R. A. ROBINSON MEMORIAL LECTURE

Thermodynamics of Hydrogen-bonded Liquids

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1 Introduction

While water is the most important of hydrogen-bonded liquids, it is also the most complex. This is because its molecule has two hydrogen bond acceptor sites and two protons which can participate in other H-bonds. This gives rise to a three-dimensional hydrogen-bonded network structure which is quite regular in ice and less well-defined but still vitally important in the liquid state.

The hydrogen-bonding in alcohols is somewhat simpler because there is only one hydroxy-group per molecule, so that the 'polymers' are chains and rings rather than three-dimensional structures. For both water[1] and alcohols[2] there have been striking recent advances in understanding the structure of the pure liquids as a result of computer studies based on the use of potential functions which more or less accurately represent both the charge distributions giving rise to hydrogen bonding, and the other intermolecular effects. These studies, however, remain very demanding on computer time and there is still an important place for the classical approach of measuring solution properties and interpreting and correlating the results in terms of chemical or 'pseudochemical' models of association through hydrogen bonds.

In principle, such studies depend on the proposition that at extremely high dilution in an inert solvent the solute consists of single molecules without H-bonds. As the concentration is progressively increased, a variety of hydrogen-bonded clusters appear, accompanied by changes in the thermodynamic, spectroscopic, and dielectric properties. (Experimentally, the reverse process of progressive dilution of the pure liquid is of course adopted). In this context, 'inert' implies that the diluent does not modify the association process except by increasing the average separation of the associating molecules. In the case of water, the association is so strong that the only solvents which will dissolve useful amounts of it cannot be described as inert towards it. Dioxan, for example, which has a low dielectric constant and is often used with water as a mixed solvent for electrolytes, is seen by a water molecule not as non-polar, but as having two oxygen atoms

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*Emeritus Professor. This review is an expanded version of the inaugural R. A. Robinson Memorial Lecture given at Imperial College London, the University of Newcastle-upon-Tyne, and St. Andrews University in October, 1981.

[1] R. O. Watts and I. J. McGee, 'Liquid State Chemical Physics', Wiley, New York, 1976.
[2] W. I. Jorgensen, *J. Am. Chem. Soc.*, 1981, **103**, 335.

which can accept hydrogen bonds. Even benzene, in which water has a modest solubility, must be considered as providing in its π-electron system an environment which lowers the energy of a water proton and hence competes with the hydrogen bonding between water molecules. The only solvents which could not be expected to show such effects are those of paraffinic type, and in these water is so insoluble that dilution of a saturated solution can only occur at concentrations too low for accurate thermodynamic study. Spectroscopy can however give some information at these low concentrations.

The study of alcohols dissolved in non-polar solvents is much easier. Some of the lower alcohols are only partially miscible with some paraffins at room temperature, *e.g.* methanol + hexane and ethanol + hexadecane, but even in these cases the range of miscibility at the low alcohol compositions includes the concentrations at which most of the alcohol association occurs. The fact that incomplete miscibility can occur, however, is evidence that interactions between the alcohol and the solvent must be considered, for it is known[3] that the association of a solute in an otherwise ideal solution cannot give rise to phase separation. The proof of this is so neat as to be worth repeating in a paraphrased form:

> No matter how assorted a set of association products is formed, the equilibrium constants for their formation must all be positive, and the stoicheiometric concentration of the solute can therefore be expressed as a polynomial in the concentration of the free monomer, with all coefficients positive. Hence the stoicheiometric concentration must be a monotonicially rising function of the free monomer concentration. Now if the various association products and the solvent form an ideal mixture, the stoicheiometric solute activity is equal to the monomer mole fraction (or concentration, if volume-scale ideality is assumed). Since this rises monotonically with the stoicheiometric solute concentration, there can never be two different solution compositions with the same solute activity, and hence never any phase separation.

My interest in liquid mixtures arose naturally out of work with Robinson on electrolytes. In 1948 we had proposed an explanation of the increase in the activity coefficient of many electrolytes at high concentrations in terms of a hydrated-ion model.[4] We treated the solution as one of hydrated cations, free anions, and free water, and assumed that the solution behaved as an ideal solution of these species except for the effects of ion–ion interactions, which were described by the usual Debye–Hückel formula. This treatment, though it had some defects, did a good deal to make hydrated ions respectable entities again after some decades of ill repute. A valuable modification of the theory was made by Glueckauf,[5] who pointed out that we had implicitly assumed mole fraction ideality for the entropy of mixing of the solvated ions, anions, and free water molecules. He suggested that the entropy of mixing would be more appropriately calculated by the volume-fraction statistics of Flory and Huggins,

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[3] E. W. Washburn, *Trans. Am. Electrochem. Soc.*, 1912, **22**, 330.

[4] R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, 1948, **70**, 1870.

[5] E. Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 1235.

and showed that this led to a more consistent set of hydration numbers. This argument was based on the fact that the hydrated ion must be considerably larger than a water molecule. It was not clear, however, that the Flory–Huggins formulae developed for high polymer solutions were necessarily right for mixtures of globular molecules such as hydrated ions and water.

I therefore suggested to K. N. Marsh at Armidale that he examine experimentally the entropy of mixing of unreactive globular molecules of similar chemical nature, but of substantially different sizes. This he undertook with great success, beginning with some highly precise vapour pressure measurements on mixtures of octamethylcyclotetrasiloxane with benzene and carbon tetrachloride.[6] Though these were accurate enough to permit a separation into enthalpy and entropy effects *via* their temperature dependence, we realized that to supplement the vapour pressures by direct calorimetric measurements of enthalpies of mixing would greatly expedite the work. We therefore developed, from H. C. Van Ness's brilliant concept[7] of the isothermal dilution calorimeter, a more refined and precise instrument using mercury displacement instead of a solid piston to eliminate the need of a vapour space.[8] Subsequently, similar continuous dilution techniques were developed for the measurement of excess volumes,[9–11] compressibilities,[12] dielectric constants,[13] and vapour pressures.[14] Marsh and collaborators[15] continued the study of globular molecules, working especially with cycloparaffins, while my group took advantage of the new techniques to study hydrogen-bonding interactions in solutions of alcohols in non-polar solvents.[16–21]

2 Experimental Techniques

The thermodynamic properties of the most direct interest for the study of association equilibria are the activity coefficients of the alcohol and the solvent, and the enthalpy of dilution from a given composition to infinite dilution of alcohol. The dielectric constant of the solution, which yields the apparent dipole

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[6] K. N. Marsh, *Trans. Faraday Soc.*, 1968, **64**, 883.

[7] C. G. Savini, D. R. Winterhalter, L. H. Kovacs, and H. C. Van Ness, *J. Chem. Eng. Data*, 1966, **11**, 40.

[8] (*a*) R. H. Stokes, K. N. Marsh, and R. P. Tomlins, *J. Chem. Thermodyn.*, 1970, **2**, 751; (*b*) M. J. Costigan, L. J. Hodges, K. N. Marsh, R. H. Stokes, and C. W. Tuxford, *Aust. J. Chem.*, 1980, **33**, 2103.

[9] R. H. Stokes, B. J. Levien, and K. N. Marsh, *J. Chem. Thermodyn.*, 1970, **2**, 43.

[10] G. A. Bottomley and R. L. Scott, *J. Chem. Thermodyn.*, 1974, **6**, 973.

[11] M. K. Kumaran and M. L. McGlashan, *J. Chem. Thermodyn.*, 1977, **9**, 259.

[12] M. B. Ewing, K. N. Marsh, and R. H. Stokes, *J. Chem. Thermodyn.*, 1972, **4**, 637.

[13] R. H. Stokes and K. N. Marsh, *J. Chem. Thermodyn.*, 1976, **8**, 709.

[14] R. P. Tomlins and K. N. Marsh, *J. Chem. Thermodyn.*, 1976, **8**, 1185.

[15] M. B. Ewing and K. N. Marsh, *J. Chem. Thermodyn.*, 1974, **6**, 1087 (and earlier papers there cited).

[16] R. H. Stokes and C. Burfitt, *J. Chem. Thermodyn.*, 1973, **5**, 623; 1975, **7**, 803.

[17] R. H. Stokes and M. Adamson, *J. Chem. Thermodyn.*, 1976, **8**, 683.

[18] R. H. Stokes and M. Adamson, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1232.

[19] R. H. Stokes, *J. Chem. Soc., Faraday, Trans. 1*, 1977, **73**, 1141.

[20] H. T. French, A. Richards, and R. H. Stokes, *J. Chem. Thermodyn.*, 1979, **11**, 671.

[21] H. T. French and R. H. Stokes, *J. Phys. Chem.*, 1981, **85**, 3347.

moment of the alcohol as a function of composition, is also informative in a more qualitative way. Excess volumes (volume change on mixing) are also of interest, but do not in general add much to the conclusions from the enthalpy measurements. Among non-thermodynamic properties, infra-red and n.m.r. spectroscopy have been extensively studied, though the conclusions show a good deal of dependence on assumptions about the assignment of frequencies to particular modes.

