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Hydration and association in solutions of tetraalkylammonium iodides

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Conductivity, self-diffusion coefficient and viscosity were measured at 298 K for tetraalkylammonium iodides in aqueous solutions, 0.5 M urea solutions and mixtures of water with *tert*-butanol. The molar conductivity was analysed *via* the Fuoss–Hsia equation. The limiting molar conductivity, the separation of ions forming the ion pairs and the association constants were determined. In all studied systems the association of opposite ions was weak, but contact ion pairs were present. The hydrodynamic radii of ions, determined from the self-diffusion coefficients, were used to compute the dynamic hydration numbers. As expected, the dynamic hydration numbers were noticeably smaller than the static numbers, because they represented the water molecules located inside the R_4N^+ ions, between the alkyl chains. Addition of *tert*-butanol reduced the hydration of Me_4N^+ and, probably, Bu_4N^+ ions, but induced aggregation of Bu_4N^+ cations only.

Introduction

Much attention has been focused on hydrophobic phenomena, which are responsible for important processes such as micelle formation and protein folding.[1] Although intuitive models of hydrophobic hydration[2–4] see water molecules forming a clathrate-like structures around non-polar molecules or non-polar groups, neutron diffraction experiments[5–7] and measurements of relaxation time[8–10] have not shown any enhancement of water structure in the shells of non-polar solutes. Aggregation of non-polar solutes, denoted 'hydrophobic association', is believed to be driven by solvent-induced attractions between non-polar molecules, but a large number of computer simulations[11–15] has not proved such hydrophobic attractions. Therefore the aggregation of non-polar solutes is probably induced by the water structure and its tendency to preserve a hydrogen-bonded network.

The aim of this work was to find a small solute, which can serve as a model in studies of the hydrophobic phenomena. Therefore we investigated aqueous solutions containing both tetraalkylammonium iodides and *tert*-butanol.

Aqueous solutions of tetraalkylammonium salts are commonly used as model systems to investigate hydrophobic phenomena, particularly hydrophobic hydration. Neutron scattering experiments[16] and molecular dynamic simulations[17–19] has shown that, in aqueous solutions, even the smallest Me_4N^+ ion is more 'apolar' than 'ionic'. Our self-diffusion measurements have confirmed that hydration of Et_4N^+ is similar to that of other non-polar solutes[20] and in aqueous solution the Et_4N^+ ion coordinates about 30 water molecules. A small amount of methanol destroys the shells of 'hydrophobic' Et_4N^+ ions, but a similar effect has been observed also for the hydrophilic Na^+ cation. MD simulations[17–19,21] and dielectric spectroscopy[10] of aqueous solutions of R_4NX salts show only pairs of opposite ions, but neutron scattering experiments[22] find also clusters consisting of three or four Pr_4N^+ ions, which can be considered as the effect of the hydrophobic association.

Self-diffusion measurements[23–25] have shown that in aqueous solutions the molecules of higher alcohols, *n*-propanol

and *tert*-butanol, behave also like non-polar solutes. Their hydration shells, which may be treated as stable molecular aggregates, consist of more than 20 water molecules. This number is consistent with the coordination number of *t*-BuOH, about 21 water molecules, deduced from neutron diffraction experiments.[26] Association of the alcohol molecules occurs when the alcohol content is high, so that there is not enough water molecules to form typical hydration shells,[25] however, clusters of three alcohol molecules have been noted in neutron scattering experiments even in dilute aqueous solutions of *t*-BuOH.[26] MD simulations of water–*tert*-butanol mixtures[27] confirmed such a picture and showed a spontaneous aggregation of alcohol molecules. The configuration of alcohol molecules is tail-to-tail and therefore these aggregates can be considered as due to the hydrophobic association.

Our studies of hydration and association in aqueous solutions of two 'apolar' solutes, *tert*-butanol and tetraalkylammonium salts should decide which of them, either R_4N^+ or *t*-BuOH, is more 'apolar' and can better serve in studies of hydrophobic effects.

Experimental

Tetraalkylammonium iodides Me_4NI (suprapur, Merck), Et_4NI (pro analysi, Fluka), Pr_4NI (pro analysi, Fluka), Bu_4NI (suprapur, Merck) and urea (pro analysi Merck) were used as received. *t*-BuOH (spectroscopy grade, Aldrich), was dried over molecular sites. Water was double distilled, deionised and degassed. All solutions were prepared by weight.

