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Self-Diffusion Coefficients of Each Component in Water+*t*-Butyl Alcohol and Water+*t*-Butylamine Binary Mixtures

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The self-diffusion coefficients of water and of the organic component have been measured for H_2O+*t*-butyl alcohol and H_2O+*t*-butylamine mixtures over the whole composition range at 301 K, using the NMR spin-echo technique. In the water-rich region below 20 mol% of cosolvent, the self-diffusion coefficients of both components for each binary solvent system decrease rapidly with increasing cosolvent content. In cosolvent-rich mixtures with more than 50 mol% cosolvent, motions of water are evidently strongly correlated with those of cosolvent molecules. The semiempirical equation proposed by Albright relating the shear viscosity of a mixture to the diffusion coefficients of its components successfully predicts the general shape of the viscosity curve for each binary system. For the composition region above 50 mol% cosolvent the Albright equation gives calculated viscosities which agree well with observed values, but in the water-rich region there are significant deviations between the observed and calculated viscosities.

Self-diffusion coefficients are a measure of the translational mobility of molecules, and can give useful information on the structure of and intermolecular interactions in pure liquids and solutions. The NMR spin-echo technique[1)] provides a method for determination of self-diffusion coefficients which has the advantage of speed of measurement compared to the isotopic tracer method.[2)] In addition, the need for isotopic labelling is eliminated, relatively small sample volumes are needed, a wide range of temperatures and pressures is accessible (including the regimes of cryogenic liquids[3)] and molten salts[4)]) and with Fourier transform techniques the self-diffusion coefficients of all components of multicomponent mixtures can often be simultaneously determined. Furthermore, the NMR technique determines 'true' self-diffusion coefficients which are not influenced by isotopic mass effects, although the latter appear to be negligibly small.[5)] While measurements by the NMR method can have low accuracy, as exemplified by the wide scatter of results reported for aqueous solutions[6,7)] in early work, an accuracy of ±1% or better can now be obtained in careful experiments,[8—11)] as evidenced by a comparison of NMR and tracer results for a variety of systems.[8,9)]

Binary liquid mixtures with water as one component are of current interest in this laboratory. These mixtures exhibit complex and challenging behavior particularly in the water-rich region, reflecting unique solvent properties of water. As part of our long-term research programme on molecular interactions in liquids and liquid mixtures, we are pursuing investigations of mass transport behavior of selected water+organic cosolvent systems. Diffusion coefficients have been measured for several aqueous binary systems including H_2O+methanol and H_2O+acetonitrile as a function of pressure, temperature, and composition.[12—16)] There are significant differences between the properties of these two systems arising from the strong hydrogen-bonding interaction between H_2O and CH_3OH, whereas there is no such interaction (though there is some disagreement on this point) between H_2O and CH_3CN. Some properties of the H_2O+CH_3OH system (and also H_2O+ethanol), however, such as the pressure dependence of the alcohol diffusion coefficient at constant temperature (particularly at 278 K), seem to require a hydrophobic-like interaction between alcohol and nearest-neighbor water molecules to be operative.

In the present study two cosolvents, *t*-butyl alcohol (Bu^tOH) and *t*-butylamine (Bu^tNH_2), were selected for investigation because they are relatively hydrophobic yet completely miscible with water in all proportions. The choice of these organic cosolvents was motivated by the expectation that they should cause significant changes in the structure of water in order to balance the hydrophobic interactions. Both H_2O+Bu^tOH and H_2O+Bu^tNH_2 systems are potentially interesting in that the large, essentially globular hydrocarbon moieties evidently have appropriate size and shape to fit into the spherical cavities of a clathrate cage of water molecules. A hydrophobic interaction is thereby promoted, so that there is an increased structuredness in the neighboring water molecule environment. At the same time the OH and NH_2 groups can form hydrogen bonds to water, leading to a destructuring effect on water in the vicinity of the organic molecules.

There have been no previous measurements, so far as we know, of the self-diffusion coefficients for H_2O+Bu^tNH_2 mixtures covering the whole composition range. Also, while a number of researchers[6,7,17,18)] have reported measurements of diffusion coefficients for H_2O+Bu^tOH mixtures, those data are incomplete in that either only the alcohol component was measured, or both components were measured over a narrow range (normally in the water-rich region only). Moreover, except in the work of Holz and co-workers[18)] numerical data have not been reported, and the accuracy of some of the reported data is low.

