Heat capacity and structure in strongly-interacting systems

Lina Andreoli-Ball, Miguel Costas, Pierre Paquet, Donald Patterson* and Marie-Esther St. Victor
McGill University, Department of Chemistry, 801 Sherbrooke St. W.,
Montreal, PQ, Canada H3A 2K6

Abstract - The heat capacity has been used to reveal H-bonded multimers, predominantly tetramers, in solutions of 1-alkanols in inert solvents, e.g., alkanes. The Treszczanowicz-Kehiaian association theory has been applied to the association part of the apparent molar heat capacity, \( \varphi_{c,\text{assoc}} \), of the alcohol in solution, giving \( \Delta H^\circ \) for H-bond formation and the volume-fraction equilibrium constant \( K_{4CP} \) for the formation of tetramers. The \( K_{4CP} \) are related to \( K_4 \), an equilibrium constant for H-bond formation in tetramers which is found to be independent of alkanol carbon number from 3 to 16 while it is slightly larger for methanol and ethanol. A common \( K_4 \) implies a single corresponding states curve (CSC) of \( \varphi_{c,\text{assoc}} \) against the number of moles of hydroxyl segments per mole of segments in the solution (essentially molarity) as introduced by Pouchly. Data for 1-alkanol + n-alkane systems follow a CSC characteristic of tetramers rather than CSC predicted by continuous association models, e.g., Mecke-Kempter or Kretschmer-Wiebe. The CSC approach can be applied to enthalpy and residual entropy data. It predicts characteristic concentration dependences of the excess functions; for instance, \( S^E \) is positive at low alcohol concentration then negative. The replacement of the inert solvent by a proton-acceptor, e.g., benzene, introduces a new association between the alcohol and the proton-acceptor. Characteristic changes occur in \( C_p^E \) and \( H^E \). Grolier and collaborators have found a wide variety of systems for which \( C_p^E \) has a surprising W-shape concentration dependence with two minima separated by a maximum, or two regions of positive curvature separated by a region of negative curvature. It is suggested that the W-shape is a consequence of local composition non-randomness caused by large values of \( H^E \) and \( G^E \) occurring in strongly-interacting systems. \( C_p^E \) is the superposition of two contributions. One is negative and of parabolic concentration dependence as found in systems where a component is polar or anisotropic in molecular shape. The other contribution due to non-randomness is positive and large toward the middle of the concentration range, i.e., the critical concentration of the system.

INTRODUCTION

The change of heat capacity on mixing, \( C_p^E \), and the apparent heat capacity, \( \varphi_{c,\text{assoc}} \), of a component, are useful thermodynamic tools to study liquid structure in solution. The disadvantage of \( H^E \) compared to \( C_p^E \) lies in the presence in \( H^E \) of a large contribution besides that of structure. This is due to the dispersive force antipathy between the two components, represented by the \( X_{12} \) parameter of the Flory theory or the interchange energy of regular solution theory. The temperature dependence of this contribution is slight so that most of \( C_p^E \) arises from structure which is usually highly temperature-dependent. Applications have been to correlations of molecular orientations in n-alkane systems (ref. 1), the formation of clathrates or "icebergs" around hydrophobic solutes (ref. 2), the micellization of surfactants (ref. 3) and the formation of micelle-like structures in aqueous mixtures of alcohols and other organic solvents (ref. 4). The present communication will deal with four other situations where structure appears in solution: (1) 1-alkanols dispersed in an inert solvent, e.g., an n-alkane, where the alcohol molecules cooperatively H-bond into tetramers. (2) 1-alkanols dispersed in an "active" solvent, e.g., CCl\(_4\), benzene, an ether or an ester or (3) dispersed in a binary mixture of an active and an inert solvent. In these systems, the alcohol molecules may either self-associate or complex with the active molecules; (4) systems of extremely high \( H^E (>1000 \text{ J mol}^{-1}) \) and \( G^E (>800 \text{ J mol}^{-1}) \). Here the antipathy between two components leads to non-randomness or concentration fluctuations with a corresponding contribution to the heat capacity of the systems, and the appearance of a characteristic W-shape concentration dependence of \( C_p^E \), negative towards the edges of the concentration range and positive toward the middle.
A molar excess quantity $X^E$ compares the apparent molar quantity $\varphi_X$ in solution with the same quantity in the pure state, i.e.,

$$X^E = x_1(\varphi_X - X^o)$$

(1)

