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ARTICLES

Diffusion and Structure in Water−Alcohol Mixtures: Water + *tert*-Butyl Alcohol (2-Methyl-2-Propanol)

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Data are reported for the intradiffusion coefficient of water (D_w) in aqueous solutions of 2-methyl-2-propanol (*tert*-butyl alcohol, TBA) as a function of pressure, temperature, and composition. In previous work (Harris and Newitt, J. Phys. Chem. B, **1998**, 102, 8874), we have shown that for this system at mole fraction $x_{TBA} \sim 0.025$ and low temperatures, D_w shows a maximum with increasing pressure to a greater relative extent than does the self-diffusion coefficient in pure water under the same conditions. It was concluded that this is consistent with the concept that the water is more structured in the TBA solution at this composition. Our present results confirm this at other concentrations below $x_{TBA} \sim 0.06$. This is also consistent with a previous, but unpublished, study of TBA intradiffusion by Woznyj, and the NMR relaxation and chemical shift results of Yoshida et al. (J. Chem. Phys., 1998, 108,1360). At higher concentrations, the normal behavior of a diminution of the diffusion coefficient with increasing pressure occurs. This is not consistent with ordering of hydration water suggested by certain models based on the presence of clathrate-like hydrates in solution.

Introduction

Much attention in the past has been directed toward the study of structural changes in water caused by the introduction of nonpolar groups, in an attempt to understand the biologically and industrially important hydrophobic effect.[1] Aqueous solutions of alcohols in particular show a number of apparently unusual effects when their thermodynamic, transport, and structural (scattering) properties are measured.[2−6]

High-pressure diffusion studies can give important information about solution structure in aqueous systems. The maxima found in the self-diffusion coefficient and fluidity isotherms for water at temperatures below 30−35 °C are well-known.[7] This phenomenon, one of the many peculiarities of liquid water, is due to competition between compression, which generally slows translational molecular motion, and the effect of pressure on the transitory, three-dimensional, H-bonded structure of liquid water, which increases water molecule mobility. The maxima move to higher pressures as the temperature is lowered, and are more pronounced for the more strongly H-bonded D_2O than for H_2O or $H_2{}^{18}O$.[8]

The phenomenon of pressure-increased self-diffusivity is an obvious tool, therefore, for an examination of the effect of solutes on water structure,[7] but there have been relatively few investigations of water−amphiphile systems to date. This paper is part of a systematic investigation of such systems and here we summarize what has been revealed by earlier work on water−alcohol mixtures.

Easteal and Woolf[6] have demonstrated that the infinite-dilution tracer diffusion coefficients of ^{14}C-labeled methanol and ethanol in water are enhanced much more than the self-diffusion coefficient of the solvent water by the application of high pressures (100−200 MPa) at low temperatures (5−15 °C). This effect for the solute alcohols was interpreted to mean that localized, more open, and highly structured microregions of the solution exist around the alcohol molecules. These regions then respond more markedly to increases in pressure, allowing solute molecules to diffuse more rapidly than bulk solvent water molecules.[6] An alternative explanation is that because of the different degree of hydrogen bonding of water and alcohol, the effect of pressure might be two-fold—(a) distortion of water structure leading to freer solute motion, and (b) changing the equilibrium for the reaction between water and the alcohol hydroxy groups, again to allow freer alcohol motion.

The initial work of Easteal and Woolf has been followed by four other studies. Woznyj[9] (see also ref 7) has examined intradiffusion (self-diffusion) of 2-methyl-2-propanol (*tert*-butyl alcohol or TBA) in its aqueous solutions to 150 MPa over a wide range of compositions. Figures 1 and 2, constructed from his data (see below), reveal positive pressure derivatives, $(\partial D/\partial p)_{T,x}$, at low compositions and temperatures ($x_{TBA} \sim 0.014$, $T \sim 5$, and 21 °C; $x \sim 0.029$, $T \sim 5$ °C), with relative diffusion coefficients becoming larger with decreasing temperature. This is similar to what Easteal and Woolf found at infinite dilution for methanol and ethanol.[6] At higher TBA concentrations ($x_{TBA} \geq 0.062$), the second derivative $(\partial^2 D/\partial p \partial T)_x$ has changed sign so that the pressure derivatives are negative, with relative diffusion coefficients becoming smaller with increasing temperature (Figure 3). It is interesting that near this composition various thermodynamic functions appear to show effects that