One of the most powerful techniques of the electrolyte chemist is the measurement of the e.m.f. of reversible cells (a method extensively and successfully used by Robinson). This technique gives a direct measure of free-energy change, and has provided extremely accurate data on activities for electrolyte solutions. It is not available for non-electrolyte solutions, and we consequently depend for non-electrolyte activities almost entirely on methods involving phase equilibria: vapour pressures, cryoscopy, and gas chromatography are the most familiar. (The qualification 'almost entirely' allows for the possibility of obtaining usefully accurate data from light-scattering studies).

A. Vapour Pressure Measurements.—Until the last decade or so, activities of liquid mixtures were usually measured in an equilibrium still,[22] where the condensed vapour is recycled to the boiler until a steady state is reached, whereupon both the liquid phase in the boiler and a condensed sample representing the vapour are analysed. The partial pressures of both components can then be calculated from the known external total pressure. This method does not work well at high dilutions of one component, and if a set of isothermal values is required the pressure must be accurately adjusted and controlled. Barker[23] pointed out that only the measurement of the total pressure is really needed, provided it covers a range of liquid compositions at one temperature, because the partial pressures of the components are connected *via* the Gibbs–Duhem relation. This eliminates the need for the analysis of the vapour phase. The method of calculation proposed by Barker was to assume a suitable functional form for the excess free energy of the solution, with a number of adjustable parameters (*e.g.* coefficients of a polynomial in the mole fraction). Expressions for the component activities and hence partial pressures are then obtained by appropriate differentiation of the free-energy function. The resulting calculated total pressures are then made to agree with the observed values by a least-squares procedure for adjusting the parameters. Although this method works well for most organic liquid mixtures, it proves difficult with alcohol solutions because of the extremely unsymmetrical nature of the partial excess free-energy functions, which arises from the breaking of the hydrogen bonds at high dilutions. An alternative method, successfully used by Marsh[6] for simpler cases, depends on the fact that modern designs of vapour pressure apparatus allow the progressive addition of very small amounts of alcohol to a large amount of solvent, with a vapour pressure measurement at each stage. At the lowest concentrations (say below 0.002 mole fraction of alcohol), the solvent activity coefficient is so close

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[22] I. Brown, *Aust. J. of Sci. Res.*, 1952, **5A**, 530.

[23] J. A. Barker, *Aust. J. Chem.*, 1953, **6**, 207.

to unity that the solvent partial pressure can be calculated as if it were ideal; the subtraction of this from the observed total pressure therefore yields the alcohol partial pressure. From this, the alcohol activity coefficient can be calculated. From a few such measurements at high dilutions, an extrapolation can be made to obtain the activity coefficient of the alcohol at infinite dilution. Integration of the Gibbs–Duhem equation then gives a more correct solvent activity coefficient, which is recycled until both solute and solute activity coefficients are unchanged. The next solvent addition is then made, and the integration and iteration are continued. This method ceases to work if a maximum in the total vapour curve is reached, but this is at higher alcohol concentrations where either the Barker method can be used, or the curve can be completed by the same marching procedure starting from the pure alcohol end.

Tucker and Christian[24,25] have obtained excellent results by the simple device of using the higher paraffins as solvents. Since these have very low vapour pressures, the measured pressure is the alcohol vapour pressure alone, which greatly simplifies the calculations.

In converting the partial pressures to activity coefficients, it is necessary to have reasonably good estimates of the second virial coefficients of the pure and mixed vapours at the temperatures of interest.[26] Lack of these is sometimes a limiting factor in the accuracy of the results. For the alcohols especially, virial coefficients are difficult to measure because (*a*) there is still some hydrogen-bonding in the vapour phase, so that the virial coefficients are large and highly temperature-dependent; (*b*) virial coefficients higher than the second have to be considered; and (*c*) the problems of adsorption are enhanced for highly polar molecules.

The routine measurement of solution vapour pressure has been greatly facilitated by technological developments such as the differential capacitance manometer and the quartz spiral pressure gauge, which make it possible to measure vapour pressures without the vapour coming into contact with mercury. The continuous dilution method[14] has also led to a considerable speeding up of the measurements, avoiding the need for much weighing of liquids in ampoules which are then broken inside the vapour pressure cell. It goes without saying that a high degree of purity is required for the liquids used; purity testing has been greatly facilitated by the commercial availability of gas chromatographic analysers. Freedom from dissolved gases is essential in vapour pressure measurements; this is most readily ensured by repeated vacuum sublimation in between passages of the vapour through a molecular sieve. Temperature control to ± 0.001 K should be aimed at, and, for the sake of cross-checking with other work, the actual temperature should be known in terms of IPTS 68 standards within at worst 0.005 K.

Since excess enthalpies can now be measured very easily, there is little point

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[24] E. E. Tucker and S. D. Christian, *J. Phys. Chem.*, 1977, **81**, 1295.

[25] E. E. Tucker and E. D. Becker, *J. Phys. Chem.*, 1973, **77**, 1783.

[26] 'Chemical Thermodynamics', ed. M. L. McGlashan, (A Specialist Periodical Report) The Chemical Society, London 1978, Vol. 2.

making vapour pressure or other free-energy measurements at more than one temperature. This may be chosen to give the range of pressures best suited to accurate measurement with the available equipment; in the case of alcohol solutions[18,20,21] we have used 45 and 52 °C.

Freezing-point measurements provide another source of free-energy information. Provided that the solid phase which freezes out is the pure solvent, its chemical potential—a measurable function of temperature—must be equal to that of the solvent in the liquid phase. Almost all aqueous electrolyte solutions satisfy this proviso, but the probability of solid solution formation is higher in the case of non-electrolyte liquid mixtures. Thus work in Armidale has shown,[27–30] by comparing the results of freezing-point and vapour pressure studies, that ethanol in *p*-xylene gives a pure xylene solid phase, but ethanol in cyclohexane appears to deposit a very dilute solid solution of ethanol in cyclohexane. The other standard objection to freezing-point measurements, that they yield results only at or near the freezing-point of the solvent, is also a minor restriction, because it is somewhat more difficult to obtain high precision temperature control below room temperature than above it.

B. Measurement of Enthalpy of Mixing.—Results of calorimetric experiments on the mixing of two liquids are usually expressed in terms of the excess enthalpy, H^E, which is defined as the heat absorbed when one mole of solution is formed from the appropriate amounts of components. The term 'excess' refers to the excess over the ideal solution value, which is of course zero. (Excess volumes are similarly defined, and again the volume change is zero for an ideal solution. The free-energy change and entropy change on mixing are however non-zero for an ideal solution). Regular solution theory indicates that for normal liquid mixtures the excess enthalpy should be of the approximate form [equation (1)]:

$$H^E \sim D(V_1V_2/V_m)x_1x_2 \qquad (1)$$

where V_1 and V_2 are the molar volumes of the components, V_m is the mean molar volume, and x denotes mole fraction; D is a parameter of the system. (Strictly speaking, the theory refers to mixing under conditions of constant volume, and to the excess energy U^E rather than to the excess enthalpy). The function H^E/x_1x_2 is therefore often used as a convenient one for plotting and tabulation, as it often changes only slowly with composition, and unlike H^E itself, it remains finite instead of going to zero at zero x_1 or x_2.

In the alcohol solutions of present interest, however, a slightly different function is often more useful. This is the excess enthalpy per mole of alcohol, H^E/x_A, which can also be called the apparent molar excess enthalpy of the alcohol. It also has a finite value at infinite dilution of alcohol, and its value relative to this limit is the relative apparent molar enthalpy, a quantity more

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[27] R. H. Stokes, *J. Solution Chem.*, 1974, **3**, 671.

[28] R. H. Stokes and M. Adamson, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 1707.

[29] R. H. Stokes and H. T. French, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 537.