Here $X$ can be $C_p$, $H$, $V$ or the residual (non-combinatorial) $S$. Trends in $X^E$ are therefore a reflection of trends in $\varphi_X$ modulated by the introduction of $X^o$ and $x_1$. In the present systems, $\varphi_X$ of an alcohol contains (1) the internal $X$, e.g., enthalpy or heat capacity of the alcohol, (2) an associational or chemical contribution, of primary interest to us, and also, (3) $\varphi_X$(phys) due to other "physical" interactions between the alcohol and its molecular surroundings. We now consider the $\varphi_X$ relative to their values in the limit of infinite dilution of the alcohol:

$$\varphi_X^{rel} = \varphi_X - \lim x_1(\varphi_{x^1} - 0)$$

(2)

Clearly $\varphi_X^{rel}$ will not contain contribution (1) but does retain $\varphi_X$(assoc) since all self-association of the alcohol vanishes at infinite dilution. $\varphi_X^{rel}$ will also contain the difference in $\varphi_X$(phys) values between finite concentration and infinite dilution. When $X = V$, this contribution is large and may dominate the associational contribution (ref. 5); for $X = H$ the difference is smaller but still important (ref. 6) and finally for $X = C_p$ the physical contribution appears to be negligible in the present systems. Thus,

$$\varphi_c^{rel} = \varphi_c(assoc) = \varphi_c - \lim x_1(\varphi_{x^1} - 0)$$

(3)

For H-bonded systems, this sensitivity of $C_p$ to association structure, and its insensitivity to the physical interaction constitutes, we believe, an important advantage. $\varphi_c$(assoc) has now been obtained (ref. 7) for seventeen 1-alkanol-n-alkane systems. A variety of curves as a function of concentration are found each with a maximum in $\varphi_c$ and $\varphi_c$(assoc) occurring at different alcohol mole fractions or weight fractions depending on the system. However, a more fundamental concentration variable has been advanced (ref. 8), i.e., a concentration of hydroxyl groups in the solution,

$$\psi_1 = \text{no. OH groups/total groups}$$

$$= x_1/(x_1r_A + x_2r_2)$$

(4)

with $r_A$ and $r_2$ being the numbers of segments in the alcohol and the inert solvent, respectively. $\psi_1$ is related to the molarity $M_1$ through

$$\psi_1 = M_1v/1000$$

(5)

where $v$ is the molar volume of the segment taken to be 40.7 cm$^3$mol$^{-1}$ the molar volume of methanol. Plotting against $\psi_1$, $\varphi_c$(assoc) for all the alcohol-inert systems now fall on a single curve with the exception of methanol and ethanol systems which deviate slightly. Fig. 1 shows the data for the dilute range, i.e., $x_1<0.1$.

The steep increase of $\varphi_c$(assoc) at very low $\psi_1$ corresponds to the onset of alcohol self-association, in fact as tetramers, followed by a maximum and a long decrease to the pure alcohol which is not seen in fig. 1. Thus the maximum in $\varphi_c$(assoc) and in "structure" does not occur for the pure alcohol where there is the highest degree of H-bond formation, but at a very low concentration, $\psi_1=0.004$ or $x_1=0.01$ where the unassociated hydroxyls would be 26 Å apart.

"Structure" implies H-bonding probability weighted by the distance through which the hydroxyls are drawn together in forming the multimers.

![Fig. 1. $\varphi_c$(assoc) = $\varphi_c^{rel}$ against $\psi_1$ in the dilute range for seventeen alkanol-n-alkane mixtures. Data for ethanol-n-decane (A).](image)
Assocation theory can be used to relate \( \varphi_c(\text{assoc}) \), to the thermodynamics of alcohol self-association. The Tresczanowicz-Kehiaian (TK) model (ref. 9) uses a H-bonding enthalpy \( \Delta \mathcal{H}^0 \) and alcohol self-association equilibrium constants \( K_i^\varphi \) for the formation of \( i \)-mers:

\[
K_i^\varphi = \varphi_{Ai} / (\varphi_A)^i
\]