Experimental

Materials. *t*-Butyl alcohol was supplied by Riedel-de Haën and *t*-butylamine by Aldrich. The stated purity of both solvents exceeded 99.0 mol%. The solvents were stored over 3 Å molecular sieves for several weeks before use. Ultrapure water from a Milli-Q reagent-grade water system was used to prepare the mixtures.

Binary mixtures were prepared by weighing appropriate amounts of the components into suitable vials or flasks with ground-glass stoppers, using a balance with accuracy ±0.1 mg. To minimise errors due to evaporation of the organic component, the water was weighed in first, followed by the organic component. The samples were transferred to 4-mm-diameter NMR tubes which were sealed with PTFE plugs.

Methods. Self-diffusion coefficients of H_2O and the organic component were determined at 60 MHz using the FT-PGSE method[19] on a JEOL FX-60 NMR spectrometer equipped with a home-built pulsed field gradient probe consisting of anti-Helmholz pair coils and current pulse programming generator. The gradient pulse duration was digitally controlled by the pulse programmer, and the experiments were computer controlled using JNM-FX 60 software. The magnetic field was locked by an external D_2O lock signal for all samples. This technique measures molecular motion by probing the change in a pulsed field gradient, using a $90°$-τ-$180°$-τ-echo pulse sequence, with two rectangular field gradient pulses of magnitude G ($1.210\ \mathrm{T\,m^{-1}}$ for $H_2O+Bu^tNH_2$, and $2.420\ \mathrm{T\,m^{-1}}$ for H_2O+Bu^tOH mixtures), separation time Δ (fixed at 10.00 ms) and duration time δ. At time 2τ the spin echo has reached its maximum intensity, and data acquisition starts. After data acquisition the spin-echo signals are Fourier-transformed into the frequency domain. Spin-echo spectra were obtained for each sample at several field gradient duration times, δ (varied from 0 to 1.80 ms in steps of 0.10 ms for each component in the sample), and the corresponding peak amplitudes, A, were recorded. The echo amplitude at time 2τ is given by

$$A(2\tau) = A(0)\exp\left[-\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D\right], \qquad (1)$$

where γ is the magnetogyric ratio for the proton. Data were analyzed by fitting the natural logarithm of the echo attenuation $A(2\tau)/A(0)$ to a linear function of $(\gamma G\delta)^2(\Delta-\delta/3)$; typical plots are shown in Figs. 1 and 2. Since τ was kept constant in each experiment the spin–spin relaxation and J-modulation effects were equal for all spectra within each experiment. The temperature over the sample space was maintained at 301.0±0.5 K by a hot air feedback system. The system had been calibrated to a precision of 1% using water.[20] In solutions comprising water and the alcohol or amine rapid proton exchange occurs between the hydroxyl group proton or the amino group protons, and water protons. Consequently the observed water diffusion coefficient is averaged over the different exchangeable proton environments. If the diffusion coefficient of the compound containing the exchangeable hydrogen is measured independently (using another peak in the spectrum, such as the CH_3 peak of Bu^tOH and Bu^tNH_2), the water diffusion coefficient can be corrected for proton exchange. The observed self-diffusion coefficient is given by

$$D_{\mathrm{W,obs}} = \{2X_{\mathrm{W}}/(2X_{\mathrm{W}}+X_{\mathrm{A}}))\}D_{\mathrm{W}} + \{X_{\mathrm{A}}/(2X_{\mathrm{W}}+X_{\mathrm{A}})\}D_{\mathrm{A}} \qquad (2)$$

for the H_2O+Bu^tOH system and

$$D_{\mathrm{W,obs}} = X_{\mathrm{W}}D_{\mathrm{W}} + X_{\mathrm{B}}D_{\mathrm{B}} \qquad (3)$$

for the $H_2O+Bu^tNH_2$ system, where D_{W}, D_{A}, and D_{B} are the self-diffusion coefficients of water, Bu^tOH and Bu^tNH_2, respectively, and X denotes mole fraction. The values of $D_{\mathrm{W,obs}}$ together with D_{A} and D_{B} were used to calculate D_{W} from Eqs. 2 and 3. The uncertainty in the organic component diffusion coefficients values did not exceed 2%, whereas the uncertainty in D_{W} in solutions with more than 70 mol% of cosolvent increased up to about 5%.

