Bull. Chem. Soc. Ethiop. **2002**, 16(2), 187-198. ISSN 1011-3924
Printed in Ethiopia

PROTON NUCLEAR MAGNETIC RESONANCE STUDY OF WATER + *t*-BUTYL ALCOHOL, WATER + *t*-BUTYLAMINE AND WATER + *t*-BUTYL ALCOHOL + *t*-BUTYLAMINE MIXTURES

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(Received November 22, 2001; revised July 4, 2002)

ABSTRACT. Hydroxyl-proton chemical shifts for water and *t*-butyl alcohol in water + *t*-butyl alcohol mixtures with ≥ 8 mol% *t*-butyl alcohol, and the average hydroxyl and amino proton chemical shift for water + *t*-butylamine mixtures, have been determined at 200 MHz for four temperatures (263, 278, 298 and 313 K) as a function of composition. Further measurements have been made for water + *t*-butyl alcohol + *t*-butylamine ternary mixtures at 310 K over the complete mole fraction range at 60 MHz. Variations in solvent composition have little effect on the resonance for the methyl protons of the cosolvent, but the signal for the hydroxylic protons is substantially influenced. The water proton resonance initially shifts to higher frequencies (low fields) as the cosolvent is added to water, and the shift to higher frequency is strongly temperature dependent, the effect being greatly enhanced at lower temperatures. As the proportion of cosolvent increases the hydroxyl proton signals in the water + *t*-butyl alcohol system and the average proton signals in water + *t*-butylamine mixtures shift to lower frequency (high field).

KEY WORDS: NMR, Hydroxyl-proton chemical shifts, Aqueous solutions, *t*-Butyl alcohol, *t*-Butyl amine, Mixtures

INTRODUCTION

Hydrophobic hydration, the solvation of an inert solute in water, is a notable property of aqueous non-electrolyte solutions [1-3]. Addition of a cosolvent to water alters the hydrogen-bonded structure of water, and many observations indicate that organic solvents such as alcohols and amines, when dissolved in water in low concentration, enhance the water structure, *i.e.* modify it in the direction of greater "crystallinity". These observations together with considerations of the anomalous thermodynamic properties of aqueous solutions led Frank and Evans to propose the "iceberg formation" model [4], which implies that the structure of the solvent water is strengthened as a result of accumulation of water molecules around the hydrophobic part of the non-electrolyte molecule. The molecular phenomena comprise two related processes. First, hydrophobic cosolvent molecules promote a stabilization of the extensive, but thermally sensitive, hydrogen-bonded network of liquid water, an effect known as 'hydrophobic hydration.' In turn, cosolvent molecules in water exhibit a tendency to aggregate, termed 'hydrophobic interaction.'

Experimental evidence for water structure stabilization by hydrophobic solutes has come from a wide variety of sources including NMR relaxation [5] and dielectric relaxation [6]. NMR is one of the most suitable techniques, particularly for systems with hydrogen-bonding and hydrophobic hydration because the chemical shifts of the nuclei are affected by structural changes in solutions. Chemical shift measurements provide direct information about hydrogen-

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bonding in liquid systems because the proton experiences a large (several parts per million) decrease in its nuclear shielding as a result of hydrogen bonding to a proton acceptor.

Binary liquid non-electrolyte mixtures with water as one component are of continuing interest in this laboratory, and current work is focused on the water + *t*-butyl alcohol (H_2O + Bu^tOH) and water + *t*-butylamine (H_2O + Bu^tNH_2) systems [7-12] which contain a large and relatively hydrophobic cosolvent which is nonetheless completely miscible in water in all proportions. These mixtures provide useful model systems for studying the special structural and microdynamical properties which occur near the hydrophobic cosolvent species in the liquid water [1, 13]. The choice of these organic cosolvents was motivated by the expectation that such cosolvents should cause major changes in the structure of water as a result of the balance between hydrogen-bonding, hydrophobic solvation and steric effects [14-16].