(6)

where \( \varphi_{Ai} \) and \( \varphi_A \) are the volume fractions of, respectively, the alcohol \( i \)-mers and monomers. \( \Delta \mathcal{H}^0 \) and \( K_i^\varphi \) have been fitted (ref. 6, 7) to the \( \varphi_c(\text{assoc}) \cdot x \) data and indicate the predominance of tetramers, as well as a rapid decrease of \( K_i^\varphi \) with increasing alcohol chain-length. The \( K_i^\varphi \) have been interpreted (ref. 10) through the more fundamental H-bonding constants using the Flory lattice theory (ref. 11). A later version (ref. 12) of this theory gives (ref. 7).

\[
(K_i^\varphi)^{1/1-1/w_A} = K_i(1)^{1/1-1/w_A^2}/z
\]

(7)

Here \( K_i \) is the H-bonding equilibrium constant for formation of the \( i \)-mer. \( V_A \) is the alcohol molar volume \( \sigma \) the \( i \)-mer vessel number, \( w \) an \( i \)-mer flexibility parameter and \( z \) the lattice co-ordination number. \( K_i = \exp(-\Delta \mathcal{H}^0 / RT) \exp(\Delta S^0 / R) \) with \( \Delta \mathcal{H}^0 \) and \( \Delta S^0 \) the enthalpy and entropy of H-bond formation in the \( i \)-mer. The \( K_i \) should be independent of the alcohol whose chain-length is taken into account by \( V_A \), but the \( K_i^\varphi \) are different, for different \( i \)-mers. If the \( K_i^\varphi \) are replaced by the more fundamental \( K_i \), then the TK theory predicts that \( \varphi_c(\text{assoc}) \) should be a universal function of \( \psi_1 \), i.e., a corresponding states curve (CSC) as found experimentally in fig. 1. A particularly simple case arises if the solution contains predominantly multimers of a single type, e.g., \( i = 4 \), as is found experimentally. Then, the co-ordinates of the maximum of the CSC are

\[
\varphi_c(\text{assoc. max}) = \frac{1}{R[(1-1)\Delta \mathcal{H}^0 / RT]^2} \quad \frac{1}{1+1^{1/2}+1^{1/2}}
\]

(8)

\[
\psi_1(\text{max}) = \frac{1}{(K_1w^2/z)^{-1}} \quad \frac{1+1^{-1/2}}{3/[2(1-1)]]}
\]

For cyclic \( i \)-mers the factor \( (1-1)\Delta \mathcal{H}^0 \) is replaced by \( i \Delta \mathcal{H}^0 \). The co-ordinates of the maximum in fig. 1 are \( \varphi_c(\text{assoc. max}) = 270 \pm 12 J \cdot K^{-1} \cdot \text{mol}^{-1} \) and \( \psi_1(\text{max}) = 4.0 \pm 0.4 \times 10^{-3} \) which with \( i=4 \) give \( \Delta \mathcal{H}^0 = -28.3 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1} \) and \( \Delta S^0 = -46.6 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1} \) for the formation of the H-bonds in linear tetramers. For cyclic tetramers each value is multiplied by \( 3/4 \). One should notice in fig. 1 that \( \varphi_c(\text{assoc. max}) \) and \( \psi_1(\text{max}) \) are different for ethanol and probably methanol. For the former \( \varphi_c(\text{assoc. max}) = 305 J \cdot K^{-1} \cdot \text{mol}^{-1} \) and \( \psi_1(\text{assoc. max}) = 3.4 \times 10^{-3} \).
The co-ordinates of the maximum may be used as scaling or reduction parameters for the CSC to give a reduced \( \phi_c \) curve where

\[
\phi_c = \phi_c(\text{assoc})/\phi_c(\text{assoc. max})
\]

\[
\rho_1 = \psi_1/\psi_1(\text{max})
\]

(9)

The reduced curves depend only on the value of \( i \) chosen, e.g., 2, 3, or 4 and are independent of \( \Delta H_i, \Delta S_i \), etc. and whether the \( i \)-mers are cyclic or linear. They are also independent of \( T \) which enters only through the scaling parameters. Thus, the same reduced CSC should be obtained not only for data from any 1-alkanol + inert solvent system, but for data at different temperatures.

The applicability at different \( T \) has not been tested but fig. 2 and 3 show the reduced CSC from the 25°C data of fig. 1 together with data at higher concentration all scaled with experimental values of \( \phi_c(\text{assoc. max}) \) and \( \psi_1(\text{max}) \).

