^{13}C spectra (Table IV). We can now estimate the relative energies of the various forms of butane. Taking the boat and chair forms of cyclohexane as models, we assume a similar pattern in ^{13}C shifts for eclipsed and gauche butane as in the model compounds, i.e., a decrease of 11.3 and 5.5 ppm for the terminal and central C atoms of eclipsed butane. The latter is thus $44.6\lambda_1 + 33.6\lambda_2 = 3.37$ kcal/mol less stable than gauche butane. Similarly, taking axial and equatorial methylcyclohexane as models for the gauche and anti forms of butane, the 6 ppm upfield shift of the C-3, C-5, and CH_3 carbons observed for the axial conformer results in a destabilization of $12\lambda_1 + 12\lambda_2 = 1.08$ kcal/mol of gauche butane with respect to its anti form. These conformational results, which are entirely derived from ^{13}C shifts, are in general agreement with currently accepted values, moreover as for these structures the variations in zero-point and thermal energies represent, in all likelihood, only minor contributions.[23]

While the examples presented here illustrate that reasonably reliable binding energies are easy to derive from ^{13}C spectral data, it also appears that in any calculation of an enthalpy of formation the real problem is now one of estimating the vibrational contributions in a simple manner. The $\Delta E_a{}^*$ energies represent nonetheless valuable information in problems of molecular stability. Since ^{13}C shifts are farther downfield as carbon atoms are closer to electroneutrality and both λ_1 and λ_2 are positive quantities, we can express the overall conclusion as a thumb rule: "in comparisons between isomers, the more stable compound is that whose carbon skeleton best approaches electroneutrality, which is reflected by larger (downfield) δ values".

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Volumes and Heat Capacities of Ternary Aqueous Systems at 25 °C. Mixtures of Urea, *tert*-Butyl Alcohol, Dimethylformamide, and Water

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Abstract: The densities and heat capacities per unit volume were measured for the systems urea (U)-*tert*-butyl alcohol (TBA)-water (W) and dimethylformamide (DMF)-TBA-W at 25 °C with a flow densimeter and a flow microcalorimeter. One of the nonaqueous components was kept at a constant low concentration and whenever possible the other component was varied over the whole mole fraction range. From these data, combined with previously published data on NaCl-U-W and on Bu_4NBr-U-W, volumes and heat capacities of transfer were calculated and compared with the corresponding excess functions of the binary systems to get an overall view of these ternary systems. In the water-rich region the thermodynamic properties are characterized by strong solute-W and solute-solute interactions. At the nonaqueous end the thermodynamic properties are reflecting mostly solute-solvent interactions. Through an understanding of the two ends it becomes easier to account for the various inflection points, maxima or minima in the transfer functions.

Mixed aqueous solvents are used intensively in chemistry, biology, and industry to control factors such as solubility, stability of systems, and kinetics of reactions. Despite numerous studies on thermodynamic, transport, and spectral properties,[2a] there is still disagreement on the nature of the interactions which are responsible for the characteristic trends in the composition dependence. For example, often maxima, minima, or inflection points are observed which are then interpreted in terms of various effects such as structural changes in the solvent, preferential hydration, or association complexes. However, depending on the property studied, these extrema or inflection points often do not occur at the same mole fraction and depend on the nature of the solute, making many of these interpretations dubious.

Much of the confusion probably comes from the limited range of most studies. A better understanding of ternary aqueous systems will necessitate systematic investigations of model systems under a large variety of conditions. Thermodynamic properties, such as enthalpies, heat capacities, and volumes, are useful in this respect since they measure the variation with temperature and pressure of the various interactions.

Model solutes or cosolvents should include ionic and nonionic components and components which are known to have vastly different effects on the structure of water. The most typical hydrophilic and hydrophobic electrolytes are probably NaCl and Bu_4NBr. On the nonionic side, *tert*-butyl alcohol (TBA) is a well-characterized hydrophobic solute completely miscible with water, urea (U) appears to be a statistical structure breaker, and dimethylformamide (DMF), being also completely miscible with water, does not seem to have any large effect on its structure. All the thermodynamic properties mentioned above of the binary systems of these components in water are now well known.

In the ternary systems it is customary to keep one of the components (the solute X) at a fixed concentration, often infinite dilution, and to vary the other one (the cosolvent Y) over the largest possible range of mole fraction. The data are then expressed as the transfer function of solute X from water (W) to the mixed solvent (W + Y),

$$\Delta F_X(W \rightarrow W{+}Y) = \bar{F}_X(W{+}Y) - \bar{F}_X(W) \qquad (1)$$

where $\bar{F}_X$ is the partial molal quantity. If the solute is in the standard state, the standard functions are expressed as $\bar{F}^\theta{}_X$. For the enthalpies, the systems Bu_4NBr in DMF-W,[2b] U in DMF-W,[3] TBA in U-W,[4] U in TBA-W,[4] Bu_4NBr in TBA-W[5] and in U-W,[6] NaCl in U-W[7] and in TBA-W,[8] and TBA in NaCl-W[9] and in Bu_4NBr-W[9] have been investigated. For heat capacities and volumes the data are scarcer; NaCl has been measured in U-W[10] and in TBA-W,[11] Bu_4NBr in DMF-W,[12,13] U-W,[14] and TBA-W,[11] and TBA in NaCl-W[9] and Bu_4NBr-W.[9] In the present paper we will present data on the systems DMF in TBA-W, U in TBA-W, and TBA in U-W and DMF-W and extending some of the other data in TBA-W. A comparison of all these ternary systems among themselves and with the corresponding binary systems should help in elucidating the nature of the interactions responsible for the concentration dependence of the various transfer functions.