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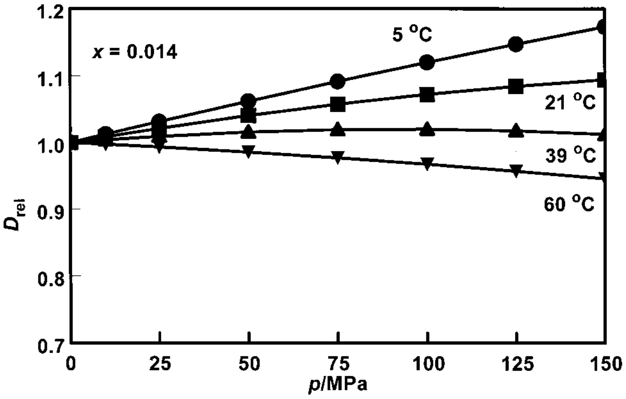

Figure 1. Relative intradiffusion coefficients for TBA in D_2O-TBA at x_{TBA} = 0.014 (calculated from the results of Woznyj[9]). Note the temperature dependence.

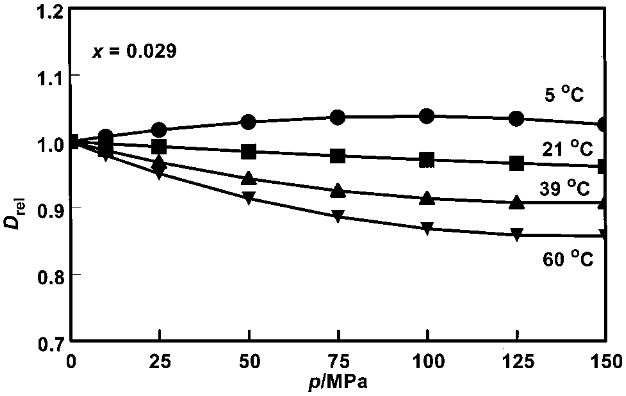

Figure 2. Relative intradiffusion coefficients for TBA in D_2O-TBA at x_{TBA} = 0.029 (calculated from the results of Woznyj[9]).

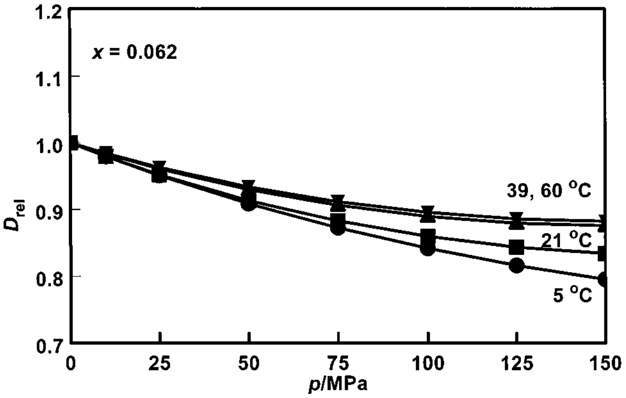

Figure 3. Relative intradiffusion coefficients for TBA in D_2O-TBA at x_{TBA} = 0.062 (calculated from the results of Woznyj[9]). The 60 °C isotherm is uppermost.

Koga et al.[5,10] have attributed to a transition from a regime where water H-bonds around a solute molecule are enhanced (and, more controversially, diminished in the "bulk" solution) and one where two kinds of microclusters exist rich in each component. We note too that at this composition, correlation lengths obtained from mutual diffusion and shear viscosities show a rapid increase consistent with long-range correlation of molecular motion.[11,12] These have been interpreted as being due to the formation of hydrated oligomeric species or, perhaps, pseudocritical enhancement.[12−15]