[30] R. H. Stokes and M. Adamson, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1236.

familiar to electrolyte workers than to liquid-mixture specialists [equation (2)]:

$$\Phi_H = H^E/x_A - \lim_{x_A \to 0}(H^E/x_A) \qquad (2)$$

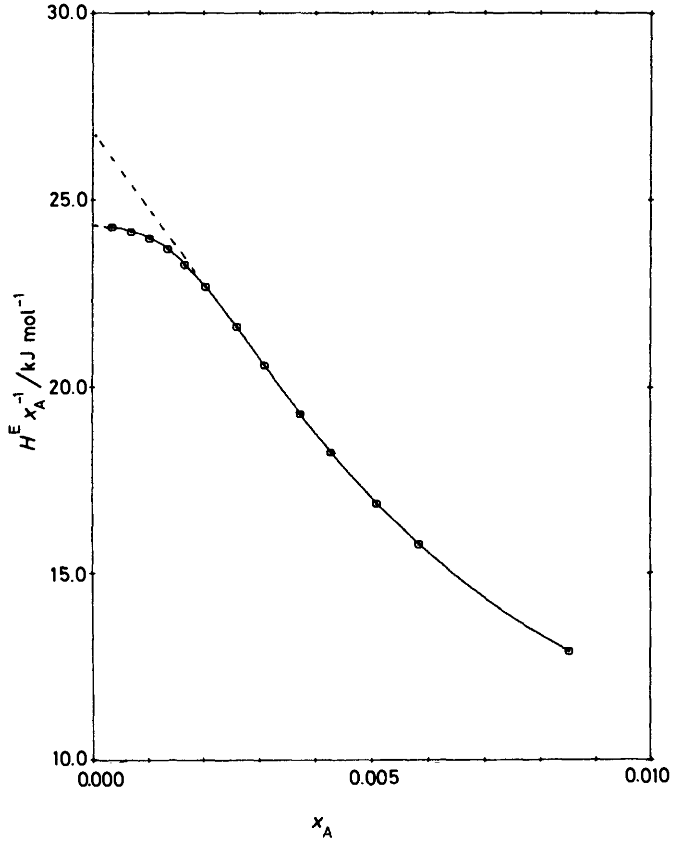

Figure 1 *Extrapolation to limiting apparent molar enthalpy. Ethanol in cyclohexane at* 10 °C. *The broken line shows how an erroneous extrapolation could be obtained in the absence of data below* 0.002 *mole fraction.*

The importance of this quantity for alcohol solutions is that its main component is the enthalpy of formation of all the H-bonds present per mole of alcohol, at the composition in question. The accurate determination of the limiting value is thus of considerable importance, and, just as with electrolytes, it requires measurements down to quite low concentrations to yield a reliable extrapolation. Figure 1 illustrates this point. If the measurements were made down to a mole fraction of 0.002, there would be an apparently straight extrapolation to approximately 26.7 kJ mol^{-1} as shown by the broken line. In fact, this extrapolation is badly in error, as the linear behaviour arises because there is a slow inflection in that region. When the measurements are extended down to another order of magnitude dilution, the much lower value of 24.0 kJ mol^{-1} is obtained.

It is only since the introduction of the isothermal dilution calorimeter by Van Ness, and its modification for higher precision work in Armidale, that it has been possible to make these extrapolations reliably. Because the amount of alcohol involved is so small at these dilutions, it is not added directly but in the form of a solution already diluted to say 0.01 mole fraction in a previous experiment, in which H^E was also measured. Then the quantity H^E/x_A shows its usefulness in another way, for if *final* refers to the result of the second dilution, and *initial* to the first, the relation [equation (3)]:

$$(H^E/x_A)_{\text{final}} = (H^E/x_A)_{\text{initial}} + \Delta H/n_A \tag{3}$$

is exact. Here ΔH is the enthalpy increase in the second dilution, and n_A is the number of moles of alcohol which is added (in the form of stock solution) to the pure solvent to make the final solution. In some cases, we have even used a third stage of dilution to give the highest accuracy in the extrapolation. The point of this method is that one need never make calculations involving an injection of less than 2 cm^3 of liquid from the piston-burette containing the alcohol or the stock solution, so that the metering error is below 0.1%. By means of a suitable arrangement of micro-ball-valves and mercury burettes, it is possible to transfer a portion of the final solution from one run into a piston-burette without exposure to air and hence possible contamination with moisture, or evaporation losses. This is then used for injection into the solvent in the next stage.

One of the features of the isothermal dilution calorimeter is that it has no vapour space. As the alcohol is added, mercury is expelled from the mixing vessel to make room for it. The sensitivity of the thermistor measurement of the solution temperature is such that it is necessary to adjust the mercury levels to a constant head of pressure on the solution, otherwise the adiabatic compression of the liquid results in a detectable heating effect, as can be shown in a blank run. The importance of having no vapour space in the calorimeter arises from the fact that the latent heat of vaporization of volatile components may be large compared to the heat of mixing. In this connection it should be noted that the volatility of alcohols at high dilutions is much higher than would be estimated on an ideal solution basis. For example, the activity coefficient of ethanol at $x_1 = 0.001$ in cyclohexane, at 6.7 °C, is 137-times the ideal solution value. This is directly due to the fact that nearly all the H-bonds are broken at this dilution, so the vapour pressure is nearly that of a solution of alcohol monomer, a much more volatile substance than the pure liquid alcohol.

C. Dielectric Constant Measurements.—As with other properties, it is necessary to carry these measurements to high dilutions in order to get a true picture of the way the apparent dipole moment varies with concentration. The method we have used[13] is again based on the principle of continuous dilution. The dielectric cell itself is the annular space between two stainless steel cylinders. The liquid is circulated by a totally immersed centrifugal pump from the cell to a mixing-vessel and back to the cell. The mixing-vessel is partly filled with mercury, and the alcohol, or a dilute solution thereof, can be added to the vessel from a piston-burette, displacing mercury. In this way the small capacitance changes resulting from the addition of as little as a few mg of alcohol can be measured with good accuracy, as they are not obscured by the circuit disturbances and variable air-contamination which result from making measurements first on the solvent and then on solutions prepared externally. Using an audio-frequency (10 kHz) capacitance bridge, we have a sensitivity of 0.001 pF in a total capacitance of about 200 pF. It is, however, not possible to get accurate measurements above about 0.2 mole fraction of alcohol as the increasing dielectric loss leads to difficulties in balancing the bridge.

3 Interpretation of the Thermodynamic Data in Terms of Association

Marsh's work[6,15] indicates that the entropy of mixing for globular molecules of different sizes lies between the values given by the mole fraction ideality expression [equation (4)]

$$\Delta S_m/R = -\Sigma x_i \ln x_i \tag{4}$$

and the volume fraction statistics (Flory–Huggins)[31] expression [equation (5)]

where x_i denotes the mole fraction of component i, ϕ_i its volume fraction, and ΔS_m is the entropy of mixing per mole of solution. In most cases a good representation of the observed entropy of mixing is given by the statistical-mechanical theories of the mixing of hard spheres (or other convex particles) which have been developed during the last two decades.[32] The experiments also show that the enthalpy of mixing is of comparable importance to the entropy in its effect on the free energy.

For calculations of association equilibria in alcohol solutions, we need to know the activity of each species involved. The only chemical potential directly accessible from experimental data is that of the monomeric alcohol, which is also the conventional chemical potential of the solute.[33] (The molecular reason for this equality is that the vapour pressure of the alcohol, used in obtaining the chemical potential, is corrected by the use of virial coefficients to that of the ideal monomeric vapour). In estimating the activity coefficients of the associated species we must therefore be guided by theory and by analogy with unassociated solutes. Though statistical-mechanical theories of liquid mixtures have had a good deal of success,[34,35] the algebraic form of the activity coefficient expressions is

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[31] P. J. Flory, *J. Chem. Phys.*, 1941, **9**, 660; M. L. Huggins, *J. Phys. Chem.*, 1941, **9**, 440.

[32] N. S. Snider and T. M. Herrington, *J. Chem. Phys.*, 1967, **47**, 2248.

[33] I. Prigogine, 'The Molecular Theory of Solutions', North-Holland, Amsterdam, 1957, p. 313.

[34] K. E. Gubbins and C. H. Twu, *Chem. Eng. Sci.*, 1978, **33**, 863.

[35] C. H. Twu and K. E. Gubbins, *Chem. Eng. Sci.*, 1978, **33**, 879.

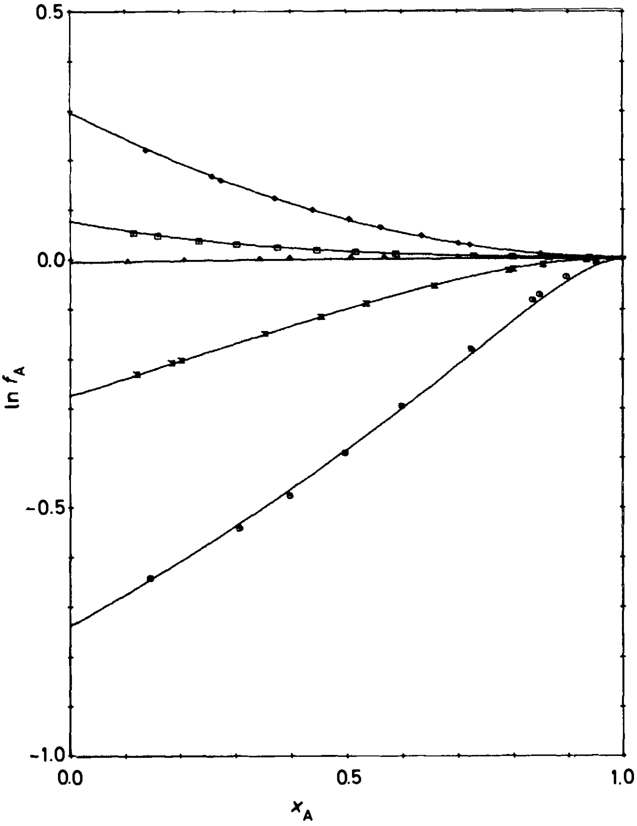

Figure 2 *Activity coefficients of component A in typical mixtures of unreactive globular molecules. Points, experimental; lines calculated from equation* (1) *with the indicated value of the interaction parameter D. In order from top the systems are:*

A	*B*	*D/J cm^{-3}*	*Temperature/ °C*
2,2-*dimethylbutane*	*cyclo-octane*	5.53	25
1,4-*dimethylbenzene*	*benzene*	2.71	35
cyclopentane	*cyclo-octane*	1.23	25
cyclopentane	*octamethyl-cyclotetrasiloxane*	5.75	25
carbon tetrachloride	*tetrakis* (2-*butoxy*)-*ethyl silane*	1.83	35

very complex even for a two-component solution, and at least one parameter (connected with the interaction energy) has still to be fixed from the experimental data. It is therefore worthwhile examining how well the classical theory of activity in non-electrolyte mixtures due to Hildebrand[36] and Scatchard[37] describe the

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[36] J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, 1933, **1**, 817.