Figs. 2 and 3 also show reduced CSC given by the TK model for \( i=2, 3 \) and 4 also for the Kretschmer-Wiebe (KW) and Mecke-Kempter (MK) continuous association models (ref. 7) where the \( K_i \) are assumed to be the same for all \( i \)-mers, the former model being based on the Flory-Huggins combinatorial entropy and the latter on the ideal entropy. It is a curious fact that with \( 1 \) seen in fig. 2 followed by a sharp upturn corresponds to the plateau of HEP1 found in a simple Flory-Huggins treatment we have

\[
\Delta H = \Delta H_0 - \Delta H_1/\psi_1(\text{max}) \psi_1(\text{max})
\]

(10)

The experimental data from ref. 13 for ethanol, + cyclohexane, + n-heptane and + n-hexadecane all fall on essentially the same CSC which is also obeyed by data at concentrations higher than those shown in fig. 4. Other data for n-propanol, n-hexanol and n-decanol in n-alkanes are available (ref. 18) and these also fall on the same CSC. This, however, is surprising since from the \( \varphi_c \) measurements ethanol constitutes a special case. Pending confirmation of values of \( \Delta H/\psi \) for these alcohols we only consider the ethanol data. The figure also shows curves of the associational \( \varphi_c^{\text{rel}} \) calculated with different models fitted to the \( \varphi_c \) results. First, the fit was made to \( \varphi_c(\text{max}) = (10 \text{ J K}^{-1} \text{ mol}^{-1}) \) and \( \varphi_1(\text{max}) = 4 \times 10^{-3} \) which are valid for the majority of the alkanols. The curves come from the following models: tetramers, dimers, KW and MK, although the last is not seen in fig. 4 since it is almost identical to KW. In fig. 4 the dimer, KW and MK models are clearly incorrect. As pointed out first by Stokes and collaborators, higher multimers are needed. Nevertheless, the MK model has been successfully used at higher concentrations in dealing with \( \Delta H \) (ref. 6). Only the tetramer curve in fig. 4 is in qualitative agreement with the data. It displays the slow decrease of \( \varphi_c^{\text{rel}} \) at low \( \psi_1 \) followed by a sharp drop characteristic of cooperative self-association. Fig. 4 shows another tetramer curve specially calculated for ethanol using constants fitted to \( \varphi_c(\text{assoc. max}) \) and \( \psi_1(\text{max}) \). This new curve passes through the data points within experimental error, which is at first sight, surprising because it seems to imply that there is no physical contribution present. In a simple Flory-Huggins treatment we have

\[
\psi_1 = \varphi_1^{\text{rel}}(\text{phys}) = z \varphi_1^{\text{rel}}(\text{phys})
\]

(11)

with \( z \) the exchange energy for the OH - CH₃ contact taken independent of the alkyl. At the low values of \( \psi_1 \) in fig. 4 the physical contribution to \( \varphi_1^{\text{rel}} \) is too small to be seen, but at higher values of \( \psi_1 = 0.1 - 0.5 \) the experimental CSC does lie below the associational curve and the difference may be interpreted as \( \varphi_1^{\text{rel}}(\text{phys}) \) which is slightly different for the ethanol-alkane and ethanol-cyclohexane systems.
Heat capacity and structure in strongly-interacting systems

It is of interest that the slopes of $\varphi^\text{rel}(\text{assoc})$ and $\varphi^\text{rel}(\text{phys})$ against $\psi_1$ are both negative, both in fig. 4 and at higher concentrations. Thus using eq. (1) both $\varphi^\text{H}(\text{assoc})$ and $\varphi^\text{H}(\text{phys})$ are positive throughout the concentration range and at all $T$. This contrasts with $\varphi^\text{SE}$ which is negative through most of the concentration range.

Fig. 5 shows the corresponding residual or non-combinatorial part of the relative apparent molar entropy $T\varphi^\text{rel}$ of ethanol in cyclohexane, n-hexane and n-hexadecane. This quantity was obtained using activity coefficient data from ref. 13, subtracting off the Flory-Huggins combinatorial free energy and making use of $\varphi^\text{rel}$. The data are seen to follow a CSC which at low $\psi_1$ looks like $\varphi^\text{rel}$. The figure also gives $T\varphi^\text{rel}$ curves calculated with the same parameters used with $\varphi^\text{H}$. The tetramers curve calculated with parameters valid for most of the alcohols is in qualitative agreement with the data, while the dimers, KW and $\varphi^\text{MK}$ do not respect the cooperative character of the experimental curve. ($\varphi^\text{MK}$ curve omitted since it is so similar to the KW). Again the special tetramers curve for ethanol is in remarkable agreement with the data. The accord at higher $\psi_1$ is shown in the insert. Again using the Flory-Huggins lattice theory we have

$$\varphi^\text{rel}(\text{phys}) = - z \nu \psi_1$$

(12)

where $\nu \psi_1$ is the physical interchange entropy for the OH-CH$_2$ contact, expected to be positive. However, the agreement between the predicted associational $T\varphi^\text{rel}$ and the experimental curve is within the experimental error, particularly in the parameters used in our calculation. It is therefore difficult to say if there is any physical contribution to $T\varphi^\text{rel}$ at all.