A second study has been made by Has and Lüdemann,[16] who examined the diffusion of heavy water and 2,2-dimethyl-1-propanol (DMP or isobutyl alcohol) in dilute solutions ($x_{DMP} < 0.006$, $p < 200$ MPa, $0 < T/°C < 130$). (The very limited composition range is due to the low solubility of the alcohol.) No enhancement of the DMP intradiffusion coefficient with increasing pressure was observed even at the lowest composition ($x_{DMP} = 0.0004$) and temperature (5 °C) studied. On the other hand, for the solvent (D_2O), the pressure derivative $(\partial D/\partial p)_{T,x}$ was positive in its DMP mixtures at the lowest temperature examined, 1 °C, at up to about $x_{DMP} \sim 0.004$. Previously, such an effect on the solvent water had only been reported for dilute ($x_{DMSO} \leq 0.036$) solutions of deuterated dimethyl sulfoxide (DMSO-d_6) at the single temperature of 25 °C.[17]

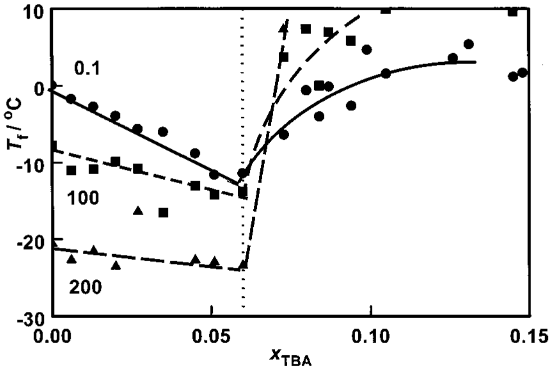

Figure 4. Phase diagram for water−TBA showing the shift in the phase boundaries with increasing pressure. The vertical dotted line corresponds to x_{TBA} = 0.06. (Drawn using the results of Woznyj[9]).

In a previous paper,[18] we made a survey of water intradiffusion at high pressure in a number of water−alcohol systems, all at the same composition (x_{ROH} = 0.025). At low temperatures, the intradiffusion coefficient of water in solutions of 2-propanol or *tert*-butanol shows a maximum with increasing *p*, to **a greater relative extent than in pure water under the same conditions**. This suggests that the water in these solutions is more "structured" than in pure water, though there is a clear distinction from the effects produced by large "structure-breaking" ions as solutes where the absolute water diffusion coefficient may show a maximum as concentration or pressure is increased. In solutions of methanol, ethanol, or 2,2,2-trifluoroethanol, the relative enhancement at this composition is similar to that of water, with no apparent additional effect.

Because of these results, we have examined the system water−TBA in more detail and report here water intradiffusion coefficients obtained as a function of temperature and pressure at other compositions. This system is unusual among the water−alcohol mixtures in that it exhibits a eutectic at low solute concentration ($x_{TBA} \sim 0.06$):[19] this eutectic moves to lower temperatures as the pressure is increased[9] and is close to that of the water−ice I−ice III triple point at 200 MPa. This provides a region of thermodynamic states not observable in other water−alcohol mixtures (Figure 4).

There have been several structural studies made on water−TBA. Some have been referred to above. Very recently, Bowron et al.[20] made a detailed study of this system at 25 °C and atmospheric pressure by H/D isotopic substitution neutron scattering techniques. Empirical potential structure refinement simulation techniques were used to reproduce the observed partial distribution functions. At the lowest accessible composition, $x_{TBA} \sim 0.06$, there was evidence that small (2−4) alcohol clusters are favored, with association through alkyl group contact rather than via hydroxyl H-bonding. As might be expected, the association is loosely structured, with fairly broad orientational distributions, becoming more so at $x_{TBA} \sim 0.11$ and 0.16, the other compositions examined. (It is interesting that a similar analysis of scattering results for pure TBA[21] suggests a similar interaction of alkyl groups coupled with H-bonding between pairs of molecules and significant polar-nonpolar interactions.) The polar−nonpolar interaction is said to be more apparent at $x_{TBA} \sim 0.16$ than in the more dilute solutions, which is consistent with hydrophobically driven association at $x_{TBA} \sim 0.06$. H-bonding seems to occur between alcohol and water molecules, with direct alcohol−alcohol H-bonding absent at the compositions studied.

Experimental Section

D_2O (Sigma, 99.8 atom %), 2-methyl-2-propanol (Aldrich, 99.5%), 2-methyl-2-propan-(ol-*d*) (Aldrich 98+%), and 2-methyl-2-propanol-d_{10} (Aldrich 99+%) were used without further purification. High-purity water (resistivity, 18 MΩ cm) was obtained by passing the product of a Millipore reverse osmosis purification system through a Milli-Q ion-exchange system (Waters-Millipore Ltd). Solutions were prepared gravimetrically from these materials; corrections were made for air buoyancy using standard methods.[22] The molar masses of TBA, TBA-*d*, and TBA-d_{10} were taken to be 74.1288, 75.135, and 84.191 g/mol, respectively.