[37] G. Scatchard, *Chem. Rev.*, 1931, **8**, 321.

activity coefficients in mixtures of globular molecules. Using the Flory–Huggins expression for the entropy of mixing this theory gives for a binary mixture [equation (6)]:

$$\ln a_1 = \ln \phi_1 + \phi_2(1 - V_1/V_2) + V_1\phi_2^2(\delta_1 - \delta_2)^2/RT \qquad (6)$$

Here a_1 is the activity of component 1 (relative to the pure liquid 1 as standard state)[1]; ϕ_1 and ϕ_2 are volume fractions; V_1 and V_2 are molar volumes; and δ_1^2 and δ_2^2 are the cohesive energy densities of the component liquids. If equation (6) held exactly, it would be possible to calculate activities in any mixture from the properties of the pure liquids, without appeal to any measurements on the mixture. In practice this is not possible with useful accuracy, but if the quantity $(\delta_1 - \delta_2)^2$ is treated as a parameter D for a particular system, to be determined from the activity at one composition, then equation (6) is a good one-parameter representation of the whole activity coefficient curve of mixtures of globular molecules of different sizes. It does not do well with the excess enthalpy (heat of mixing) and excess entropy considered separately. This failure has been explained by Hildebrand and Scott;[38] is it due to the fact that deficiencies in the theory, leading to first-order errors in the enthalpy and entropy separately, cancel in the free energy leaving only second-order errors there. This cancellation occurs essentially because the free energy is a minimum at equilibrium.

A. Species Activity Coefficients for Associated Solutes.—In using equation (6) to estimate activity coefficients for association equilibria in solutions of alcohols, two further reasonable approximations are required:

(*a*) that the volume of an associated cluster of *i* molecules is *i*-times that of a single molecule, and

(*b*) that the non-H-bonding interactions between the alcohol species and the solvent can all be described by a single parameter D [corresponding to $(\delta_1 - \delta_2)^2$ in equation (6)].

Assumption (*a*) is demonstrably inexact, since the limiting partial volumes of alcohols in non-polar solvents are several cm^3 mol^{-1} greater than those of the pure alcohols; nevertheless the resulting error in activity coefficient *ratios* should be minor. Assumption (*b*) amounts to saying that the H-bonding and Van der Waals interactions may be treated independently. With these assumptions, the molarity-scale activity coefficient y_i of the *i*-fold associated species can be deduced from the generalisation of equation (6) to several components as:

$$\ln y_i = iV_A[\Sigma c_k - 1/V_B] + iDV_A(\phi_B^2 - 1)/RT \qquad (7)$$

where V_A is the (conventional) molar volume of the alcohol and V_B that of the solvent; ϕ_B is the volume fraction of solvent. The summation Σc_k refers to all the distinct species present at equilibrium including the solvent.

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[38] J. H. Hildebrand and R. L. Scott, 'Solubility of Non-Electrolytes', 3rd Ed. Dover, New York, 1967 (Chap. VIII).

B. Association Equilibria.—The important point about equation (7) for present purposes is that in calculating a stepwise equilibrium at any chosen solution composition (where c_i and ϕ_B are fixed), we have

$$K_i = (c_i/c_{i-1} \cdot c_1)(y_i/y_{i-1} \cdot y_1) \qquad (8)$$

and by equation (7) the activity coefficient factor is always unity, even though the separate activity coefficients are not. This vastly simplifies the calculation of the equilibrium properties. The standard state used here is the one used in dealing with electrolyte equilibria, *i.e.* a hypothetical one molar solution of the species in question, magically prevented from dissociating or associating.

The stoicheiometric alcohol concentration c_A can be expressed as a polynomial in the monomer concentration c_1 and the overall formation constants of the various i-fold associated clusters (i-mers)

$$c_A = c_1 + \sum_{i=2,\ldots} i\beta_i c_i^i \qquad (9)$$

Here β_i is the formation constant for species i.

C. The Free Monomer Concentration.—Another equation connects the free monomer concentration c_i with the measured alcohol activity. This is based on the theorem[33] that in an association equilibrium the stoicheiometric chemical potential of the associating substance is equal to the chemical potential of the free monomer. Therefore if we can calculate the activity coefficient of the monomer in the mixture, we can express the monomer concentration c_i in terms of the measured activity. Though the activity coefficients given by equation (7) cancel from the equilibrium constant expressions, it is necessary now to know the value of the parameter D in order to calculate the monomer activity coefficient. Then equation (1) leads to equation (10)

$$\ln c_1 = \ln(x_A f_A/f_A^0) - \ln V_B + (V_A/V_B)\ln(c_B V_B/a_B) + 2D\phi_A V_B/RT \qquad (10)$$

where f_A^0 is the limiting alcohol activity coefficient at zero alcohol concentration.

The mole-fraction-scale activity coefficients f_A and f_B of the alcohol and the solvent can also be expressed in terms of c_1 and the 'species sum' [equation (11)]

$$\Sigma c_i = c_1 + \sum_{i=2,\ldots} \beta_i c_1 \qquad (11)$$

which is summed over all the alcohol species (but not the solvent):

$$\ln f_A - \lim_{x_A \to 0}(\ln f_A) = \ln(c_1/c_A) + \ln\{1 + c_A(V_B - V_A)\}$$
$$+ V_A(c_A V_A/V_B - \Sigma c_i) + DV_A(\phi_B^2 - 1)/RT \qquad (12)$$

$$\ln f_B = \ln\{1 + c_A(V_B - V_A)\} - V_B \Sigma c_i + c_A V_A + DV_B\phi_A^2/RT \qquad (13)$$

Equation (10) shows that the vital quantity c_i can be evaluated from the activity coefficient data, without any detailed knowledge of the association process, provided equation (7) holds and that D is known. In principle, it is then possible to use equation (9) to determine the β's. In practice, some simplifying assumption must be made, as two infinite sets of arbitrary equilibrium constants can be neither calculated nor interpreted.

D. Relations between Successive Constants.—The simplest assumption that can be made about the association process is that all the stepwise association constants are equal. If this hypothesis is to mean anything, it must be true at all temperatures; hence the enthalpies of formation of the successive hydrogen bonds must be the same. From this model one can obtain an expression for Φ_H the apparent molar enthalpy of the alcohol, relative to infinite dilution. It is of course a function of the alcohol concentration, the equilibrium constant, and the enthalpy of formation of the H-bond, and it can be shown that it cannot give rise to an inflexion in the curve of Φ_H *versus* concentration. Such an inflexion is invariably found, as shown in Figure 4, so the assumption of equal stepwise constants is too simple.

E. Cyclic Species.—Probably the most important additional effect is the formation of cyclic associated species. If a strain-free cyclic hydrogen-bonded cluster is formed from an open chain, there is an enthalpy loss corresponding to the extra hydrogen-bond formed, though the number of molecules in the cluster is unchanged. The entropy change arises mainly from the loss of flexibility of the ring compared with the chain, and would not be expected to be as great as for the the addition of another molecule to a chain. Hence the cyclic forms should be favoured once the cluster gets large enough to permit strain-free cyclization.

Cyclic forms with as few as two molecules have been suggested, but these must have an O—H···O angle much more acute than the 180° which is the lowest energy configuration for the hydrogen bond. (This favoured configuration is seen very clearly in the structure of ice, where the mean position of each proton is on the line of centres of two oxygen atoms). Jorgensen,[39] using an admittedly simplified but still quite reasonable potential function (in which the H-bonding arises from Coulomb interactions of a charge distribution) finds that the anti-parallel configuration of the methanol dimer has an energy some 6 kJ higher than the open or end-on configuration. This would suggest that the open form of the dimer would be favoured by a factor of about 10 at room temperature. Since the H—O···H angle has approximately the tetrahedral value (109°) it follows that five or more hydroxy-groups are necessary to give a strain-free ring. A ring of four should not be severely strained, but it seems reasonable to ignore the contributions of two- or three-membered rings to the thermodynamic properties.