Self-diffusion coefficients were measured by the open-end capillary method,[28] using the following radioactive tracers: *t*-BuOH labelled with ^3H in methyl group, water labelled with ^3H, R_4NI labelled with ^{127}I and Me_4NI labelled with ^{14}C. Radioactivity of samples was measured in Ultima Gold XR (Packard) liquid scintillation cocktail by liquid scintillation counter RackBeta (LKB). Self-diffusion coefficients were measured for at least three different times of experiment within the range 50–90 h. All self-diffusion coefficients were independent

of time. The D-values presented here were calculated as the mean values of no less than nine independent results and their experimental errors were obtained at 0.95 confidence level. Viscosities of all solutions were measured using the Ubbelohde type viscosimeter AVS-100 (Schott–Geräte).

Conductance of solutions was measured using LKB 5300 B conductometer at the constant frequency 1 kHz. Specific conductivities of alcohol and water, used to prepare all solutions, were <0.1 and 0.5 μS cm^{-1}, respectively.

Results

Molar conductivities of Me$_4$NI, Et$_4$NI, Pr$_4$NI and Bu$_4$NI were measured at 298 K in aqueous and 0.5 M urea solutions. Molar conductivities of two salts, Me$_4$NI and Bu$_4$NI, were also determined in mixtures of water with t-BuOH, for $x_{t\text{-BuOH}} \leq 0.25$. In all experiments the concentration of salts covered the range 10^{-4}–0.1 M, except Bu$_4$NI, where for $0.1 \leq x_{t\text{-BuOH}} \leq 0.25$ the highest salt concentration was 0.05 M.

Experimental data of molar conductivity λ were analysed using the Fuoss–Hsia[29] dependence on the salt concentration c for the partially dissociated (1:1) electrolytes:

$$\lambda = \alpha\left[\lambda^0 - S\sqrt{(\alpha c)} + E(\alpha c)\ln(\alpha c) + J_1(R)(\alpha c) + J_2(R)\sqrt{(\alpha c)^3}\right] \tag{1}$$

All parameters proposed by Fernandez-Prini,[30] S, E, $J_1(R)$ and $J_2(R)$, depend on the solvent static dielectric constant ε and the viscosity η. The parameters $J_1(R)$ and $J_2(R)$ depend also on the separation of ions in the ion pair.

Fitting procedure, used to compute three adjustable parameters: the limiting molar conductivity λ^0, the fraction of free ions α and the distance R, separating ions in the ionic pair, has been described previously.[31]

Then the association constant was calculated from eqn. (2):

$$K_A = \frac{(1-\alpha)f_p}{\alpha^2 c f_\pm^2} \tag{2}$$

The activity coefficient of the ion pair f_p was assumed to be unity and the activity coefficient of free ions $f_\pm$ was computed from eqn. (3):

$$f_\pm = \exp\left[-\frac{A\sqrt{(\alpha c)}}{1 + BR\sqrt{(\alpha c)}}\right] \tag{3}$$

Temperature dependent parameters A and B, for the distance R given in Å, are $2.791 \times 10^6/(\varepsilon T)^{3/2}$ and $50.29/(\varepsilon T)^{1/2}$, respectively. The ε-values for the t-BuOH + H$_2$O mixture were reported by Kaatze et $al.$[32] and those for urea solutions we measured previously.[33]

The fitting procedure was made for the series of R-values, starting from the sum of ionic radii in crystals, using the data reported by Marcus et $al.$[34] The standard deviation σ, of the experimental conductivity λ(exptl.) from the calculated one λ(calc.), for three adjustable parameters λ^0, α and R, was computed as follows:

$$\sigma = \sqrt{\frac{\Sigma[\lambda(\exp\text{tl.}) - \lambda(\text{calc.})]^2}{(n-3)}} \tag{4}$$

According to Fuoss[35] the dependence of σ on R should exhibit a minimum, indicating the most probable separation of ions in the pair. For all investigated solutions the functions $\sigma(R)$ were different. They decreased rapidly than it became independent of R, but did not show any minimum. Thus the smallest R-value, for which $\sigma = $ const., was treated as the distance between ions in the pair. These R-values and other results of the fitting procedure: the limiting molar conductivity λ^0 and the association constant K_A, are summarized in Tables 1 and 2.