Intradiffusion coefficient measurements were carried out by the NMR spin-echo technique at 20 MHz using a Be−Cu pressure vessel in a glass Dewar thermostat. The techniques used have been described previously.[18,23,24] The NMR signal-to-noise ratio naturally is worse at the lowest TBA concentrations, so the accuracy is estimated to lie between ± 2% at TBA mole fraction 0.15 in D_2O to ±1% for mixtures of H_2O and TBA-d_{10} where the water signal is quite strong.

Results and Discussion

The results for each of the systems studied are presented in detail in Table 1S and summarized in Table 1. Figure 5 shows a comparison between the results of this work at 25 °C and those of Kipkemboi and Easteal[25] obtained at 28 °C for solutions of unlabeled TBA; the curves are of very similar shape. However, it should be noted that their values for the intradiffusion coefficient of TBA seem a little high, as the infinite dilution value is some 26% higher than that obtained from mutual diffusion measurements at 25 °C,[15] rather more than might be expected for the small difference in temperature.

Figures 6−12 show relative diffusion coefficients [$D_{rel} = D(p)/D(0.1\ \mathrm{MPa})$] plotted against pressure, p. At low compositions, D passes through a maximum as the pressure is increased, but declines with increasing pressure above $x_{TBA} \sim 0.06$. The corresponding values for pure water are given in Figure 13 for comparison.

At $x_{TBA} \sim 0.1$ and $x_{TBA} \sim 0.15$ it is possible to fit D as a function of molar volume and temperature using an analogue of an equation used for self-diffusion[26,27] and tracer diffusion in nonaqueous molecular liquids,[28] either unassociated such as *n*-hexane or H-bonded such as methanol. Details are given in Table 2 and *Appendix 1*. At these compositions, diffusion in the water−TBA mixture is slowed by compression because of a reduction in free volume as in the majority of liquids, and the effects of water cooperativity appear to be absent.

In our earlier study, we reported that at $x_{TBA} \sim 0.025$ the maxima are larger at 0 °C and −5 °C and are displaced to higher pressures than for pure water. This suggests greater structure around the solute molecules than in pure water under the same conditions, which requires greater pressure to distort and hence facilitate molecular motion. The present results at $x_{TBA} \sim 0.01$ under the same conditions are similar, though the maxima occur at pressures closer to those for pure water as might be expected.

TABLE 1: Coefficients for $D(H_2O; H_2O + \text{TBA-}d_{10}) = D_0(1 + a_1p + a_2p^2 + a_3p^3)$ for Each Composition and for $D(\text{TBA}; D_2O + \text{TBA})$ at $x_{TBA} = 0.5$, at Various Temperatures