The clearest indication that cyclic groups are important comes from dielectric constant studies on the solutions. The typical form of the apparent dipole moment of an alcohol in a paraffinic solvent is shown in Figure 3; the important features are clearest at low temperatures. There is a small initial increase in apparent moment, which is ascribed to formation of small non-cyclic associates (dimer and trimer). Still at quite low concentrations, this increase is overwhelmed

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[39] W. L. Jorgensen, *J. Am. Chem. Soc.*, 1981, **103**, 341.

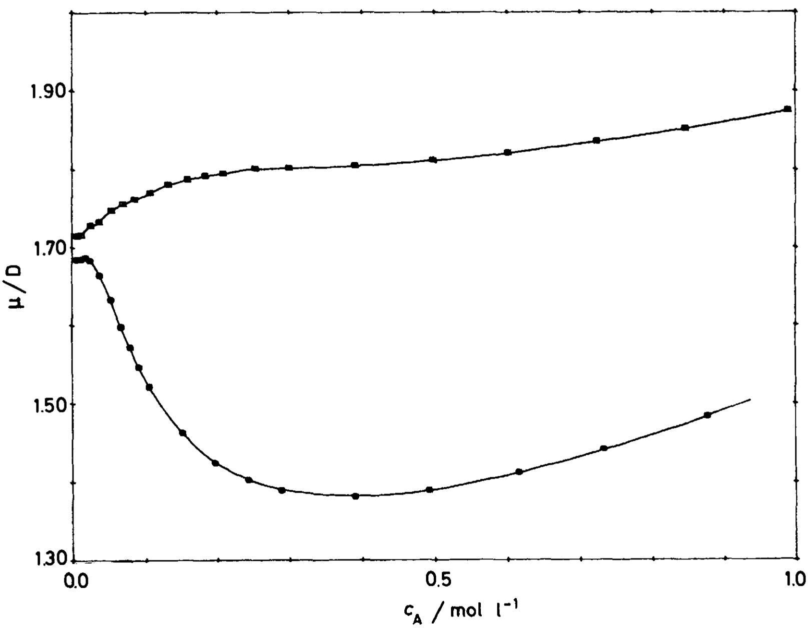

Figure 3 *Apparent dipole moments of ethanol at* 25 °C *in* 1,4-*dimethylbenzene (upper curve) and n-hexane (lower curve). These curves are typical of alcohols in aromatic and aliphatic solvents respectively*

by a rapid drop ascribed to the formation of cyclic species, which would be expected to have nearly zero net moment. As the concentration is further increased, the apparent moment rises again. This is probably because longer chains are forming, and there are entropy factors opposing the cyclization of long chains. There is a striking contrast with the behaviour in aromatic solvents, also shown in Figure 3. It will be argued later that the aromatic solvents reduce the proportion of rings present by 'solvating' the free hydroxy-groups at the ends of chains which would otherwise tend to close to form rings.

The activity data cannot themselves provide any means of telling whether a cluster is open or cyclic; both forms occupy nearly the same volume, and their effect on the activity is the same. In principle, however, the difference should show up in the enthalpy of dilution, since the ring has a larger (more negative) enthalpy of formation.

F. Equation involving the Enthalpy.—The enthalpy of formation of the various H-bonded clusters is most readily considered as a contribution to the relative apparent molar enthalpy of the alcohol, Φ_H [equation (2)]. To a first approximation, one may expect that the energy of formation of a hydrogen bond should be independent of the size of cluster in which it occurs, provided only strain-free configurations are accepted. There is, however, known to be a co-operative effect in multiply hydrogen-bonded systems, according to which adjacent bonds mutually enhance each other. To allow for this, we assign an enthalpy of formation h_2 to the H-bond in a linear dimer, and a constant value h in all other cases. The strain-free cyclic groups are assumed to start with five or possibly four alcohol molecules in the ring. The total contribution of the H-bonds to Φ_H in a solution containing c_A moles of alcohol per unit volume is therefore as shown in equation (14):

$$c_A\Phi_H(\text{H-bonds}) = c_2h_2 + h\sum_{i=3,\ldots}(i-1)c_i(\text{linear}) + h\sum_{i=(4\text{or}5),\ldots} ic_i(\text{cyclic}) \qquad (14)$$

where c_i denotes the equilibrium concentration of associated species i in the solution. Equation (14), through the respective factors $(i - 1)$ and i, allows for the fact that a linear i-chain contains $(i - 1)$ bonds, but a cyclic i-group contains i bonds.

At concentration below about 0.1 molar (typically $x_A < 0.01$), the H-bonding terms are the only significant contribution to Φ_H. The other contribution is what may be called the 'ordinary' or Van der Waals enthalpy of mixing. Though we have remarked that this is not accurately given by the Scatchard–Hildebrand expression [equation (6)], there is nothing better which can be used in a practical calculation without a lot of parameters.

Equation (1) gives rise to a term in the relative apparent molar enthalpy

$$\Phi_H(\text{SH}) = -DV_A\phi_A$$

With typical values of D and V_A, this term is unlikely to exceed -0.2 kJ mol^{-1} at $x_A = 0.1$, in contrast to typical experimental values of approximately -20 kJ mol^{-1} for Φ_H. Thus, the imperfection of equation (1) is not of great importance as long as we confine ourselves to alcohol solutions of less than say one molar. This does not mean that the H-bonding forces are hundreds of times stronger than the van der Waals forces, but that the latter change little with concentration in dilute solutions, whereas the amount of H-bonding changes rapidly. If, however, we wish to consider properties nearer the pure alcohol composition, and in particular the other limit

$$\lim_{x_A\to 0}(H^E/x_Ax_B)\,,$$

the non-H-bonding term is of major importance.

G. Cyclization Equilibria.—The presence of cyclic H-bonded groups may be formally accounted for in many ways. For example, a five-molecule ring could be thought of as formed from five monomers, a linear dimer plus a linear trimer, or a linear tetramer plus a monomer, or a linear pentamer alone. All of these are thermodynamically equivalent, and the cyclization equilibrium constant could be expressed in terms of any of these processes. However, it is obviously simplest to consider only the last-named one, the cyclization of an open chain to a ring of the same length. This process must clearly have an equilibrium constant of the form [equation (15)]:

$$k'_i = c_i(\text{cyclic})/c_i(\text{linear}) = q_i \exp(-h/RT) \tag{15}$$

where q_i is an entropy factor and the exponential factor deals with the enthalpy loss in forming the new H-bond. Since $h \approx -24$ kJ mol^{-1} the exponential factor is of the order of 10^4 at room temperatures, and even a strongly unfavourable entropy factor is likely to leave k_i still large enough to cause a significant amount of the cyclic form to be present.

To find an exact expression for q_i would be a difficult exercise in statistical mechanics. Clearly it will depend for one thing, on the detailed geometry of the alcohol molecule in question; steric effects may restrict the number of configurations possible for cyclic groups, and the internal degrees of freedom may change in different ways on cyclization. There is, however, one effect that must always be relevant, and is fairly easily dealt with. This is the dependence of q_i on the chain length i. Apart from the fact that we are excluding the possibility of cyclization for $i < 4$ on the grounds of excessive ring strain, it is clear that in unstrained rings q_i should decrease as i increases. There are two ways of justifying this proposition: either a greater chain length reduces the probability of the ends coming close enough to form the new H-bond, or the larger ring has an increasing probability of breaking, because it has more H-bonds to break. Indeed, there seem no good reason why both these processes should not operate at once, but it is probably sufficient to consider only the second, which would lead us to expect a q_i inversely proportional to i for a given alcohol. Thus the simplest form one could expect for the cyclization constant k_i' is given in equation (16)

$$k_i' = \theta/i \tag{16}$$

with

$$\partial \ln\theta/\partial T = h/RT^2 \tag{17}$$

and θ independent of i.

There seems to be no way of estimating θ from any thermodynamic property except through optimizing the whole fit of the expressions for the activities and enthalpies to the observed data. Likewise, although the cyclization process plays a major role in determining the shape of the apparent dipole-moment curve, it requires several further assumptions about the moments of linear species to make possible any quantitative estimate of θ. Nor does there seem to be any spectroscopic property which is *directly* related to the presence of cyclic species. There is, however, an infra-red absorption at ~3620 cm^{-1} which is certainly attributable to non-H-bonded hydroxy-groups. There is some disagreement as to whether it arises only from free monomeric alcohol molecules, or from all hydroxy-groups in which the proton is not participating in an H-bond, even though the oxygen is the acceptor of another H-bond. That is to say, does the band come only from the completely free —OH groups of the monomer, or from these as well as from the terminal —OH groups of H-bonded chains? This is the sort of discussion in which a non-specialist hesitates to take part, and I have adopted the monomer-and-terminal view on the basis that it seems to fit in better with the thermodynamic data. However, the spectroscopic data still do not provide on their own a value for the cyclization constant θ; they have to be combined with the thermodynamic data and the association model to yield a value of θ, and even then the best value of θ is obtained only from a rather flat minimum in a standard deviation. For ethanol in cyclohexane at 25 °C, the value of $\theta = 20$ was so obtained.[19] This means that at 25 °C, the cyclic pentamer is four-times as abundant as the linear pentamer; for the icosamer the ratio has fallen to unity.