The self-diffusion coefficients of iodide ions D_I^- were measured at 298 K in Me$_4$NI and Bu$_4$NI solutions in t-BuOH + H$_2$O mixtures. The salt concentration varied within the range 10^{-4} and 0.1 M for Me$_4$NI and 10^{-4}–0.05 M for Bu$_4$NI. The experimental data were used to compute the limiting self-diffusion coefficients D_I^∞, from the equation derived previously:[36]

$$D_{I^-} = D_I^\infty\left[1 - \frac{2.801 \times 10^6}{\sqrt{(\varepsilon T)^3}}\left(1 - 0.5\sqrt{3 - \frac{2F^2 D_I^\infty}{RT\lambda^0}}\right)\sqrt{c}\right] \tag{5}$$

R and F denote gas and Faraday's constants, respectively, and the λ^0 values are taken from Table 2. Then the self-diffusion coefficients of both cations, Me$_4$N$^+$ and Bu$_4$N$^+$, were obtained from the Nernst relation:

$$D_{cat}^\infty = \frac{RT}{F^2}\lambda^0 - D_I^\infty \tag{6}$$

The influence of the solvent composition on the ion self-diffusion coefficients in t-BuOH–water mixtures are shown in Fig. 1. For some of the mixture compositions the self-diffusion coefficient of Me$_4$N$^+$ was measured using the cation labelled with ^{14}C. The experiments were done for very diluted, 10^{-5} M, solutions of Me$_4$NI. As seen from Fig. 1 all the measured D-values are in excellent agreement with the D^∞ coefficients computed from eqn. (6).

The self-diffusion coefficient of t-BuOH, labelled with ^{14}C and the diffusion coefficient of tritium were measured in 0.1 M Me$_4$I and 0.05 M Bu$_4$NI solutions. The water self-diffusion coefficient was recalculated from the tritium diffusion coefficient using the procedure described previously.[37] The results are listed in Table 3. Viscosity, summarized in Table 3, was used to compute the 'structure coefficient' $F_{solvent}$, described below. Variations the self-diffusion coefficients of t-BuOH and water of the structure coefficients, $F_{solvent}$ in 0.1 M Me$_4$I and 0.05 M Bu$_4$NI solutions are shown in Fig. 2.

Table 1 Limiting molar conductivity λ^0 (S m^2 mol^{-1}), association constants K_A and distance parameters R (in nm) for tetraalkylammonium iodides in aqueous and 0.5 M urea solutions at 298 K

	Aqueous solution				0.5 M urea solution			
	Me$_4$NI	Et$_4$NI	Pr$_4$NI	Bu$_4$NI	Me$_4$NI	Et$_4$NI	Pr$_4$NI	Bu$_4$NI
$10^4\lambda^0$	121.74	109.45	100.25	96.48	121.03	104.11	108.67	99.59
R	0.584	1.10	0.654	0.700	0.580	0.850	0.601	0.633
K_A	5.6 ± 0.7	10 ± 1	13.1 ± 0.9	15.3 ± 0.6	5.1 ± 0.7	10 ± 2	10.7 ± 0.8	11.1 ± 0.7
$(r_c + r_a)_{cryst}{}^a$	0.500	0.557	0.601	0.633				

^{a} Crystallographic radii of ions (in nm) taken from ref. 34.

Table 2 Limiting molar conductivity λ^0 (S m² mol⁻¹), association constants K_A and distance parameters R (in nm) for Me₄NI and Bu₄NI in *tert*-butanol–water solutions at 298 K

	Me₄NI			Bu₄NI		
x_{BuOH}	R	$10^4\lambda^0$	K_A	R	$10^4\lambda^0$	K_A
0.00	0.584	121.75	5.6 ± 0.5	0.700	96.48	15.3 ± 0.6
0.025	0.582	87.42	5.9 ± 0.7	0.726	64.23	18.2 ± 0.3
0.050	0.585	64.37	6.3 ± 0.6	0.808	46.81	20.6 ± 0.9
0.075	0.603	50.15	7.5 ± 0.4	0.708	38.40	23.1 ± 1
0.100	0.598	42.31	8.4 ± 0.9	0.714	32.13	26.3 ± 0.8
0.150	0.598	33.89	9.9 ± 0.8	0.720	27.46	31.1 ± 1
0.200	0.592	28.77	13.3 ± 0.4	0.700	24.20	37.3 ± 0.9
0.250	0.606	26.11	15.1 ± 0.7	0.750	24.27	45.2 ± 0.7

Table 3 Viscosity η (N s m²) and self-diffusion coefficients (in m² s⁻¹) of *tert*-butanol D_{BuOH} and water D_W in *tert*-butanol–water solutions of Me₄NI and Bu₄NI at 298 K