x_{TBA}	T/°C	10^9D_0/ m^2s^{-1}	10^3a_1/ MPa^{-1}	10^5a_2/ MPa^{-2}	10^8a_3/ MPa^{-3}	δ/%[a,b]
0.01	−5	0.765	2.054 82	−0.805 57	0.874 24	1.1
	0	0.900	1.417 42	−0.527 98	0.490 12	0.8
	5	1.059	1.165 15	−0.493 61	0.501 59	0.2
	15	1.496	0.444 51	−0.157 92	0.0	0.5
	25	2.010	0.173 46	−0.101 87	0.0	0.7
	45	3.323	−0.457 96	0.0	0.0	1.1
0.025[c]	−5	0.495	1.6903	−0.300 96	−0.156 97	1.2
	0	0.616	1.5714	−0.598 69	0.747 76	1.7
	15	1.143	0.534 01	−0.259 24	0.253 56	0.6
	25	1.595	−0.059 65	−0.056 40	−0.106 82	0.7
	50	3.017	−0.452 21	0.0	0.0	0.3
0.06	−10	0.149	−0.005 165	0.592 47	−1.655 63	0.2
	−5	0.216	0.404 93	−0.086 60	0.0	0.9
	0	0.305	−0.129 19	0.0	0.0	0.3
	5	0.417	−0.382 59	0.033 92	0.0	0.5
	15	0.707	−0.537 57	0.0	0.0	0.8
	25	1.076	−0.657 76	0.0	0.0	1.0
	−5	0.166	−2.183 02	0.548 44	0.0	0.5
	0	0.242	−1.992 62	0.296 48	0.0	1.2
	25	0.936	−1.592 30	0.156 63	0.0	0.5
0.1	0	0.217	−3.235 84	0.573 40	0.0	1.0
	5	0.304	−2.719 41	0.356 47	0.0	0.3
	15	0.530	−2.107 54	0.195 37	0.0	0.3
	25	0.831	−1.876 92	0.170 00	0.0	0.7
0.15	5	0.244	−3.670 87	0.843 36	0.0	0.5
	15	0.398	−2.813 82	0.349 79	0.0	0.3
	25	0.674	−2.493 67	0.301 91	0.0	0.3
0.5	0	0.0824	−7.524 00	0.0	0.0	2.5
	5	0.112	−9.168 28	4.008 00	0.0	0.5
	15	0.190	−8.718 11	4.708 42	−12.220	1.0
	25	0.284	−7.327 24	2.816 34	−4.414 33	1.1
	50	0.807	−7.121 93	2.878 00	−4.787 47	1.5

[a] δ is the standard deviation of the fit expressed as a percentage of D_0, the value of D at atmospheric pressure. [b] D_{rel} values were fitted rather than absolute D values. [c] From ref 23.

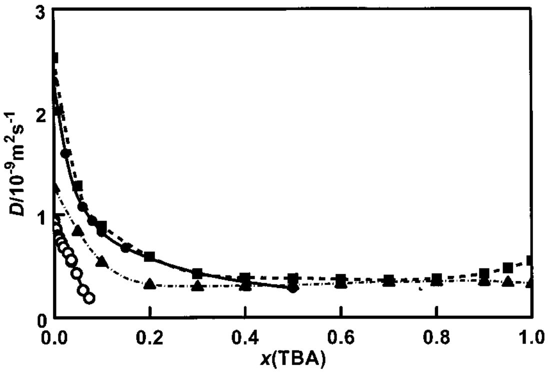

Figure 5. Comparison of the intradiffusion coefficient of water in water−TBA−d_{10} at 25 °C and atmospheric pressure (●, this work), the intradiffusion coefficient of water in water−TBA at 28 °C (■, Kipkemboi and Easteal[25]), the intradiffusion coefficient of TBA in water−TBA at 28 °C (▲, Kipkemboi and Easteal[25]), and the mutual diffusion coefficient for water−TBA at 25 °C (O, Harris and Lam[15]).

At these two compositions it is not possible to fit the diffusion data using the equation referred to above. At $x_{TBA} \sim 0.06$, the maximum in D_{rel} has decreased in magnitude and is present only below 0 °C (Figure 8); the temperature dependence begins to reverse above this composition (Figure 9) and the reversal is complete above mole fraction 0.1 (Figure 10).

As mentioned in the *Introduction*, Woznyj[9] measured the self-diffusion coefficient of TBA-d_{10} in aqueous mixtures at pressures to 150 MPa at temperatures between 5 °C and 162 °C. He did not compare the pressure dependence of different

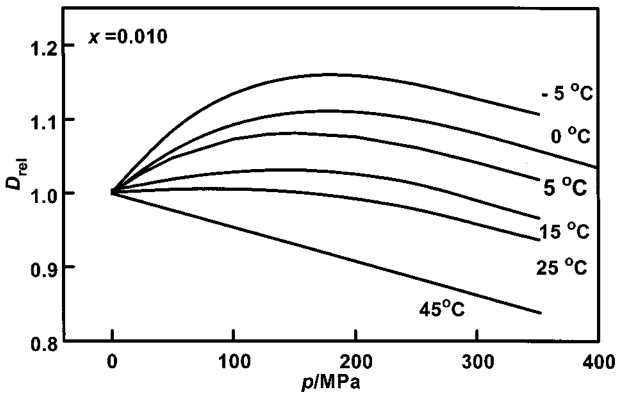

Figure 6. Relative intradiffusion coefficients for water in water−TBA-d_{10} (x_{TBA} = 0.010).