H. Association Constants for the Linear Association Species.—It is in general more helpful to work with the stepwise equilibria, *i.e.* those for the addition of a further monomer to an existing chain. Then for the formation of a chain of length i [equation (18)]:

$$K_i = c_i/c_1 \, . \, c_{i-1} \tag{18}$$

(since we have shown that activity coefficients cancel). Again, since one new H-bond is formed, it is useful to write [equation (19)]:

$$K_i = a_i \exp(-\Delta H/RT) \tag{19}$$

where ΔH is the enthalpy increase in forming the new bond, and a_i is an entropy factor. Since we are proposing that the co-operative enhancement of the H-bond energy is noticeable only between the cases of one and two bonds, the dimer has one bond of strength h_2, and all other linear i-mers have $(i - 1)$ bonds of the enhanced strength h. Hence the first few stepwise constants should be [equations (20)—(22)]

$$K_2 = a_2 \exp(-h_2/RT) \tag{20}$$

$$K_3 = a_3 \exp[(-2h + h_2)/RT)] \tag{21}$$

and

$$K_i = a_i \exp(-h/RT) \text{ for all } i > 3 \tag{22}$$

If h is taken as the normal bond strength, then K_2 will have a smaller temperature dependence than normal, and K_3 a larger one; and the temperature coefficient of all the linear steps after the trimer formation should be the same as for the cyclization. (Strictly speaking a small enthalpy term arising from the thermal expansion has to be included in the temperature dependence of the linear species K_i's, but not in that of the cyclization constant θ). This leaves the question of how the entropy factors a_i vary with i. In discussion of chainwise association equilibria it is commonly argued that the first step should have a different constant from the rest, because in the first step the two reactants are the same, whereas in all later steps they are different. In some of our applications of this model we have allowed both a_2 and a_3 to have different values from the subsequent ones. This, however, does increase the number of parameters to be fixed from the data, and it is not unreasonable to try the approximation of setting $a_2 = a_3 = a_i$ $(i > 3)$. This is more reasonable in the alcohol case than in cases of weaker association because it turns out that the proportion of dimer is small in most of the solutions of interest, the higher association products rapidly predominating as the concentration increases. Also a difference between a_2 and a_i can be at least partially compensated for by 'sophisticating' the value of h_2 (this delicious term for fudging is borrowed from the science of ballistics, with which I was peripherally concerned in my youth).

4 Expressions for the Thermodynamic Properties

Using the model outlined above, expressions may be written for the thermodynamic properties in terms of the equilibrium constants. The concentration of free monomer, c_1, is the natural independent variable to use; its values can be calculated from the activity data, independently of the details of the association, provided that one assumes a value for the non-H-bonding interaction parameter D of equation (6). For notational convenience we put

$$K_i = k \quad (i > 3) \tag{23}$$

and retain K_2 and K_3 as distinct quantities with temperature dependence given by equations (20) and (21). It is convenient to use the dimensionless argument

$$y = kc_1$$

in the various series summations which arise from the theory; the cyclization constant θ is already dimensionless.

Two important quantities in the theory are the species sum S_1 and the stoicheiometric sum S_2. These are respectively the total number of solute entities (monomer, dimer, *etc.*) and the total number of moles of solute (calculated as monomer), in unit volume of solution. Obviously S_2 is identical with c_A, the stoicheiometric alcohol concentration.

$$S_1 = \Sigma c_i = c_1 + K_2 c_1^2 + (K_2 K_3/k^3)\,[y^3/(1 - y) - \theta\{\ln(1 - y) + y + y^2/2 + y^4/3\}] \tag{24}$$

$$S_2 = c_A = c_1 + K_2 c_1^2 + (K_2 K_3/k^3) y^3[(3 - 2y)/(1 - y)^2 + \theta y/(1 - y)] \tag{25}$$

Equations (24) and (25) are for the case where cyclization is taken to set in at $i = 4$. If it does not occur until $i = 5$, equation (24) has a further term $+y^3/4$ following $y^3/3$, and in equation (25) the term $\theta y/(1 - y)$ becomes $\theta y^2/(1 - y)$.

It is not possible to set up expressions in which all the equilibrium constants appear linearly so that linear least-squares methods can be applied directly. The procedure we have found most practical is to assign a trial value to the interaction parameter D; then the monomer concentration c_1 can be calculated from the experimental activities by equation (10). The equilibrium constants k, K_2, K_2K_3 and θ are then adjusted so that the concentrations c_A given by equation (25) reproduce the experimental values as closely as possible. Alternatively, one may assume D and a set of equilibrium constants, and using c_1 as a parameter calculate both the activity coefficients and the alcohol concentration c_A to match the experimental curve. This is most conveniently done using an interactive computer program in conjunction with a plotter or a high-resolution graphic monitor. As is to be expected with any but an exact theory, the parameters obtained show some dependence on the range fitted. If interest is mainly in the hydrogen bonding, it is best to fit only the range up to about 1 molar. Figures 6—9, however, show that a fairly satisfactory description of the whole composition range up to the pure alcohol can be obtained; the enthalpy function is less well reproduced than the activities.

In the case of ethanol in n-hexadecane, the constants which fit the activity data also predict phase separation, which does indeed occur, as shown in Figure 7. The conjugate phase compositions can be found by plotting $\ln a_A$ against $\ln a_B$, using c_1 as a parameter to calculate both activities and the corresponding stoicheiometric composition x_A. Where the curve crosses itself, the two x_A

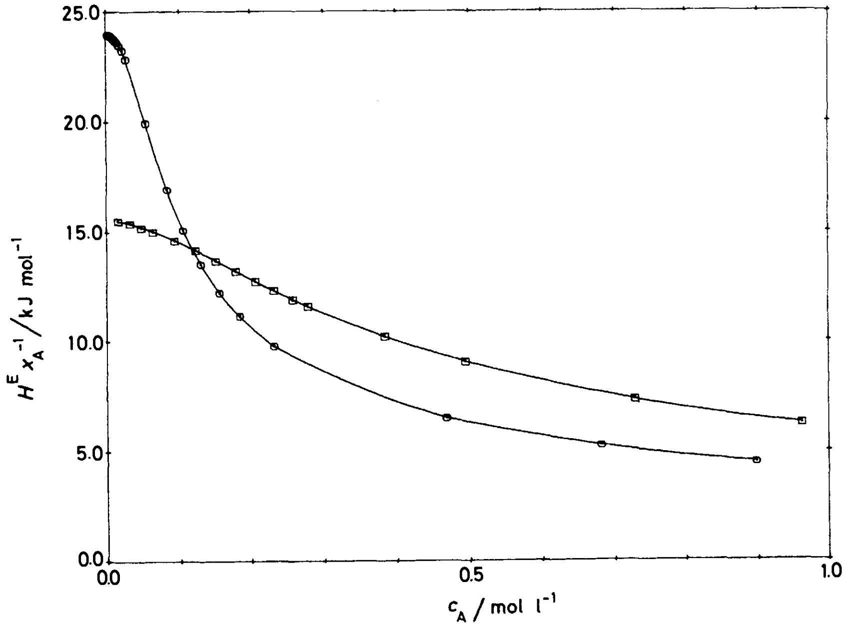

Figure 4 *Showing inflexions characteristic of the apparent molar excess enthalpy of alcohols in dilute solutions. (a) Ethanol in cyclohexane and (b) ethanol in* 1,4-*dimethylbenzene* (25 °C)

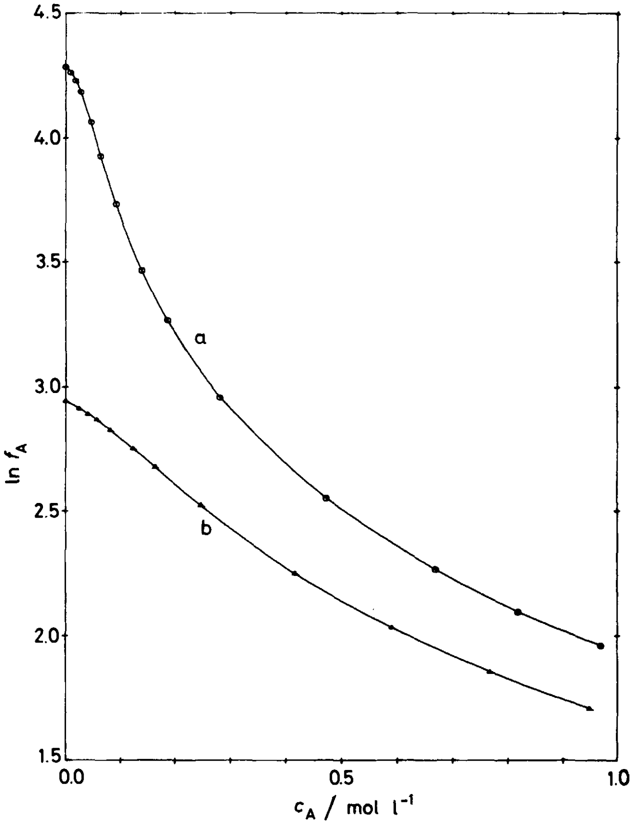

Figure 5 *Activity coefficients f_A of ethanol at* 25 °C *in* (*a*) *Cyclohexane and* (*b*) 1,4-*dimethylbenzene*

values are the predicted compositions of the conjugate phases. These are close to the observed values at 25 °C but do not change rapidly enough as the temperature rises towards the observed U.C.S.T. at 52.5 °C.