Experimental Section

The volumes and heat capacities have been measured using a flow densimeter[15] and a Picker flow microcalorimeter.[16,17] Experimental details and tests of the instruments have been given before. Also the origin and any purification of the different substances have been published previously.[10,11,14,18] The density[19] and heat capacity per unit volume[20] of pure water were taken from the literature. All solutions were prepared by weight and the measurements were carried out at 25.00 ± 0.01 °C.

In order to use the differential flow instruments under optimal conditions, all ternary systems were measured relative to the corresponding binary systems so that the measured quantities immediately corresponded to the effect of addition of the third component to the binary mixture. Precise volumes and heat capacities of the U-W,[10,14] DMF-W,[18] and TBA-W[21] systems have been published elsewhere.

The temperature increment for the differential specific heat capacity measurements was 0.5 K, the flow rate was 0.6 $cm^3\ min^{-1}$, and the basic power was 21 mW.

Results

With the present techniques it is not possible to obtain directly $\bar{V}$ and $\bar{C}_p$; usually the apparent molal quantities ϕ_V and ϕ_C are measured as a function of concentration, and the values extrapolated to infinite dilution are by definition equal to $\bar{V}^\theta$ and $\bar{C}^\theta{}_p$. However, at low solute concentration, the concentration dependences of ϕ_F (F stands for V or C_p) in the binary and ternary systems are usually sufficiently similar that

$$\Delta F^\theta{}_X(W \rightarrow W{+}Y) \simeq \phi_F(W{+}Y) - \phi_F(W) \qquad (2)$$

provided the concentration of X is kept relatively constant in all measurements.[11]

The choice of the proper concentration scale for component X is not obvious. At low cosolvent concentrations, the MacMillan-Mayer approach[4,22] requires that we express all concentrations relative to the pure solvent (m is the number of moles of solute per kg of W). On the other hand, at higher cosolvent concentrations, this scale becomes meaningless and scales such as mean molalities $\bar{m}$ (number of moles of solute per kg of mixed solvent) or aquamolalities (number of moles of solute per 55.51 moles of mixed solvent) are more convenient. We felt that it might be preferable to keep the number of moles of mixed solvent rather than the weight constant. Therefore, all measurements were made at an aquamolality of about 0.3. At this nonelectrolyte concentration the changes in densities and heat capacities can be measured with sufficient precision and eq 2 is usually a good approximation.

The apparent molal volumes and heat capacities of the solute X can be calculated from

$$\phi_V = M_X/d - \frac{1000 + m_Y M_Y}{m_X}\frac{(d - d_0)}{dd_0} = M_X/d - \frac{1000(d - d_0)}{dd_0\bar{m}_X} \qquad (3)$$

and

$$\phi_C = M_X c_p + \frac{1000 + m_Y M_Y}{m_X}(c_p - c_{p0}) = M_X c_p + \frac{1000(c_p - c_{p0})}{\bar{m}_X} \qquad (4)$$

where M is the molecular weight of components X or Y and d, d_0, c_p, and c_{p0} are the corresponding densities and specific heat capacities of the ternary and binary mixtures. With the flow microcalorimetric technique[16] the relative change in heat capacities per unit volume $(\sigma - \sigma_0)/\sigma_0$, where the subscript 0 refers to the reference solvent, is measured directly. The difference in specific heat capacities can however readily be calculated from

$$c_p - c_{p0} = c_{p0}[\{1 + (\sigma - \sigma_0)/\sigma_0\}d_0/d - 1] \qquad (5)$$

The experimental results, which are average values of at least three determinations, for ϕ_V and ϕ_C of DMF in TBA-W, U in TBA-W, TBA in U-W, and TBA in DMF-W are summarized in Tables I to IV (see Supplementary Material Available paragraph at end on paper).