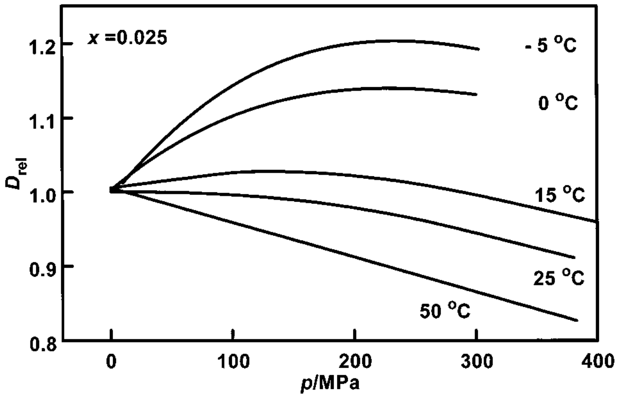

Figure 7. Relative intradiffusion coefficients for water in water−TBA-d_{10} (x_{TBA} = 0.025).[18]

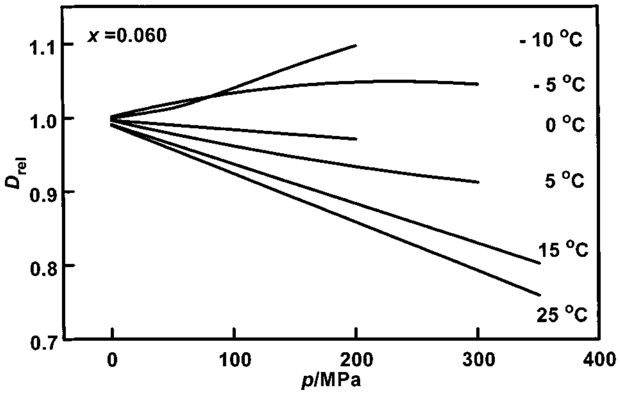

Figure 8. Relative intradiffusion coefficients for water in water−TBA-d_{10} (x_{TBA} = 0.060).

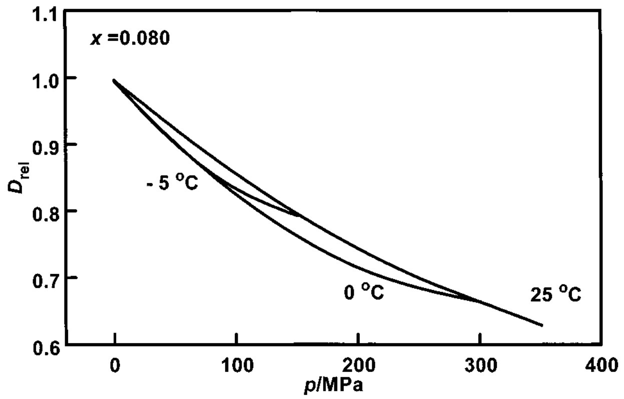

Figure 9. Relative intradiffusion coefficients for water in water−TBA-d_{10} (x_{TBA} = 0.080).

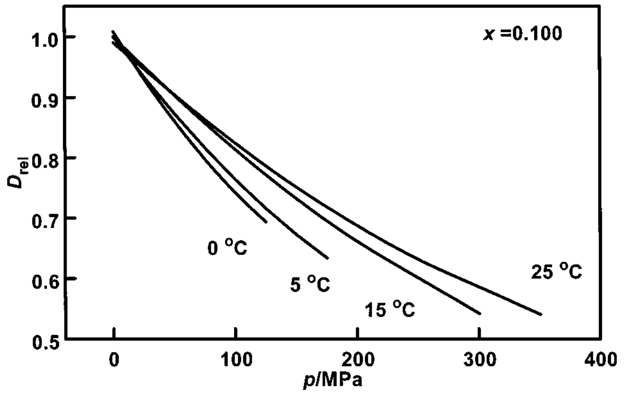

Figure 10. Relative intradiffusion coefficients for water in water−TBA-d_{10} (x_{TBA} = 0.100).