The qualitative aspects of $T\varphi^\text{rel}$ curve are interesting. The negative values of course indicate the non-randomness introduced into the solution through tetramer formation. The slope of $T\varphi^\text{rel}$ against $\psi_1$ is first negative and then for higher concentration it becomes positive (fig. 5, insert) whereas the slope for $\varphi^\text{H}$ continued negative, this feature being seen experimentally and for all theoretical models. Thus, in spite of continuously increasing H-bonding as $\psi_1$ increases, a minimum in the residual entropy occurs at low $\psi_1$ after which the residual entropy increases. This behaviour arises from non-randomness or "structure" reflecting the distance through which the alcohol molecules are drawn together to form the multimers. The residual entropy of alcohol molecules in the pure state is higher than in the solution at all but the most dilute concentrations. Thus according to eq. (1) $T\varphi^\text{S}(\text{residual})$ is positive at low concentration and negative through the remainder of the concentration range. The Flory-Huggins combinatorial contribution to $T\varphi^\text{H}$ is positive but can hardly eliminate the negative sign when added to $T\varphi^\text{S}(\text{residual})$ to give the total. Thus the S-shape $T\varphi^\text{S}$ concentration dependence is expected to be general for all alcohols and all $T$. Finally, the same approach described here for $H$ and $S$ may be applied to $\varphi^\text{rel}(\text{A.J. Tresczczanovicz, unpublished}).
1-ALKANOLS + A PROTON ACCEPTOR

Fig. 6 shows $H_E^E$, $C_p^E$ and $\varphi_c$ for ethanol mixed with the inert solvent hexane (I) and also with benzene, of similar molar volume to hexane. Benzene is a proton acceptor (PA) with which the ethanol can H-bond as well as self-associating into tetramers. In the fig. $H_E^E$ (PA) < $H_E^E$(I) at extremely low x but is considerably larger throughout most of the concentration range. It is surprising that the introduction of the PA increases $H_E^E$ even though it interacts favourably with the alcohol. For $C_p^E$ and $\varphi_c$ three concentration regions are visible. For both these thermodynamic functions, (I), at very low x=0.01, PA<I; (2), for higher x=0.1, PA<I; and finally, (3), x>0.2, PA>I. These qualitative effects of a PA on the thermodynamic functions seem to hold generally unless the alcohol-PA interaction is stronger than the alcohol-alcohol interaction and unless there is a large difference in molecular size of the two components. The present article also compares $\varphi_c$ for hexanol + n-C12 and + methyl acetate in fig. 9. In apparent contradiction to the above there is no region (3) where $C_p^E$, $\varphi_c$ are larger for the PA system. However, the molar volume of n-C12 is considerably larger than that of MA and this increases $\varphi_c$ and $C_p^E$ of the former system causing the region 3 to disappear.

These effects of changing an inert to a PA solvent can be understood through the alcohol energy, $\varphi_H$, shown in fig. 7 as a function of temperature. The fig. is schematic but based on TK calculations fitted to $\varphi_c$ for the ethanol-benzene system using a variation of eq. 1 in ref. 20. Three energy levels are seen corresponding to self-associated tetramers ($A_4^T$) at $\Delta H_0 = -21,290$ J mol$^{-1}$, the alcohol-PA complex (AB) at $-13,900$ J mol$^{-1}$ fitted to the ethanol-benzene system, and finally complete dissociation of the alcohol at 0 J mol$^{-1}$.