As mentioned above, the concentration of component X was fixed at approximately 0.3 aquamolality. Since the molecular weights of the various cosolvents are all significantly larger than that of water, the mean molalities decrease as the mixed solvent becomes rich in nonaqueous component. In the case of TBA in DMF-W some experimental problems arose from these low mean molalities. Therefore, we checked the effect of the concentration dependence of TBA in pure DMF, the extreme case, and found that ϕ_V and ϕ_C showed little concentration dependence for molalities in the range 0.4 to 2 mol kg^{-1}. At low concentration, $m < 0.2$ mol kg^{-1}, a substantial concentration dependence was observed, probably as a result of preferential solvation with the contaminant water. For these reasons the concentration of TBA was held at a constant aquamolality in the water-rich region and above $X_{DMF} = 0.2$ at a constant mean molality of approximately 0.4 mol kg^{-1}. Such difficulties did not arise with the other systems. We believe that even in the case of TBA in DMF-W the reported values of ϕ_V and ϕ_C deviate at most 0.5 $cm^3\ mol^{-1}$ and 10 J

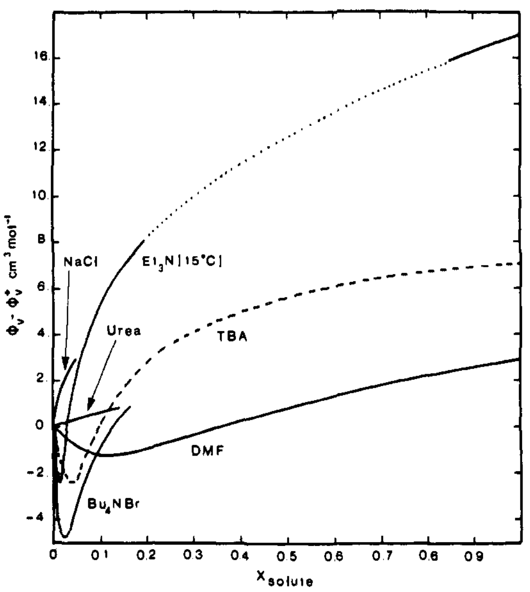

Figure 1. Apparent molal excess volumes of various solutes in water at 25 °C.

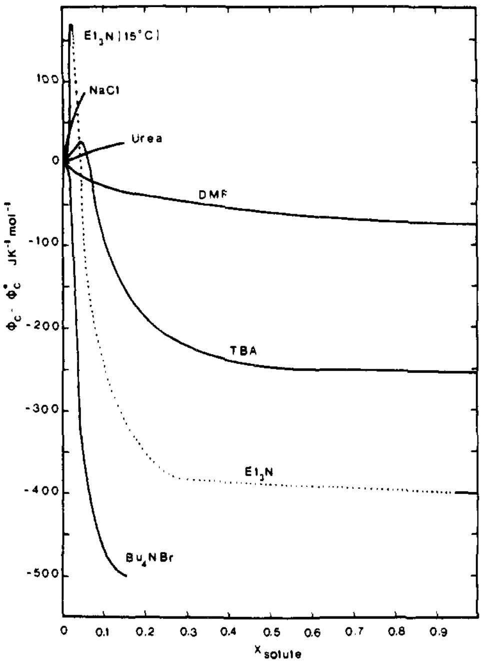

Figure 2. Apparent molal excess heat capacities of various solutes in water at 25 °C.

K^{-1} mol^{-1} respectively from the standard infinite dilution values and the signs and trends of the transfer functions will hardly deviate from those we would obtain from eq 1.

Discussion

The concentration dependence of the transfer functions is a measure of the perturbation of the components Y and W in the vicinity of solute X as the mole fraction of the mixed solvent is varied. It is therefore informative to compare the transfer functions with the corresponding excess functions of the binary system. The total excess function of the component Y is defined[23] by

$$F^E_Y = m(\phi_F - \phi^\theta_F) \qquad (6)$$

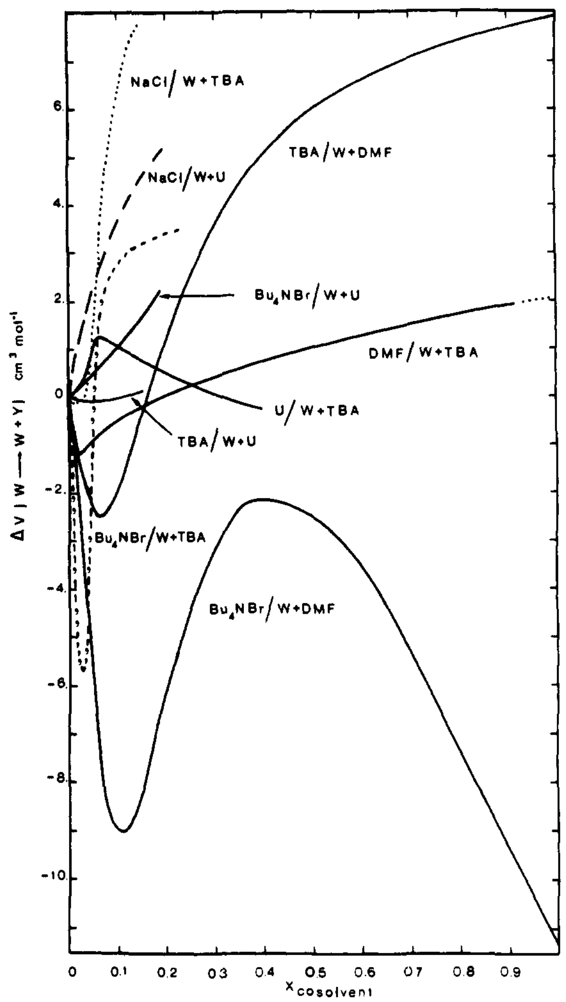

Figure 3. Volumes of transfer of various solutes from water to mixed aqueous solvents at 25 °C.