	0.1 M Me₄NI solution			0.05 M Bu₄NI solution		
x_{BuOH}	η	D_{BuOH}	D_W	η	D_{BuOH}	D_W
0.000	–	–	2.23 ± 0.03	–	–	2.22 ± 0.03
0.025	1.522	0.71 ± 0.03	–	1.516	0.72 ± 0.03	–
0.050	2.181	0.44 ± 0.03	0.99 ± 0.03	2.183	0.44 ± 0.05	1.01 ± 0.03
0.075	2.643	0.36 ± 0.02	0.77 ± 0.03	2.596	0.35 ± 0.03	0.78 ± 0.03
0.100	3.273	0.29 ± 0.03	0.67 ± 0.04	3.336	0.28 ± 0.04	0.66 ± 0.03
0.150	3.846	0.26 ± 0.04	0.55 ± 0.04	4.209	0.25 ± 0.04	0.54 ± 0.05
0.200	4.605	0.26 ± 0.03	0.48 ± 0.05	4.882	0.24 ± 0.04	0.47 ± 0.04
0.250	5.022	0.26 ± 0.02	0.46 ± 0.04	5.502	0.23 ± 0.05	0.44 ± 0.04

Discussion

Measurements of molar conductivity provide information concerning association of ions and character of the ion pairs. R-values reflect the most probable separation between the ions in the ion pair. As seen from Table 1 the R-values for R_4N^+ ions, except Et_4N^+, are very close to the sum of the ionic radii in the crystal. This means that iodides of Me_4N^+, Pr_4N^+ and Bu_4N^+ form contact ion pairs. Dielectric spectroscopy studies[10] of aqueous solutions of R₄NBr and R₄NCl also show that contact ion pairs are preferred. These results suggest penetration of the anion inside the R_4N^+ cations, between the alkyl chains. Contact ion pairs and the pairs with anions located inside cations, were observed for moderate concentration of salts, below 0.5 M, when solvent separated pairs were expected. This suggests that association of opposite ions cannot be driven by electrostatic forces only. Formation of the contact ion pairs, instead of the solvent separated ones, were found experimentally and was confirmed by MD simulation in methanol–water solutions of NaI. Such behaviour protects the hydrogen bond network.[38] The different behaviour of Et₄NI is consistent with that tendency, because the 'cage-like' structure around the Et_4N^+ ion, formed by the H-bonded water molecules, is more stable than that around the other cations.[39] As seen from Tables 1 and 2, the addition of urea and *t*-BuOH does not affect the R-values and the separation of ions in the pairs remains close to the sum of the ion radii in the crystal. It means that neither *t*-BuOH nor urea influences the character of the ion pairs.

Though in aqueous solutions the K_A values are slightly higher than those reported for tetraalkylammonium chlorides and bromides,[10] association of opposite ions is negligible. As might be expected, the addition of *t*-BuOH induces association of the opposite ions, and K_A increases. Enhancement of association is due to the decrease of the static dielectric constant, as can be deduced from linear dependences of $\ln K_A$ on $1/\varepsilon$, shown in Fig. 3.

At constant temperature, the limiting molar conductivity λ^0 depends on the solvent viscosity, thus a variation of the Walden product, $\lambda^0\eta$, might reflect a change of hydration of ions. The molar conductivity depends however on mobilities of both ions, thus the self-diffusion coefficient, which reflects the motions of one ion, is more informative and provides information concerning the size of every ion independently.

As seen from Fig. 1 the D^∞ coefficients of iodide ions in both solutions, of Me₄NI and Bu₄NI, are the same, which means that translations of I⁻ are not influenced by the counter-ion motions. Although lack of correlation has been expected, this confirms that the association of opposite ions, for the studied salt concentrations, below 0.1 M, is negligible. Therefore the self-diffusion coefficients of R_4N^+ cations, computed from eqn. (6), represent motions of free ions and, maybe, their environment. An excellent agreement of the Me_4N^+ self-diffusion coefficients, determined with the cation labelled with ¹⁴C with those calculated from eqn. (6), see Fig. 1, justifies the above statement.