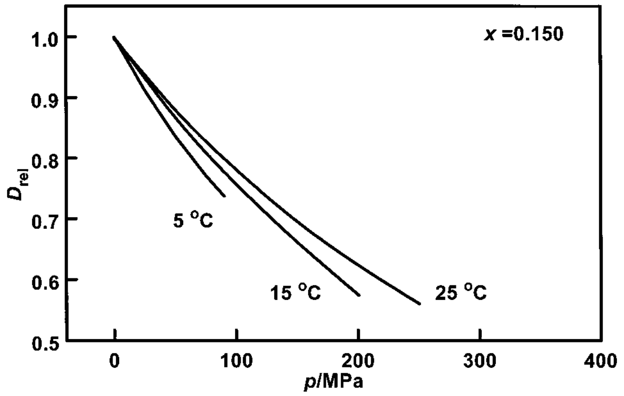

Figure 11. Relative intradiffusion coefficients for water in water−TBA-d_{10} (x_{TBA} = 0.150).

isotherms at constant composition, but rather the temperature dependence of different isobars. His data are reported as smoothed curves of the form

$$D(p,T) = \exp[a_1(T) + a_2(T)p + a_3(T)p^2] \qquad (1)$$

the a_i (T) being fitted coefficients. We have used eq 1 and Woznyj's coefficients to construct isothermal plots of the relative TBA intradiffusion coefficients − Figures 1−3. These show similar behavior to those of water in the same mixtures, with maxima at temperatures below 39 °C at $x_{TBA} \sim 0.014$, below 5 °C at $x_{TBA} \sim 0.029$. At compositions above $x_{TBA} \sim 0.06$, normal behavior returns. This behavior is consistent with what we have observed with the intradiffusion of water.

Therefore our results, and those of Woznyj, are consistent with strengthened water structure in dilute solutions of TBA at low temperatures. The network is distorted by moderately high pressure, which allows accelerated diffusion of both solute and solvent, relative to the molecular motion at atmospheric pressure. At very high pressure the competing effect of the reduction in free volume dominates, so that maxima are observed in the intradiffusion isotherms. We note that this model is supported by the recent high-pressure study of ^{2}H spin-lattice relaxation times and ^{1}H chemical shifts in D_2O-TBA by Yoshida et al.[29]

Finally, we consider the models of hydrated TBA oligomers that have been proposed to explain the experimentally observed peak in correlation lengths in this system. This peak lies in the composition range $0.05 < x_{TBA} < 0.35$ and increases in magnitude with increasing temperature.[11,12] We have reviewed these models in an earlier publication.[15] These models consider that TBA and water form large labile aggregates of the form $(TBA)_m(H_2O)_n$ based on clathrate-like hydrates with shared faces

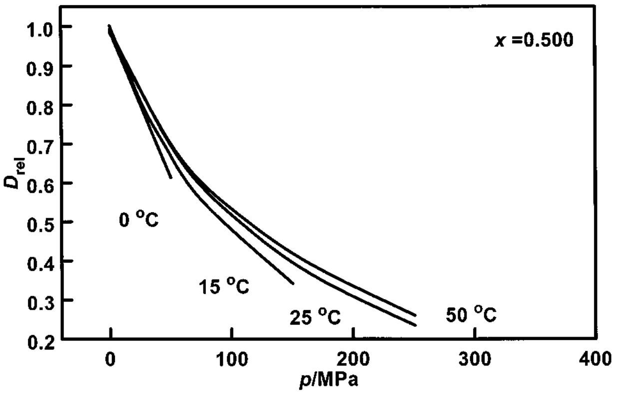

Figure 12. Relative intradiffusion coefficients for water in water−TBA-d_{10} (x_{TBA} = 0.500).

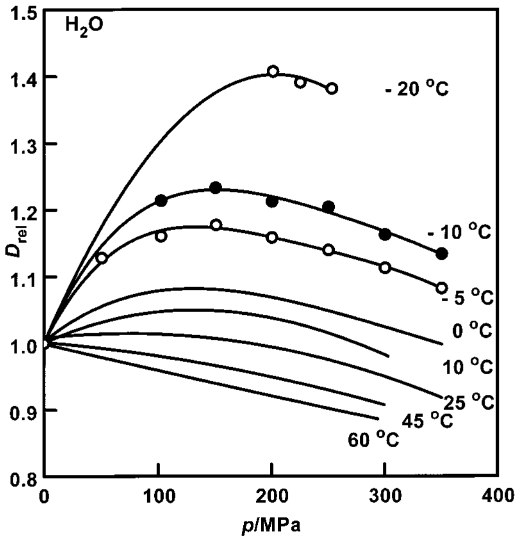

Figure 13. Relative self-diffusion coefficients for water.[18]