where ϕ^θ_F, the apparent molal quantity at infinite dilution, is equal to $\overline{F}^\theta_Y$. The corresponding partial molal excess function is

$$\overline{F}^E_Y = (\partial F^E_Y/\partial m)_{T,P} = \overline{F}_Y - \overline{F}^\theta_Y \qquad (7)$$

It is also possible to define an apparent molal excess function by

$$\phi^E_F = F^E_Y/m = \phi_F - \phi^\theta_F \qquad (8)$$

which is qualitatively equivalent to $\overline{F}^E_Y$ but which has the advantage of being directly measurable.

The data for the binary systems we are interested in, DMF-W,[18] TBA-W,[21] U-W,[10,14,24] Bu_4NBr-W,[24-26] and NaCl-W,[16,17] have all been published elsewhere and ϕ^E_V and ϕ^E_C are summarized in Figures 1 and 2. Some preliminary results with triethylamine-W[27] are also included. For the ternary systems, the transfer functions calculated from Tables I to IV, combined with previously published data, are given in Figures 3 and 4. The present figures summarize the interactions between typical ionic and nonionic structure breakers and hydrophobic solutes; DMF is also representative of a class of solutes[28] including dioxane, dimethyl sulfoxide, and possibly acetone which are only weakly hydrophobic and probably have little overall influence on the structure of water.

In order to examine all these interactions in a comprehensive way, it is convenient to divide the mole fraction range into three regions where different types of interactions and different models apply: (a) the nonaqueous solvent region, (b) the water-rich region, and (c) the intermediate region.

(a) The Nonaqueous Solvent Region. In cases where it was possible to obtain data over the whole mole fraction range the

Table V. Volumes and Heat Capacities of DMF and TBA at 25 °C

System	Function	Volume, $cm^3\ mol^{-1}$	Heat capacity, $J\ K^{-1}\ mol^{-1}$
DMF in TBA[a]	$\bar{F}_{DMF}(TBA)$	76.5	135
DMF in W	$\bar{F}^{\theta}{}_{DMF}(W)$	74.3	221
Pure DMF	$F^0{}_{DME}$	77.4	148
TBA in DMF[b]	$\bar{F}_{TBA}(DMF)$	95.20	182
TBA in W	$\bar{F}^{\theta}{}_{TBA}(W)$	87.76	463.3
Pure TBA	$F^0{}_{TBA}$	94.97	210

[a] 0.3 aquamolal. [b] 0.4 molal.

transfer and excess functions were found to be nearly constant in the nonaqueous end. Although TBA is a solid at 25 °C, it is relatively easy to extrapolate the data to get the molar volume and heat capacity of supercooled liquid TBA at 25 °C. With the solutes DMF and TBA, the infinite dilution (or low concentration) values $\bar{V}^{\theta}$ and $\bar{C}^{\theta}{}_p$ in different solvents are compared with the molar V^0 and $C^0{}_p$ in the pure liquid phase in Table V.

The partial molal quantities in nonaqueous solvents are not too different from the molar quantities, but the partial molal quantities in water are significantly different. Benson et al.[29] have estimated the molar heat capacities of many organic molecules in the gas phase. Although the uncertainty can be appreciable, the values for DMF and TBA seem to be smaller than all the data in Table V. This is a general observation. Liquids usually have higher heat capacities than gases or solids, and this is related to the much larger temperature dependence of the intermolecular forces in the liquid phase. If the heat capacity can be taken as some measure of the amount of structure in the system, then the present data suggest that there might be slightly more structure when TBA or DMF are surrounded by like molecules than by unlike ones (TBA in DMF or DMF in TBA). On the other hand, for these solutes in water, the situation is different since $\bar{C}^{\theta}{}_p$ is much larger, especially with TBA. It is through these kinds of observations that hydrophobic solutes were said to promote the structure of water.[30] However, it must be remembered that heat capacities are not measuring the interaction energies but the energy fluctuations. Therefore the extra structure near hydrophobic solutes must be more temperature dependent (melt more easily or with a larger ΔH) than that of pure water.

With the volumes, $\bar{V}^{\theta}$ in water are significantly smaller than the molar volumes, again the effect being larger with TBA. This contraction in volume when an hydrophobic solute goes from an nonaqueous phase to an aqueous one is in agreement with the statements that say that hydrophobic hydration occurs with an economy of space.[31]

It is not possible to obtain corresponding data with U, BU_4NBr, and NaCl, but the trends in the high concentration data are consistent with Bu_4NBr being hydrophobic like TBA and U and NaCl being structure breakers. It seems that the heat capacities of Bu_4NBr in DMF and TBA are not too different from what we would expect for pure liquid Bu_4NBr, whereas in water $\bar{C}^{\theta}{}_p$ is much more positive. Similarly, if we assume that ϕ_C of NaCl and U in nonaqueous solvents are tending to their pure liquid values at high concentration, then $\phi^{\theta}{}_C$ of both solutes in water are smaller than their intrinsic values as expected from their structure breaking effects.

