. We could then compare the values of <u>both</u> the association equilibrium constant and the standard enthalpy of association for chloroform + triethylamine with the values determined by other workers. In practice, analysis of our calorimetric results in this manner is complicated by the need for corrections due to chloroform/cyclohexane and triethylamine/cyclohexane interactions and leads to large uncertainties in the values of K and ΔH^{θ}. We have, therefore, chosen to assume that the value of K = 2.6 (Hepler et al., 1985) is correct and to calculate the molar enthalpy of association as described above.

Discussion

Table 3-4 shows that the values of the molar enthalpy of chloroform-triethylamine complex dissociation determined in this work are independent of both the ratio of chloroform to triethylamine and the amount of

Table 3-4. Molar enthalpies of dissociation of the complex formed between chloroform and triethylamine.

	$n(CHCl_3)/n(TEA)^a$	$\Delta H^{\theta\ b}$/kJ mol^{-1}	$\pm\sigma^c$/kJ mol^{-1}
concentrated solutions	3/1	16.59	0.25
	1/1	17.34	0.18
	1/3	16.39	0.19
dilute solutions	3/1	16.47	0.08
	1/1	16.95	0.16
	1/3	16.34	0.07

[a] Approximate molar ratio of chloroform ($CHCl_3$) to triethylamine (TEA).

[b] Average molar enthalpy of complex dissociation, based on six experiments for concentrated solutions and four experiments for dilute solutions.

[c] One standard deviation of the set of enthalpies from the listed average enthalpy.

cyclohexane in the mixture within the uncertainties of the calculations and the measurements. Our average value of the average enthalpy of complex dissociation is $\Delta H^{\theta} = 16.7 \pm 0.6$ kJ mol^{-1}. The magnitude of this average enthalpy is in excellent agreement with the value of -17.0 ± 0.5 kJ mol^{-1} that Hepler et al. (1985) obtained for the enthalpy of complex association in the binary (no solvent) chloroform + triethylamine system from results of calorimetric experiments and the ideal associated solution model. This agreement shows that the same thermodynamic quantities ($\Delta H_{diss} = 17$ kJ mol^{-1}, $K = 2\ 6$) can be used to describe the chloroform + triethylamine system both as a pure binary system and as a binary system dissolved in cyclohexane (and by inference, other "inert" solvents). We therefore conclude that the ideal associated solution model can provide a useful approach to the analysis of data for A + B = AB systems when these systems are dissolved in some inert solvent.

That the model can provide a good approximation to associated systems in dilute solutions in an "inert" solvent is fortunate because there exists a large body of spectroscopic work in which dilute solutions of associated systems have been studied. The results of these studies are almost always analysed according to the ideal associated solution model. That is, it is assumed that physical interactions between the components are unimportant compared with the chemical interactions. A second assumption is then usually made: the thermodynamic properties of associated systems in dilute solution are the same as those that would be observed in binary mixtures (A + B = AB, no solvent). In this Chapter we have shown that, at least in the case of chloroform + triethylamine in cyclohexane, both assumptions are justified. Further experimentation is necessary to investigate whether these assumptions are valid in general or are valid only for certain specific cases.

CHAPTER 4

Complex Formation between Dissolved Gas and Solvent: Association Equilibrium Constants and Henry's Law Constants. Application to Chloroform + Ammonia

Introduction

Chapters 2 and 3 and the studies of other workers show that the ideal associated solution model can be applied successfully to many associated systems (A + B = AB) in which the A and B are liquids. This success raises the possibility that the model may be useful in the investigation of systems in which a dissolved gas, B, interacts chemically with the solvent, A, to form an associated complex, AB. In this case the solubility of the gas (and hence the equilibrium speciation of the system) is determined by both the liquid-vapour equilibrium and the association (in the liquid phase) equilibrium. The liquid-vapour equilibrium represents the physical process of dissolution of gas. For a dilute solution this process can be described by Henry's law. The association equilibrium represents the chemical interaction that results in the formation of complex. As we have seen earlier, this type of chemical interaction can be approximated by the ideal associated solution model if the complex is sufficiently stable (see Chapter 2).

In this Chapter we present a method based on the ideal associated solution model, in which data collected in investigations of gas solubility can be used to evaluate the equilibrium constant and the Henry's law constant for any system in which a stable 1:1 complex forms between the gas and the solvent. We illustrate the use of this method by applying it to results of our measurements of the solubilities of ammonia in chloroform at three temperatures and several pressures.

Derivation of Equations

Consider a system in which a gas B is dissolved in a solvent A and a complex forms between the gas and the solvent according to the equilibrium

[4-1] $A + B = AB$

The gas molecules in solution exist either as dissolved B or as the complex AB. Therefore, the solubility of the gas depends on the Henry's law constant, k_H, for the system and on the equilibrium constant, K, for reaction [4-1]. The solubility of a gas in a solvent can be determined experimentally. In this section we derive a relationship between this experimental quantity and the two constants (K and k_H) using the ideal associated solution model.

Assuming that the ideal associated solution model is a valid approximation to the system (i.e., assuming that the system is an ideal solution of A + B + AB), we can express the association equilibrium constant in terms of the equilibrium mole fractions, z_i, as in Chapters 2 and 3:

[4-2] $K = z_{AB}/z_A z_B$

From mass balance considerations for an A + B ⇌ AB system (discussed in Chapter 2) we can rewrite equation [4-2] in terms of the extent of association, r, and the stoichiometric mole fraction (mole fraction solubility) of B, x_B:

[4-3] $K = r(1 - r)/[x_B(1 - x_B) - r + r^2]$

The mass balance also shows (see Appendix A) that

[4-4] $r = (x_B - z_B)/(1 - z_B)$

Substitution of this expression for r into equation [4-3] yields

[4-5] $K = (x_B - z_B)/[z_B(1 - 2x_B + z_B x_B)]$

Equation [4-5] expresses the equilibrium constant for process [4-1] in terms of the mole fraction solubility of B in A and the mole fraction of unassociated B in the solution at equilibrium.

Now we write Henry's law (in terms of the equilibrium mole fraction of B) as

[4-6] $p_B = k_H z_B$

where p_B represents the partial pressure of gas above the solution and k_H represents Henry's law constant. Combination of equations [4-5] and [4-6] leads to

[4-7] $K = (k_H x_B - p_B)/[p_B(1 - 2x_B + p_B x_B/k_H)]$

Equation [4-7] contains two unknowns, K and k_H, and cannot be rearranged to obtain a function that is linear in p_B and x_B. In order to evaluate the two constants from equation [4-7] we must employ an iterative method. Note also that if no association occurs then $K = 0$ and $z_B = x_B$ and equation [4-7] reduces to the usual form of Henry's law ($p_B = k_Hx_B$).

A first estimate of k_H can be obtained by ignoring the last term in the denominator of the right-hand side of equation [4-7]. Remembering that $p_Bx_B/k_H = z_Bx_B$ (equation [4-6]), the neglect of this term is equivalent to saying that $1 - 2x_B + z_Bx_B = 1 - 2x_B$. That this is reasonable (at least as a first approximation) can be seen by considering the relative magnitudes of x_B and z_B. Due to the association equilibrium some B is converted to AB and hence $z_B < x_B$. Also $x_B < 1$ and so $z_Bx_B < 2x_B$. The resulting approximate version of equation [4-7] is

[4-8] $K \sim (k_Hx_B - p_B)/[p_B(1 - 2x_B)]$

If the associated complex is strong (K is relatively large) then $z_B << x_B$ and hence $z_Bx_B << 2x_B$. Thus the accuracy of equation [4-8] is best when the complex is stable (large K). Rearrangement of equation [4-8] yields

[4-9] $x_B/p_B \sim 1/k_H + (1 - 2x_B)K/k_H$

Equation [4-9] indicates that the intercept of a plot of x_B/p_B against $(1 - 2x_B)$ will be approximately equal to the reciprocal of k_H. Substituting this first estimate of k_H in equation [4-7] allows the value of the equilibrium constant to be calculated at each partial pressure of gas. Since the association equilibrium constant should be independent of the composition of the solution, the estimate of

Henry's law constant is then adjusted in such a way as to reduce the variation of the equilibrium constant with composition. The final values of the constant are taken to be the values which correspond to the least variation of the equilibrium constant.

Evaluation of the equilibrium constant and Henry's law constant for a particular chemical system by application of the method described above requires experimental determination of the solubility of the gas in the solvent at a number of gas partial pressures. Only the total pressure of gas can be measured directly. If the vapour pressure of the solvent is negligible, then the partial pressure of the gas is equal to the total pressure and the data can be treated directly to yield the two constants. If the vapour pressure of the solvent is appreciable, then the contribution of this pressure to the total pressure must be taken into account. One method of accounting for the solvent vapour pressure, using an iterative procedure, is described in Appendix B.

Experimental

Chloroform (Caledon Lab Ltd.) was purified and stored as described in Chapter 2. Ammonia (Medigas Ltd.) was used without further purification.

The measurements of gas solubility were made using an isobaric equilibrium solubility method and apparatus similar to that previously described by Morrison and Billett (1948) and Hayduk, Walter, and Simpson (1972). In this method a known amount of solvent is injected in a thin film into apparatus containing a known pressure of gas. As the gas dissolves in the solvent, a constant pressure is maintained inside the apparatus by addition (or removal) of a known volume of mercury. The amount of gas dissolved is then calculated from the change in gas volume, using an equation of state for the gas. The experimental quantities measured in this technique are the mass of solvent injected, m_A, the mass of mercury added to maintain the system at constant pressure, m_{Hg}, and the total pressure, P_t. Further details of the design and operation of this apparatus are given by Singh (1987) and Yan, Zhang, Singh, and Hepler (manuscript in preparation).

The experimental quantities, m_A and m_{Hg}, were measured for the chloroform + ammonia system at 298.15 K, 303.15 K and 308.15 K over a pressure range of 80-300 kPa. Three values of m_A and m_{Hg} were measured at each temperature and pressure.

Pycnometers were used to measure the density of chloroform and values of 1.4793 g cm^{-3} at 298.15 K, 1.4733 g cm^{-3} at 303.15 K and 1.4679 g cm^{-3} at 308.15 K were obtained.

The method and apparatus described in Chapter 7 were used to obtain a value of 30.3 cm^3 mol^{-1} for the partial molar volume of ammonia in chloroform at infinite dilution.

Results and Discussion

Since the vapour pressure of chloroform at 298 K is 26 kPa, the solvent makes a significant contribution to the measured total pressure at all of the temperatures and pressures investigated. For each estimate of Henry's law constant a consistent set of (K, p_B, x_B) values was found using the method described in Appendix B. Values of the second virial coefficient of ammonia were obtained by interpolation based on data compiled by Dymond and Smith (1980). Vapour pressures of pure chloroform of 26.220 kPa at 298.15 K, 32.329 kPa at 303.15 K, and 39.542 kPa at 308.15 K were taken from the compilation of Smith and Srivastava (1986). During each iteration the value of x_B at a particular total pressure was taken to be the mean of three x_B values calculated from the three replicate measurements of m_A and m_{Hg} at that total pressure. The maximum number of iterations required to obtain a consistent set of (K, p_B, x_B) values was four. The values of the equilibrium constant were then averaged and the standard deviation was calculated. A new value of Henry's law constant was chosen, and a new set of (K, p_B, x_B) values consistent with this new value of k_H was calculated. The process was repeated until the standard deviation of the equilibrium constant had been minimised. The average value of K and the value of k_H corresponding to this minimum in the standard deviation were taken to be the "best" values of the association equilibrium constant and the Henry's law constant for the chloroform +

ammonia system. The values of these constants at each of the temperatures investigated are listed in Table 4-1. The values of the partial pressure of ammonia and the stoichiometric mole fraction solubility of ammonia (consistent with our best values of K and k_H) for each of our experiments are listed in Table 4-2.

No published reports of the equilibrium constant for the formation of chloroform-ammonia complex are available for comparison with our results. Thus, we cannot yet examine quantitatively the use of the ideal associated solution model as a tool for investigating complex formation between dissolved gas and solvent. Qualitatively, our results are consistent with the expected strength of chloroform-ammonia association as we now show.

Ammonia is generally considered to be a weaker base than triethylamine (due to the positive inductive effect of the ethyl group) and a stronger base than benzene. We therefore expect the chloroform-ammonia complex to be less stable than the chloroform-triethylamine complex and more stable than the chloroform-benzene complex. On this basis we predict that the association equilibrium constant for chloroform + ammonia should be smaller than that for chloroform + triethylamine (K = 2.6 at 298 K; Hepler, Kooner, Roux-Desgranges, and Grolier, 1985) and larger than that for chloroform + benzene (K = 0.45 at 298 K; Chapter 2). We have found, using the ideal associated solution model, that the chloroform + ammonia association equilibrium constant has a value of K = 0.58 at 298 K (see Table 4-1). This value is intermediate between K = 2.6 and K= 0.45 and thus is consistent

Table 4-1. Values of K and k_H for chloroform + ammonia.

T/K	K	$\pm \sigma^a$	k_H/MPa	$\pm \sigma^a$/MPa
298.15	0.58	0.04	1.04	0.04
303.15	0.50	0.04	1.15	0.04
308.15	0.62	0.02	1.39	0.05

[a] Standard deviation at the 95% confidence level.

Table 4-2. Partial pressure (p_B) and stoichiometric mole fraction solubility (x_B) of ammonia in chloroform at total pressure (P_t).

P_t/kPa	p_B/kPa	x_B
	T = 298.15 K	
300.21	283.67	0.336
227.85	209.10	0.263
186.29	166.07	0.214
159.21	138.24	0.188
134.51	112.44	0.151
130.91	108.96	0.152
111.95	89.06	0.122
103.86	80.74	0.114
95.36	71.83	0.099
	T = 303.15 K	
287.97	265.79	0.291
271.41	248.39	0.268
226.77	202.11	0.223
171.58	144.90	0.166
160.73	133.86	0.161
136.99	109.05	0.130
118.29	89.65	0.110
82.06	51.86	0.065

Table 4-2 continued.

P_t/kPa	p_B/kPa	x_B
	T = 308.15 K	
292.53	263.81	0.253
293.33	208.62	0.208
188.24	155.29	0.158
146.54	111.98	0.121
122.41	86.67	0.093
98.43	61.65	0.068

with our prediction. Further studies (possibly spectroscopic) are necessary to investigate the accuracy of association equilibrium constants determined using the method described in this Chapter.

Combining our values of K and k_H with a rearranged version of equation [4-7], we calculate the mole fraction solubility of ammonia in chloroform at 298.15 K and a partial pressure of ammonia of 101.325 kPa to be 0.139. This is in excellent agreement with the value of 0.141 obtained by extrapolation of the results of Seward (1932) at 298.2 K to a partial pressure of ammonia of 101.325 kPa .

Matsui, Hepler, and Fenby (1973) showed that in a dilute solution of B in A (where A and B associate according to the A + B = AB) the equilibrium amount of B (n_B) is related to the stoichiometric amount of B (N_B) by

[4-10] $n_B = [K/(K + 1)]N_B$

where K represents the association equilibrium constant. Substitution of our value of $K_{298} = 0.58$ into equation [4-10] we calculate that in a dilute solution of ammonia in chloroform 63% of the ammonia is in the uncomplexed form and 37% is in the complexed form.

The analysis of the chloroform + ammonia system presented in this paper is based on the premise that a 1:1 associated complex forms between the two components. That this is a reasonable proposal is seen by comparing the solubility of ammonia in chloroform with that of ammonia in carbon tetrachloride. The mole fraction solubility of ammonia in carbon tetrachloride is

0.0281 at 293.2 K and a partial pressure of ammonia equal to 101.325 kPa (IUPAC Solubility Data Series, 1985; Bell, 1931). We would expect a slightly smaller value at 298.15 K. The much larger solubility of ammonia in chloroform than in carbon tetrachloride indicates that interactions other than dissolution occur in the chloroform + ammonia system. Since chloroform (unlike carbon tetrachloride) has the capacity to form hydrogen bonds with ammonia, we attribute the high solubility of ammonia in chloroform to the formation of hydrogen bonds between the two components.

The enthalpy of solution of ammonia in chloroform can be separated into a contribution from dissolution (no complex formation) and a contribution from formation of the complex. The contribution from the dissolution process, ΔH^{θ}_{d}, can be obtained from the temperature dependence of Henry's law constant, $(\partial \ln k_H/\partial T)_p = \Delta H^{\theta}_{d}/RT^2$. Using this equation and the values of k_H listed in Table 4-1, we calculate a value of $\Delta H^{\theta}_{d} = -22.2$ kJ mol^{-1}. Over the temperature range of our investigations the relative uncertainties in the association equilibrium constant are too large for the van't Hoff equation, $(\partial \ln K/\partial T)_p = \Delta H^{\theta}/RT^2$, to yield reliable values of ΔH^{θ} for the formation of the chloroform-ammonia complex.

We have shown that our combination of Henry's law and the ideal associated solution model leads to values of the association equilibrium constant which are in qualitative agreement with values predicted from basic chemical principles. Furthermore, our values of the association equilibrium constant and Henry's law constant lead to [illegible] value [illegible] solubility of ammonia in chloroform at 298.15 K and a partial pressure of ammonia of 101.325 kPa that is within 2% of the literature value. These agreements are good evidence that the model (combined with Henry's law) provides reliable results for systems in which a dissolved gas and solvent interact chemically.