The primary objective of the present investigation was to establish whether proton chemical shifts can provide insight into the nature of structural changes which occur as the composition of the mixtures is varied. NMR studies of exchangeable protons of water + amine mixtures over the whole composition range, and alcohols in dilute aqueous solution are severely hampered by fast proton exchange so that separate resonances from the water hydroxyl protons and alcohol-OH or amine-NH_2 protons are normally not observed. Aqueous sugar solutions are similar to alcohol solutions in that respect and separate hydroxyl proton resonances are not usually resolved in the water-rich region. However, under favourable conditions above a certain concentration of Bu^tOH, for example, it is possible to observe the alcohol hydroxyl proton resonance separately from the water proton resonance at relatively low alcohol concentrations.

Recently, several groups have reported success in observing separate signals for water and sugar-OH protons for dilute solutions of certain sugars in water, by lowering the temperature to slow exchange, and/or by using pulse sequences that suppress the water signal [17-21]. It has also been shown that at very low alcohol concentration the OH signals for water and alcohol can be separated by replacing H_2O by D_2O. Cernicki [22] and Shuiskii and Naberukhin [23] have reported separate signals for water and ethanol in D_2O + ethanol mixtures with less than 20 mol% alcohol. Although numerous NMR studies have been reported for the H_2O + Bu^tOH system the available chemical shift data have been limited by the fact that the rates of hydroxyl proton exchange are fast on the NMR time-scale, so that in the water-rich region of much interest (mixtures with less than about 20 mol% Bu^tOH), separate signals from water and alcohol hitherto have not been recorded [24-28]. Separate hydroxyl resonances at concentration ≥ 30 mol % Bu^tOH at 298 K (60 MHz) were reported by Kingstone and Symons [28], whereas Mavel's smallest Bu^tOH content for resolved signals [24] was 72 mol% (25 MHz), while Wen and Hertz [26] have reported the lowest limiting Bu^tOH content to date of 20 mol% Bu^tOH at 258 K and 60 MHz. By using low temperature, moderately high frequency and D_2O we have been able to resolve the hydroxyl proton signals and obtain separate resonances for H_2O and Bu^tOH in relatively dilute (down to 8 mol%) aqueous solution.

Except for the H_2O + pyridine system, the NMR technique has been little employed for investigation of water + amine mixtures, and there have been no previous NMR measurements, so far as we know, of H_2O + Bu^tNH_2 mixtures covering the whole composition range. The only NMR data available in the literature were reported by Wen and Hertz [26] at 273 K and 60 MHz for the water-rich region (0-10 mol% Bu^tNH_2). In this communication we present chemical shift data for the H_2O + Bu^tNH_2 system at various temperatures over the whole composition range. In addition, we have obtained data at one temperature for the ternary system water + Bu^tOH + Bu^tNH_2.

EXPERIMENTAL

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 thermally activated 3X molecular sieves for several weeks before use. Deuterated water, utilized both as the field frequency lock solvent and cosolvent, was obtained in 99.9% isotopic purity from several sources and used without further purification. Ultra-pure water from a Milli-Q reagent-grade water system was used to prepare the ternary aqueous mixtures for the proton NMR measurements at 60 MHz.

The ^{1}H NMR spectra were recorded at 200 MHz on a Bruker AC-200 spectrometer equipped with a variable-temperature control unit and a 5-mm ^{1}H/^{13}C probe. Measurements were performed at 263, 278, 298 and 313 K. Sixteen scans were collected using 32 k data points over a sweep width of 6000 Hz. It was necessary to re-shim the field for each sample and at each temperature to improve the accuracy of the measurements. The temperature of the probe head was kept constant to within 0.1 K by means of a gas flow thermostat. Each sample and the thermocouple assembly was allowed to thermally equilibrate for 10 min in the NMR probe, while temperature changes required a 30-min equilibration time before data acquisition. Measurements could not be made in the water-sparse region above 95 mol% cosolvent or above 90 mol% for low temperatures as the D_2O signal could not be locked. Consequently, the chemical shifts for pure organic cosolvents and for pure water at 263 K were estimated by linear extrapolation. Additional measurements were carried out on a Varian T-60 spectrometer at the probe temperature (310 ± 0.5 K). In all cases 3-(trimethylsilyl)-1-propane-sulfonic acid (DSS) was used as an internal standard in the highly water-rich region below 20 mol% and tetramethylsilane (TMS) above 30 mol% cosolvent due to its low solubility in water. In the 20-30 mol% cosolvent region, both internal standards gave the same chemical shifts. Chemical shifts (δ) were calculated as parts per million (ppm) relative to TMS; δ is always positive and increases with increasing frequency (decreasing applied field).