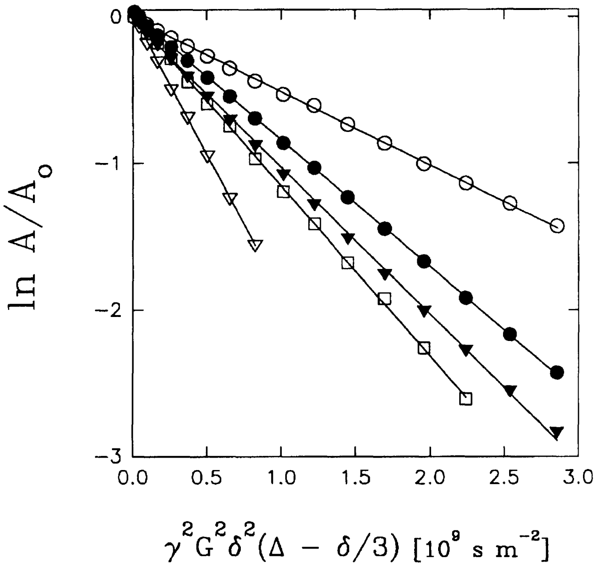

Fig. 1. Proton spin-echo attenuation plots for $H_2O+Bu^tNH_2$ mixtures at various compositions (mol% Bu^tNH_2): ○, 20%; □, 40%; ●, 50%; ▽, 80%; ▼, 90%.

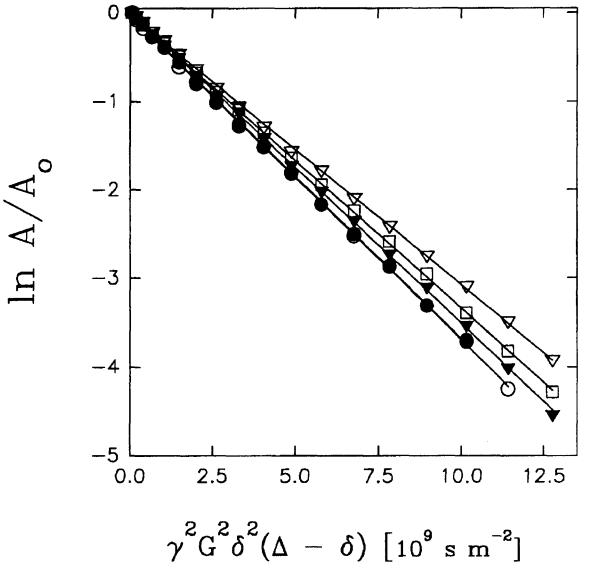

Fig. 2. Proton spin-echo attenuation plots for H_2O+Bu^tOH mixtures at various compositions (mol% Bu^tOH): ○, 20%; ▽, 30%; ●, 50%; ▼, 80%; □, 100%.

Viscosities of the binary mixtures were measured at 301.0±0.05 K using factory-calibrated Cannon Ubbelohde suspended-level viscometers, and densities were measured at the same time using an Anton Paar Model DMA 02C vibrating-tube digital densimeter, as reported previously.[21] The estimated uncertainty in the measured viscosities was within ±0.005 mPa s.

Results and Discussion

The self-diffusion coefficients of H_2O, Bu^tOH and Bu^tNH_2 in H_2O+Bu^tOH and $H_2O+Bu^tNH_2$ mixtures together with the estimated limiting values are listed in Table 1, and density and viscosity data for the two systems are given in Table 2. The diffusion coefficient for pure Bu^tOH is in excellent agreement with the value reported by Holz and co-workers.[18] So far as we know no data have been reported hitherto for pure Bu^tNH_2.