We cannot draw unambiguous conclusions with ϕ_V of Bu_4NBr in nonaqueous solvents since here, contrary to heat capacities, coulombic type interactions are just as important as structural effects. Electrostriction around the Br^- is very pronounced in nonaqueous solvents and accounts for the large concentration dependence of ϕ_V in the nonaqueous solvent end.[13]

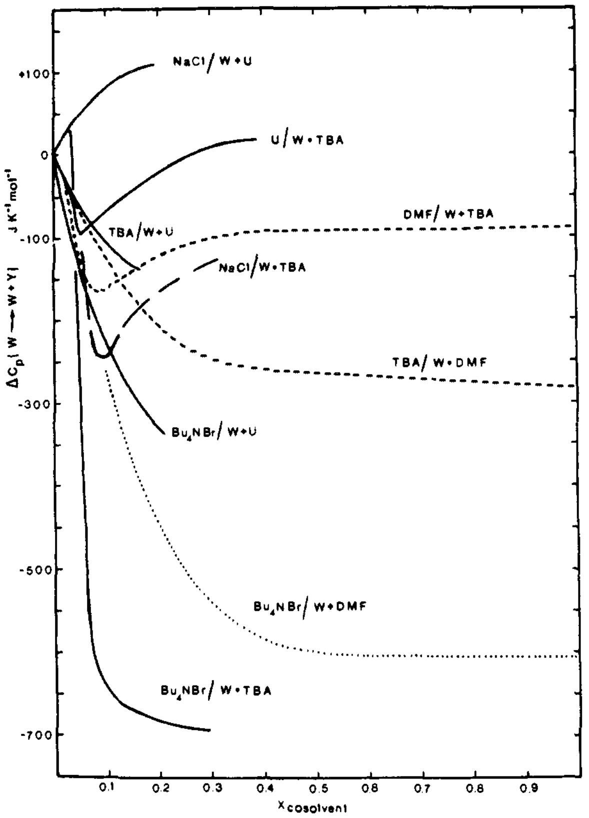

Figure 4. Heat capacities of transfer of various solutes from water to mixed aqueous solvents at 25 °C.

(b) Water-Rich Region. When water is in large excess the transfer functions show a large concentration dependence and it is convenient to interpret the transfer functions in terms of solute-solute interactions between the reference solute and the cosolvent.[4,9] This is best done using the MacMillan-Mayer approach as suggested by Kozak et al.,[32] Friedman and Krishnan,[22] Franks et al.,[33] and Schrier et al.[34] The general formalism used here has been described elsewhere.[4] Essentially, the nonideal contributions to the total thermodynamic functions are expressed as a series of pair, triplet, and higher interaction terms between like and unlike solutes, $f_{XX}, f_{YY}, f_{XY}, f_{XXY}$, etc. For volumes and heat capacities, the interaction terms are obtained directly from the apparent molal quantities. For the binary system of solute Y in W

$$\phi_F(W) - \phi^{\theta}{}_F(W) = f_{YY}m_Y + f_{YYY}m_Y{}^2 + \ldots \quad (9)$$

With electrolyte solutions eq 9 must also include terms for the long-range Debye-Hückel forces. For the ternary systems

$$\phi_F(W+Y) - \phi_F(W) = 2f_{XY}m_Y + 3f_{XXY}m_Xm_Y + 3f_{XYY}m_Y{}^2 + \ldots \quad (10)$$

In these equations the molalities m are always expressed in number of moles of X or Y per kg of W.

The parameters f_{XX} and f_{YY} of nonelectrolyte solutions can be derived from the initial slopes of the excess functions and the triplet terms from the deviations from linearity. Similarly, the parameters f_{XY}, f_{XXY}, and f_{XYY} can be obtained from the transfer functions provided the solute being transferred is kept at sufficiently low concentrations. The system TBA-DMF-W can serve as a check of this formalism since both solutes were in turn varied in concentration. For the variable DMF and variable TBA the mixed pair interaction terms c_{pXY} and c_{pYX} are respectively -11.5 and -10.7 $J\ K^{-1}\ mol^{-2}\ kg$ and v_{XY} and v_{YX} are -0.93 and -1.01 $cm^3\ mol^{-2}\ kg$. These parameters are identical inside the experimental uncertainty. The agreement

Table VI. Pair and Triplet Interaction Terms for Binary and Ternary Aqueous Solutions at 25 °C (Reference to Original Data Given in Parentheses)