RESULTS AND DISCUSSION

At the highest temperature (313 K) the signals for H_2O and Bu^tOH hydroxyl protons are resolved above 35 mole % Bu^tOH, whereas at the lowest temperature (263 K) separate signals for hydroxyl protons are resolved down to 8 mole % BuOH. Chemical shifts for water and Bu^tOH are presented in Figures 1 and 2. For the $H_2O + Bu^tNH_2$ system the average $(OH + NH_2)$ proton chemical shift is given in Figure 3. For mixtures containing both organic cosolvents again only one proton resonance (apart from methyl proton signals) was seen, and the chemical shifts are given in Table 1.

In both of the systems studied, the chemical shifts of hydroxyl protons vary strongly with composition whereas the chemical shift of the methyl protons of Bu^tOH or Bu^tNH_2 remains unchanged (the shift being < 0.03 ppm for all compositions and temperatures measured; Figures 1 and 2). The resonance frequency for the hydroxyl protons of Bu^tOH is always at higher frequency than for the water protons, the chemical shift versus composition graphs are approximately parallel for water and Bu^tOH protons over much of the composition range, and all resonances shift to higher frequency as the temperature is lowered. In the water-rich region the reported [25-28] shift of the water proton resonance to higher frequency is confirmed. The chemical shift of water increases initially when Bu^tOH is added to water, attaining a maximum value at about 6-8 mole % Bu^tOH. Another feature of the composition dependence of the chemical shift is that at 278 K and to a larger extent at 263 K, in Bu^tOH-rich mixtures, there is a pronounced minimum in the Bu^tOH hydroxyl proton chemical shift (Figure 2).

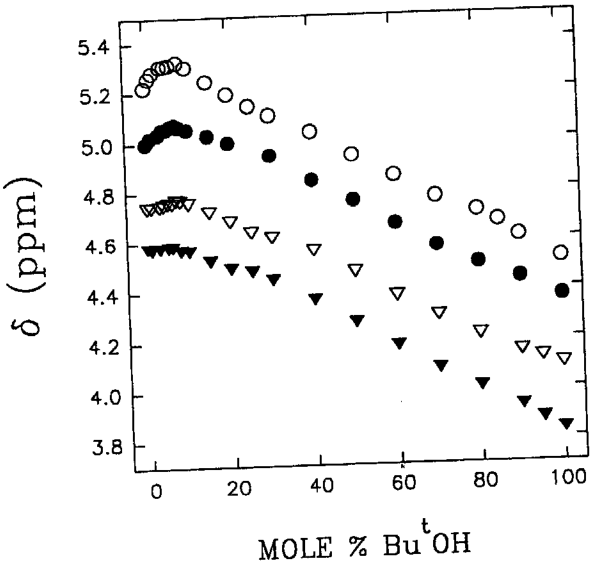

Figure 1. Chemical shift of water in D_2O + Bu^{t}OH mixtures at 200 MHz as a function of composition. Temperature (K): O, 263; ●, 278; ▽, 298; ▼, 313.

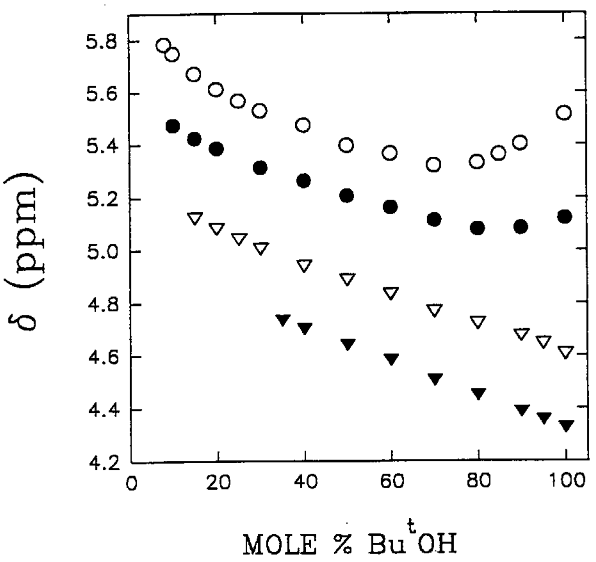

Figure 2. Chemical shifts of the hydroxyl protons of alcohol in D_2O + Bu^{t}OH mixtures at 200 MHz as a function of composition. Temperature (K): O, 263; ●, 278; ▽, 298; ▼, 313.