CHAPTER 5

Extension of the Ideal Associated Solution Model. Application of Solubility Parameter Theory to Estimation of Physical Contributions to Non-Ideality.

Introduction

In earlier chapters it has been demonstrated that the ideal associated solution model can be applied successfully to a variety of real systems in which there are association equilibria of the type A + B = AB. However, the model does not give an exact description of any system. For example, the true standard state thermodynamic properties (K, ΔH^{θ}, ΔC_p^{θ}, ΔS^{θ}, and ΔV^{θ}) of an association reaction should be independent of composition. The properties calculated using the ideal associated solution model (model properties) always exhibit some variation with composition. When the complex species (AB) is weakly associated this variation may be so large, relative to the values of the properties, that the model no longer provides a useful approximation (see Chapter 2).

The variation of the model thermodynamic properties with composition arises from the basic assumption of the model: the physical contributions to the deviations from ideality in an associated system are negligible with respect to the chemical contributions (see Chapter 1). Therefore, model properties account only for the chemical contributions. Although the physical contributions to non-ideality are small for many associated systems, they are always finite and may be significant. Furthermore, the physical contributions are composition dependent. The true standard state thermodynamic properties are given by the sum of the chemical and physical contributions. Therefore, since the true thermodynamic properties are constant with composition and the physical contributions are composition dependent, the chemical contributions must also be (at least slightly) composition dependent. For associated systems in which the effect of chemical interactions (association) are large compared to the effect of physical interactions, the variation of the chemical contributions with composition is relatively unimportant and the model is a good approximation. When neither contribution is dominant over the other, the ideal associated solution model does not provide a good approximation and we expect to observe a relatively large variation of the model thermodynamic properties with composition.

The problem to be discussed in this Chapter is how do we treat associated systems in which the physical contributions to non-ideality are important. As we have already seen, the composition dependence of the physical contributions is reflected in a composition dependence of the chemical contributions. We can further say that since the sum of the chemical and physical contributions (as expressed in terms of ΔG^{θ}, ΔH^{θ} etc. for the association equilibrium under consideration) is constant, the variation with composition of the physical contributions should be equal in magnitude and opposite in sign to that observed for the chemical contributions. This information can be combined with an appropriate theory of activity coefficients (measures of physical interactions) to obtain a quantitative assessment of the contribution of physical interactions between the components (A, B, and AB) to the non-ideality of an associated system.

Using the above argument, we have developed an extension of the ideal associated solution model; this extension allows the activity coefficients of an associated system to be evaluated. We have used a theory of activity coefficients based on solubility parameter theory, but we emphasise that any appropriate one-parameter theory could be used without altering the principles of the method. Pure component standard states have been chosen for A, B, and AB . This choice was convenient because the method requires the results of experiments conducted across the entire composition range and is also consistent with usual practice in analysing many properties of binary mixtures (no solvent).

We have applied our extended ideal associated solution model to an evaluation of the activity coefficients and thence to evaluation of the thermodynamic equilibrium constant for the chloroform + triethylamine system at 283.14 K and 298.15 K. Many workers have shown that 1:1 complex formation is the only important chemical interaction in this system (Howard, Jumper, and Emerson, 1963; Stapleton, Bellay, Wulff, and Hepler, 1966; Wiley and Miller, 1972). Application of the ideal associated solution model to chloroform + triethylamine has shown that physical interactions make a small but significant contribution to the observed non-ideality (Hepler, Kooner, Roux-Desgranges, and Grolier, 1985). Due to the large difference in the cohesive energy densities of chloroform and triethylamine, we expect that solubility parameter theory may well account for the physical contributions to non-ideality.

Previously, Bertrand (1975) and Fenby, Chand, Inglese, Grolier, and Kehiaian (1977) have improved the ideal associated solution model by combining the model with solubility parameter theory. These workers then applied their improved ideal associated solution models to chloroform + triethylamine. The advantages of our extended ideal associated solution model over these improved models are discussed. Comparison is made between values of the association equilibrium constant for chloroform + triethylamine at 298.15 K obtained using the ideal associated solution model (no improvements or extensions), the improved versions of the model proposed by Bertrand and Fenby et al., and our new, extended ideal associated solution model.

Derivation of Equations

Relationship between Activity Coefficients and Equilibrium Constant

The thermodynamic equilibrium constant, K^o, for the association reaction

[5-1] $A + B = AB$

can be expressed in terms of activities, a_i:

[5-2] $K^o = a_{AB}/a_A a_B$

Equation [5-2] can also be written as

[5-3] $K^o = (z_{AB}/z_A z_B)(\gamma_{AB}/\gamma_A \gamma_B)$

where z_i represents the equilibrium mole fraction of species i and γ_i represents the activity coefficient of species i.

In the ideal associated solution model all activity coefficients are unity (see Chapter 1). If we let K_z represent the equilibrium constant determined using the model then

[5-4] $K_z = z_{AB}/z_A z_B$

In earlier Chapters we have used the symbol K (instead of K_z) to represent the ideal associated solution model equilibrium constant. In this Chapter we are examining the relationship between the thermodynamic equilibrium constant, K^o, and the model equilibrium constant. The subscript z on our symbol for the latter emphasises that the model equilibrium constant is determined solely by the equilibrium speciation in the associated solution (equation [5-4]).

Substituting equation [5-4] into equation [5-3] we can relate the thermodynamic equilibrium constant to the model equilibrium constant and the ratio of activity coefficients:

[5-5] $K^o = K_z (\gamma_{AB}/\gamma_A \gamma_B)$

Taking logarithms of both sides of equation [5-5] we obtain

[5-6] $\ln K^o = \ln K_z + \ln(\gamma_{AB}/\gamma_A \gamma_B)$

Equation [5-6] shows that the logarithm of the thermodynamic equilibrium constant can be separated into a "chemical" contribution and a "physical" contribution. The chemical contribution arises from the association process [5-1] which results in the redistribution of A and B in the solution. This chemical contribution is represented in equation [5-6] by $\ln K_z$ (the logarithm of the ideal associated solution model equilibrium constant). The physical contribution to $\ln K^o$ arises from all interactions between A, B, and AB molecules other than that represented by process [5-1]. This physical contribution is represented in equation [5-6] by the logarithm of the ratio of activity coefficients. That the contributions to the thermodynamic equilibrium constant can be separated in this way suggests that we can use knowledge of the model equilibrium constant (K_z) together with an appropriate theory of activity coefficients to obtain values of the thermodynamic equilibrium constant (K^o).

Since we have adopted pure component standard states for A and B, we know that in pure A (and "nearly" pure A) the activity coefficient of A is unity and that in pure B (and "nearly" pure B) the activity coefficient of B is unity. If we let P be the point on the composition surface corresponding to pure A and R be the point corresponding to pure B, then $\gamma_A(P) = 1 = \gamma_B(R)$. We can use this information in equation [5-6] to write simplified expressions for the themodynamic equilibrium constant at P and R:

[5-7] $\ln K^{o}(P) = \ln K_z(P) + \ln\gamma_{AB}(P) - \ln\gamma_B(P)$

[5-8] $\ln K^{o}(R) = \ln K_z(R) + \ln\gamma_{AB}(R) - \ln\gamma_A(R)$

Because the thermodynamic equilibrium constant is independent of composition, $K^{o}(P) = K^{o}(R)$, we equate the right-hand sides of equations [5-7] and [5-8] and rearrange to obtain

[5-9] $\ln K_z(P) - \ln K_z(R) = \ln\gamma_{AB}(R) + \ln\gamma_B(P) - \ln\gamma_{AB}(P) - \ln\gamma_A(R)$

This equation specifies the relationship between the activity coefficients at pure A and pure B in terms of the model equilibrium constant at these endpoints.

A method for evaluating model equilibrium constants from vapour pressure measurements is described in Appendix A. The general principles of this method can also be applied to the results of spectroscopic experiments to obtain values of the model equilibrium constant. Here we confine ourselves to a discussion of model equilibrium constants calculated from vapour pressure results. If the vapour pressure above the associated system has been measured over the entire composition range (i.e., stoichiometric mole fraction of A ranging from close to 1.0 to close to 0.0), then the model equilibrium constant can be calculated over this same range of composition. The results can then be expressed by a polynomial:

[5-10] $\ln K_z = \ln K_z(R) + f(z_A)$

The only restriction on $f(z_A)$ is that $f(z_A) = 0$ at $z_A = 0$ (point R). Evaluation of equation [5-10] at $z_A = 1$ (point P) and $z_A = 0$ (point R) yields $\ln K_z(P)$ and

$\ln K_z(R)$, respectively. In this way the term $\ln K_z(P) - \ln K_z(R)$ on the left hand side of equation [5-9] can be calculated.

Solubilty Parameter Theory

In order to proceed further some theory of activity coefficients must be introduced. We have chosen to use solubility parameter theory (Hildebrand and Scott, 1962). In solubility parameter theory the molar excess Gibbs free energy, G^E, of a binary liquid mixture (A + B) is given by

[5-11] $G^E = (z_A V_A + z_B V_B)(\delta_A - \delta_B)^2 \phi_A \phi_B$

where z_i represents the equilibrium mole fraction of species i, V_i represents the molar volume of species i, δ_i represents the solubility parameter of species i, and ϕ_i represents the volume fraction of species i. The solubility parameter of i is related to the molar energy of vapourisation of i, ΔU_i^{vap}, and the molar volume of i:

[5-12] $\delta_i = (\Delta U_i^{vap}/V_i)^{0.5}$

The volume fraction of i is defined by the expression

[5-13] $\phi_i = (z_i V_i)/(\Sigma z_j V_j)$

In the case where components A and B interact chemically to form a 1:1 associated species AB we can consider the mixture to be a three component mixture of A, B, and AB. There are three types of binary interactions in this ternary mixture; A + B interactions, A + AB interactions, and B + AB interactions. We can, therefore, express the excess Gibbs free energy of the mixture as the sum of three terms. Each term accounts for one type of binary interaction and has the form of equation [5-11]. The excess Gibbs free energy of the three component mixture is given by

[5-14] $G^E = (z_A V_A + z_B V_B + z_{AB} V_{AB})(J_{A,B}\,\phi_A \phi_B + J_{A,AB}\,\phi_A \phi_{AB} + J_{B,AB}\,\phi_B \phi_{AB})$

where

[5-15] $J_{i,j} = (\delta_i - \delta_j)^2$

The excess Gibbs free energy is also related to the activity coefficients of the components of the mixture, γ_i, by the thermodynamic equation

[5-16] $G^E = RT(z_A \ln\gamma_A + z_B \ln\gamma_B + z_{AB} \ln\gamma_{AB})$

Here R represents the gas constant and T represents the temperature. Taking the derivative of equation [5-16] with respect to the amount of component i in the mixture, n_i, we obtain the standard expression for the partial molar excess Gibbs free energy of i, $G^E{}_i$

[5-17] $(\partial G^E/\partial n_i)_{n,T,p} = G^E{}_i = RT\ln\gamma_i$

Taking the derivative of equation [5-14] with respect to n_A we obtain the solubility parameter expression for the partial molar excess Gibbs free energy of A in the ternary mixture:

[5-18] $G^E{}_A = V_A[J_{A,B}\,\phi_B{}^2 + (J_{A,B} + J_{A,AB} - J_{B,AB})\phi_B \phi_{AB} + J_{A,AB}\,\phi_{AB}{}^2]$

Similar differentiation of equation [5-14] with respect to n_B and n_{AB} yields

$$[5\text{-}19] \quad G^E{}_B = V_B[J_{A,B}\ \phi_A{}^2 + (\ J_{A,B} + J_{B,AB} - J_{A,AB})\phi_A\phi_{AB} + J_{B,AB}\ \phi_{AB}{}^2]$$

and

$$[5\text{-}20] \quad G^E{}_{AB} = V_{AB}[J_{A,AB}\ \phi_A{}^2 + (\ J_{A,AB} + J_{B,AB} - J_{A,B})\phi_A\phi_B + J_{B,AB}\ \phi_B{}^2]$$

respectively. Equating the expressions for the partial molar excess Gibbs free energies of A, B, and AB given by equation [5-17] with those given by equation [5-18], [5-19], and [5-20] we obtain the solubility parameter expressions for the activity coefficients in an associated mixture:

$$\ln\gamma_A = (V_A/RT)\left[J_{A,B}\,\phi_B{}^2 + (J_{A,B} + J_{A,AB} - J_{B,AB})\phi_B\phi_{AB} + J_{A,AB}\,\phi_{AB}{}^2\right]$$

$$[5\text{-}21] \quad \ln\gamma_B = (V_B/RT)\left[J_{A,B}\,\phi_A{}^2 + (J_{A,B} + J_{B,AB} - J_{A,AB})\phi_A\phi_{AB} + J_{B,AB}\,\phi_{AB}{}^2\right]$$

$$\ln\gamma_{AB} = (V_{AB}/RT)\left[J_{A,AB}\,\phi_A{}^2 + (J_{A,AB} + J_{B,AB} - J_{A,B})\phi_A\phi_B + J_{B,AB}\,\phi_B{}^2\right]$$

At any composition the values of the activity coefficients of all species are given by this theory, provided that the solubility parameter and the molar volume of each species is known.

For components which can exist in the pure state (A and B in this case) the solubility parameter is given by equation [5-12]

$$[5\text{-}14] \quad \delta = (\Delta U_i{}^{vap}/V_i)^{0.5}$$

where $\Delta U_i{}^{vap}$ is the energy of vapourisation of pure component i. The molar volumes of these pure components can be obtained from the molar mass and the density ($V_i = M_i/d_i$). For species which do not exist in the pure state (AB in this case) the solubility parameter and molar volume must be obtained by indirect methods.

An estimate of the molar volume of complex can be obtained from the results of excess volume measurements for A + B mixtures. In the ideal associated solution model the excess volume, V^E, of the system is related to the volume change of the association reaction, ΔV^θ, by

[5-22] $V^E = r\,\Delta V^\theta$

where r is the extent of the association reaction. The volume change of the association reaction can also be calculated in terms of the molar volumes of A, B, and AB (V_A, V_B, and V_{AB}) by

[5-23] $\Delta V^\theta = V_{AB} - V_A - V_B$

Combining equations [5-22] and [5-23] we find that the molar volume of complex is given by

[5-24] $V_{AB} = V^E/r + V_A + V_B$

If the model is a perfect representation of the system, then the value of V_{AB} calculated from equation [5-24] and excess volumes will be independent of the composition of the solution. In practice the model is never a perfect representation of a system (as discussed earlier in this Chapter) and the calculated values of V_{AB} do vary with composition. However, the variation is usually small relative to the value of V_{AB}. Therefore, a good estimate of V_{AB} can be obtained by taking the average of V_{AB} values calculated using equation [5-24] and excess volume results that cover the entire range of composition.

The only quantity that must still be evaluated in order to obtain the activity coefficients of A, B, and AB at any composition is the solubility parameter of AB. As was shown in the first part of this section (equation [5-11]) the activity coefficients (and hence the solubility parameters) of A, B, and AB are not independent and are related by the variation of the model equilibrium constant with composition. Substituting (see below) the expressions for the activity coefficients from solubility parameter theory into equation [5-[illegible]] leads to an expression for δ_{AB} that is consistent with both the ideal associated solution model and solubility parameter theory.

At point P (pure A) the volume fraction of A is unity [$\phi_A(P) = 1$] and the volume fractions of B and AB are zero [$\phi_B(P) = 0 = \phi_{AB}(P)$]. Substituting this information into equations [5-21], we obtain

$$\ln\gamma_A(P) = 0$$

$$\ln\gamma_B(P) = (V_B\, J_{A,B})/RT \qquad [5\text{-}25]$$

$$\ln\gamma_{AB}(P) = (V_{AB}\, J_{A,AB})/RT$$

Similarly at point R (pure B), $\phi_B(R) = 1$ and $\phi_A(R) = 0 = \phi_{AB}(R)$. Substitution into equations [5-21] gives

$$\ln\gamma_A(R) = (V_A\, J_{A,B})/RT$$

$$\ln\gamma_B(R) = 0 \qquad [5\text{-}26]$$

$$\ln\gamma_{AB}(R) = (V_{AB}\, J_{B,AB})/RT$$

We see that solubility parameter theory yields $\ln\gamma_A(P) = 0 = \ln\gamma_B(R)$, which shows that this theory is consistent with our choice of pure component standard states for A, B, and AB.

Combining the expressions for $\ln\gamma_B(P)$, $\ln\gamma_{AB}(P)$, $\ln\gamma_A(R)$, and $\ln\gamma_{AB}(R)$, given by equations [5-25] and [5-26], with equation [5-9] we find

$$[5\text{-}27] \quad \ln K_z(P) - \ln K_z(R) = 1/RT\,[V_{AB}(J_{B,AB} - J_{A,AB}) + J_{A,B}(V_B - V_A)]$$

We are now in a position to express the solubility parameter of the AB complex (δ_{AB}) in terms of variables that can be determined independently. Combining equations [5-15] and [5-27] and rearranging leads to

$$[5\text{-}28] \quad \delta_{AB} = [1/(2\,V_{AB}\,(\delta_A - \delta_B))]\,[RT(\ln K_z(P) - \ln K_z(R)) + (\delta_A - \delta_B)^2(V_A - V_B) + V_{AB}\,(\delta_A{}^2 - \delta_B{}^2)]$$

All of the variables on the right-hand side of equation [5-29] can be obtained from the results of independent experiments, as described earlier in this section. Therefore, the value of δ_{AB} can be calculated from equation [5-28] for any A + B = AB system provided that the necessary experimental data are available. Evaluation of the solubility parameter of AB in this way allows solubility parameter theory to be incorporated into the ideal associated solution model without losing the information on the nature of the activity coefficients that is given by the variation of the model equilibrium constant with composition.