The self-diffusion coefficients for each component in the binary system are plotted against cosolvent concentration in Figs. 3 and 4. The limiting diffusion coefficients of both Bu^tOH and Bu^tNH_2 in water are relatively small in comparison to tracer diffusion coefficients for other organic liquids in water.[12] They are also much smaller than the self-diffusion coefficient for water. Our value for Bu^tOH is significantly higher than that reported by Tominaga and Matsumoto[22] (0.940×10^{-9} $m^2\,s^{-1}$ by interpolation of listed data) and closer to the value obtained by Gary-Bobo and Weber[23] (1.02×10^{-9} $m^2\,s^{-1}$ by interpolation). It is interesting to note that the limiting diffusion coefficient of Bu^tNH_2 is about 17% smaller than the limiting diffusion coefficient for Bu^tOH: Evidently Bu^tNH_2 is more effectively 'trapped' in the surrounding water network than is Bu^tOH. While the limiting diffusion coefficient of water in Bu^tOH is (relatively) very small, and its value in Bu^tNH_2 is fairly large and comparable to those given in the literature for pyridine, nitrobenzene and butyl acetate,[24] the limiting diffusion coefficients of water in the two solvents are very nearly in inverse proportion to the viscosities of the cosolvents. The self-diffusion coefficient of water is larger than that of either organic component over nearly the whole composition range, but particularly in the water-rich composition region, for both systems. So far as the composition dependence of the diffusion coefficients is concerned, the $H_2O+Bu^tNH_2$ system has a strong similarity to the H_2O+methanol system investigated by Easteal and co-

Table 1. Self-Diffusion Coefficients (in $m^2\,s^{-1}\times10^9$) for H_2O (D_W), Bu^tOH (D_A) and Bu^tNH_2 (D_B) in H_2O+Bu^tOH and $H_2O+Bu^tNH_2$ Mixtures at 301.0±0.5 K

$X^{a)}$	D_A	D_W	D_B	D_W
0	1.267	2.530	1.050	2.530
5	0.840	1.281	0.770	1.381
10	0.540	0.890	0.600	1.037
20	0.322	0.591	0.498	0.782
30	0.303	0.424	0.558	0.790
40	0.307	0.386	0.670	0.850
50	0.313	0.379	0.854	1.001
60	0.328	0.369	1.110	1.375
70	0.344	0.361	1.540	1.837
80	0.348	0.375	1.880	2.230
90	0.353	0.425	2.310	2.360
95	0.341	0.478	2.560	2.450
100	0.330	0.549	2.740	2.557

a) X=mol% Bu^tOH or Bu^tNH_2.

Table 2. Density and Viscosity Data for H_2O+Bu^tOH and $H_2O+Bu^tNH_2$ Mixtures at 301.00±0.05 K

$X^{c)}$	$\rho/\mathrm{kg\,m^{-3}}$		$\eta/\mathrm{mPa\,s}$	
	(a)	(b)	(a)	(b)
$0^{d)}$	996.24	996.24	0.833	0.833
5	968.75	956.61	1.921	1.740
10	939.94	918.22	2.839	2.373
20	894.48	861.64	3.899	2.827
25		840.75		2.762
30	863.64	822.65	4.265	2.573
35	851.62		4.312	
40	841.30	792.61	4.303	2.041
50	824.30	768.12	4.186	1.518
60	810.73	747.24	4.057	1.113
70	799.68	728.89	3.820	0.829
80	790.75	712.57	3.677	0.640
90	783.32	697.74	3.618	0.509
95	780.26	690.68	3.651	0.460
100	777.37	683.65	3.755	0.418

a) H_2O+Bu^tOH; b) $H_2O+Bu^tNH_2$. c) X=mol% Bu^tOH or Bu^tNH_2. d) Data from "Handbook of Chemistry and Physics," CRC Press, 69th ed, Boca Raton (1988—1989).