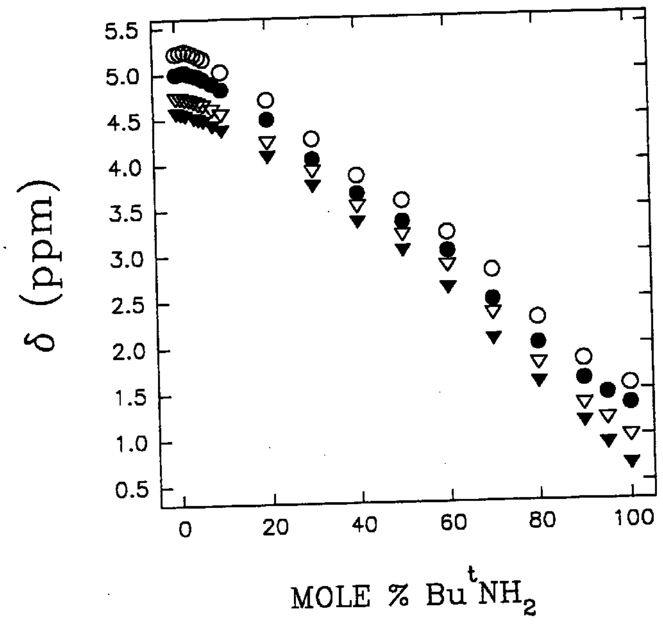

Figure 3. Average (OH + NH$_2$) proton chemical shift in D_2O + Bu^{t}NH$_2$ mixtures at 200 MHz as a function of composition. Temperature (K): O, 263; ●, 278; ▽, 298; ▼, 313.

Table 1. Average chemical shift for H_2O + Bu^{t}OH + Bu^{t}NH$_2$ mixtures at 310 K.

Y	δ (ppm)				
	Z = 0	Z = 25.0	Z = 50.0	Z = 75.0	Z = 100
1.0	4.65	4.63	4.66	4.66	4.61
2.0	4.66	4.64	4.70	4.68	4.64
3.0	4.67	4.65	4.68	4.64	4.62
4.0	4.68	4.66	4.66	4.59	4.60
5.0	4.70	4.68	4.64	4.57	4.58
6.0	4.72	4.66		4.56	4.50
8.0	4.67		4.61	4.51	
10.0	4.65	4.61	4.59	4.48	4.42
20.0	4.63	4.52	4.42	4.25	4.13
30.0	4.58	4.45	4.25	3.99	3.83
40.0	4.48	4.32	4.08	3.69	3.45
50.0	4.38	4.14	3.85	3.42	3.13
60.0	4.28	4.02	3.62	3.11	2.66
70.0	4.18	3.89	3.32	2.66	2.27
80.0	4.12	3.75	3.03	2.24	1.83
90.0	4.06	3.62	2.80	1.89	1.46
95.0	3.98	3.49	2.65	1.76	1.30
100	3.88	3.39	2.53	1.58	1.16

Y = mol% cosolvent, Z = mol% Bu^{t}NH$_2$ in cosolvent.

Figure 3 shows the proton chemical shift for H_2O + Bu^tNH_2 mixtures as a function of composition and temperature. Addition of Bu^tNH_2 to water produces initially a small increase in the proton chemical shift with a maximum at very low Bu^tNH_2 concentrations (1-2 mole % Bu^tNH_2). Thereafter the chemical shift decreases almost linearly as the Bu^tNH_2 content is increased, with marked temperature dependence. The proton chemical shifts obtained in the present work indicate that the structure breaking effect of Bu^tNH_2 on water, above about 5 mole % Bu^tNH_2 at low temperature or over the whole concentration range at elevated temperatures (≥313 K), is similar to the effect of acetonitrile [29, 30] on water.