Substitution of the value of δ_{AB} calculated from equation [5-28] into equation [5-15] yields values of $J_{A,AB}$ and $J_{B,AB}$. These values can then be inserted into equations [5-21] to obtain functions for the activity coefficients of A, B, and AB which can be evaluated at any composition. By evaluating these functions at P (pure A, equation [5-18]) we obtain values of $\ln\gamma_B(P)$ and $\ln\gamma_{AB}(P)$. Similarly we can use equation [5-19] to evaluate $\ln\gamma_{AB}(R)$ and $\ln\gamma_A(R)$.

Thermodynamic Properties

Substitution of our calculated values of $\ln\gamma_A(R)$, $\ln\gamma_{AB}(R)$, and $\ln K_z(R)$ into equation [5-8] (or alternatively $\ln\gamma_B(P)$, $\ln\gamma_{AB}(P)$, and $\ln K_z(P)$ into equation [5-7]) yields the thermodynamic equilibrium constant, K^o. The physical contribution to the logarithm of the thermodynamic equilibrium constant, $\ln(\gamma_{AB}/\gamma_A\gamma_B)$, can be determined by subtracting the chemical contribution (given by equation [5-6]) from $\ln K^o$. We can therefore write

$$[5\text{-}29] \quad \ln(\gamma_{AB}/\gamma_A\gamma_B) = \ln[\gamma_{AB}(R)/\gamma_A(R)\,\gamma_B\,(R)] - f(z_A)$$

If values of $\ln K^o$ are obtained at several temperatures, then we can use the van't Hoff equation, $(\partial \ln K^o/\partial T)_p = \Delta H^\theta/RT^2$, to evaluate the enthalpy of the association process. In a similar fashion the chemical and physical contributions to the enthalpy can be determined from the temperature dependences of the model equilibrium constant and the ratio of activity coefficients, $\gamma_{AB}/\gamma_A\gamma_B$. From $\Delta S^\theta = R\ln K^o + \Delta H^\theta/T$ the entropy change due to association and the chemical and physical contributions to the entropy can be calculated. If the temperature range of the study is wide enough, the heat capacity of the association reaction may also be examined.

Application to Chloroform + Triethylamine

The equations developed in the preceeding section have been applied to the chloroform (A) + triethylamine (B) system at 283.14 K and 298.15 K. Molar energies of vapourisation, molar volumes, and solubility parameters that are necessary for the analysis of this system are listed in Table 5-1. Vapour pressures above mixtures of chloroform + triethylamine (mole fractions of chloroform ranging from close to 0.0 to close to 1.0) have been measured at 283.14 K by Handa, Fenby, and Jones (1975) and at 298.15 K by Handa and Jones (1975). The equilibrium compositions and the model equilibrium constants were calculated using these data and the method described in Appendix A.

Plots of the logarithm of the model equilibrium constant ($\ln K_z$) against equilibrium mole fraction of chloroform (z_A) for the chloroform + triethylamine system at 283.14 K and 298.15 K are presented in Figures 5-1a and 5-1b, respectively. These plots show that at 283.14 K the relationship between $\ln K_z$ and z_A can be described by

$$[5\text{-}30] \quad \ln K_{z,283} = 1.311 + 0.165 z_A^2 + 4.545 z_A^3 - 3.548 z_A^4$$

and at 298.15 K the relationship between $\ln K_z$ and z_A can be described by

$$[5\text{-}31] \quad \ln K_{z,298} = 0.920 + 0.178 z_A$$

Table 5-1. Molar energies of vapourisation (ΔU^{vap}), molar volumes (V), and solubility parameters (δ) for chloroform + triethylamine at 283.14 K and 298.15 K.

	chloroform	triethylamine	complex
ΔU^{vap}/kJ mol^{-1}	28.5[a]	32.5[a]	-
V(283)/cm^3 mol^{-1}	79.2[b]	137.2[b]	208.2[c]
V(298)/cm^3 mol^{-1}	80.715[d]	139.98[d]	212.4[e]
δ(283)/10^3 Pa$^{1/2}$	18.97[f]	15.39[f]	-
δ(298)/10^3 Pa$^{1/2}$	18.79[f]	15.24[f]	-

[a] Calculated from $\Delta U^{vap} = \Delta H^{vap} - RT$. Values of ΔH^{vap} taken from Handbook of Chemistry and Physics(1986).

[b] Handa, Fenby, and Jones (1975).

[c] Calculated assuming $V_{AB}(283)$ is 2% smaller than $V_{AB}(298)$.
Note that $V_A(283)$ is 2% smaller than $V_A(298)$ and $V_B(283)$ is 2% smaller than $V_B(298)$.

[d] Hepler, Kooner, Roux-Desgranges, and Grolier (1985).

[e] Calculated from excess volumes; equation [5-20].

[f] Calculated using equation [5-17].

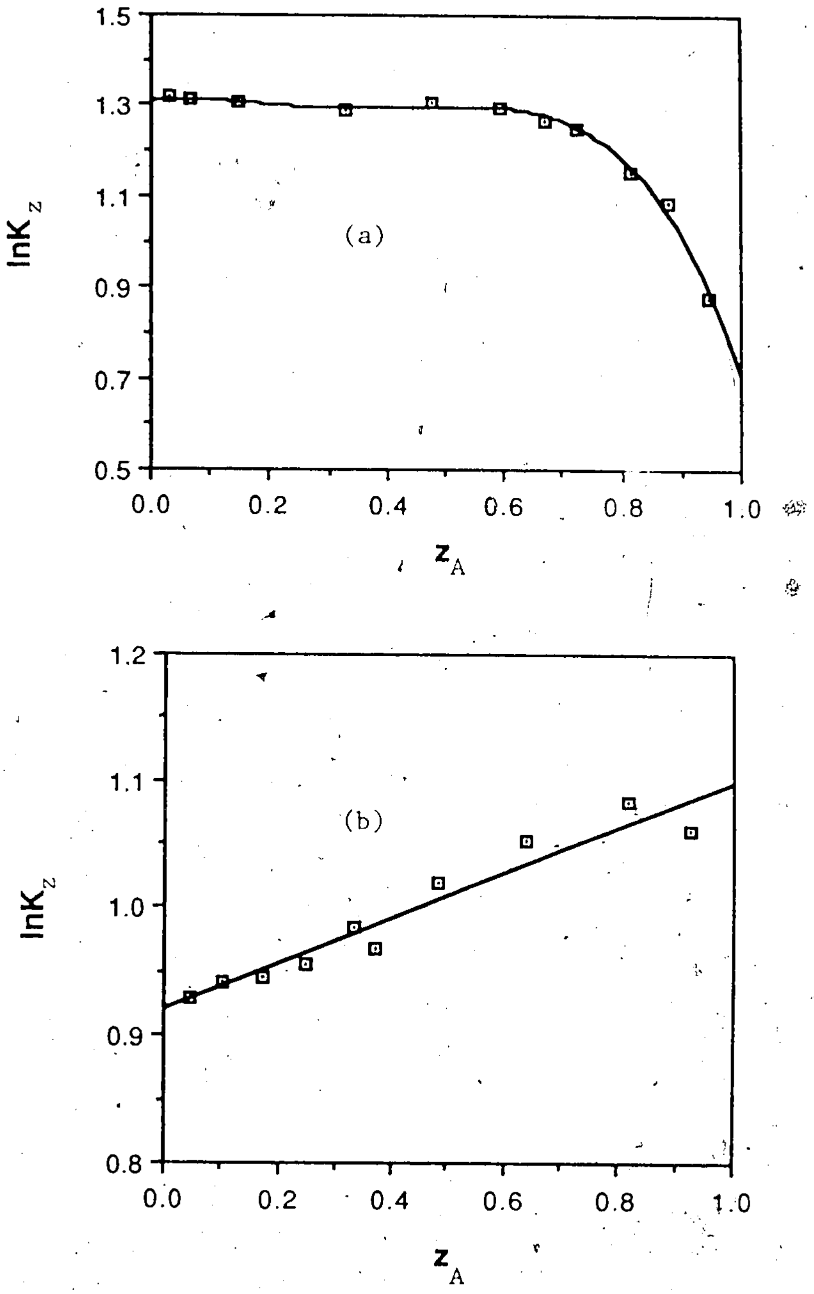

Figure 5-1. Dependence of $\ln K_z$ on z_A for chloroform (A) + triethylamine (B): (a) 283.14 K; (b) 298.15 K. Points are calculated; solid lines represent fitted equations.

Equations [5-30] and [5-31] yield values of $[\ln K_z(P) - \ln K_z(R)]_{283} = -0.601$ and $[\ln K_z(P) - \ln K_z(R)]_{298} = 0.178$. Substituting these values of $[\ln K_z(P) - \ln K_z(R)]$ and the molar volumes and solubility parameters given in Table 5-1 into equation [5-28], we obtain $\delta_{AB}(283) = 1.57 \times 10^4$ $Pa^{1/2}$ and $\delta_{AB}(298) = 1.68 \times 10^4$ $Pa^{1/2}$. Combining these values with the values of δ_A and δ_B in Table 5-1, we calculate (using equation [5-15]) values of $J_{A,B}$, $J_{A,AB}$, and $J_{B,AB}$ at each temperature, as listed in Table 5-2. We now use the values of $J_{A,B}$, $J_{A,AB}$, and $J_{B,AB}$ in equations [5-25] and [5-26] to obtain the values of $\ln\gamma_B(P)$, $\ln\gamma_{AB}(P)$, $\ln\gamma_A(R)$, and $\ln\gamma_{AB}(R)$ that are listed in Table 5-3. Since $z_A = 1$ at point P and $z_A = 0$ at point R, $\ln K_z(P)$ and $\ln K_z(R)$ at the two temperatures can be calculated by inserting these values of z_A into equations [5-30] and [5-31]. The values obtained are $\ln K_z(P)_{283} = 0.709$, $\ln K_z(P)_{283} = 1.311$, $\ln K_z(P)_{298} = 1.098$, and $\ln K_z(R)_{298} = 0.920$. Combining these values of the model equilibrium constant at pure A and pure B with the appropriate values of the activity coefficients (Table 5-3) in equations [5-7] and [5-8] we can evaluate the thermodynamic equilibrium constant for association in the chloroform + triethylamine system. We find that $K^o_{283} = 2.43$ and $K^o_{298} = 2.06$.

Because the equilibrium constant has been evaluated at only two temperatures and the difference in these temperatures is only 15 K, calculation of the enthalpy of association using the van't Hoff equation is not justified.

Table 5-2. Values of the parameters $J_{i,j}$[a] for the chloroform (A) + triethylamine (B) + chloroform-triethylamine complex (AB) system.

	283.14 K	298.15 K
$J_{A,B}/10^6$ Pa	12.82	12.60
$J_{A,AB}/10^6$ Pa	10.48	3.91
$J_{B,AB}/10^6$ Pa	0.11	2.47

[a] Calculated using equation [5-13]

Table 5-3. Logarithms of activity coefficients[a] of chloroform (A), triethylamine (B), and chloroform-triethylamine complex (AB) in pure A (P) and pure B (R).

	A	B	AB
$\ln\gamma_i(P)_{283}$	0	0.747	0.927
$\ln\gamma_i(R)_{283}$	0.431	0	0.010
$\ln\gamma_i(P)_{298}$	0	0.712	0.335
$\ln\gamma_i(R)_{298}$	0.410	0	0.212

[a] Calculated using equations [5-14] and [5-15].

Discussion

As noted in the Introduction, Bertrand (1975) and Fenby et al. (1977) have previously combined the ideal associated solution model with solubility parameter theory to obtain an estimate of the thermodynamic equilibrium constant for chloroform-triethylamine complex formation. In both of these studies two approximations were made that we have been able to avoid. The first approximation was that K_z (the model equilibrium constant) is equal to K_z in the (stoichiometric) equimolar mixture. As displayed in Figure 5-1, K_z can vary dramatically with composition. The second approximation was that the solubility parameter of AB could be represented as a weighted average of the solubility parameters of the pure components:

$$[5\text{-}32] \quad \delta_{AB} = (\Gamma_A\delta_A + \Gamma_B\delta_B)\,(\Gamma_A + \Gamma_B)$$

where Γ_A and Γ_B are weighting factors. Fenby et al. took the weighting factors of A and B (Γ_A and Γ_B) to be equal, i.e. the solubility parameter of AB was obtained as the arithmetic mean of the solubility parameters of A and B (evaluated in the usual way, equation [5-12]). Bertrand estimated the values of the weighting factors by treating the solubility parameters of A and B as adjustable parameters in conjunction with the partial molar excess enthalpies of the components in the pure solvents and in the equimolar mixture.

In contrast to the improved ideal associated solution models of Bertrand and Fenby et al., our extended ideal associated solution model does take into account the variation of the model equilibrium constant with composition and the interdependence of the activity coefficients of A, B, and AB. The result is a model which is consistent with the requirements of the ideal associated solution model and solubility parameter theory. The only assumptions that are made when our extended model is applied to an associated system is that the ideal associated solution model provides a good account of the chemical contributions to non-ideality and that solubility parameter theory provides a good account of the physical contributions.

The improved models of Bertrand and Fenby et al. both yield values of $K^o_{298} = 2.0$. These are in excellent agreement with the value of $K^o_{298} = 2.06$ obtained from our new extended model. However, this agreement occurs only because $\ln K_z$ (the logarithm of the model equilibrium constant) varies linearly with composition at 298 K. When $\ln K_z$ is an odd function of composition about $z_A = 0.5$ (for example a linear function) very little error is introduced to the calculation of K^o by ignoring the composition dependence of K_z and assuming that K_z is given by K_z of the equimolar mixture. This is because the error introduced at z_A values less than 0.5 is offset by the error (equal in magnitude but opposite in sign) at z_A values higher than 0.5. Thus, although the averaging method is not strictly correct, it does lead to values similar to those obtained using our extended model in the special case of $\ln K_z$ being an odd function of composition about $z_A = 0.5$. When $\ln K_z$ is a function of composition which is not odd about $z_A = 0.5$, our extended model should lead to equilibrium constants which are significantly different than those obtained using the improved models of Bertrand and Fenby et al. We examine this expectation by considering chloroform + triethylamine at 283 K where the logarithm of the model equilibrium constant is a non-linear function of z_A (see Figure 5-1).

At 283.14 K the model proposed by Fenby et al. yields a value of K^o_{283} = 2.86, which is 17% larger than the value determined using our new extended model (2.43). Partial molar excess enthalpies of the components in the pure solvents and in the equimolar mixture are not available at 283 K so we cannot calculate K^o_{283} using Bertrand's model. We anticipate that the difference between results obtained from our extended model and Bertrand's model would be similar to the difference between results obtained from our model and the model of Fenby et al.

Hepler, Kooner, Roux-Desgranges, and Grolier (1985) have used the simple ideal associated solution model (no improvements or extensions) to obtain a value of 2.6 for the equilibrium constant of chloroform + triethylamine association at 298.15 K. This value is approximately 25% larger than the value of 2.06 determined using our extended model. From this comparison we conclude (as have by both Bertrand (1975) and Fenby et al. (1977)) that neglect of physical contributions to the deviations from ideality may lead to significant errors in calculated equilibrium constants even for those systems in which chemical interactions are dominant over physical interactions.

CHAPTER 6

Self-Association of Chloroform in Pure Chloroform and in Chloroform + n-Hexane Mixtures

Introduction

Self-association is a well recognised phenomenon that occurs in many liquids and gases. One of the best known examples of self-association is the dimerisation of NO_2 to form N_2O_4. It has been shown that the deviations from ideality in gaseous NO_2 can be explained in terms of the equilibrium, $2NO_2 = N_2O_4$. The gas is then treated as an ideal mixture of monomer (NO_2) and dimer (N_2O_4). Treatment of NO_2 in this way is equivalent to applying the ideal associated solution model to self-association in nitrogen dioxide. We anticipate that many other self-associated fluids may be analysed successfully in terms of a similar ideal association model.

That the ideal associated solution model is a good approximation for fluids in which self-association occurs can be seen by considering the chemical species in a "pure" self-associated fluid, A. If m molecules of monomer A combine to form the self-associated species C according to the equilibrium

[6-1] $mA = C$

then there are two species present at equilibrium, A and C. The physical contributions to the non-ideality of the fluid arise from non-chemical interactions between unlike components. Therefore, the only physical interactions that lead to deviations from ideality in a pure self-associated fluid A are those between monomer and m-mer. The m-mer molecules are simply collections of monomer molecules so we expect that interactions between monomer and m-mer are very nearly ideal. All this means that physical contributions to non-ideality are very small. On this basis we suggest that the assumption of the ideal associated solution model that physical contributions to deviations from ideality are negligible with respect to chemical contributions - is valid in the case of self-association in a pure fluid.