Curves 1, 2, and 3 give the temperature variation of the alcohol energy $\varphi_H$, at the above-mentioned concentrations 1, 2, and 3 in an inert solvent (dotted) and in the PA solvent (full). Curve * represents the pure alcohol. For every curve, at low enough T, the alcohol is part of a self-associated tetramer and hence lies at the lowest energy level. With increasing T, $\varphi_H$ rises and ultimately reaches the top level, i.e., 0. At any T the slope $\frac{d\varphi_H}{dT}$ of the curve against T gives $\varphi_c$. In the inert case the $A_4^T$ break up to give monomers directly, while in the PA case they first give AB complexes which then dissociate to give monomers. In both cases the temperature at which the $A_4^T$ break up increases with alcohol concentration, i.e., from curve 1 to curve 3 and then the curve for the pure alcohol. However, the temperature in the PA case is lower than in the inert case since the AB level is lower than the monomer level and hence is more easily attained. In contrast to the tetramers, the AB complexes only contain a single alcohol molecule and hence dissociate at a concentration-independent temperature which in our case lies below T' the experimental temperature. The curves for the PA case seen in the fig. correspond to a resultant of the $A_4^T$-$AB$ and $AB$ dissociations.

Fig. 6. (above and at left) Comparison between $H_E^E$, $C_p^E$ and $\varphi_c$ for ethanol - inert n-C6 (A) and ethanol - PA benzene (+). $H_E^E$ data for ethanol - inert from ref. 13 and Smith and Robinson. 1, 2 and 3 indicate concentration regions mentioned in the text.
Heat capacity and structure in strongly-interacting systems

Fig. 7. (at left) Schematic of energy $\phi_H$ of alkanol in inert solvent (dotted curves) and proton acceptor (full curves). Energy levels correspond to tetramers $A_4$, alcohol-PA complex $AB$ and dissociation 0. Increasing concentration 1, 2 and 3 and pure alcohol 0. $T$ corresponds to experimental temperature.

Fig. 8. Schematic of energy $\phi_H$ of alcohol at the same low concentration in the following inert solvent (C), increasing concentration of PA in PA - inert mixture ($C_1$, $C_2$ and $C_3$), the pure PA ($C'$) and pure alcohol.

Fig. 9. $\phi_c$ of hexanol as a function of its concentration in (a) n-dodecane, (f) methyl acetate(NA) and in MA-dodecane mixtures having the following MA wt %: b. 2.0; c. 4.3, d. 10.2; e. 30.0.

The different dissociations take place at different $T$. For the lowest concentration, (1), the $A_4$ dissociate in the PA at the lowest temperature, then the $A_4$ dissociate in the inert solvent, and finally the $AB$ dissociation lies at the highest temperature. Thus at $T'$ the alcohol in the inert is almost dissociated, i.e., $\phi_H$ and $\phi_c$ are at the 0 level. However, in the PA case the alcohol is still freeing itself from the AB complex and $\phi_H$ is still negative and $\phi_c$ positive. According to eq. (1), $H^E$ and $C_p^E$ are found through subtracting $H^E$ and $C_p^E$ from $\phi_H$ and $\phi_c$. $H^E$ is close to the lowest level and $C_p^E$ is small. Thus $H^E$ is $+\phi_c$ for both inert and PA cases but $H^E$ is larger than $H^E$ in the PA case, and $C_p^E$ is larger than $C_p^E$ in the PA case.

At the higher concentration (2), the temperature of dissociation in the inert has caught up with the temperature of AB dissociation which has hardly changed. Then in the fig. $\phi_H(FA)=\phi_H(1)$ and the HE values are equal for the inert and PA systems. However, the slope against $T$ of the inert curve is larger than in the PA case and hence $\phi_c(FA)=\phi_c(1)$ as seen in fig. Finally at conc. (3), the dissociation temperature of $A_4$ in the inert is now at the highest temperature, higher than the full line resultant of the $A_4$-$AB$ and AB dissociations which has been "held back" by the AB dissociation. In neither the inert nor the PA case is the alcohol substantially dissociated, but dissociation is even less for the inert than the PA case, and hence $H^E(FA)>H^E(1)$. Correspondingly, $d\phi_H/dT$ and also $\phi_c$ and $C_p^E$ are larger for the PA system.