High-resolution NMR has been used in several different ways to infer the existence of hydrogen-bonding. In studies of model compounds such as alcohols, it has been observed that hydrogen-bonding causes an increase in chemical shifts of the hydroxyl protons, and that increasing temperature leads to decreases in δ. In addition, it has been reported that alcohols stabilize the water structure at low concentration [31] and that the shift of the water hydroxyl signal to higher frequency is evidence of the enhancement of water structure [1, 32, 33]. Coccia and co-workers [33] attributed the shift to higher frequency to hydrogen-bonding between water and ethanol and to the enhanced hydrogen-bonding between water molecules owing to the hydrophobic hydration of ethyl groups. Thus it is expected that for any liquid mixture capable of forming hydrogen-bonds, an increase in the strength of the hydrogen-bonds or in the concentration of hydrogen-bonded species should result in a shift of the corresponding NMR signal to higher frequency [34]. If dissolving a nonpolar non-electrolyte has a structure-promoting effect, one should then find that the water proton signal moves downfield by an amount proportional to the concentration, and to the number of water molecules that each cosolvent molecule is able to affect. This corresponds precisely to the effects that we have observed on the water proton chemical shift in the H_2O + Bu^tOH system and to a lesser extent in H_2O + Bu^tNH_2 binary mixtures. Since hydrogen-bond formation causes a shift of the proton signal to higher frequencies [34], the initial increase in the water proton chemical shift in these systems can be attributed to a structure-enhancing effect on water induced by the hydrophobic Bu^tOH and Bu^tNH_2, in agreement with the interpretation of other data [7-12] for these binary systems.

The maximum in the chemical shift of water for H_2O + Bu^tOH mixtures at about 8 mole % Bu^tOH is of considerable interest. There is no evidence for a similar maximum in the alcohol OH resonance (at least down to about 8 mole % alcohol at 263 K) implying that in this water-rich composition region enhancement of water-water hydrogen-bonding is promoted by the dissolved alcohol, as is envisaged in the hydrophobic hydration concept, rather than formation of alcohol (OH)-water hydrogen-bonds.

At moderately dilute to higher concentrations of cosolvent, strong hydrogen-bonds between water molecules are replaced by weaker H_2O-cosolvent hydrogen-bonds, leading to the decrease in the water chemical shift observed for the H_2O + Bu^tOH system. In a similar fashion, the decrease in the Bu^tOH hydroxyl chemical shift with increasing Bu^tOH suggests that hydrogen-bonds between Bu^tOH molecules at low concentration in water are stronger than the water-Bu^tOH hydrogen-bonds formed at higher Bu^tOH concentrations. It is envisaged that at low concentration in water, Bu^tOH molecules form hydrogen-bonded clusters, analogous to reverse micelles, that present a hydrophobic exterior to surrounding water molecules.

An interesting feature of the H_2O + Bu^tOH system is that addition of water to pure Bu^tOH and to dilute solutions of water in Bu^tOH at low temperature shifts the resonance frequency of the alcohol hydroxyl proton to lower frequency, with a broad minimum at about 70-80 mole % Bu^tOH. Analogous behaviour in the alcohol-rich region for this system was observed in the variation of permittivity and viscosity [7, 8] with composition. Since the minima of the permittivity, viscosity and alcohol OH proton chemical shift occur at about the same Bu^tOH content, the behaviour of the system in this composition region appears to be a consequence of a

Bu^{t}OH solvent structure induced by water addition, for example the formation of clusters in which each water molecule is 'solvated' by about four alcohol molecules.

The temperature dependence of hydrogen-bonded proton resonances has been attributed to an energy separation between hydrogen-bonded and non-hydrogen-bonded states [34, 35]. A change in temperature will alter the populations of the hydrogen-bonded and non-bonded states, giving rise to changes in the chemical shift of the resonance of interest. The observed proton resonances for the two binary systems investigated in the present work are strongly temperature dependent (Figures 4 and 5). The variation of δ with temperature is linear to a good approximation, and the temperature coefficient of δ is negative in every case. For water + Bu^{t}OH mixtures dδ/dT for water protons is -0.014 ± 0.001 ppm K^{-1} for the whole composition range. The magnitude of dδ/dT for the Bu^{t}OH hydroxyl protons is about -0.016 ppm K^{-1} for most of the composition range, but dδ/dT changes rapidly to about -0.024 ppm K^{-1} as the Bu^{t}OH content of the mixtures increases from 70 to 100 mole % (Figure 6). Evidently hydrogen-bonding intermolecular interactions in pure Bu^{t}OH at low temperatures weaken substantially as temperature increases. For the water + Bu^{t}NH$_2$ system, the temperature dependence of the average (OH + NH$_2$) proton chemical shift varies significantly with composition (Figure 7). At very low Bu^{t}NH$_2$ contents (1-3 mole %) dδ/dT passes through a sharp minimum, so that the chemical shift (which is to a good approximation the water proton chemical shift at these compositions) is about 13% more temperature dependent than the chemical shift for pure water.