In Chapter 2 we showed how the ideal associated solution model is applied to associated liquid mixtures of unlike components, A and B. Using the method described in Appendix A, the vapour pressures of stoichiometric mixtures of A + B were combined with the pure component vapour pressures to obtain a value of the equilibrium constant at each composition. An average value of the equilibrium constant was then used to interpret measured thermodynamic properties of A + B mixtures in terms of complex formation. In order to apply a similar calculation scheme to the treatment of self-association in a pure liquid, we need to know the stoichiometry of the dominant self-associated species (i.e., the value of m in equation [6-1]) and the vapour pressure of pure monomer, $p^{\bullet}_{A}$.

The stoichiometry of the complex in associated mixtures of unlike components (A + B) can be obtained from the results of spectroscopic investigations, from measurements of dielectric properties, or from studies of cooling curves. All of these techniques require examination of the dependence of certain physical properties on the stoichiometric composition of the A + B mixtures. Since self-association involves chemical interaction between molecules of the same species, the stoichiometric ratio of the components undergoing the association cannot be varied. Therefore, we must obtain the value of m by indirect methods. Vapour pressures of pure components are determined by direct experimental measurement. However, in a self-associated liquid we can never physically separate monomer from m-mer. For this reason the vapour pressure of pure monomer must be obtained indirectly.

In this Chapter we describe a method whereby the vapour pressure of pure monomer can obtained by considering the vapour pressure above very dilute solutions of the self-associated component, A, in some "inert" solvent, S. Combination of this value of $p_A^{\bullet}$ with results of vapour pressure measurements for mixtures of A + S over the entire composition range yields the value of m and also the value of the self-association equilibrium constant.

We have applied our method to the evaluation of the self-association equilibrium constant for chloroform by using experimental vapour pressures of mixtures of chloroform and n-hexane. This equilibrium constant was then combined with published excess volumes and excess enthalpies of chloroform + n-hexane mixtures to obtain values for the standard volume and standard enthalpy of chloroform self-association. Chloroform was chosen as the self-associated component because it is a common organic solvent with a known capacity to undergo self-association (Pimentel and McClellan, 1960;

Suzuki, Tsutsui, and Fujiyama, 1981; Evans, 1983). Also, chloroform has only one proton so the number of possible stoichiometries of self-associated chloroform is rather more limited than for substances with a larger number of sites at which self-association could occur. This means that there is a high probability that one stoichiometric form of self-associated chloroform is dominant over the others; this permits us to focus on only one equilibrium of type [6-1]. We chose n-hexane as the inert solvent because it has no apparent chemical reactivity towards chloroform and because the physical interactions between alkanes and other substances are usually weak. Furthermore, there exists a large body of high quality experimental data for the vapour pressures, excess volumes, and excess enthalpies of chloroform + n-hexane mixtures.

Derivation of Equations

Consider a mixture with a stoichiometric composition of N_A moles of a self-associating component, A, and N_S moles of an inert solvent, S. If m molecules of A associate to form the self-associated species, C, (as represented by equation [6-1]) then the equilibrium composition of the mixture can be related to the stoichiometric composition by way of the mass balance given in Table 6-1. In Table 6-1 r represents the extent of self-association (the amount of self-associated A relative to the stoichiometric amount of mixture).

The expression given in Table 6-1 for the equilibrium mole fraction of

Table 6-1. Mass balance for the self association $mA \rightleftharpoons C$ in a stoichiometric mixture of A + S.

Species	Stoichiometric Amount/mol	Stoichiometric Mole Fraction	Equilibrium[a] Amount/mol	Equilibrium[b] Mole Fraction
A	N_A	x_A	$N_A - mn_C$	$[x_A - mr)/(1 - r(m - 1)] = z_A$
C	-	-	n_C	$r/[1 - r(m - 1)] = z_C$
S	N_S	x_S	N_S	$x_S/[1 - r(m - 1)] = z_S$

---

[a] Total number of moles at equilibrium = $N_A + N_S - (m - 1)n_C$

[b] $r = n_C/(N_A + N_S)$.

monomer A, z_A, can be rearranged to obtain an expression for r:

[6-2] $r = (x_A - z_A)/[z_A + m(1 - z_A)]$

where x_A represents the stoichiometric mole fraction of A.

A similar rearrangement of the expression for z_S (given in Table 6-1) yields

[6-3] $r = (x_S - z_S)/[z_S(1 - m)]$

where x_S represents the stoichiometric mole fraction of inert solvent.

Equating the right-hand sides of equations [6-2] and [6-3] and rearranging leads to the equilibrium mole fraction of inert solvent in terms of the equilibrium mole fraction of monomer and the stoichiometric composition of the mixture:

[6-4] $z_S = x_S[z_A + m(1 - z_A)]/(x_A + mx_S)$

The total (experimental) pressure above the mixture of A and S, P_t, can be expressed in terms of the partial pressures, p_i, of each of the components:

[6-5] $P_t = p_A + p_S + p_C$

Since the mixture is considered to be ideal when the ideal associated solution model is applied, we express the partial pressure of component i in terms of its <u>equilibrium</u> mole fraction and the vapour pressure of pure component i, $p_i^\bullet$:

[6-6] $p_i = z_i p_i^\bullet$

If self-associated A is present in negligible amounts in the vapour phase at low pressures and thus makes no contribution to the measured total pressure, then we can combine equation [6-6] with equation [6-5] to obtain

[6-7] $P_t = z_A p^{\bullet}_A + z_S p^{\bullet}_S$

where p_A represents the vapour pressure of hypothetical pure monomer.

Substituting our expression for z_S from equation [6-4] into equation [6-7] and rearranging we obtain

[6-8] $z_A = (P_t(x_A + mx_S) - mx_S p^{\bullet}_S)/(p^{\bullet}_A(x_A + mx_S) - (m - 1)x_S p^{\bullet}_S)$

For any mixture of a self-associating component and an inert solvent the quantities $p^{\bullet}_A$, $p^{\bullet}_S$, and m are constants. The vapour pressure of pure inert solvent, $p^{\bullet}_S$, can be measured directly. If $p^{\bullet}_A$ and m are known, then we can use equation [6-8] to calculate the equilibrium mole fraction of monomer A, z_A, for any mixture of A + S for which the total vapour pressure has been measured. The value of z_A can then be substituted into equation [6-4] to obtain the equilibrium mole fraction of inert solvent, z_S. Because the sum of the equlibrium mole fractions of all the species in the mixture is unity, the equilibrium mole fraction of self-associated A (C) can be calculated by difference:

[6-9] $z_C = 1 - z_A - z_S$

The equlibrium constant for the self-association is given by

[6-10] $K = (a_C)/(a_A)^m = (z_C\gamma_C)/(z_A\gamma_A)^m$

where a_i represents the activity of species i and γ_i represents the activity coefficient of species i. Since in the ideal associated solution model we assume that the activity coefficients of all species are unity at all temperatures and compositions, equation [6-10] can be simplified to

[6-11] $K = z_C/(z_A)^m$

We can calculate the equilibrium constant for the self-association reaction [6-1] by inserting our values of z_A and z_C (obtained as described above) into equation [6-11].

Using the method outlined in this section, the self-association equilibrium constant for a liquid, A, can be calculated from vapour pressure data for mixtures of A + inert solvent provided that the number of A monomers in self-associated A and the vapour pressure of pure monomer A are known.

Self-Association in Chloroform

Equilibrium Constant

Application of the method described in the preceding section to the calculation of a self-association equilibrium constant for a real chemical system presents two difficulties. First, the vapour pressure above pure monomer cannot be measured since monomers can never be physically separated from m-mers. Second, the number of monomers that associate to form the self-associated species is generally unknown. In this section we illustrate how these difficulties may be overcome by considering the specific case of self-association in chloroform.

In the following discussion A represents monomeric chloroform and C represents self-associated or complexed chloroform. The vapour pressure above hypothetical pure monomeric chloroform can be estimated by considering the vapour pressure above a very dilute solution of chloroform in some inert solvent.. In these dilute solutions the amount of self-associated chloroform is negligible in comparison with the amount of monomeric chloroform; thus the equilibrium mole fraction of monomeric chloroform, z_A, is equal to the stoichiometric mole fracti[illegible]f chloroform, x_A. Since the solvent is inert with respect to chloroform, we consider the dilute solutions as ideal mixtures of monomer chloroform + inert solvent. The vapour pressure of these solutions, P_t, can be expressed by

$$[6\text{-}12] \quad P_t = x_S p^{\bullet}_S + x_A p^{\bullet}_A$$

where $p^{\bullet}_S$ is the vapour pressure of pure inert solvent and $p^{\bullet}_A$ is the unmeasureable vapour pressure of hypothetical pure monomeric chloroform. Noting that the sum of the stoichiometric mole fractions is unity ($x_A + x_S = 1$) we can rewrite equation [6-12] as

$$[6\text{-}13] \quad P_t = p^{\bullet}_S + x_A(p^{\bullet}_A - p^{\bullet}_S)$$

Equation [6-13] shows that at infinite dilution of chloroform the vapour pressure-mole fraction curve for chloroform + inert solvent has a slope of $p^{\bullet}_A$ -

$p^{\bullet}_S$. Since the vapour pressure of the pure inert solvent can be measured directly, we obtain an estimate of the vapour pressure of pure monomeric chloroform from:

[6-14] $p^{\bullet}_A = [\lim_{x_A \to 0}(\partial P_t/\partial x_A)] + p^{\bullet}_S$

Bissell and Williamson (1975) have measured the vapour pressures of chloroform + n-hexane mixtures at 298.15 K. From a graphical fit to this data we estimate that at infinite dilution of chloroform the slope of the vapour pressure-mole fraction curve is 21.35 kPa. Using the value of 20.141 kPa for the vapour pressure of pure n-hexane (Bissell and Williamson, 1975), we estimate (using equation [6-14]) that the vapour pressure of pure monomeric chloroform at 298.15 K is 41.5 kPa.

In order to determine the value of m (the number of monomeric chloroform molecules which comprise the self-associated species), we recognise that the equilibrium constant of the self-association process should be independent of the composition of the solution. Since the ideal associated solution model is an approximation, an equilibrium constant calculated using the model will exhibit some composition dependence. However, if the model is a good approximation to the system (which we expect in the case of self-association, as discussed earlier) this dependence will be small. Correct choice of the value of m should lead to an equilibrium constant that is nearly independent of composition. Therefore, we choose as the value of m the integral value which leads to the least variation of the equilibrium constant with composition.

Bissell and Williamson (1975) report the vapour pressures at 298.15 K of 13 chloroform + n-hexane mixtures with stoichiometric mole fractions of chloroform ranging from 0.1312 to 1.0000. Using the equations developed in the previous section and our value of 41.5 kPa for the vapour pressure of hypothetical pure monomeric chloroform, we can evaluate the self-association equilibrium constant for each mixture, provided that the value of m is fixed.

We have calculated the self-association equilibrium constant for each of the 13 mixtures using values of m = 2, 3, and 4. The results of these calculations are given in Table 6-2.

Table 6-2 shows that the self-association equilibrium constant is almost independent of composition when m = 3. The average value of K(m = 3) is 1.33 with a standard deviation of 0.07. Table 6-2 also shows that values of m = 2 and m = 4 lead to equilibrium constants with a large composition dependence. We, therefore, conclude that the dominant form of self-associated chloroform is chloroform trimer (i.e., the symbol C is equivalent to A_3), and that the equilibrium constant for trimerisation has the value K = 1.33.

Standard Volume Change and Enthalpy of Trimerisation

Other molar excess properties of chloroform + n-hexane mixtures can be interpreted in terms of self-association of chloroform. When n-hexane is added to chloroform some trimers dissociate and, hence, the number of trimers decreases and the number of monomers increases. Due to the presence of chloroform-chloroform "bonds" in the trimer molecules we expect that

Table 6-2. Equilibrium constants for $mCHCl_3 = (CHCl_3)_m$ in stoichiometric mixtures of x(chloroform) + (1 - x)(n-hexane).

x	K(m=2)	K(m=3)	K(m=4)
0.1312	0.235	1.471	9.784
0.2441	0.363	1.387	5.617
0.3445	0.432	1.291	4.095
0.4052	0.471	1.274	3.653
0.4442	0.500	1.283	3.492
0.5022	0.536	1.280	3.251
0.5345	0.556	1.285	3.156
0.6013	0.598	1.298	2.996
0.6169	0.596	1.269	2.870
0.7015	0.658	1.315	2.788
0.7898	0.715	1.333	2.630
0.8937	0.798	1.378	2.477
1.0000	0.923	1.461	2.314

chloroform trimers occupy less volume than three chloroform monomers and, therefore, that the effect of trimer dissociation is to increase the volume occupied by liquid chloroform. On this basis we anticipate that mixtures of chloroform and n-hexane will exhibit positive excess volumes. Bond dissociation is always endothermic so we expect to see positive excess enthalpies for chloroform + n-hexane mixtures. Experimental results show that the excess volumes and enthalpies ~~do~~ have the sign that is predicted from the assumption that chloroform self-association is the main contributor to the non-ideality ($V^E \neq 0$, $H^E \neq 0$) in chloroform + n-hexane mixtures.

In order to obtain estimates of the standard volume and standard enthalpy for the trimerisation of chloroform from experimental excess volume and excess enthalpy results, we need to know the equilibrium speciation in a chloroform + n-hexane mixture. We take the trimerisation equilibrium constant to have a value of K = 1.33 as calculated in the first part of this section. The equilibrium constant can be written in terms of the equilibrium amount of each species, n_i:

[6-15] $K = n_C(n_A + n_C + n_S)^2/(n_A)^3$

The mass balance in Table 6-1 shows that

[6-16] $n_A = N_A - 3n_C$

where N_A represents the stoichiometric amount of chloroform. We also note that the amount of n-hexane is unchanged by the self-association of chloroform and so the equilibrium amount of n-hexane equals the stoichiometric amount:

[6-17] $n_S = N_S$

Combining equations [6-16], [6-17], and [6-17] and rearranging we obtain a cubic equation in n_C:

[6-18] $$0 = (n_C)^3(4 + 27K) - (n_C)^2(4(N_A + N_B) + 27KN_A) +$$
$$n_C((N_A + N_S)^2 + 9KN_A^2) - KN_A^3$$

Equation [6-16] can be solved by an iterative method (or analytically) to obtain the equilibrium amount of trimeric chloroform in a mixture of chloroform and n-hexane. The equilibrium amount of monomeric chloroform can then be calculated using equation [6-14].

The amount of trimer dissociated when N_S moles of n-hexane are added to N_A stoichiometric moles of chloroform can be calculated by considering the amount of trimer present before and after the addition of n-hexane. By solving equation [6-18] with $N_S = 0$ and $N_A = N_A$ the amount of trimer present before the addition of n-hexane (n_C') can be determined. The amount of trimer present after the addition of n-hexane (n_C'') is calculated by setting $N_S = N_S$ and $N_A = N_A$ in equation [6-18]. The amount of trimer dissociated, Δn_C, is then given by

[6-19] $$\Delta n_C = n_C'' - n_C'$$

The amount of monomer formed on addition of n-hexane, Δn_A, can be calculated from

[6-20] $$\Delta n_A = -3\Delta n_C$$

We turn now to the calculation of the standard volume of the trimerisation of chloroform. Using the approximation that trimerisation of chloroform is the only important interaction in chloroform + n-hexane mixtures, we can relate the excess volume of these mixtures to the molar volumes of monomeric and trimeric chloroform (V_A and V_C):

[6-21] $V^E = \Delta n_A V_A + \Delta n_C V_C$

Equation [6-21] contains two unknowns, V_A and V_C. We therefore require more of information before equation [6-21] can be used to calculate V_A or V_C.

From equations [6-16] and [6-18] we calculate that one stoichiometric mole of pure chloroform contains 0.2079 moles of trimer and 0.3762 moles of monomer. Also, one stoichiometric mole of chloroform has a volume of 80.715 cm^3 at 298.15 K (Handa and Jones, 1975). We can, therefore, write

[6-22] $80.715 = 0.3762V_A + 0.2079V_C$

Rearranging equation [6-20] we find

[6-23] $V_C = 388.24 - 1.8095V_A$

which can be combined with equation [6-21] and rearranged to obtain

[6-24] $V_A = (388.24\Delta n_C - V^E)/(1.8095\Delta n_C - \Delta n_A)$

Using equation [6-24] we can calculate the molar volume of monomeric chloroform in any mixture of chloroform and n-hexane for which the excess volume is available. This molar volume can be substituted into equation [6-21] to obtain the molar volume of trimeric chloroform. The molar volumes of monomeric and trimeric chloroform can then be combined in

[6-25] $\Delta V^\theta = V_C - 3V_A$

to give the standard volume change for the trimerisation of chloroform, ΔV^{θ}.

Bissell, Okafor, and Williamson (1971) have measured the excess volumes of 16 mixtures of chloroform + n-hexane. Mole fractions of chloroform in the 16 mixtures range from 0.1398 to 0.8666. Note that for one stoichiometric mole of mixture ($N_A + N_S = 1$) the stoichiometric amount of A (or S) is equal to the stoichiometric mole fraction of A (or S). Using these results and the method described above, the standard volume change for the trimerisation of chloroform at 298.15 K was calculated. A value of $\Delta V^{\theta} = -7.30$ cm^3 mol^{-1} with a standard deviation of 0.15 cm^3 mol^{-1} was obtained.