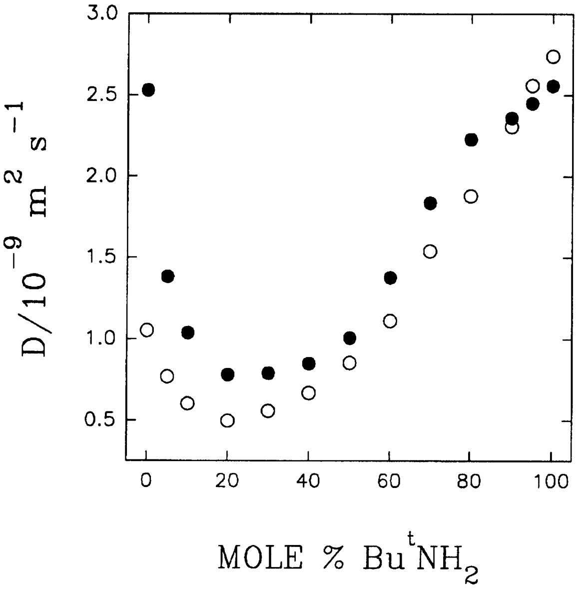

Fig. 3. Self-diffusion coefficients for $H_2O+Bu^tNH_2$ mixtures as a function of composition at 301.0±0.5 K: ●, H_2O; ○, Bu^tNH_2.

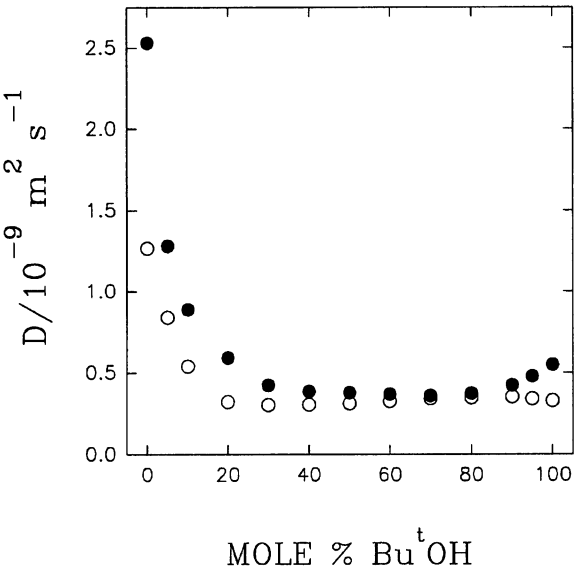

Fig. 4. Self-diffusion coefficients for $H_2O + Bu^tOH$ mixtures as a function of composition at 301.0±0.5 K: ●, H_2O; ○, Bu^tOH.

workers[15)] and the H_2O+acetone system measured by Mills and Hertz.[25)] In addition, the pronounced minima in D_W and D_B occur at very nearly the same composition as the viscosity maximum, and the diffusion coefficient of the organic component is highly correlated with the inverse of the solution viscosity, as shown (Fig. 5) by the near constancy of the $D_B\eta$ product for about 80% of the composition range. A similar trend is shown by the product $D_A\eta$ in the H_2O+Bu^tOH system (Fig. 6): For both systems the $D\eta$ product for the organic component varies significantly only for solutions with less than about 20 mol% of the organic component.

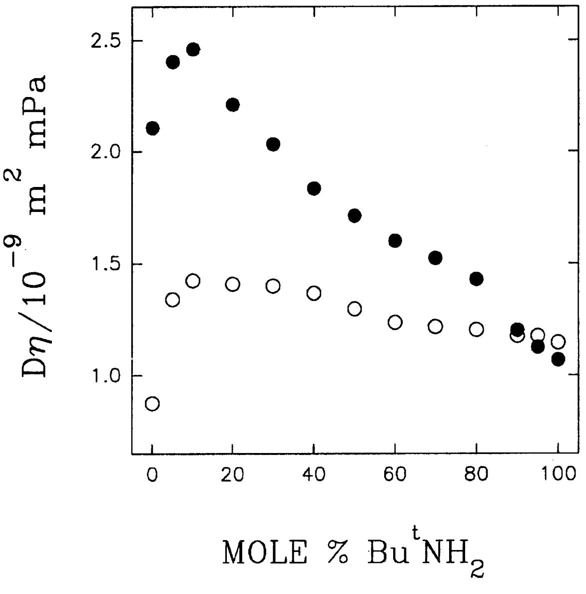

Fig. 5. Variation of the product $D\eta$ with composition for $H_2O+Bu^tNH_2$ mixtures at 301 K: ●, D_W; ○, D_B.