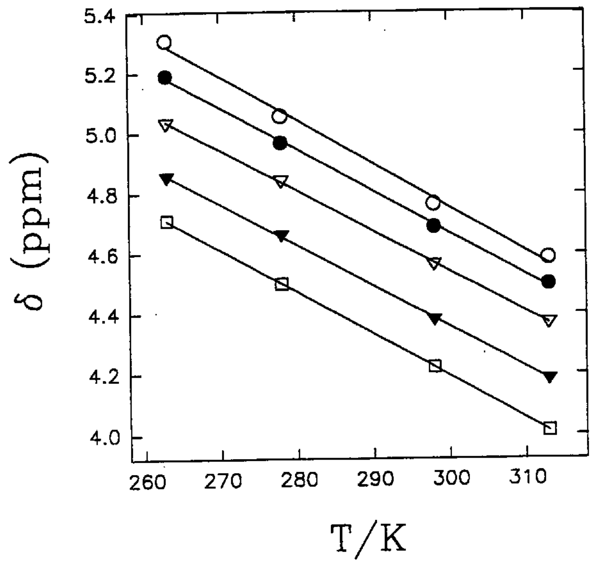

Figure 4. Chemical shift of water in D$_2$O + Bu^{t}OH mixtures at 200 MHz as function of temperature. Mole % Bu^{t}OH: O, 5; ●, 20; ▽, 40; ▼, 60; □, 80.

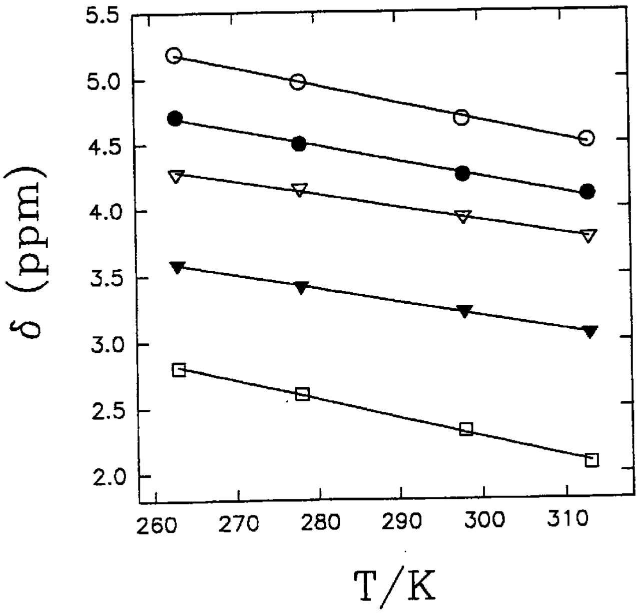

Figure 5. Average (OH + NH_2) proton chemical shift in D_2O + Bu^tNH_2 mixtures at 200 MHz as a function of temperature. Mole % Bu^tNH_2: O, 5; ●, 20; ▽, 40; ▼, 50; □, 70.