Calculation of the standard enthalpy of trimerisation of chloroform, ΔH^{θ}, is less complicated than the calculation of the standard volume. The measured excess enthalpy arises from the dissociation of chloroform-chloroform bonds in the trimer. The excess enthalpy of a chloroform + n-hexane mixture is, therefore related to the standard enthalpy of trimerisation, ΔH^{θ}, by

[6-26] $H^E = \Delta n_C \Delta H^{\theta}$

where Δn_C represents the number of trimers which dissociate on the addition of n-hexane, as before.

Excess enthalpies for the chloroform + n-hexane system have been measured by Bissell, Okafor, and Williamson (1971). Mixtures of 10 different compositions were investigated. The mole fraction of chloroform in these mixtures ranged from 0.106 to 0.907. Using these experimental results and equation [6-24] we have calculated 10 values of the standard enthalpy of trimerisation. The values show significant composition dependence and are accurately summarised by

[6-27] ΔH^{θ}/kJ mol^{-1} = -11.952 - 9.900x_A

where x_A represents the stoichiometric mole fraction of chloroform. The variation of the standard enthalpy of trimerisation with composition is discussed in the final section of this Chapter.

Discussion

In the previous section we proposed that chloroform + n-hexane mixtures can be considered as ideal mixtures of monomeric chloroform + trimeric chloroform + n-hexane. The equilibrium constant of chloroform trimerisation was found to have a value of K = 1.33 and the standard volume of trimerisation was found to have a value of ΔV^{θ} = -7.30 cm^3 mol^{-1}. Both of these thermodynamic properties are nearly independent of the composition of the mixture. However, the calculated standard enthalpy of trimerisation shows a strong composition dependence. This dependence can be explained by considering the structure of a chloroform trimer.

It is possible to imagine two different structures in which three chloroform molecules are collected to form a chloroform trimer. One of these is a cyclic structure with three chloroform-chloroform bonds. The other is a chain structure, which contains two chloroform-chloroform bonds. These two structures are very similar and hence we expect that the energy difference between them will be very small. It follows that very small changes in the composition of the chloroform + n-hexane mixtures may well shift the equilibrium between the two forms. For example one form may be favoured when the mixture is concentrated in n-hexane and the other form favoured when the mixture is dilute in n-hexane. Since the two structures contain a different number of chloroform-chloroform bonds, interconversion between the structures involves absorption or emission of heat. Therefore, some of the measured excess enthalpy may arise from a change in trimer structure due to a change in the composition of the mixture. We have no way of predicting quantitatively the contribution to the measured excess enthalpies arising from reorganisation of trimers. However, we do expect that this contribution is significant since it involves breaking or making one hydrogen bond for every trimer molecule that reorganises. The value of ΔH^θ calculated from a measured excess enthalpy and equation [6-24] will depend on the degree of trimer reorganisation occuring at the composition of the measurement. This means that the calculated values of ΔH^θ will vary with composition, as is observed.

Our calculations demonstrate that the vapour pressures, excess volumes, and excess enthalpies of chloroform + n-hexane mixtures are consistent with the view that trimerisation of chloroform is the most important contribution to non-ideality in these mixtures. The lack of variation of our calculated values of K and ΔV^θ with composition of the mixtures indicates that interactions between chloroform and n-hexane can be neglected for the purpose of evaluating these properties. That is to say, our assumption that n-hexane is inert with respect to chloroform is valid for the analysis of vapour pressures and excess volumes. Therefore, the value of the trimerisation equilibrium constant and the standard volume of trimerisation can be attributed to the chloroform alone (no n-hexane) and are the values of these properties in pure chloroform. As we have discussed, the measured excess enthalpies of chloroform + n-hexane mixtures appear to contain a contribution which arises from the influence of chloroform + n-hexane interactions on the structure (cyclic or linear) of the trimer. For this reason it is difficult to determine the value of the standard enthalpy of trimerisation in pure chloroform.

One method for estimating the standard enthalpy of trimerisation in pure chloroform is to evaluate equation [6-25] at $x_A = 1$ (pure chloroform). This leads to a value of $\Delta H^\theta = -21.85$ kJ mol^{-1}. Combining this value with our value of $K = 1.33$ in $\Delta S^\theta = R\ln K + (\Delta H^\theta/T)$ we obtain an estimate of the standard entropy of trimerisation of chloroform, $\Delta S^\theta = -70.9$ J K^{-1} mol^{-1}.

The success of the calculation scheme presented in this Chapter in interpreting the properties of pure chloroform in terms of self-association indicates that, as expected, the ideal associated solution model can be a very useful tool for investigating self-association in pure liquids. An important limitation of the method we have described is that the self-associated molecules must exist predominantly in one stoichiometric form (only one m value).

CHAPTER 7

Complex Formation between Sulphur Dioxide and Electron Donors: Partial Molar Volumes

Introduction

Many workers have shown that sulphur dioxide forms charge-transfer complexes with electron donors. Evidence has been reported for complex formation between sulphur dioxide and aromatic hydrocarbons, olefinic hydrocarbons, and hydrocarbons containing a heteroatom. Some representative studies are those of Locket (1932), Andrews and Keefer (1951), de Maine (1957), Booth, Dainton, and Ivin (1959), Smith and Smith (1965), Santos and Isolani (1979), Tse and Ripmeester (1983), Adams, Kruus, and Patraboy (1983), and Gardener and Day (1983).

Formation of charge-transfer complexes between SO_2 and electron donors suggests that the solubility of sulphur dioxide in electron donating solvents will be greater than its solubility in non-electron donating solvents. This increased solubility has industrial importance because of the possibility that electron donors (such as unsaturated hydrocarbons or hydrocarbons containing a heteroatom) may be good absorbents for removing sulphur dioxide from gaseous effluents (Benoit and Milanova, 1979). Further investigation of this possibility requires knowledge of the solubility of sulphur dioxide in electron donating solvents. At low pressures of sulphur dioxide the solubility can be calculated from the appropriate Henry's law constant and equilibrium constant of complex formation. However, in order to calculate the solubility at higher pressures we need to know the dependence of both the Henry's law constant and the equilibrium constant on pressure.

At pressures above the saturation pressure of the solvent the logarithm of the ratio of the fugacity (f_2) of a gas to its solubility (x_2) - defined as the logarithm of the Henry's law constant at that pressure, $\ln k_H{}^P$ - in a particular solvent may be obtained from the Krichevsky-Kasarnovsky equation (Krichevsky and Kasarnovsky, 1935; Dodge and Newton, 1937; Prausnitz, Lichtenthaler, and de Azevedo, 1986):

[7-1] $$\ln(f_2/x_2) = \ln k_H{}^P = \ln k_H{}^o + V_2{}^o\,(P - p_1)/RT$$

In equation [7-1] $k_H{}^o$ represents the Henry's law constant at the saturation pressure of the solvent and $V_2{}^o$ represents the partial molar volume of the gas at infinite dilution (limiting partial molar volume); P and p_1 represent the pressure of gas and the partial pressure of the solvent, respectively; R represents the gas constant and T represents the temperature. The only assumptions required in deriving equation [7-1] are that the partial molar volume of dissolved gas is independent of pressure and that the solution is dilute enough that Henry's law holds.

Use of equation [7-1] to predict solubilities of sulphur dioxide in electron donating solvents as a function of pressure requires values for the limiting partial molar volume of sulphur dioxide in these solvents. Evaluation of the limiting partial molar volume of sulphur dioxide in electron donating solvents is the primary aim of the work presented in this Chapter. We have also used these results to estimate the pressure dependence of the equilibrium constant for the complexation reaction between sulphur dioxide and benzene.

Summaries of the experimental methods for obtaining partial molar volumes of dissolved gases have been given by Battino and Clever (1966) and Clever and Battino (1975). Although several precise investigations have led to accurate and reliable values of the desired limiting partial molar volumes of several gases in several liquids, the experimental methods that have been used are unattractively complicated. We have undertaken the research described here and in the next Chapter for two reasons: (i) to develop another (less complicated) method for obtaining the desired limiting partial molar volumes of gases in liquids; (ii) to obtain limiting partial molar volumes of selected gases in selected liquids.

We begin by defining the apparent molar volume of a solute ($V_{\phi,2}$) in terms of the total volume of a solution (V_{soln})

$$[7\text{-}2] \qquad V_{soln} = n_2 V_{\phi,2} + V_1$$

where n_2 represents the number of moles of dissolved gas and V_1 represents the volume occupied by the pure solvent before dissolution of gas. The partial molar volume of a dissolved gas at infinite dilution is defined by

[7-3] $V_2 = (\partial V_{soln}/\partial n_2)_{n,T,p}$

Taking the derivative of equation [7-2] with respect to n_2 and combining the result with equation [7-3] yields the limiting partial molar volume in terms of the apparent molar volume:

[7-4] $V_2 = V_{\phi,2} + n_2 (\partial V_{\phi,2}/\partial n_2)_{n_1,T,p}$

As we approach infinite dilution ($n_2 \rightarrow 0$), the sec [illegible] the right side of equation [7-4] goes to zero, and the partial molar volume of the dissolved gas is equal to the apparent molar volume at infinite dilution. For small values of $(\partial V_{\phi}/\partial n_2)_{n,T,p}$ the second term on the right hand side of equation [7-4] is small relative to $V_{\phi,2}$, and V_2^o is in effect equal to $V_{\phi,2}$.

We have designed and built a new dilatometer which allows speedy measurement of apparent molar volumes of dissolved gases to 1% precision. The dilatometer is inexpensive and relatively easy to operate. As we described in the previous paragraph, measurements of apparent molar volume of dissolved gas at very low gas concentrations provide good estimates of the limiting partial molar volume of the gas. We have used our new dilatometer to measure the apparent molar volume, and thence to obtain values for the limiting partial molar volume of sulphur dioxide, in eleven electron donating solvents, seven unsaturated hydrocarbons, and four hydrocarbons containing oxygen. Preliminary measurements showed that $V_{\phi,2}$ is nearly independent of the amount of sulphur dioxide dissolved; thus $(\partial V_{\phi}/\partial n_2)_{n_1,T,p}$ is close to zero and our measured apparent molar volumes (in dilute solution) are essentially equal to the desired partial molar volumes at infinite dilution.

In addition to obtaining limiting partial molar volumes of sulphur dioxide in eleven electron donating solvents, we were also interested in comparing these volumes with those of sulphur dioxide in solvents that do not donate electrons. The aim of this comparison was to see if the limiting partial molar volume of sulphur dioxide is significantly different in electron donors than in non-electron donors. Our question was, does the formation of a charge-transfer complex alter the limiting partial molar volume of sulphur dioxide? To this end we have measured the apparent molar volume of sulphur dioxide in six saturated hydrocarbons (non-electron donors).

Design and Operation of the Dilatometer

Apparatus

The dilatometer consists of a Pyrex glass bulb, capacity 68 cm^3, wall thickness 1.5-2.0 mm, fitted with a straight capillary tube 100 mm long and 3 mm in bore. As a reference mark a thin copper wire was attached halfway up the capillary tube. The open end of the capillary tube can be closed with a loose fitting Nylon cap. A diagram of the dilatometer is presented in Figure 7-1.

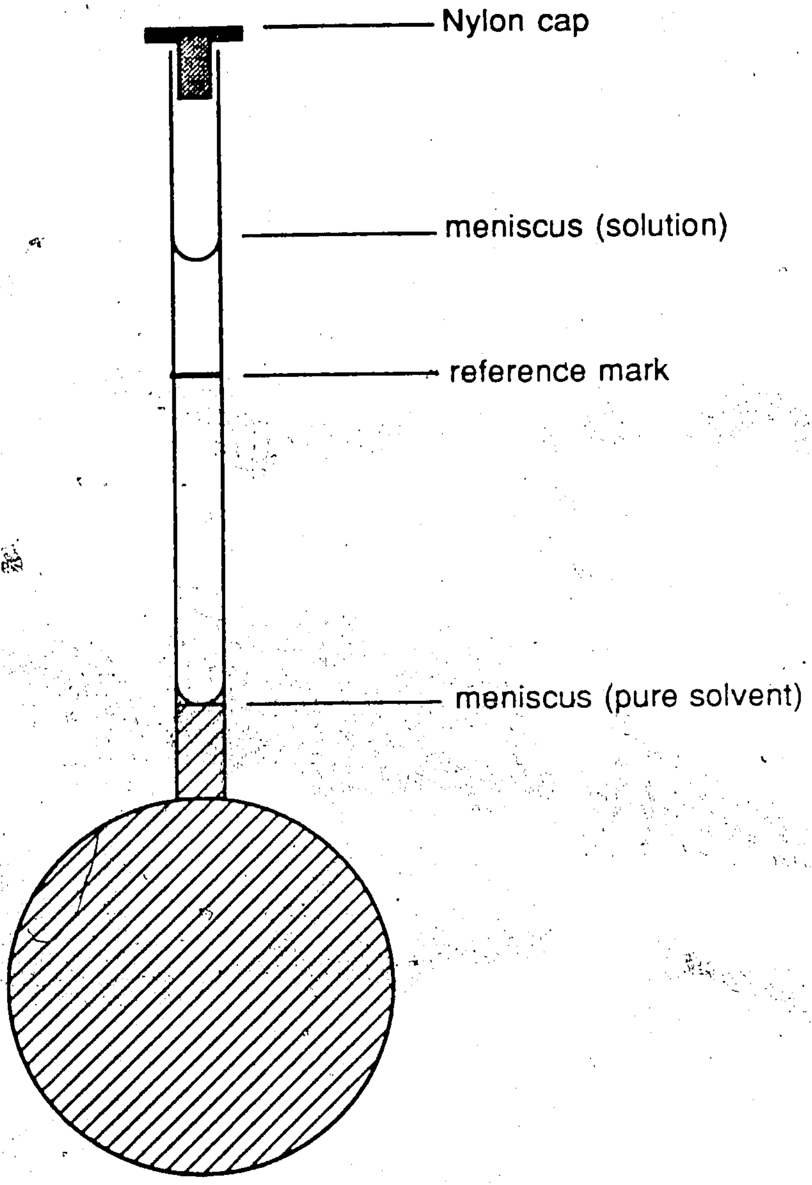

Figure 7-1. Diagram of dilatometer for measuring apparent molar volumes of dissolved gases

Operation

The solvent is degassed with an oil pump vacuum for three to five minutes and then loaded into the dilatometer through a 100 cm^3 hypodermic syringe fitted with a 200 mm needle. Solvent is loaded into the dilatometer until the solvent meniscus is about 10 mm up the capillary tube. The dilatometer is then closed with the Nylon stopper and allowed to equilibrate in a constant temperature bath. When equilibrium has been achieved the height of the meniscus relative to the reference mark is measured with a cathetometer to ±0.2 mm. The loaded dilatometer is then removed from the water bath, carefully dried, and weighed to ±0.0002 g.

The solute gas is introduced to the dilatometer under hydrostatic pressure very slightly above atmospheric pressure by connecting the top of the capillary tube to a gas cylinder with Tygon tubing. The bulb is then placed in ice-water which causes the solvent to contract and a gas space of approximately 1 cm^3 is produced. This space is large enough that easy solution of the solute gas is achieved by gentle rocking and shaking of the dilatometer. The intention is not to reach saturation but merely to gain sufficient mass of gas for suitable determination of the solute concentration by direct weighing.

The dilatometer is disconnected from the Tygon tubing, closed with the Nylon stopper, returned to the water bath, and left to equilibrate for 20-30 minutes. The final level of the meniscus relative to the reference mark and the final mass of the loaded dilatometer are then measured.

The difference between the initial and final values of the height of the meniscus is combined with a previously determined value (see section on calibration) for the average cross-sectional area of the capillary tube to obtain the volume expansion on solution. Division of this volume expansion by the number of moles of gas in solution (found from the difference in mass of the dilatometer before and after addition of the solute gas) yields the apparent molar volume of the solute gas in the solvent.

Temperature control to 0.005 K and pressure control to 10 kPa is sufficient to make all temperature, dilatation and compressibility corrections negligible. We found that at 25°C, even with the dilatometer uncapped, toluene (one of our more volatile solvents) was lost at a rate less than 1 mg per hour indicating that no corrections need be made for solvent losses due to diffusion of solvent up the capillary.

Provided that the amount of solute taken up by the solvent results in a rise of the meniscus of at least 40 mm and a gain in mass of about 0.5 g, the precision and accuracy of this technique are of the order of 1%. A complete experiment requires only 1.5 to 2 hours.

Calibration

A liquid of known density was injected into the dilatometer and, when equilibrium had been achieved, the height of the meniscus relative to the reference mark and the mass of the dilatometer were determined. A small volume of the same liquid was then added to the dilatometer and the measurement process repeated. The change in mass, combined with the density, gives the change in volume of liquid in the dilatometer. The average cross-sectional area of the capillary tube was obtained by dividing the volume change by the change in meniscus height.

Experimental

We have measured the apparent molar volume of sulphur dioxide in seven unsaturated hydrocarbons (benzene, toluene, m-xylene, mesitylene, cyclohexene, 1-methylnaphthalene, and tetralin), six saturated hydrocarbons (cyclohexane, methylcyclohexane, 1,3-dimethylcyclohexane, decalin, n-octane, and n-hexadecane) and four oxygen containing hydrocarbons (2-nonanone, diphenylether, dimethylphthalate, and 1-octanol) at 25°C using our new style of dilatometer. For the purpose of comparing the results obtained with our new dilatometer with those of other workers we have also measured the apparent molar volume of ethane in n-octane.