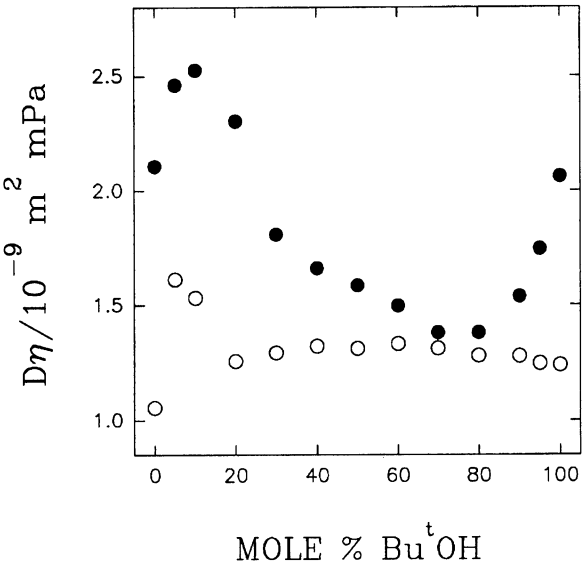

Fig. 6. Variation of the product $D\eta$ with composition for H_2O+Bu^tOH mixtures at 301 K: ●, D_W; ○, D_A.

In marked contrast, the $D_W\eta$ product for both systems varies strongly throughout the composition range, suggesting that the diffusional mobility of water in these mixtures is dependent on factors additional to solution viscosity. It has been proposed frequently in the literature that the product $D_i\eta$, where D_i is the diffusion coefficient of mixture component i, should be constant (at constant temperature) for mixtures of non-interacting components. The basis for that proposal is the Stokes–Einstein equation

$$D_i = RT/6\pi\eta a_i, \tag{4}$$

where a_i is a molecular size parameter for the diffusing species. The composition invariance of $D\eta$ has been established, at least approximately, for several binary organic mixtures such as benzene+nitromethane[26)] and chloroform+carbon tetrachloride.[27)] For the D_2O+dioxane and D_2O+pyridine systems[28)] $D_W\eta$ decreases linearly with increasing D_2O content. The non-invariance of $D\eta$ in these cases was tentatively attributed to an increase in the effective molecular size of the organic molecule as the water content is increased. A similar interpretation can be advanced for the monotonic (and approximately linear) decrease in $D_W\eta$ for the water+Bu^tNH_2 system, viz. the progressive formation of aggregates of the organic component as the cosolvent content increases beyond about 20 mol%. The composition dependence of $D_W\eta$ for water+Bu^tOH is less simple, but at least up to about 80 mol% Bu^tOH there is again a monotonic decrease in $D_W\eta$ which may well have a similar origin, but evidently the trend toward aggregation is reversed in mixtures containing more than about 80 mol% Bu^tOH.

The initial rapid decrease in D for both mixture components as organic solvent is added to water can be attributed to hydrophobic interaction effects. At low concentrations of cosolvent water is mostly ordered in clusters and the organic component fills the cavities among them exerting a geometric effect and promoting a region of highly structured neighboring water molecules. Increasing the organic solvent content leads to replacement of the small proportion of monomeric water molecules[21] by organic solvent molecules. We have previously concluded from a study of solvent polarity[29] of these systems that this effect is operative up to about 10—15 mol% of the organic component, and it is consistent with that conclusion that addition of 10 mol% Bu^tOH or Bu^tNH_2 to water reduces D_W by roughly 60%. The diffusional mobility of the organic component is less strongly, but nonetheless also markedly reduced by initial addition of cosolvent to water.

It is further proposed that addition of organic cosolvent beyond about 15 mol% leads to a gradual breakdown in the hydrophobic interaction-enhanced water structure, as the Bu^tOH or Bu^tNH_2 molecules participate to an increasing extent in hydrogen-bonding to nearest neighbor water molecules. With two hydrogen-bonding sites Bu^tNH_2 should be more effective than Bu^tOH, and correspondingly the diffusion coefficients of both components in water+Bu^tNH_2 mixtures increase substantially with Bu^tNH_2 content (Fig. 3), whereas for water+Bu^tOH mixtures (Fig. 4) the diffusion coefficient of each component is nearly composition invariant for much of the composition range.