In this qualitative treatment $H^E(\text{phys})$ has been ignored since the main trends are determined by the association contribution. It seems to us that alcohol-PA thermodynamics is a fruitful area in which simple models can lead to a satisfying qualitative picture.
ALCOHOL + PROTON ACCEPTOR + INERT SOLVENT SYSTEMS

An alcohol dispersed in a proton acceptor-inert solvent mixture is capable of the same three energy levels as in fig. 7. They are seen again in fig. 8 where the curves represent an alcohol in its pure state, and at the same very low alcohol concentration in an inert solvent (C), in binary mixtures of the inert with increasing amounts of a proton-acceptor, \( C_1, C_2, C_3 \) and in the pure proton-acceptor \( C' \). As the concentration of PA is increased the AB level is increasingly attractive to the alcohol, so that the \( \varphi_0(\text{assoc}) \) curves above the AB energy level are displaced towards higher temperature and below the AB level towards lower T.

Fig. 8 is helpful in understanding the experimental \( \varphi_p(\text{assoc}) \) curves for the 1-hexanol + methyl acetate + n-dodecane mixtures shown in fig. 9. Substitution of an inert hydrocarbon solvent by a proton-acceptor + hydrocarbon mixture produces drastic changes in the concentration dependence of \( \varphi_p(\text{assoc}) \). In fig. 8 at the experimental temperature \( T' \) and at constant very low alcohol concentration increasing PA concentration causes the slope \( \varphi_p(\text{assoc})/dT \) to rise from its value in the inert (curve C) to a maximum (curve C2) and then drop to the value in the proton acceptor solvent (curve C'). This corresponds to the experimental behaviour seen in fig. 9 for infinite dilution of the 1-hexamol as the methyl acetate concentration is increased.

At higher alcohol concentration, as the concentration of methyl acetate is increased \( \varphi_p(\text{assoc}) \) drops continuously from the alcohol + inert to the alcohol + PA curve. This behaviour is also understandable from a higher concentration version of fig. 8.

In fig. 9 the experimental \( \varphi_p(\text{assoc}) \) is compared with the TK calculations. Parameters of the theory were fitted to the alcohol + inert \( \varphi_p(\text{assoc}) \) curve and to the infinite dilution value for \( \varphi_p(\text{assoc}) \) in the binary alcohol + proton acceptor. The curves in fig. 9 for the ternary and the alcohol + proton acceptor system are thus predictions and not the result of a fitting procedure. Qualitatively, the drop in \( \varphi_p(\text{assoc}) \) on increasing methyl acetate concentration corresponds to a lowering of the degree of alcohol structure in solution through replacing self-associated multimers by AB complexes. The latter bring together the associating A and B species over shorter distances compared with the association of A monomers at low alcohol concentration, and hence correspond to greater non-randomness and structure.

SOLUTION NON-RANDOMNESS IN HIGHLY NON-IDEAL MIXTURES

Grolier and collaborators (ref. 21) have found a wide variety of systems for which the concentration dependence of the excess heat capacity has a "W-shape", i.e., two minima occur, separated by a maximum or two regions of positive \( C_p^E(x) \) curvature separated by a region of negative curvature. Both types of W-shape \( C_p^E \) curves are schematically represented in fig. 10.

Component 1 can be a linear or cyclic ether, ester, nitrile, ketone or chloroalkane while component 2 is a normal, branched or cyclic alkane. A common characteristic of these systems is that they have large \( H^E>1200 \text{ J mol}^{-1} \) and \( G^E>800 \text{ J mol}^{-1} \) values and often are close to phase separation. Recently (ref. 22) it has been proposed that the W-shape \( C_p^E \) concentration dependence is due to a deviation of local from bulk composition, i.e., non-randomness in the solution. Here the structure is due to the antipathy between unlike molecules forcing like molecules to "associate".

The W-shape arises then from two \( C_p^E \) contributions depicted in fig. 10: a random contribution which is negative and of parabolic concentration dependence and a non-random contribution which, as shown qualitatively by the Guggenheim quasi-chemical theory (ref. 22) is positive, concave downwards in the middle of the concentration range, but concave upwards at the extremes. The non-randomness contribution falls to zero at both ends of the concentration range in accordance with the intuitive requirement that when either component is dispersed at high dilution in the other, it must tend to be randomly distributed. As a result, the non-random \( C_p^E \) contribution has the correct concentration dependence to give the W-shape when added to the random contribution.
A more direct measurement of non-randomness is given (ref. 23) by the concentration-concentration correlation function $S_{cc}$ which is related to the inequality of distribution of component 1 molecules around a component 2 molecule or a component 1 molecule, i.e., non-randomness. $S_{cc}$ is given by

$$S_{cc} = \left( \frac{\beta^2 G/RT}{\partial x^2} \right)^{-1} - \frac{x_2 RT}{(\partial \mu_1/\partial x_1)_{p,T}}$$