In all experiments the mole fraction of sulphur dioxide was less than 0.03; thus the measured apparent molar volumes are very close to the desired partial molar volumes at infinite dilution.

The temperature of the water bath was controlled to ±0.005 K with a Thermomix 1460 temperature controller.

Sulphur dioxide (Matheson), benzene (Anachemia), toluene (Anachemia), m-xylene (BDH), mesitylene (Fluka), cyclohexene (MCB), 1-methylnaphthalene (J. T. Baker), tetralin (Anachemia), cyclohexane (Caledon), decalin (Fisher), n-hexadecane (Alfa Products), 1,3-dimethylcyclohexane (Fisher), n-octane (Fisher), nonanone (Fisher), diphenylether (Fisher), dimethylphthalate (BDH), and 1-octanol (Fisher) were used without further purification. All of these chemicals were reagent grade except dimethylphthalate, 1-methylnaphthalene, and tetralin which had purities of 97% or higher.

Results and Discussion

As stated in the preceding section, we take our measured apparent molar volumes to be equal to the limiting partial molar volumes. The limiting partial molar volumes of sulphur dioxide in the seventeen solvents that we investigated are listed in Table 7-1. The reliability of the values obtained using our new dilatometer is demonstrated by comparison with values published by others. Handa, D'Arcy, and Benson (1982) found the limiting partial molar volume of ethane in n-octane to be 66.6 $cm^3\ mol^{-1}$, and Horiuti (1931) reported 46.8 $cm^3\ mol^{-1}$ for the limiting partial molar volume of sulphur dioxide in benzene. Our values for ethane in n-octane (65.8 $cm^3\ mol^{-1}$) and sulphur dioxide in benzene (47.8 $cm^3\ mol^{-1}$) agree with these reported values within the stated uncertainties of the measurements.

Table 7-1 shows that the limiting partial molar volumes of sulphur dioxide in electron donating solvents (unsaturated hydrocarbons and oxygen-containing hydrocarbons) are significantly smaller than the limiting partial molar volume of sulphur dioxide in non-electron donating solvents (saturated

Table 7-1. Limiting partial molar volumes of sulphur dioxide in organic solvents

Solvent	Limiting Partial Molar Volume[a,b]
Unsaturated Hydrocarbons	
Benzene	47.8
Toluene	46.1
m-xylene	46.2
Mesitylene	46.1
Cyclohexene	48.7
1-methylnaphthalene	44.6
Tetralin	44.3
Saturated Hydrocarbons	
Cyclohexane	55.4
Methylcyclohexane	54.7
1,3-dimethylcyclohexane	55.0
Decalin	52.6
Octane	56.2
Hexadecane	53.5
Oxygen-Containing Hydrocarbons	
2-nonanone	45.8
Diphenylether	45.4
Dimethylphthalate	43.1
1-octanol	44.1

[a] Units: $cm^3 mol^{-1}$

[b] Maximum uncertainty is less than 2%

hydrocarbons). We attribute this difference to the existence of a charge-transfer complex between electron donors and sulphur dioxide because formation of the charge transfer complex draws the sulphur dioxide molecules towards the solvent molecules. Stated another way, the relative equilibrium positions of sulphur dioxide and solvent molecules are closer to each other when a complex is formed than when no complex is formed.

Our limiting partial molar volumes (Table 7-1) can be used in equation 7-1 to calculate the pressure dependence of the Henry's law constant for each of the sulphur dioxide + solvent systems that we have investigated. However, as noted in the Introduction to this Chapter, in order to predict the solubility of sulphur dioxide in electron donating solvents as a function of pressure, we need to know the pressure dependence of the equilibrium constant, K, for the complexation reaction

[7-5] $SO_2 + e^- \text{ donor} = \text{complex}$

Here e^- donor refers to the electron donating solvent in the pure liquid state. SO_2 refers to uncomplexed sulphur dioxide in solution, and complex (also in solution) refers to the charge-transfer complex formed between SO_2 and e^- donor. The variation of the equilibrium constant for reaction [7-5] with pressure is given by the thermodynamic equation

[7-6] $(\partial \ln K/\partial p)_T = -\Delta V^\theta/RT$

where ΔV^θ represents the standard volume change of reaction [7-5] and all other symbols are as previously defined. Thus, in order to calculate the equilibrium constant for reaction [7-5] at pressures other than the standard state pressure we need to know the value of ΔV^{θ}.

As shown in Chapters 2 and 6 the standard volume change for a complexation reaction can be calculated from measured excess volumes, using the ideal associated solution model. However, no published measurements of excess volumes for SO_2 + e^- donor systems are available. Thus approximate methods must be used to obtain values of ΔV^{θ} for complex formation between sulphur dioxide and an electron donating solvent. In this connection we have applied the scaled particle theory of liquids (Reiss, 1965; Pierotti, 1976). As a specific example we consider the formation of a complex between sulphur dioxide and benzene.

Scaled particle theory gives an expression for the reversible work of forming in the solvent a cavity of size sufficient to contain the solute molecule. That is, the theory allows calculation of the free energy, G_{cav}, of transferring a non-interacting hard sphere (same diameter as a solute molecule) from an ideal gas phase to infinite dilution in the solvent. Taking the derivative of G_{cav} with respect to pressure, we obtain the scaled particle theory expression for the hard sphere contribution, V_{cav}, to the limiting partial molar volume:

$$[7\text{-}7] \qquad V_{cav} = \beta RT[(1 - y)^2 + 3(1 - y)(\sigma_2/\sigma_1) + 3(1 + 2y)(\sigma_2/\sigma_1)^2]/(1 - y)^3 + (N\pi(\sigma_2)^3)/6$$

In equation [7-7] σ_1 and σ_2 represent the hard sphere diameters of solvent and solute molecules, respectively, β represents the isothermal compressibility of the pure solvent, N represents Avogadro's constant, and y represents the reduced density

[7-8] $= (N\pi(\sigma_1)^3)/(6V_1)$

where V_1 represents the molar volume of the pure solvent.

In addition to the hard sphere contribution there are two other contributions to the limiting partial molar volume of a solute in a solvent:

[7-9] $V_2^o = V_{cav} + V_{int} + \beta RT$

The term V_{int} in equation [7-9] represents the pressure derivative of the free energy of solute/solvent interactions and βRT is the kinetic contribution of the hard sphere to the partial molar volume of solute. The first and third terms on the right-hand side of equation [7-9] can be evaluated for any solute/solvent system for which the compressibility of the solvent and the diameters of solvent and solute molecules are known. Therefore, if the limiting partial molar volume of a gas in a solvent has been determined experimentally, we can calculate the contribution to this volume arising from solute/solvent interactions, V_{int}:

[7-10] $V_{int} = V_2^o - V_{cav} - \beta RT$

For mixtures of sulphur dioxide + benzene we know that both chemical and physical interactions occur between the solute and the solvent. Accordingly, we separate V_{int} into chemical and physical contributions:

[7-11] $V_{int} = V_{int}(chem) + V_{int}(phys)$

Physical contributions to V_{int} arise from all interactions between solute and solvent that do not lead to the formation of the sulphur dioxide-benzene complex. We approximate $V_{int}(phys)$ for sulphur dioxide + benzene by $V_{int}(phys)$ for sulphur dioxide + a non-electron donating "model of benzene", such as cyclohexane. Cyclohexane is similar to benzene in size and polarisability (see Table 7-2) and, like benzene, has no dipole moment. This similarity suggests that $V_{int}(phys)$ for sulphur dioxide + cyclohexane is approximately equal to $V_{int}(phys)$ for sulphur dioxide + benzene. Since cyclohexane is not an electron donor, $V_{int}(chem) = 0$ for sulphur dioxide + cyclohexane. On this basis we interpret the difference between V_{int} for the sulphur dioxide + benzene system and V_{int} for the sulphur dioxide + cyclohexane system as being entirely due to chemical interactions between sulphur dioxide and benzene. That is to say, the standard volume change arising from the complexation reaction is given by

[7-12] $\Delta V^{\theta} = V_{int}(SO_2/C_6H_6) - V_{int}(SO_2/C_6H_{12})$

Values of the molecular diameters of sulphur dioxide, benzene, and cyclohexane are given in Table 7-2. This Table also lists the molar volumes and isothermal compressibilities of benzene and cyclohexane. Inserting these

Table 7-2. Molecular diameters (σ) of SO_2, C_6H_6, and C_6H_{12}. Molar volumes (V), isothermal compressibilities (β) at 298.15 K of C_6H_6 and C_6H_{12}. Molecular polarisabilities (α) of C_6H_6 and C_6H_{12}.

	σ/nm	$10^4\beta$/MPa^{-1}	V/cm^3 mol^{-1}	$10^{24}\alpha$/cm^3 molec^{-1}
C_6H_6	0.5455[a]	9.66[b]	89.408[b]	10.32[c]
C_6H_{12}	0.5771[a]	11.20[b]	108.755[b]	10.78[c]
SO_2	0.4102[a]	-	-	-

[a] Mourits and Rummens (1976).

[b] Tardajos, Diaz Pena, Lainez, and Aicart (1986).

[c] Pierotti (1976).

values into equation [7-7] we calculate $V_{cav}(SO_2/C_6H_6)$ and $V_{cav}(SO_2/C_6H_{12})$. Combining these values of V_{cav} with our values of $V^o(SO_2/C_6H_6)$ and $V^o(SO_2/C_6H_{12})$ in equation [7-10] leads to $V_{int}(SO_2/C_6H_6)$ = -60.0 cm^3 mol^{-1} and $V_{int}(SO_2/C_6H_{12})$ = -46.7 cm^3 mol^{-1}. From equation [7-12] we then calculate a value of ΔV^θ = -13.3 cm^3 mol^{-1} for the standard volume change for the benzene + sulphur dioxide complexation reaction.

Scaled particle theory might be used also to estimate ΔV^θ for other SO_2 + e$^-$ donor systems, provided that a non-electron donating model compound with physical properties (molecular diameter, dipole moment, and polarisability) similar to those of the electron donor of interest exists.

CHAPTER 8

Partial Molar Volumes and Solubilities of Gases in Bitumen

Introduction

Simulation and mathematical modelling of various *in situ* processes for production of bitumens from Alberta oil sands requires basic physico-chemical information on these bitumens. Such information includes partial molar volumes of gases dissolved in bitumen. Partial molar volumes can be used to calculate solubilities of gases at pressures above the Henry's law region. In particular, the partial molar volume used in these calculations is the partial molar volume at infinite dilution or limiting partial molar volume.

Limiting partial molar volumes of dissolved gases cannot be measured directly. In Chapter 7 we described how measurements of apparent molar volume made with our new dilatometer could be used to obtain partial molar volumes of dissolved gases at infinite dilution. It was shown that the limiting partial molar volume, V_2^o, is equal to the apparent molar volume at infinite dilution of gas. It follows that measurements of the apparent molar volume in very dilute solutions of the gas lead to good estimates of the limiting partial molar volume.

Measurement of the apparent molar volumes of gases in bitumen using our new dilatometer is complicated by the high viscosity of bitumen at temperatures that are of practical importance and by the low solubility of the gases of interest. This means that we cannot obtain an estimate of the limiting partial molar volume of a gas in bitumen by simply measuring the apparent molar volume in a very dilute solution of the gas in bitumen.

In this Chapter we present four alternate methods for obtaining values of the limiting partial molar volume of a gas in bitumen. The results obtained from the various methods are compared and discussed, and values of the partial molar volumes of carbon dioxide, ethane, propane, and sulphur dioxide in bitumen are recommended.

Our first method for obtaining the partial molar volume of a gas in bitumen requires measurements of the apparent molar volume of the gas (low concentration) in mixtures of bitumen and some organic solvent. On the basis of the argument presented above and in Chapter 7 we assume that the measured apparent molar volumes of solutes in dilute solutions are equal to the limiting partial molar volumes in these mixed solvents. Plotting the limiting partial molar volumes of gas in the mixed solvent against bitumen mole fraction of the solvent and extrapolating to pure bitumen gives an estimate of the limiting partial molar volume of the gas in bitumen. We have measured the apparent molar volumes of gases dissolved in bitumen/toluene and bitumen/mesitylene solutions and have used this extrapolation method to estimate the limiting partial molar volumes of the gases in bitumen.

A second estimate of the limiting partial molar volumes of gases in bitumen can be obtained by measuring the apparent molar volumes of gases dissolved in a liquid that has some of the same solvent properties as bitumen. In terms of solvent properties a "model bitumen" might consist of an appropriately weighted mixture of a long chain hydrocarbon, an aromatic or partially hydrogenated aromatic system containing two or more rings, and possibly a cyclic system containing a sulphur atom. Representative substances that we have chosen are hexadecane, 1-methylnaphthalene, and decalin. No suitable sulphur containing compound without an intensely disagreeable odour could be found. The weighting factors for each of the components of this model bitumen that would make the model most like real bitumen are unknown and hence we make the following approximation. Since solute partial molar volume is only moderately solvent dependent, the proportion of each component in the model bitumen is relatively unimportant. An estimate of the limiting partial molar volume of any gas in bitumen can be made by taking an average of the limiting partial molar volumes of a gas dissolved in each of the pure components of the model bitumen. Accordingly we have used our new dilatometer to measure the apparent molar volumes of gases dissolved in hexadecane, 1-methylnaphthalene, and decalin. Limiting partial molar volumes of the gases in these solvents were obtained from the measured apparent molar volumes as described earlier.

Another possible model for bitumen is automobile engine oil. Engine oil is chemically similar in some respects to bitumen but has a much lower viscosity, making it suitable for investigation in our new dilatometer. We have measured the apparent molar volume of carbon dioxide in Valvoline 10W-30 (automobile engine oil).

Because the densities of bitumen/gas solutions contain information on the partial molar volumes of the dissolved gases, measurements of densities of bitumen/gas solutions provide a third method of estimating the limiting partial molar volumes of gases in bitumen. The limiting partial molar volume of the dissolved gas can be calculated by considering the volume of a bitumen/gas solution to be the sum of a volume due to the pure bitumen at the particular applied pressure and a volume due to the dissolved gas. We have analysed recently reported densities of bitumen/carbon dioxide, bitumen/nitrogen and bitumen/methane solutions to obtain limiting partial molar volumes for carbon dioxide, nitrogen, and methane in bitumen.

Our fourth method is based on the empirical equation of Handa and Benson (1982), which correlates the limiting partial molar volume of a dissolved gas with the critical constants of the solute gas and the internal pressure of the solvent. By assuming that the limiting partial molar volume of one gas in bitumen (obtained by one or more of our other methods) is reliable, we can evaluate the internal pressure of bitumen from the correlation equation. We can then use this value of the internal pressure of bitumen in the correlation equation to estimate the limiting partial molar volumes of other gases in bitumen.

Experimental

Apparent molar volumes of carbon dioxide, sulphur dioxide, ethane, and propane in toluene, mesitylene, hexadecane, 1-methylnaphthalene, and decalin (normal commercial mixture of cis and trans isomers) were measured at 25°C using our new dilatometer (see Chapter 7). Apparent molar volumes of carbon dioxide, sulphur dioxide, and ethane in the solvents bitumen/toluene (60/40 by mass) and bitumen/mesitylene (60/40 by mass) were similarly determined. Apparent molar volumes of carbon dioxide in bitumen/mesitylene (80/20 by mass) at 45°C and undiluted Valvoline 10W-30 (automobile engine oil) at 25°C were also measured. In all of our experiments the mole fraction of dissolved gas was less than 0.03. Thus, the measured apparent molar volumes are very close to the desired partial molar volumes at infinite dilution.

The apparent molar volume of carbon dioxide in bitumen/mesitylene (80/20 by mass) was measured at 45°C because at 25°C this solution is too viscous to be loaded into our dilatometer. Because of the low thermal conductivity of this solution even at 45°C 2-3 hours are required for the meniscus to reach its equilibrium height in the dilatometer. Mesitylene was used as the second component of the solvent for this experiment because the low vapour pressure of mesitylene at 45°C (< 1 kPa) ensures that solvent losses by diffusion up the capillary tube are negligible despite the duration of the experiment.

Some of the above measurements were made using a modified version of the dilatometer described in Chapter 7. This second version was fitted with a

Kontes 3 mm bore tap and Viton O-ring seal so that gases could be delivered at pressures up to 150 kPa above atmospheric pressure. This version of the dilatometer was used to measure the apparent molar volumes of gases that have a low solubility in the solvent of interest.

Toluene (Anachemia), mesitylene (Fluka), hexadecane (Alfa Products), 1-methylnaphthalene (J. T. Baker), decalin (Fisher), n-octane (Fisher), benzene (Anachemia), carbon dioxide, sulphur dioxide, ethane and propane (Matheson) were used without further purification. All of these chemicals were reagent grade except for 1-methylnaphthalene which had a purity of 97% or higher. Valvoline 10W-30 (Valvoline) was obtained from a retail sample.

Bitumen was obtained from the Oil Sands Bank of the Alberta Research Council. The average molecular weight of this bitumen was found to be 481 g mol^{-1} by vapour phase osmometry.