	U	DMF	TBA	Bu_4NBr	NaCl
			(a) c_{pXY}, J K^{-1} mol^{-2} kg		
U	5.2 (16)		−10	−25 (24)	12 (10)
DMF		−8.3 (18)	−11.1		
TBA			7.9 (24)	23 (11)	−33 (11)
Bu_4NBr				−32.5 (25,24)	−35 (36)
NaCl					15.6 (16)
			(b) v_{XY}, cm^3 mol^{-2} kg		
U	0.12 (16)		−0.01	0.30 (24)	0.4 (10)
DMF		−0.42 (18)	−0.97		
TBA			−1.89 (24)	−7.0 (11)	−0.3 (11)
Bu_4NBr				−9.81 (24)	−2 (36)
NaCl					−0.008 (37)

	c_{pXXY}	v_{XXY}
U-U-TBA	0.4	0.01
U-TBA-TBA	−2.4	0.04
DMF-DMF-TBA	0.2	0.07
DMF-TBA-TBA	−3.2	0.21
TBA-TBA-TBA	1.8 (24)	0.39 (24)
U-U-U	−0.3 (16)	−0.004
DMF-DMF-DMF	+0.03	0.03

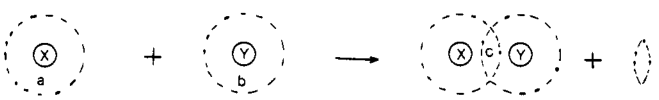

Figure 5. Structural interactions for the pair functions.

is not quite as good with the system U-TBA-W. The respective values of c_{pXY} are −11.7 and −8.0 J K^{-1} mol^{-2} kg and of v_{XY} 0.08 and −0.09 cm^3 mol^{-2} kg. These differences could result from the nonzero concentration of the solute at constant concentration but most probably are reflecting a larger uncertainty with this system. A summary of the pair and triplet interaction parameters is given in Table VI. With electrolytes the pair parameters were identified with the B_F parameters of the Redlich[35] type equation,

$$\phi_F(W) = \phi^\theta{}_F(W) + A_F m^{1/2} + B_F m + \ldots \quad (11)$$

where A_F is the limiting slope of the Debye-Hückel law.

These pair interaction parameters are related to second virial coefficients and are essentially a measure of the change in the thermodynamic function as two molecules move from infinite separation to some finite small distance. As illustrated in Figure 5 the molecules may not necessarily come into contact. As the two hydrated molecules approach each other, in addition to the usual electrostatic, inductive, and dispersion interactions, there will be some changes in the hydration of the molecules. Also the structure of water in the zone c need not necessarily be the same as in the cospheres a or b. These kind of structural interactions have been discussed by Desnoyers et al.,[37] Friedman and Krishnan,[22] and Franks et al.[33]

General trends can be observed for the interaction terms of the various types of solutes.

(i) Hydrophilic-hydrophilic interactions, such as U-U, U-NaCl, and Na^+-Cl^-, lead to positive heat capacities and volumes. Since the hydration contribution (mostly structure-breaking with heat capacities) causes a negative contribution to both $\bar{C}^\theta{}_p$ and $\bar{V}^\theta$ in pure water, an increase in concentration decreases the overall hydration effect as expected from the destructive overlap models.[37] Interaction between ions of the same sign Na^+-Na^+ or Cl^--Cl^- may lead to the opposite effect[37] but these interactions are usually small compared with interactions between ions of opposite sign, e.g., Na^+-Cl^-.

(ii) The interaction between hydrophilic and hydrophobic solutes (U-TBA, NaCl-TBA, Bu_4N^+-Br^-) causes a negative contribution to heat capacities and a small (negative) contribution to volumes. Hydrophobic hydration causes an overall positive contribution to $\bar{C}^\theta{}_p$ and negative contribution to $\bar{V}^\theta$. However, with volumes, structural models attribute the decrease in volume to the filling of natural cavities in the structure of water,[31] the increase in the structure of water causing a smaller but significant increase in volume. The interaction between hydrophobic and hydrophilic solutes reduces the hydration of both types of ions as shown in Figure 5. The reduction in hydrophobic hydration seems to be the leading effect with heat capacities and there is a near cancellation with volumes. If one of the solutes has little overall structural effect (DMSO, dioxane, DMF) then the reduction in hydrophilic hydration of the other solute predominates.[28]