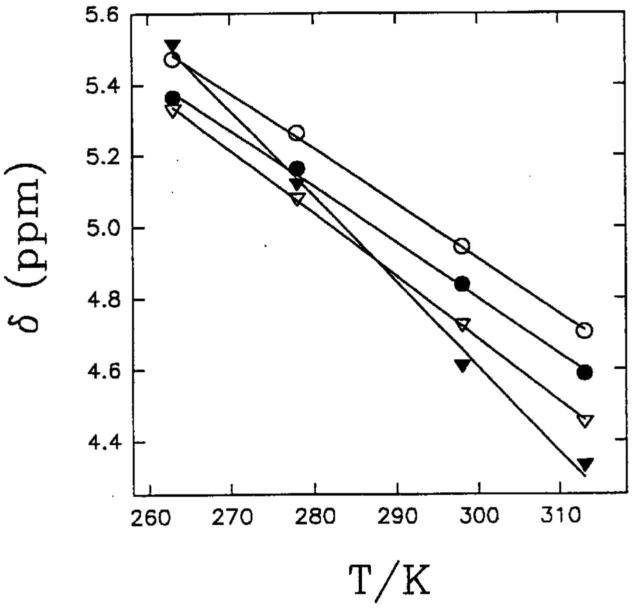

Figure 6. Chemical shift of the alcohol hydroxyl proton in D_2O + Bu^tOH mixtures at 200 MHz as a function of temperature. Mole % Bu^tOH: O, 40; ●, 60; ▽, 80; ▼, 100.

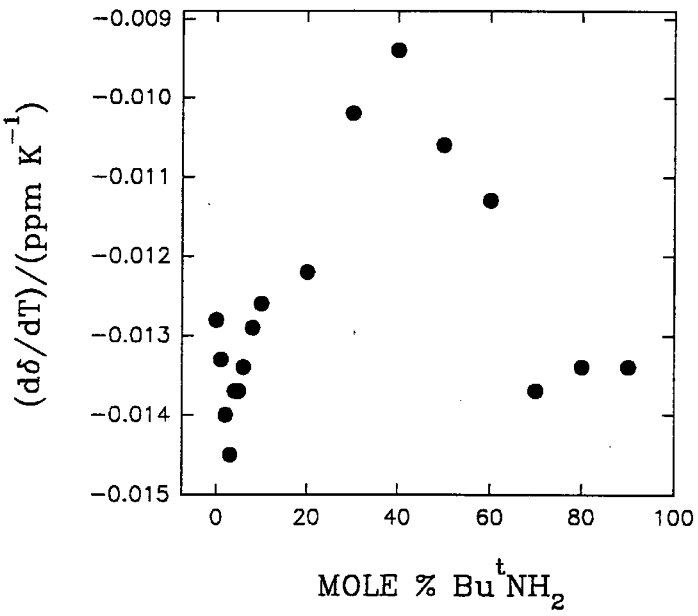

Figure 7. Composition variation of dδ/dT for D_2O + Bu^{t}NH$_2$ mixtures.

The minimum in dδ/dT is in the composition region for which minima or maxima in other properties of the system have been observed [7-12]. It seems that the water structure that is promoted by hydrophobic interaction at very low cosolvent contents is more thermally labile than the unperturbed structure of water. The situation changes dramatically at higher Bu^{t}NH$_2$ mole fractions. At about 40 mole % Bu^{t}NH$_2$ (where water and amine protons contribute roughly equally to the observed chemical shift) the magnitude of dδ/dT is about 26% smaller than for pure water. In this composition region the pure water structure has essentially been replaced by a less thermally labile molecular rearrangement in which water-amine hydrogen-bonds predominate. As further cosolvent is added, water-amine hydrogen-bonds are progressively replaced by amine-amine bonds as cosolvent aggregates are formed, and the amine-amine bonds weaken more rapidly as the temperature is changed.

It is noteworthy that the structure promoting effect of Bu^{t}OH on water (manifest as a maximum in the water hydroxyl chemical shift) persists over a considerable range of temperature, up to 313 K. For the water + Bu^{t}NH$_2$ system, on the other hand, the maximum in the proton chemical shift for dilute solutions of Bu^{t}NH$_2$ in water is only just detectable at 298 K and absent at higher temperatures. The implication is that Bu^{t}NH$_2$ is a weaker structure promoter than Bu^{t}OH under similar conditions.

The concurrent presence of two non-electrolytes in ternary mixtures with water can propose new questions concerning the possibility of a cooperative intervention of them on the structure of water, and the characterization of the organic mixed solvent as a whole. Chemical shifts measured at 60 MHz for water + Bu^{t}OH + Bu^{t}NH$_2$ mixtures at 310 K are given in Table 1. For each mixture only one proton signal (in addition to the methyl proton signal) was observed. Figure 8 shows the proton chemical shift for water + Bu^{t}OH + Bu^{t}NH$_2$ ternary mixtures as a function of composition. Addition of the mixed non-electrolyte (Bu^{t}OH + Bu^{t}NH$_2$ mixture) to water produces initially a very small increase in the proton chemical shift with a maximum at very low non-electrolyte content thereafter the chemical shift decreases monotonously to lower frequencies. Furthermore, either the addition of water to a mixed organic non-electrolyte of a given composition or the increase of the content of Bu^tOH in the non-electrolyte shifts the resonance of these protons to higher frequencies.