Results and Discussion

As stated in the preceding section, our measured apparent molar volumes are taken to be equal to the limiting partial molar volumes. Our values for the limiting partial molar volume of gas in the systems that we investigated are listed in Table 8-1.

We turn now to the evaluation of the limiting partial molar volumes of gases in bitumen. The limiting partial molar volumes of carbon dioxide in mesitylene, bitumen/mesitylene (60/40), and bitumen/mesitylene (80/20) (see Table 8-1) were plotted against the mole fraction of bitumen in the solvent. The resulting

Table 8-1. Limiting partial molar volumes[a] of gases at 25°C

	Solute gas			
Solvent	CO_2	C_2H_6	SO_2	C_3H_8
Toluene	46.5	65.0	46.1	82.9
Bitumen/Toluene (60/40)[b]	45.2	61.4	42.3	-
Mesitylene	46.9	64.7	46.1	81.9
Bitumen/Mesitylene (60/40)[b]	44.6	62.9	44.4	-
Bitumen/Mesitylene (80/20)[b]	44.4[c]	-	-	-
Hexadecane	48.6	65.1	53.5	82.5
1-Methylnaphthalene	43.4	62.1	44.6	79.6
Decalin	47.5	62.5	52.6	79.5
Valvoline 10W-30	43.4	-	-	-

[a] Units: $cm^3\ mol^{-1}$

[b] Percentage by mass

[c] Temperature = 45°C

curve indicates that the limiting partial molar volume of carbon dioxide in bitumen/mesitylene is nearly independent of bitumen mole fraction above a bitumen mole fraction of 0.2. Extrapolation of the curve to pure bitumen (bitumen mole fraction = 1) yields a value of 43 cm^3 mol^{-1} for the limiting partial molar volume of carbon dioxide in bitumen. This extrapolation is necessarily long because solutions containing a mole fraction of bitumen higher than 0.5 were too viscous to be loaded into the dilatometer. However, as we have already mentioned, the slope of the curve at bitumen mole fractions above 0.2 is close to zero. Therefore the extrapolation is acceptable.

We have assumed that the dependence of the limiting partial molar volume of other dissolved gases on bitumen mole fraction is the same as that observed for carbon dioxide. We have also assumed that replacing mesitylene with toluene as the second component of the solvent will not affect this dependence. Using these assumptions and the results in Table 8-1 we constructed plots of limiting partial molar volume of dissolved gas against mole fraction of bitumen in the solvent for sulphur dioxide and ethane in bitumen/mesitylene and bitumen/toluene. A similar plot was also constructed for carbon dioxide in bitumen/toluene. Extrapolation of the resulting curves to pure bitumen yields two values for the limiting partial molar volumes of each of carbon dioxide, sulphur dioxide and ethane in bitumen. Taking the mean of the two values we obtain 43 cm^3 mol^{-1} for the limiting partial molar volume of carbon dioxide in bitumen, 42 cm^3 mol^{-1} for the limiting partial molar volume of sulphur dioxide in bitumen, and 60 cm^3 mol^{-1} for the limiting partial molar volume of ethane in bitumen.

As described in the first section of this Chapter, we have also estimated limiting partial molar volumes of gases in bitumen by considering a mixture of hexadecane, 1-methylnaphthalene, and decalin to provide a model of the solvent properties of bitumen. Table 8-1 shows that the limiting partial molar volume of carbon dioxide is about 10% higher in hexadecane than in 1-methylnaphthalene. This solvent dependence is small enough that we do not need to know the relative proportions of components in the model bitumen. A reasonable estimate of the limiting partial molar volume of carbon dioxide in bitumen can be found by taking an average of the limiting partial molar volumes of carbon dioxide in each of hexadecane, 1-methylnaphthalene, and decalin. On this basis we estimate the limiting partial molar volume of carbon dioxide in bitumen to be 45±2 $cm^3\ mol^{-1}$.

Applying the model bitumen method to our results for the limiting partial molar volumes of sulphur dioxide, ethane, and propane in the pure solvents hexadecane, 1-methylnaphthalene, and decalin (Table 8-1) leads to values of 47±3 $cm^3\ mol^{-1}$ for sulphur dioxide in bitumen,60±1 $cm^3\ mol^{-1}$ for ethane in bitumen, and 80±1 $cm^3\ mol^{-1}$ for propane in bitumen.

We have also used Valvoline 10W-30 (automobile engine oil) as a model for bitumen. The value of 43.4 $cm^3\ mol^{-1}$ that we obtained for the limiting partial molar volume of carbon dioxide in Valvoline 10W-30 provides further evidence that 43 $cm^3\ mol^{-1}$ is a good estimate of the limiting partial molar volume of carbon dioxide in bitumen. The agreement between the value obtained with Valvoline 10W-30 as a model for bitumen and those values found by other methods indicates that Valvoline 10W-30 is a good model solvent for bitumen.

Due to the well documented (see Chapter 7 and references therein) charge transfer interaction between sulphur dioxide and aromatic substances, the limiting partial molar volume of sulphur dioxide is strongly dependent on the degree of aromatic character of the solvent. Therefore, uncertainties associated with the extrapolation and model bitumen methods for obtaining the limiting partial molar volumes of gases in bitumen are larger for sulphur dioxide than for solutes which do not exhibit this type of interaction.

The limiting partial molar volumes of carbon dioxide, ethane, and sulphur dioxide in bitumen obtained from the extrapolation and model bitumen methods are in good agreement with each other. It appears that these methods together with our new dilatometer provide reliable and efficient approaches to the evaluation of the limiting partial molar volumes of gases dissolved in bitumen. If for some reason (e.g. low gas solubility) the extrapolation and model bitumen methods cannot be used, qualitative estimates of the limiting partial molar volumes of gases in bitumen may still be found by either of the following methods. One of these is based on the densities of bitumen/gas solutions (measureable only with considerable difficulty) of known composition while the other uses an empirically developed correlation equation.

Kalra and Robinson (1983) have collected data on the densities of bitumen/gas solutions and on the effect of pressure on the density of bitumen.

In order to obtain estimates of the limiting partial molar volumes of gases from these data we have assumed that the volume change associated with the dissolution of a gas can be regarded as the sum of two effects: a volume change of the pure bitumen due to the applied pressure alone and a volume change due to dissolution of the gas. From the results of Prowse, Wallace, Lott, Daigneault, and Shelley (1987) at 15°C we obtain the following expression relating V(P), the volume per gram of bitumen at pressure P, to V(P=0), the volume per gram of bitumen at zero pressure:

$$[8\text{-}1] \quad V(P)/V(P=0) = 1 - (0.00141)P/\mathrm{MPa}$$

We have used equation [8-1] to describe the compressibility of bitumen at temperatures between 15°C and 35°C. Since the contribution of the applied pressure to the overall volume change is very small, any error introduced by using equation [8-1] at temperatures above 15°C will have little effect on the values calculated for the partial molar volume of the dissolved gas.

The results of Svrcek and Mehrotra (1982) show that bitumen at 25°C under a pressure of carbon dioxide of 5.75 MPa contains 8.75 wt% carbon dioxide and has a volume of 0.9615 $cm^3\ g^{-1}$. These results also show that the volume of pure bitumen at zero applied pressure is 0.9615 $cm^3\ g^{-1}$. Since each gram of the bitumen/carbon dioxide solution contains 0.9125 g of bitumen, the volume per gram of solution occupied by the bitumen at zero applied pressure is 0.8774 $cm^3\ g^{-1}$. From equation [8-1] we obtain 0.8703 $cm^3\ g^{-1}$ for the volume of bitumen per gram of bitumen/carbon dioxide solution at 5.75 MPa. The remaining volume per gram of solution, 0.0912 $cm^3\ g^{-1}$, is due to the dissolved carbon dioxide. Dividing this volume by 0.0199 mol g^{-1}, the number of moles of carbon dioxide dissolved per gram of bitumen/carbon dioxide solution, we obtain 46 cm^3 mol^{-1} for the limiting partial molar volume of carbon dioxide in bitumen. We estimate the uncertainty in this value to be of the order of 20%. The value is in good agreement with that of 43 cm^3 mol^{-1} found using the extrapolation and model mixture methods.

Applying this method to results (Svrcek and Mehrotra, 1982) for methane in bitumen and nitrogen in bitumen we obtain 75±15 cm^3 mol^{-1} for the limiting partial molar volume of methane in bitumen and -230±50 cm^3 mol^{-1} for the limiting partial molar volume of nitrogen in bitumen. The value calculated by this method for the limiting partial molar volume of methane in bitumen is larger than expected. On the basis of the survey of Handa and Benson (1982) it appears that 58 cm^3 mol^{-1} is not an unreasonable value for the limiting partial molar volume of methane in typical solvents. The sign and magnitude of our calculated value of the limiting partial molar volume of nitrogen in bitumen have their origin in the data of Svrcek and Mehrotra (1982) that show a steep increase in density of bitumen with increasing pressure of nitrogen. Although such a density increase is possible if the bitumen undergoes some type of chemical reaction with the solute gas, this seems unlikely in the case of nitrogen.

Another approach to the limiting partial molar volumes of gases dissolved in bitumen may be found using the correlation equation of Handa and Benson (1982). This equation empirically relates the limiting partial molar volume at infinite dilution of a dissolved gas, V_2^o, to the critical temperature and pressure of the gas, T_2^c and P_2^c, and the internal pressure of the solvent, P_1^i:

[8-2] $$V_2^o = R[0.092\,(T_2^c / P_2^c) + 2.674(T/P_1^i)]$$

The symbols R and T in equation [8-2] represent the gas constant and the temperature, respectively. We now consider the use of equation [8-2] to estimate limiting partial molar volumes of gases dissolved in bitumen.

No value for the internal pressure of bitumen is available. However, by substituting our value of 43 cm^3 mol^{-1} for the limiting partial molar volume of carbon dioxide in bitumen into equation [8-2] and rearranging we obtain 576 MPa as the internal pressure of bitumen. This means that, in terms of internal pressure, bitumen is comparable with acetonitrile, P^i = 581 MPa, and 2-propanol, P^i = 552 MPa, (Dack, 1975). The high internal pressures of acetonitrile and 2-propanol result from the hydrogen bonding in these liquids. Bitumen also has properties that suggest significant chemical interactions between its components. For example, dissolved carbon dioxide markedly reduces the viscosity of bitumen, and we have recently noted that even a 1% solution of sulphur dioxide in bitumen lowers the viscosity considerably. We conclude that 576 MPa is a reasonable value for the internal pressure of bitumen.

Combining our value for the internal pressure of bitumen with the appropriate critical constants (Handbook of Chemistry and Physics,1986) we obtain the following limiting partial molar volumes of gases dissolved in bitumen: methane 43 cm^3 mol^{-1}, ethane 59 cm^3 mol^{-1}, propane 78 cm^3 mol^{-1}, nitrogen 40 cm^3 mol^{-1}, sulphur dioxide 53 cm^3 mol^{-1} and hydrogen 31 cm^3 mol^{-1}. These results conform to a considerable degree with the trends shown in Table 8-1.

Table 8-2 gives a summary of the results obtained using the four methods presented in this Chapter. Of the four methods for obtaining the limiting partial molar volumes of gases dissolved in bitumen, the most reliable results are obtained using our new dilatometer together with the extrapolation and model bitumen methods. We estimate that for reasonably soluble gases with moderate molar masses (e.g. carbon dioxide, propane) the values obtained from these two methods are accurate to within 5%. Our best estimates of the limiting partial molar volumes of carbon dioxide, ethane, sulphur dioxide, and propane in bitumen are given in Table 8-3.

For less soluble gases with smaller molar masses (e.g. nitrogen, hydrogen) it is difficult to use either of the more accurate methods to find reliable quantitative estimates of the limiting partial molar volumes of gases in bitumen. In these cases qualitative estimates can be made from the densities of bitumen/gas solutions (as described) or, if these are unavailable, from equation [8-2]. It may also be possible to construct a "high pressure" version of our dilatometer which could tolerate pressures up to 10 atmospheres. Measurements could then be made of the apparent molar volume of gas in pure bitumen at 10 atmospheres and 80°C. Limiting partial molar volumes of the gas in pure bitumen would then be estimated from the results of the

Table 8-2. Limiting partial molar volumes[a] of gases in bitumen using the four methods presented in this Chapter.

Gas	Extrapolation method	Model bitumen method	Densities of bitumen/gas mixtures	Correlation equation
CO_2	43	45	46	-
C_2H_6	60	60	-	59
C_3H_8	-	80	-	78
SO_2	42	47	-	53
N_2	-	-	-230[b]	40
H_2	-	-	-	31
CH_4	-	-	75[b]	43

[a] Units: cm^3 mol^{-1}

[b] Probably incorrect as discussed in text

Table 8-3. Recommended limiting partial molar volumes[a] of gases in bitumen at 25°C.

CO_2	C_2H_6	SO_2	C_3H_8
43	60	44	80

[a] Units: cm^3 mol^{-1}

measurements of apparent molar volume as we have described earlier.

Limiting partial molar volumes of dissolved gases can be used to predict gas solubilities at pressures above the usual Henry's law region by way of the Krichevsky-Kasarnovsky equation (Krichevsky and Kasarnovsky, 1935; Dodge and Newton, 1937; Prausnitz, Lichtenthaler, and de Azevedo, 1986):

[8-3] $\ln(f_2/x_2) = \ln k_H{}^o + V_2{}^o P/RT$

In equation [8-3], f_2 represents the fugacity of the solute, x_2 represents the mole fraction of the solute, and $k_H{}^o$ represents the Henry's law constant at the saturation pressure of the solvent. All other symbols are as previously defined. Derivation of equation [8-3] requires three assumptions: the limiting partial molar volume of the dissolved gas is independent of pressure, the saturation pressure of the solvent is negligible compared to the total pressure, and the solution is dilute enough that Henry's law holds. All assumptions are valid for the case of a dilute solution of a gas in bitumen at 25°C. Our values for the partial molar volumes of carbon dioxide, ethane, sulphur dioxide and propane in bitumen with equation [8-3] allow prediction of the solubility of these gases in bitumen as a function of pressure.

Lu, Chung, Adachi, and Boublik (1986) have recently assessed existing solubility data for methane, nitrogen, and carbon dioxide in bitumen on the basis that the ratio of gas fugacity to mole fraction solubility in logarithmic form is expected to be a smooth function of pressure. This function is non-linear in general but approaches equation [8-3] in the limit of low gas solubility. These authors rejected 33 of 100 data points on this test as being too discordant. Provided that the gas solubility is low, the remaining points together with equation [8-3] yield values for the limiting partial molar volumes of the gases in bitumen.

Of the data recommended by Lu et al. (1986) the lowest experimental mole fraction of methane in bitumen at 300 K was 0.027, the highest 0.313. These workers have constructed a plot of $\ln(f_2/x_2)$ against pressure for methane + bitumen mixtures . The plot is reasonably linear. From the slope of this plot we have calculated a value of 66 cm^3 mol^{-1} for the limiting partial molar volume of methane in bitumen. Slightly larger values are obtained at 318 K and 431 K, and a much larger value is found at 373 K.

For nitrogen in bitumen at 326 K and at mole fractions similar to those for methane, we obtained (from the recommended data of Lu et al.) a value of 169 cm^3 mol^{-1} for the limiting partial molar volume of nitrogen. Similar calculations led to a value of 134 cm^3 mol^{-1} for the limiting partial molar volume of carbon dioxide in bitumen at 297.7 K.

All of the limiting partial molar volume values that we calculated from the solubilities recommended by Lu et al. (and cited here) are surprisingly large in comparison with typical values for the same gases in common solvents and the estimates of partial molar volumes of gases in bitumen discussed earlier in this work.

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Appendix A. Calculation of model association equilibrium constant from vapour pressure-composition data

Consider a mixture containing N_A moles of A and N_B moles of B; here we are focussing on chemical systems in which equilibrium $A + B = AB$ is supposed to be the sole cause of deviations from Raoults law (ideal solution). We can view the association in terms of a mass balance as shown in Table 2-3 in which n_{AB} represents the amount of AB formed and $r = n_{AB}/(N_A + N_B)$. From Table 2-3 we obtain

[A-1] $z_A = (x_A - r)/(1 - r)$

and

[A-2] $z_B = (x_B - r)/(1 - r)$

Solving [A-1] and [A-2] for r and equating the two expressions leads to

[A-3] $z_B = 1 + (z_A - 1)x_A/x_B$

We now assume (can be checked by experiment) that there is a negligible amount of the complex AB in the gas phase at low pressure and express the total pressure (P_t) as the sum of the partial pressures of A and B (p_A and p_B)

[A-4] $P_t = p_A + p_B$

In accord with the ideal associated solution model, we take the partial pressures of A and B to be given by the Raoult's law expressions written in terms of the equilibrium mole fractions of A and B:

[A-5] $p_A = z_A p_A^{\bullet}$

[A-6] $p_B = z_B p^{\bullet}_B$

where $p^{\bullet}_i$ represents the vapour pressure above pure i. Substitution of [A-5] and [A-6] into [A-4] gives

[A-7] $P_t = z_A p^{\bullet}_A + z_B p^{\bullet}_B$

which can be combined with [A-3] to give

[A-8] $z_A = [x_B P_t - p^{\bullet}_B(x_B - x_A)]/(x_B p^{\bullet}_A + x_A p^{\bullet}_B)$

A similar derivation with subscripts A and B reversed leads to a similar expression for z_B:

[A-9] $z_B = [x_A P_t - p^{\bullet}_A(x_A - x_B)]/(x_B p^{\bullet}_A + x_A p^{\bullet}_B)$

Also, since the sum of the equilibrium mole fractions is unity we can express z_{AB} by

[A-10] $z_{AB} = (1 - z_A - z_B)$

Now, we can use equations [A-8], [A-9], and [A-10] in

[A-11] $K = z_{AB}/z_A z_B$

to obtain the desired values of the model equilibrium constant, K. In Chapter 5 we have used K_z to denote the model equilibrium constant.