TABLE 2: Coefficients of Eqs A1 and A4 for Intradiffusion of Water in Water−TBA at x_{TBA} = 0.1 and 0.15

x	0.1	0.15
ζ_1	−0.580 334	-0.938 642
$10^1\ \zeta_2$/mol cm^{-3}	0.111 562	0.173 855
$10^{-2}\ \zeta_3$/cm mol^{-1}	−0.131 669	-0.136 349
$10^2\ \xi_1$/K^{-1}	−3.039 02	-0.483 033
$10^4\ \xi_2$/K^{-2}	6.169 88	-0.105 504
μ/g mol^{-1}	23.625	
T_{ref}/K	273.15	273.15
stand. devn./%	3.5	3.3
T range/K	278−298	278−298

in this composition range. Such models have been supported by X-ray scattering[13,30] studies. Our present results, on the other hand, do not support the ordering of hydration water structure suggested by these models. The neutron scattering results of Bowron et al.[20] are also inconsistent with the formation of aggregates of this kind, as their data suggest direct alcohol−alcohol molecular contact rather than caged structures in this composition range. This is supported to a degree by the molecular dynamics simulations of Tanaka and Nakanishi.[31] It seems then that the suggestion of Sorenson and co-workers[13,32] that the correlation length peak is due to pseudocritical behavior (that is, exhibiting concentration fluctuations as if the system were approaching a consolute point) is more likely to be correct. Using Kirkwood−Buff theory and thermodynamic data, Shulgin and Rukenstein[33] have been able to make estimates of the sizes of water-rich and TBA-rich “clusters” in this system, reinforcing the strength of this suggestion. It is known that the addition of small amounts of electrolyte[9,34] do, in fact, produce phase separation.

In fitting the data, molar volumes were interpolated from *pVTx* data published previously.[36] As these do not include x_{TBA} ~ 0.5 (0.44 was the closest), diffusion data at this composition were not fitted.

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Appendix

The equation used to fit the data at x_{TBA} ~ 0.1 and 0.15 was

$$D^* = \zeta_1 + \zeta_2 V_{ref}/(1 + \zeta_3/V_{ref}) \qquad \text{(A1)}$$

where D^* is a reduced diffusion coefficient introduced by Dymond[35] as an aid in the application of the hard-sphere model to real fluids. V_{ref} is a reference molar volume (see below) and the ζ_i are fitted coefficients. D^* is given by

$$D^* \equiv \frac{nD}{(nD)^\infty}\left(\frac{V}{V_0}\right)^{2/3} \qquad \text{(A2)}$$

n is the number density, and $(nD)^\infty$ is the density−diffusion coefficient product for a dilute gas of hard spheres given by the Chapman−Enskog equation in its first (composition independent) approximation

$$(nD)^\infty = \frac{3}{8\sigma_{12}^2}\left(\frac{kT}{2\pi\mu}\right)^{1/2} \qquad \text{(A3)}$$

In this equation, μ is the apparent molecular mass, $(x_1m_1+x_2m_2)$, k is Boltzmann’s constant, and σ_{12} the mean diameter of the two species. V_0 in eq 2 is $\sigma_{12}^3/V2$. Inspection of these equations shows D_{T2}^* to be independent of σ_{12}, so it is a function of only the molecular masses, temperature, and density. For many fluids, the reduced diffusion coefficient isotherms on a D^*-V plot are similar in the geometric sense and may be superposed onto a single reference isotherm, T_{ref}, chosen arbitrarily, by the coordinate transformation

$$V_{ref} = V[1 - \xi_1(T - T_{ref}) - \xi_2(T - T_{ref})^2] \qquad \text{(A4)}$$

In fitting the data, molar volumes were interpolated from *pVTx* data published previously.[36] As these do not include x_{TBA} ~ 0.5 (0.44 was the closest), diffusion data at this composition were not fitted.

Supporting Information Available: Table 1S contains all the diffusion data. This material is available free of charge via the Internet at http://pubs.acs.org.

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