(iii) The interaction between two hydrophobic solutes is certainly the most fascinating and intriguing one. Destructive overlap models[37] would suggest a decrease in heat capacity and volume, as the two solutes approach each other but do not come in contact, as in Figure 5. This is generally observed with volumes. This is also true for heat capacities with some hydrophobic solutes. For example ϕ_C of DMF decreases monotonically with concentration. This is better seen if ϕ_C is plotted against volume fraction as in Figure 6. The small hydration contribution to the heat capacity decreases regularly and ϕ_C tends in a nearly statistical way to $C^0{}_p$ as the volume fraction tends to 1. Continuing studies in our laboratory show that the same general behavior is observed with low molecular weight ketones, ethers and esters. On the other hand, with some alcohols,[21] alkoxyethanols, trialkylamines, and carboxylic acids, the concentration dependence of ϕ_V is similar to other organic solutes in water, but the shape of ϕ_C is remarkably different. At low temperatures there is an initial decrease in ϕ_C (negative c_{pXX}), then a pronounced increase in ϕ_C, and eventually a large decrease. As the temperature increases the initial slope becomes more positive or less negative, and with many systems, such as alcohols or amines, c_{pXX} is positive at 25 °C (see Figure 2). The general trends are more obvious if $\phi_C - \phi^\theta{}_C$ is plotted against volume fractions as in Figure 6. If the line going from pure water to the pure organic liquid is taken as the ideal behavior, then there is a positive deviation from ideality with these hydrophobic solutes at all temperatures. The positive hump in ϕ_C, which results from positive c_{pXXX} and higher terms, suggests that the interactions in this region are cooperative. The positive value of c_{pXY} observed with the system

Bu_4NBr-TBA (see Table VI) also suggests that the interactions between Bu_4N^+ and TBA are similar to those between TBA and TBA. Heat capacity is a very sensitive probe for studying structural interactions but, as discussed by Ben-Naim,[38] its interpretation is often ambiguous. Still we can speculate on possible explanations. For example, as it will be shown in the next section, the large decrease in ϕ_C at high mole fractions of TBA and other similar solutes is suggesting a microphase separation in a way analogous to micellization. It seems that a positive c_{pXX} or a positive hump in the concentration dependence of ϕ_C is characteristic of the systems that have a strong tendency to associate through hydrophobic interactions. It is also appealing to interpret these maxima in ϕ_C in terms of the formation of some intermediate metastable complex, e.g., something that would resemble a time-average clathrate hydrate where each solute is separated by a cage of water one molecule thick. These cages would collapse when there is not enough water available, and ϕ_C would then decrease rapidly upon further addition of solute. Unfortunately, such models are not unique and further work with properties such as compressibilities, expansibilities, ultrasonic absorption, light scattering, etc., will be required before a definite model can be confirmed.

Savage and Wood[39] have shown recently that with enthalpies and free energies the pair interaction parameters show group additivity. Not enough systems are available at the moment to test the group additivity for the parameters v_{XY} and c_{pXY} but there is not too much hope here in view of the rather large temperature dependence of c_{pXY}[21,24] and the small magnitude of v_{XY}.

Not much can be said regarding the triplet interaction terms except that they are in general opposite in sign to the leading corresponding pair term. The hydrophobic-hydrophobic-hydrophobic triplet term is an exception in that it usually has the same sign as the pair term.

The pair interaction terms are also known for enthalpies[4] and free energies[40] for the system U-TBA-W. At 25 °C, there are respectively $h_{XY} = 715$ J mol^{-1} kg and $g_{XY} = 46$ J mol^{-1} kg. Again the signs of these terms are the same as for NaCl-TBA-W[9] which is again consistent with U acting as a structure breaker.

(c) Intermediate Region. In the water-rich region there are often strong solute-cosolvent structural interactions while very little specific effects are observed in the nonaqueous end. The initial slope of the transfer function is reflecting the solute-cosolvent pair interactions while the transfer function from water to the pure nonaqueous solvent $\Delta F^{\theta}_X(W \rightarrow Y)$ measures the change in the solvation of the solute X. Whenever f_{XY} is of opposite sign to $\Delta F^{\theta}_X(W \rightarrow Y)$ a maximum or minimum *must* occur. Therefore, in many ternary aqueous systems, the extrema have no particular significance and should not be taken as evidence for the formation of complexes, maximum structure of the mixed solvent, etc. In some cases, however, particularities in the general shape of the concentration dependence of the transfer and excess functions in the intermediate zone lead to interesting conclusions.

There is a remarkable similarity between the general concentration dependence of hydrophobic solutes such as TBA, Bu_4NBr, and triethylamine on the one hand and surfactants on the other. In the binary systems (see Figures 1 and 2) the volumes pass through a minimum and level off to the molar value. With heat capacities the trends are reversed; ϕ_C goes through a maximum (TBA, triethylamine) and decreases sharply to C^0_p. If partial molal quantities are used instead of apparent molal ones the transitions are even sharper. For example, $\bar{C}_p$ of TBA in W nearly reaches its molar value at 0.1 mol fraction. This implies that the hydrophobic solute or hydrophobic part of the solute is only seeing other hydrophobic entities at these high concentrations somewhat as in the case of micelles. Therefore something that approaches a microphase separation or higher order transition is occurring, as suggested by Kruus.[41] In the ternary system Bu_4NBr-TBA-W[11] the same general trend is observed but the transition is even sharper and larger. At low concentration of TBA, Bu_4N^+ (kept also at low concentration) interacts strongly with TBA without forming a contact pair. At higher TBA concentration, Bu_4N^+ binds with the TBA aggregates in a way analogous to the interaction of a dye with a micellar surfactant.