The values of h_2 and K_2 are subject to large uncertainties, as the amount of dimer is always small. Indeed the only place where the dimer contribution is noticeable is for the apparent molar enthalpy in the region up to about $x_A = 0.005$. Consequently it is better to take as the adjustable linear chain constants

$$K_2, (K_2K_3), \text{ and } k$$

rather than

$$K_2, K_3, \text{ and } k$$

The choice of (K_2K_3) is also advantageous in that the theory requires that the ratio (K_2K_3/k^2) should be independent of temperature. Some typical fits to the theory are shown in Figures 6—9.

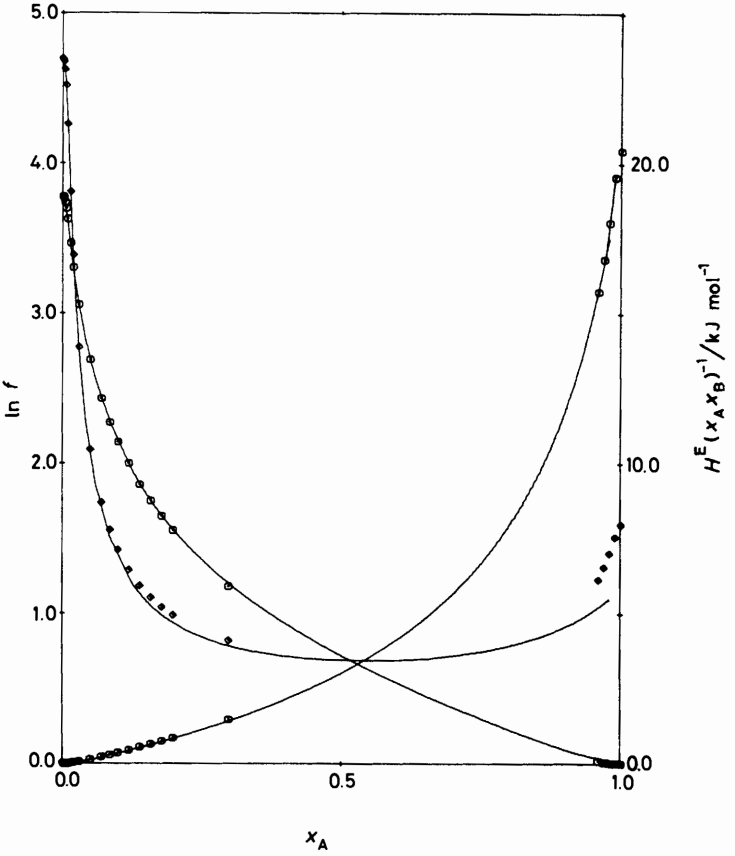

Figure 6 *Activity coefficients and the excess enthalpy function* versus *mole fraction for ethanol in hexadecane at* 25 °C, *showing the extreme steepness in the low alcohol region*

5 Alcohols in Aromatic Solvents

In aromatic solvents and to lesser extent in carbon tetrachloride, and carbon disulphide, the thermodynamic behaviour of alcohols is markedly different (Figures 4—5). The limiting partial excess enthalpy is much lower (in aromatics about 15 kJ mole^{-1}) than in aliphatic solvents; the apparent molar enthalpy of dilution is much less steep in the low-alcohol region; and the limiting activity coefficient f_A of the alcohol is substantially lower (Figure 5). The shift in the limiting partial excess enthalpy can also be looked upon as an enthalpy of transfer of a (monomeric) alcohol molecule from infinite dilution in the aliphatic solvent to infinite dilution in the aromatic solvent; the enthalpy change in this process is about -9 kJ mol^{-1}. In an initial survey of ethanol in several solvents, I examined whether this could be explained by the move of the hydroxyl dipole

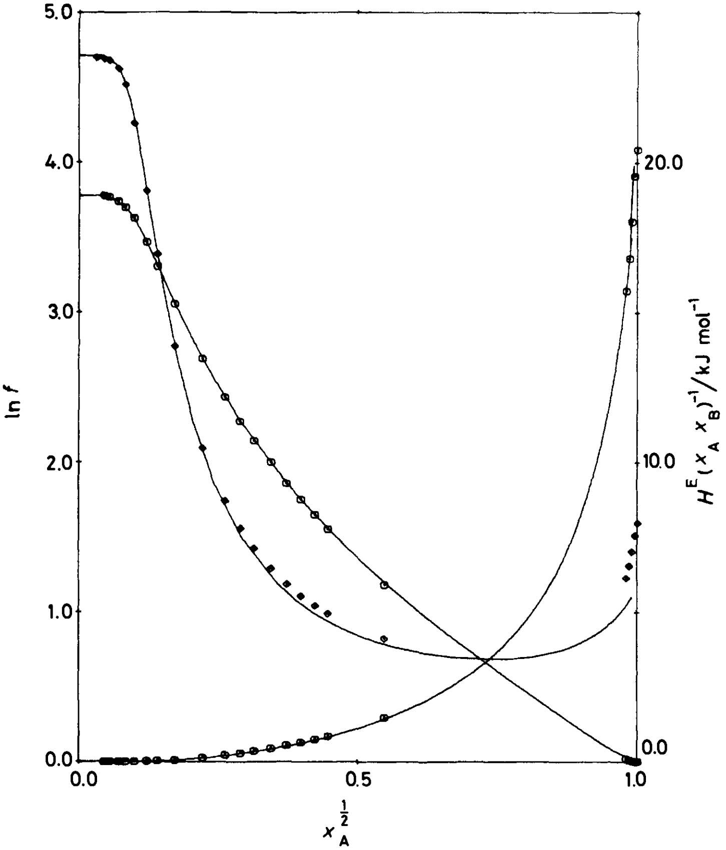

Figure 7 *The same data as in Figure 6, plotted against* $x_A^{\frac{1}{2}}$; *to expand the abscissa scale at low alcohol concentrations. The calculated curves are continued through the phase-separation region where there are no points plotted*

moment to a higher dielectric constant medium, but this attractive idea was invalidated by the observation that in carbon disulphide, with by far the highest dielectric constant of the non-polar solvents used (2.633), the enthalpy of transfer is only -3 kJ mol^{-1}. It therefore appears that the effects are due to a specific interaction between the solvent and the alcohol hydroxy-group. In the case of carbon tetrachloride, the concept of a weak H-bond from the hydroxy-group to a chlorine atom is acceptable. With the aromatic solvents, however, one must think of the somewhat exposed hydroxyl proton as finding a lower-energy environment in the π-electron cloud of the solvent; in fact a solvation of the hydroxy-group occurs.

Besides affecting the limiting partial excess enthalpy, this interaction substantially reduces the amount of H-bonding between alcohol molecules as

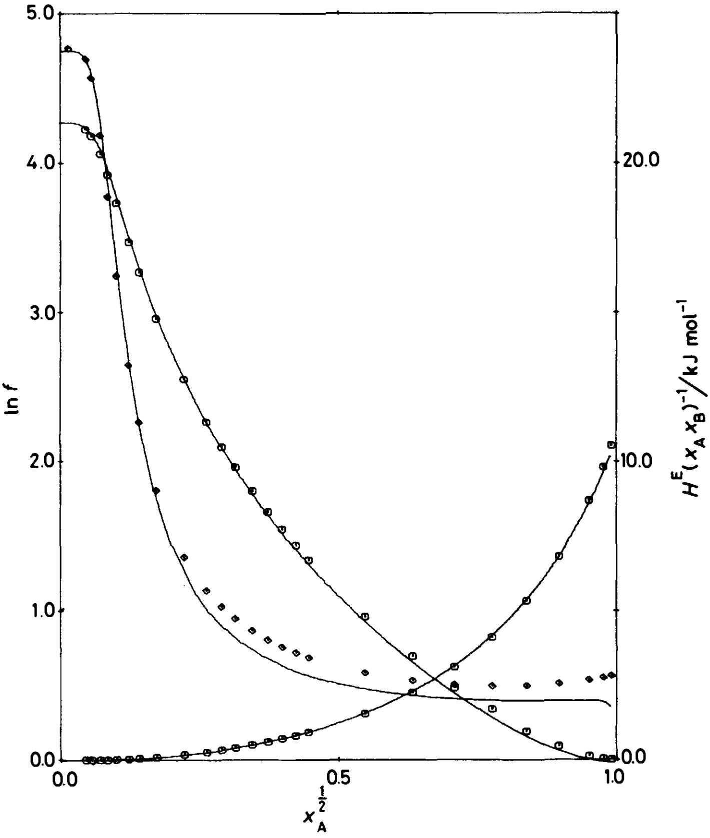

Figure 8 *Observed and calculated properties of ethanol in cyclohexane at* 25 °C

compared with aliphatic solvents at similar concentrations. In effect, the solvent competes with the solute–solute hydrogen bonding interactions; a hydroxy-group buried in π-electrons is not available for H-bonding with other alcohol molecules. Clearly, if an isolated alcohol molecule can be solvated by a benzene ring, so can the terminal hydroxy-group of an open H-bonded chain, and a chain thus solvated will no longer participate in the cyclization equilibria. This situation can be treated formally by introducing a solvation equilibrium for each of the open-chain clusters, including the monomer