Calculation of the equilibrium mole fractions (equations [A-8], [A-9], [A-10]) and thence the equilibrium constant (equation [A-11]) as described here makes use of the accurately known quantities $p^{\bullet}_A$, $p^{\bullet}_B$, x_A, and x_A. Previously (for example Handa and Jones, 1975) the equilibrium constant has been calculated using $p_i = y_i p_i^{\bullet}$ (y_i = vapour phase mole fraction) in

[A-12] $K = [1 - (p_A/p_A^{\bullet}) - (p_B/p_B^{\bullet})]/ (p_A/p_A^{\bullet}) (p_B/p_B^{\bullet})$

Partial pressures of gases cannot be measured and must be obtained by indirect methods. For this reason, partial pressures of gas are not known as accurately as the quantities that are used to calculate the equilibrium constant by our method. Therefore calculation of the equilibrium constant by the method described in this Appendix leads to values of K that are slightly more accurate than those calculated from equation [A-12].

Appendix B. Iterative procedure for obtaining consistent values of equilibrium constant, partial pressure of gas, and mole fraction solubility of gas from measurements of gas solubility when the solvent has an appreciable vapour pressure.

Calculation of the value of the equilibrium constant that is consistent with a value of the Henry's law constant from results obtained using the isobaric equilibrium solubility technique is made more difficult if the solvent has an appreciable vapour pressure. In this case we take the measured pressure, P_t, to be the sum of the partial pressures of the gas, p_B, and the solvent, p_A:

[B-1] $P_t = p_A + p_B$

We obtain a first estimate of p_B from [B-1] by taking the value of p_A to be equal to the pressure above pure solvent A, $p^{\bullet}_A$.

We let ΔV represent the change in volume of the vapour space of the solubility apparatus that occurs when the solvent is introduced. Then we write

[B-2] $\Delta V = V_A + \Delta N_B V_B^{o} + V_{Hg}$

where V_A represents the volume of solvent in the apparatus, ΔN_B represents the amount (moles) of B dissolved in A, V_B^{o} represents the partial molar volume of B in A, and V_{Hg} represents the volume of mercury added to maintain constant pressure in the apparatus. A first estimate of ΔV is obtained by setting ΔN_B equal to zero in equation [B-2].

The volume of the vapour space (V) and the amount of gas in the vapour space, N_B, are related by the virial equation

[B-3] $p_BV = N_B(RT + \beta p_B)$

where β represents the second virial coefficient of component B. From equation [B-3] we can see that when the volume of the vapour space changes by ΔV (at constant p_B and T) the change in the amount of gas in the vapour space, ΔN_B, is given by

[B-4] $N_B = p_B\Delta V/(RT + \beta p_B)$

We now insert our estimates of p_B and ΔV into equation [B-4] to obtain a first approximation of ΔN_B, the amount of gas dissolved in the solvent at equilibrium. Combination of this estimate of N_B with the value for the number of moles of solvent, N_A, (obtained experimentally) in

[B-5] $x_B = \Delta N_B/(\Delta N_B + N_A)$

yields the first approximation for x_B, the mole fraction solubility of gas B in solvent A.

We carried out this series of calculations for each set of experimental results to obtain first approximations for p_B and x_B, corresponding to each measured total pressure pressure. We plotted x_B/p_B against $(1 - 2x_B)$ to obtain an estimate of the Henry's law constant (k_H) as indicated by equation [4-9]. We then calculated the value of the association equilibrium constant (K) that is consistent with this value of k_H as follows.

Combination of the estimate of k_H with each p_B, x_B pair yields (equation [4-7]) an "estimate" of K. The average of these K values was taken to be our first estimate of K. This estimate of K was then inserted into

[B-6] $z_A = 1 - [K + 1 - [(1 + K - 2Kx_A)^2 + 4Kx_A^2]^{1/2}] /2Kx_A$

to obtain estimates of the equilibrium mole fraction of solvent, z_A, corresponding to each measured total pressure. In equation [B-6] $x_A = 1 - x_B$. Substitution of these z_A estimates into

[B-7] $p_A = z_A p_A^{\bullet}$

yields new estimates of the partial pressure of solvent, p_A, and thence new estimates of p_B (equation [B-1]). New estimates of ΔV were calculated from equation [B-2] using the values of ΔN_B calculated above. These new estimates of ΔV lead to new estimates of ΔN_B (equation [B-4]) and thence to new estimates of x_B (equation [B-5]). Combination of our estimate of k_H (see above) and the new p_B, x_B pairs yields a new series of K values. The average of these K is calculated. We repeat this procedure until the value obtained for the equilibrium constant from successive iterations is unchanged to one part in a thousand. The last value of the equilibrium constant and the corresponding p_B, x_B values are the values that are consistent with our estimate of k_H.

The iterative procedure described here is designed expressly for use with results obtained from the apparatus employed in our experiments. However, the basic principles, described by equations [B-1], [B-4], [B-5], [B-6], and [B-7], can be applied to the development of an iterative procedure for analysis of results from other methods of determining isobaric gas solubility.

Appendix C. Operation of the isoperibol calorimeter

The design of the calorimeter has been described in Chapter 3 (pp 27 and 28). A diagram of the calorimeter is given in Figure C-1. To begin an experiment the reaction mixture is weighed into the Dewar flask (B). The flask is then clamped to the inside of the brass can (A) as shown in Figure C-1 and the calorimeter is placed in a constant temperature water bath. The resistance of the thermistor (F) is monitored using a resistance bridge. When the resistance of the thermistor attains a value that has been shown by separate experiments to correspond to the temperature of the water bath, a known volume of titrant is introduced to the Dewar flask from the outlet of the titrant delivery tube (D). The interaction of the titrant with the reaction mixture leads to a change in the temperature of the mixture in the Dewar and a corresponding change in the resistance of the thermistor. The temperature of the mixture then gradually relaxes back towards the temperature of the surrounding water bath. During this relaxation period the resistance of the thermistor is recorded as a function of time. When the change in resistance of the thermistor with time has been constant for several minutes, the calibration heater is switched on. The voltage across the heater, V_h, and the time of heating, t, are recorded using the circuit shown in Figure C-2. The current through the heater, I_h, is calculated from the measured voltage across a standard resistor (SR). After the heater has been switched off the resistance of the thermistor as a function of time is again recorded.

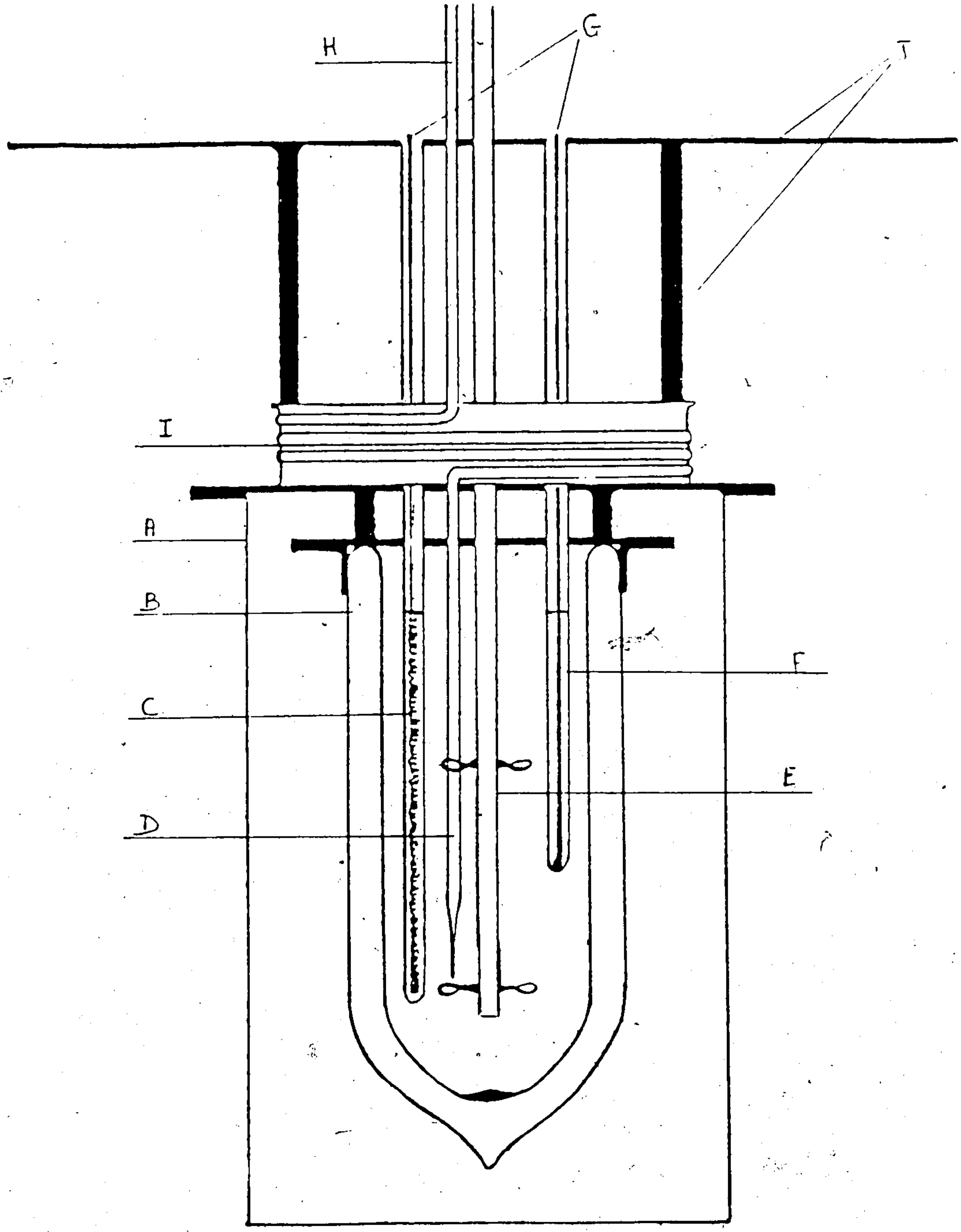
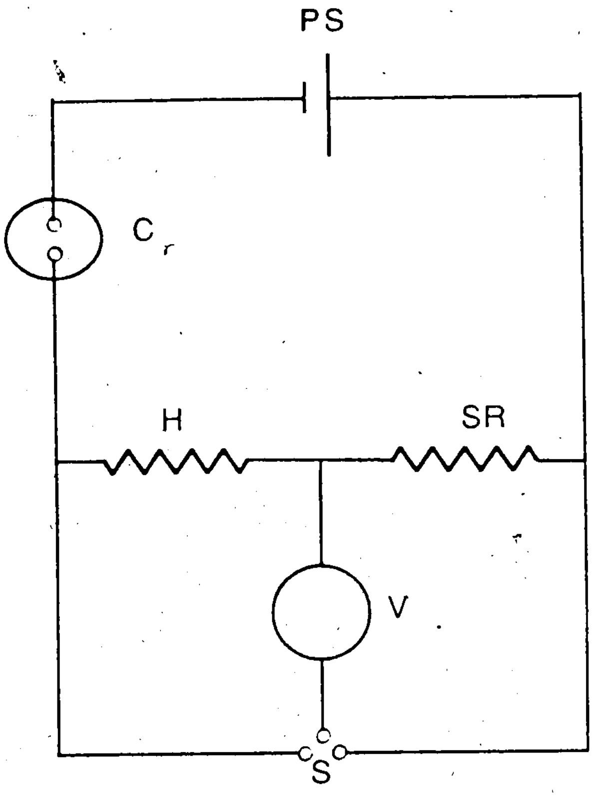


Figure C-1. Cross-sectional diagram of isoperibol calorimeter (captions on following page)

A	brass can
B	Dewar flask
C	heating element immersed in paraffin oil
D	outlet of titrant delivery tube
E	stirrer
F	thermistor immersed in paraffin oil
G	exit tubes for heater and thermistor lead wires
H	titrant delivery tubing
I	heat exchange coil to bring titrant solution to the temperature of the constant temperature bath surrounding the calorimeter
J	brass lid and supports.



PS	power supply
SR	standard resistor, 10.004 Ω
V	voltmeter
H	heater
C	clock
S	switch

Figure C-2. Diagram of electrical calibration circuit

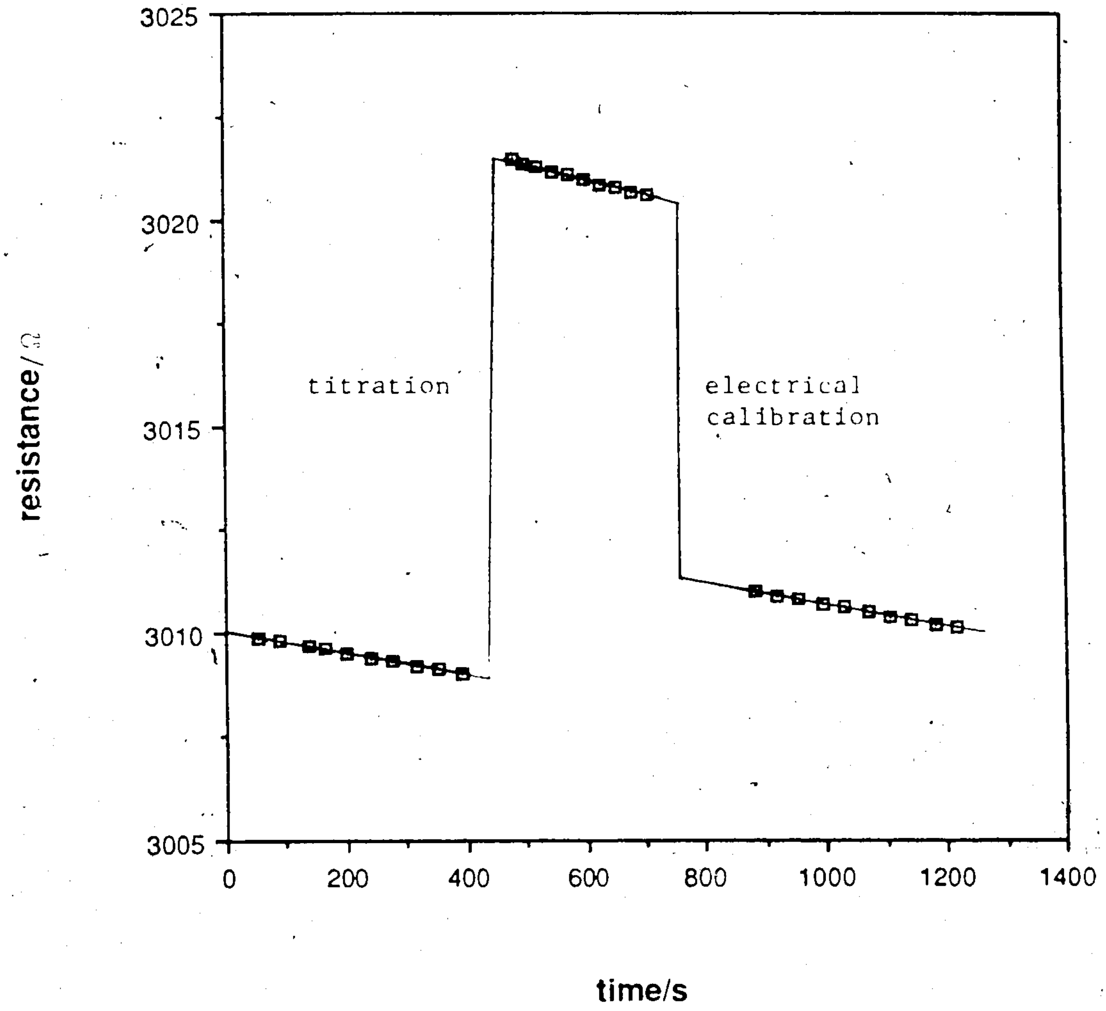


Figure C-3. Typical plot of the resistance of the thermistor against time. Points are experimental; solid line represents the reconstructed calorimetric record.

A typical plot of the resistance of the thermistor as a function of time for one complete calorimetric experiment is given in Figure C-3. The solid lines in Figure C-3 represent the reconstructed calorimetric record that was determined using the method of Vanderzee (1981). The two vertical lines in Figure C-3 represent the instantaneous changes in resistance of the thermistor due to the titration and the electrical calibration. Since the total heat capacity of the calorimeter is the same for the titration and the electrical calibration, the ratio of the heights of the vertical lines in Figure C-3 is equal to the ratio of the energies associated with the two processes. The electrical energy of the calibration is known from $Q_c = I_h V_h t$ and hence the energy associated with the titration can be calculated.