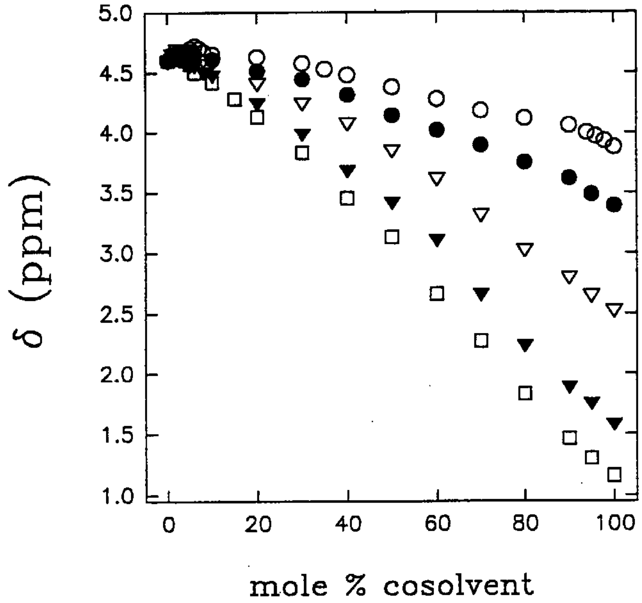

Figure 8. Average ($OH + NH_2$) proton chemical shift at 60 MHz as a function of the proportion of nonelectrolyte in $H_2O + Bu^tOH + Bu^tNH_2$ ternary mixtures at 310 K. Mole % Bu^tNH_2 in cosolvent: O, 0; ●, 25; ▽, 50; ▼, 75; □, 100%.

It is instructive to examine the extent to which the effect of the two cosolvents is additive, by considering the variation of δ with the proportion of Bu^tNH_2 in the cosolvent at constant total cosolvent content. For each total cosolvent content a relative excess chemical shift can be defined as

$$\delta^{ex} = 100\,(\delta - \delta_{add})/\,\delta_{add} \qquad (1)$$

δ_{add} is the additive chemical shift defined by

$$\delta_{add} = \delta_0 + (Z/100)(\,\delta_{100} - \delta_0) \qquad (2)$$

where δ_0 and δ_{100} are the chemical shifts for solutions with 0 and 100 mole % Bu^tNH_2 respectively, and Z is mole % Bu^tNH_2 in the cosolvent. For total cosolvent content less than 40 mole % the relative excess chemical shift is small (less than about 1%) and the chemical shift is approximately additive. At intermediate cosolvent contents (40-60 mole %) δ^{ex} is mostly positive with a maximum at about 50 mole % Bu^tNH_2 and δ^{ex} increases with increasing proportion of Bu^tNH_2 in the cosolvent. The implication is that when the proportions of water and cosolvent are roughly equal, replacement of Bu^tOH by Bu^tNH_2 enhances hydrogen-bonding interactions between cosolvent and water. When the proportion of cosolvent exceeds 70 mole %, the dependence of the relative excess chemical shift on Bu^{t}NH$_2$ content is different. δ^{ex} has a maximum positive value at about 25 mole % Bu^{t}NH$_2$ and the maximum value is only slightly dependent on the cosolvent composition. When the Bu^{t}NH$_2$ content exceeds 50-60 mole % however, δ^{ex} is negative and becomes increasingly negative as water is replaced by cosolvent. The variation of δ^{ex} confirms that hydrogen-bonding interactions in Bu^{t}OH are considerably stronger than in Bu^{t}NH$_2$.

ACKNOWLEDGEMENTS

The authors are indebted to the New Zealand government for the award of a Commonwealth Scholarship to P.K.K., and to the University of Auckland Research Committee for equipment funding. P.K.K. also thanks Moi University, Kenya for a study leave.

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