$$\text{solvated open } i\text{-mer/unsolvated open } i\text{-mer} = K_S$$

or

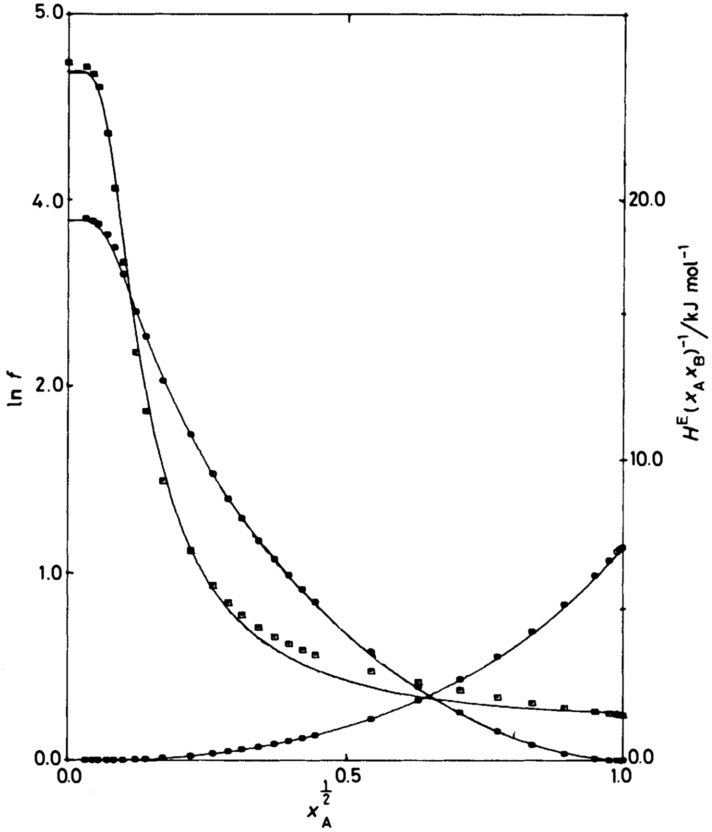

Figure 9 *Observed and calculated properties for butan-*1*-ol in cyclohexane at* 25 °C

$$\text{unsolvated open } i\text{-mer/total open } i\text{-mer} = 1/(1 + K_S)\,.$$

A single K_S independent of i should be a good first approximation. The equilibrium constants relating the unsolvated monomer, open chains, and cyclic forms should on this model be the same as for the aliphatic case, provided that all the other assumptions of the model are satisfied.

The detailed working out of the thermodynamic properties of ethanol in *p*-xylene on this model has been presented. The calculations prove to be extremely recalcitrant when the volume-fraction statistics equations for the species activity coefficients are used; hence the mole-fraction statistics were used, and the calculation confined to alcohol mole fractions up to 0.2, where the effects of the statistics are quite minor. Using only two new parameters, the equilibrium constant and enthalpy change for the solvation process, it proved possible[29] to obtain a reasonably good prediction of the properties of the xylene solution from those of the cyclohexane solution.

6 Dielectric Constant

The prediction of the dielectric constant of pure polar liquids has been the subject of numerous theoretical papers using advanced mathematical techniques.[40] A special difficulty is associated with the long-range nature of dipole-dipole forces, which in some treatments makes the result highly dependent on the size of the body of liquid considered. Also, some simplified models such as point dipole in the centre of a dielectric sphere, though of value as a starting point, cannot be expected to reproduce with accuracy the complexity of behaviour of real hydrogen-bonded liquids. By taking more realistic potential functions for the water molecule, considerable progress has been made with the problem of water itself by computer techniques, but little such work has yet been done with alcohols or their solutions in non-polar solvents.

One of the earliest treatments of the dielectric properties of alcohols was due to Lennard–Jones and Pople,[41] who proposed an association into unbranched chains through hydrogen bonds. This idea has remained the basis of most later treatments of pure alcohols and their solutions in non-polar solvents.

The typical behaviour of the apparent dipole moment of alcohols in paraffinic solvents is shown in Figure 3. There is initially a small rise in the apparent moment, followed by a marked fall to a rather flat minimum followed by a slow rise which continues to the highest concentrations studied. (One should note, however, that the concept of the apparent dipole moment is in any case of decreasing usefulness as the pure alcohol composition is approached). The association model which we have used for the thermodynamic properties would require, for its detailed application to the dielectric properties, the assignment of a net dipole moment to each of the associated species. While bolder spirits have not shrunk from the necessary guesswork, and have even calculated association constants from our dielectric data alone without cross-reference to the thermodynamic data, I do not feel confident enough in our knowledge of the charge distributions and the internal molecular motions of the associated species to attempt this assignment more than qualitatively. There is one important case, however, where I believe that no guesswork is needed. This is in the assumption that for any hydrogen-bonded *cyclic* group, the net dipole-moment is zero. This is automatically true if the dipole moments of the constituent molecules of the ring are vectorially additive, and there seems to be no reason for this not to hold, even though the individual moments may each be enhanced from the free-molecule value by co-operative effects. There is clearly no reason why any particular molecule in a ring should make a different contribution from the rest.

The apparent dipole moment of an associated mixture, in which the i-fold associated species i has an effective dipole moment μ_i and concentration c_i may

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[40] G. Still, G. N. Patey, and J. S. Høye, *Adv. Chem. Phys.*, 1981, **48**, 183.

[41] J. A. Pople, *Proc. R. Soc. London, Ser. A*, 1951, **205**, 163.

be written:

$$c_{\mathrm{A}}\mu_{\mathrm{app}}^{2} = \Sigma c_i \mu_i^{2}(\text{linear}) + \Sigma c_i' \mu_i'^{2}\ (\text{cyclic})\ (i = 1, 2 \ldots .)$$

where c_{A} is the stoicheiometric concentration.

If the cyclic species have zero moments, the summation need be taken only over the linear species. Although we still do not know how the μ_i's for these depend on i, we can estimate the effect of the omission of the cyclic species by calculating a different average moment of the non-cyclic species:

$$\begin{aligned}\mu_{\mathrm{nc}} &= \textstyle\sum c_i \mu_i^{2}\,(\text{linear})/\sum i c_i(\text{linear})\\ &= c_{\mathrm{A}}\mu^{2}_{\mathrm{app}}/\textstyle\sum i c_i(\text{linear})\end{aligned}$$

If we use the values of $\Sigma i c_i$ calculable from the model which fits the thermodynamic data, μ_{nc} turns out to be the monotonically increasing function of c that one would expect.[19] It is in fact much like the apparent moment found for solutions in aromatic solvents, where cyclization is to a considerable extent replaced by solvation of the hydroxy-groups, a process which is expected to have little effect on the dipole moments. The limiting moments extrapolated to infinite dilution are not very different between aliphatic and aromatic solvents (or indeed between one alcohol and another).

Acknowledgements. Many of the results presented here are the work of Dr. Han Tin French; I also acknowledge with thanks the help of K. N. Marsh and his students, and the technical staff of the Chemistry Department of the University of New England in both the construction and the operation of the equipment. The Australian Research Grants Council has provided financial support over a long period.

Tribute. R. A. Robinson, who gave me my first introduction to physical chemistry in Auckland in 1937, was a firm believer in the value of accurate thermodynamic measurements on solutions, and his own contributions to our knowledge of electrolytes have been of immense value not only to experimentalists, but also to those who have been developing theories of single and mixed electrolyte solutions during the past half-century. Though for the past fifteen years most of my own work has been in the field of non-electrolyte solutions, I can attribute such success as I have had in large measure to the grounding he gave me in thermodynamics.

I must also acknowledge his personal generosity to me, which made possible the endowment of this memorial lecture. Those who knew him know also that his modesty would not have allowed him to endow it himself.