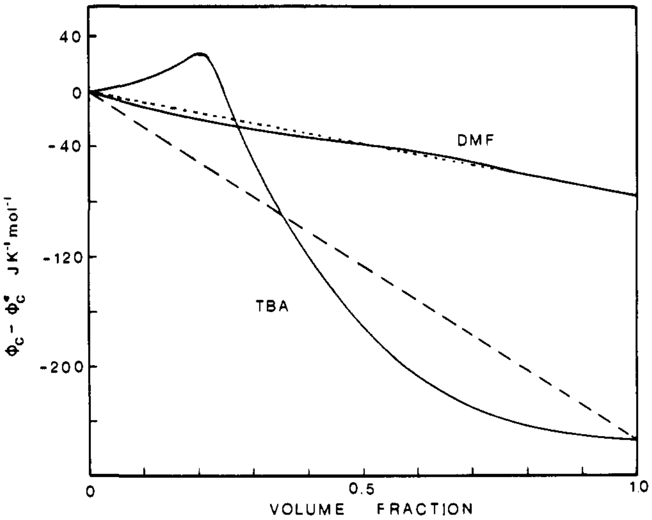

Figure 6. Apparent molal excess heat capacities in water at 25 °C; dotted line represents the ideal behavior.

The system U in TBA-W is qualitatively similar to NaCl in TBA-W.[11] The negative deviation from the limiting slope (pair interaction) for $\Delta C_{pU}(W \rightarrow W+TBA)$ and positive deviation for $\Delta V_U(W \rightarrow W+TBA)$ is in the direction of enhanced hydrophobic bonding between TBA molecules in the presence of U. A similar trend was also observed with $\Delta H_U(W \rightarrow W+TBA)$.[4] Here the analogy with surfactants fails since NaCl lowers the critical micelle concentration while U raises it. Again the maximum and minimum have no special significance and depend on the value of ϕ_C and ϕ_V in pure TBA relative to that in W.

The system DMF in TBA-W presents no particular features and the shape of the transfer function is largely fixed by the sign of the pair interaction function and the difference of ϕ_C and ϕ_V in pure TBA and pure W.

The two nonelectrolytes U and DMF have opposite excess functions but are similar in that they actually show little specific solute-solute interactions in W. This is especially true with ϕ_C. With both solutes, ϕ_C is tending to its molar value (see Figure 6). In both cases nonelectrolyte-W interactions are being replaced by nonelectrolyte-nonelectrolyte interactions in a near statistical way. In the same way, with the ternary systems, ϕ_C of TBA and Bu_4NBr in U-W and in DMF-W decrease regularly from their high values in W to approximately their molar values as the DMF-W or U-W[24] mixtures tend to the pure nonaqueous phase. The volume behavior is somewhat complicated since there is a slight minimum in the DMF-W binary system which automatically appears in the TBA-DMF-W system. The volumes of the ternary system Bu_4NBr-DMF-W[13] are further complicated at high DMF mole fractions by the electrostriction of Br^- which causes the large decrease in ϕ_V.

(d) Enthalpies and Entropies of Ternary Systems. The general interpretation of the ternary aqueous systems we have used for heat capacities and volumes can be applied in the same way to enthalpies and entropies whenever the experimental data are available.[2b-9] The water-rich end is reflecting the strong structural solute-cosolvent pair interactions and the nonaqueous end shows little specificity. There is also evidence for high order transitions with hydrophobic cosolvents in the intermediate zone, but, as in the case of micellization, the enthalpic contribution during these transitions is rather small.

(e) Transfer Functions of Hydrophobic Solutes and the Scaled Particle Theory. Recently one of us has shown[42] that the Scaled Particle theory can be used successfully to predict the concentration dependence of the transfer function of Bu_4N^+ in mixed solvents. Similar success would also hold for TBA in the various mixed solvents since TBA behaves qualitatively in the same way as Bu_4N^+. However, since this theory uses experimental data for the binary system, it does not give us much insight into the nature of the interactions in the ternary system.

Conclusion

The thermodynamic properties of ternary aqueous solutions often appear to be quite complicated with inflection points, maxima and minima occurring at different mole fractions. However, the overall picture is much clearer once we understand what is going on at both ends. In the water-rich region the properties are characterized by strong solute-W, cosolvent-W, and solute-cosolvent structural interactions while in the nonaqueous end the solute-cosolvent interactions predominate. While theoretical models[22,43] can account for the existence of such structural interactions no theory can at present predict their magnitude or even their sign. To get a good understanding of aqueous ternary mixtures it is therefore essential to determine precisely the initial concentration dependence in the water-rich region and to obtain or estimate the data for the solute in the pure cosolvent. This is the kind of information theoreticians will require. Studies which are limited to properties of solutes in mixed solvents at concentrations such as 20, 40, and 60% by weight of cosolvent are near to useless from the theoretical point of view.

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Supplementary Material Available: Molal volumes and heat capacity of *N,N*-dimethylformamide, urea, and *tert*-butyl alcohol, Tables I-IV (4 pages). Ordering information is given on any current masthead page.

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