(13)

where $\mu_1$ is the chemical potential of component 1. Hence, $S_{cc}$ reflects the concentration fluctuations and is attainable through light scattering measurements. Using the Flory-Huggins (FH) expression for $G^E$, eqn (13) becomes

$$S_{cc} = \frac{x_1x_2}{1 + \frac{x_1x_2(x-1)^2}{(x_1 + x_2)^2} + \frac{2x_1x_2x_2^2}{(x_1 + x_2)^3}}$$

(14)

where $r = v_2/v_1$ and $x_1 = z\Delta w/KT$ with $\Delta w$ being the interchange free energy per mole of segments normalized to size of the component 1 molecule and $z$ the lattice coordination number. It also indicates that molecular size has different effects depending on the size of $r$. For small values of $x_1$, the first term in eqn (14) dominates and $S_{cc}$ decreases as $V_2$ and $r$ increases. If $x_1$ is large, the second term in the denominator of eqn (14) dominates and the maximum in $S_{cc}$ occurs at high concentration of the smaller component. If $V_2$ and $r$ are increased $S_{cc}$ increases and the maximum moves to higher $x_1$. The correlation between non-randomness in solution, as measured by $S_{cc}$ and the appearance of W-shape $C_p^E$ curves is illustrated in fig. 11 where $S_{cc}$ and $C_p^E$ are shown for hexafluorobenzene (HFB) mixed with several alkanes. $S_{cc}$ for HFB+brC$_8$ is small and skewed slightly to high HFB concentration whereas for HFB+cC$_6$ $S_{cc}$ is larger and skewed to lower HFB concentration. Also in fig. 11 calculated $S_{cc}$ values using eqn (14) are displayed; here, $x_1$ values were fitted so that theoretical $S_{cc}$ has the same maximum value as the experimental, although not necessarily occurring at the same concentration. This gives $x_1 = 0.61$ and 1.27 for brC$_8$ and cC$_6$ respectively. Theoretical $S_{cc}$ values using eqn (14) are seen to give the correct skewing of the curves. For the small $S_{cc}$ mixture, i.e., HFB+brC$_8$, $C_p^E$ curves are of normal shape both at 25 and 10°C; the negative $C_p^E$ and positive $dC_p^E/dT$ values are consistent with the presence of order in pure HFB and its destruction upon mixing. For HFB+cC$_6$, although $S_{cc}$ is now larger than for HFB+brC$_8$, $C_p^E$ still does not have a W-shape; it is less negative, however, and on decreasing the temperature to 10°C the W-shape becomes evident. This change in $C_p^E$ shape is clearly due to increasing non-randomness, i.e., increasing $S_{cc}$.

Fig. 11 also shows $C_p^E$ for HFB + dicyclohexyl and +brC$_{16}$. Here, components 2 are of similar chemical character to cC$_6$ and brC$_8$ but are of greater molecular size. For HFB + cC$_6$ and dicyclohexyl, it is clear that the effect of increasing molecular size of component 2 is to enhance the W-shape character and to move the maximum from low cyclic concentration to
high. On the other hand, comparing HFB + brC₈ and + brC₁₆, the effect of increasing molecular size is the opposite: Cᵣ shows no W-shape for brC₁₆ and is in fact more negative than for brC₈. These effects are explained by non-randomness and S_{cc} given by eqn (14), where the χ₁ values for dicyclohexyl and brC₁₆ may be taken equal to the values found for cc₆ and brC₈ respectively. Fig. 11 shows that in going from cc₆ to dicyclohexyl, the increase of r has made the second term in eqn (14) dominant increasing S_{cc} and displaying it to higher HFB concentration. Clearly, this increase and displacement of S_{cc} corresponds to the behaviour of Cᵣ. For HFB + brC₁₆ and + brC₈ (low χ₁ value) the first term in eqn (14) dominates and then S_{cc} decreases as r is increased from brC₈ to brC₁₆. Correspondingly, Cᵣ is more negative for brC₁₆ and there is no W-shape concentration dependence.

Acknowledgements

Financial support of the Natural Science and Engineering Research Council of Canada and the Ministère de l’Education du Québec is gratefully acknowledged. We thank the Journal of the Chemical Society, Faraday Transactions 1 for permission to reprint figs. 1-3.

REFERENCES

22. P. Paquet and D. Patterson, to be published.