Semi-empirical equations relating the intradiffusion coefficients for all components of a mixture to the shear viscosity η, have been proposed by Dullien,[30] and by Albright[31] using a simple model of the liquid state. For a two-component system

$$\eta = \alpha V_m^{2/3} RT(c_1 D_1 + c_2 D_2), \qquad (5)$$

where V_m is the molar volume of the mixture, c_1 and c_2 are molar concentrations (in $mol\,cm^{-3}$) of the components and α is a constant. This equation was later modified[31] to

$$\eta = RT\{(\xi_1 c_1 V_1^{2/3}/D_1) + (\xi_2 c_2 V_2^{2/3}/D_2)\} \qquad (6)$$

with V_i the respective partial molar volumes. The values of the parameter ξ_i are chosen to make the equation exact for pure solvent and solute. Albright and co-workers[32] have shown that equations of this type (Eq. 6) give a good approximation, usually within experimental error, for the shear viscosity of mixtures where association between the components is not significant; the approach is usually much less successful when association such as hydrogen bonding is important. Viscosities calculated using Eq. 6 for H_2O+Bu^tNH_2 and H_2O+Bu^tOH systems are compared with measured viscosities in Figs. 7 and 8, respectively. The partial molar volumes have been derived from the measured densities. Eq. 6 reproduces correctly the general shape of the experimental curve including the position of the maximum in both systems but not their magnitude in the water-rich regions. Accordingly, Eq. 6 provides a poor prediction of viscosity for both systems in the water-rich regions. However, the agreement between calculated and measured viscosity is excellent for compositions in cosolvent-rich regions above 50 mol% cosolvent in both systems.

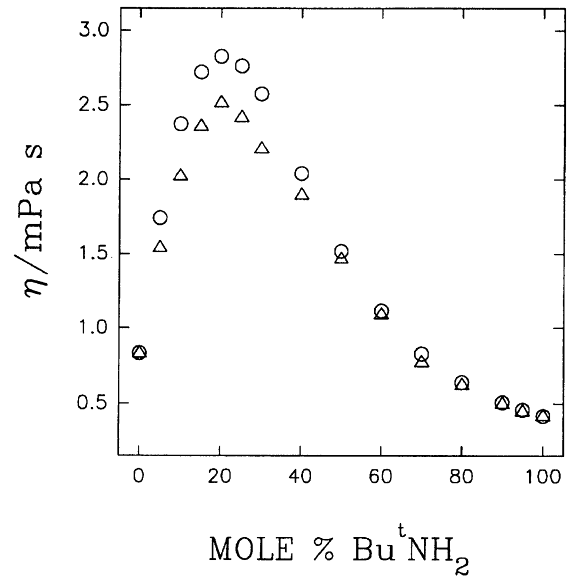

Fig. 7. Shear viscosity of H_2O+Bu^tNH_2 mixtures at 301.00±0.05 K: ○, measured values; △, values calculated from Eq. 6.

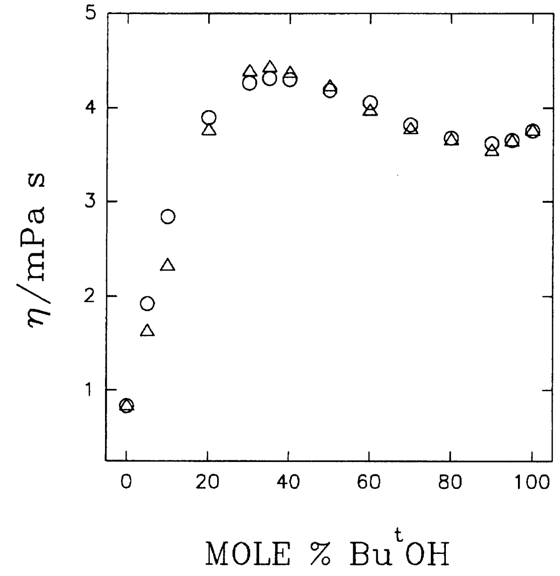

Fig. 8. Shear viscosity of H_2O+Bu^tOH mixtures at 301.00±0.05 K: ○, measured values; △, values calculated from Eq. 6.

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