The hydrodynamic radii of the R_4N^+ and I⁻ ions in all studied solutions were calculated from the Stokes–Einstein equation:

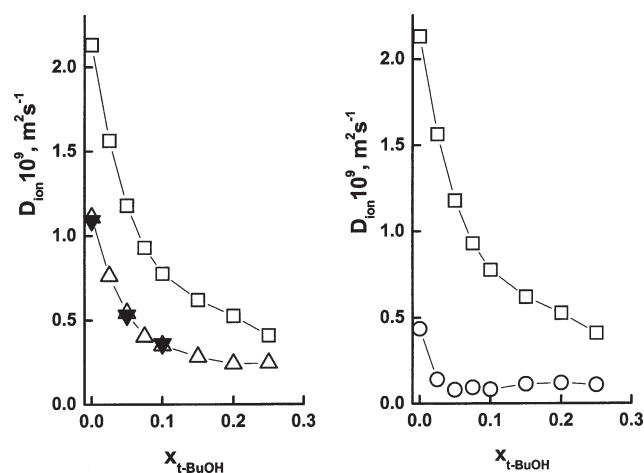$$r_{hydr} = \frac{kT}{\alpha\pi\eta D_{ion}} \qquad (7)$$

Fig. 1 Dependence of self-diffusion coefficient of I⁻ (□), Me₄N⁺ (△), ¹⁴C-Me₄N⁺ (▼) and Bu₄N⁺ (○) ions on the mole fraction of BuOH in solutions of Me₄NI (left) and Bu₄NI (right) at 298 K.
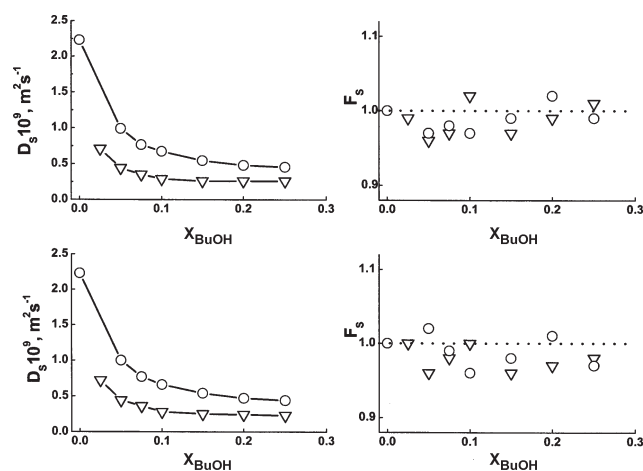

Fig. 2 Self-diffusion coefficients (left) and ratios of solvent hydrodynamic radii, computed from eqn. (10), (right) for water (○) and *tert*-butanol (▽) in solutions of Me₄NI (upper) and of Bu₄NI (bottom) at 298 K.
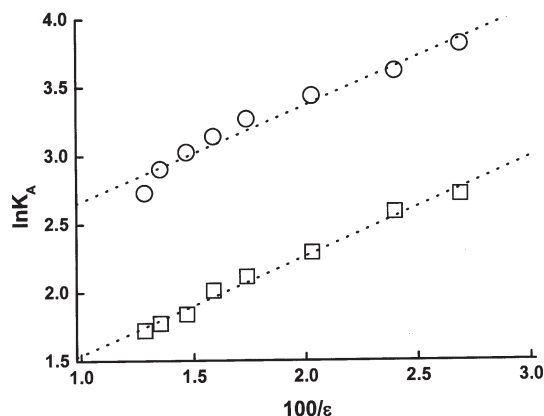
Fig. 3 Variations of $\ln K_A$ of Me$_4$NI ($\square$) and Bu$_4$NI ($\bigcirc$) on $1/\varepsilon$ in aqueous t-BuOH solutions at 298 K.

Fig. 4 Variations of the hydrodynamic radii, computed from eqn. (7), of I$^-$ ($\bigcirc$), Me$_4$N$^+$ ($\triangle$) and Bu$_4$N$^+$ ($\square$) and the corrected radii in solution, computed from eqn. (8) of I$^-$ ($\bullet$) and Me$_4$N$^+$ ($\blacktriangle$) with the mole fraction of BuOH in solutions of Me$_4$NI (left) and Bu$_4$NI (right).

For small ions, Me$_4$N$^+$ and I$^-$, we assume the perfect slipping conditions and $\alpha = 4$, whereas for bigger Bu$_4$N$^+$ ion the perfect sticking conditions, for which $\alpha = 6$, seem to be more appropriate. The hydrodynamic radii of Et$_4$N$^+$ and Pr$_4$N$^+$ ions were computed for both assumptions. The question arises whether the hydrodynamic radius of the ion can serve as the radius of the solvated ions. For the ions with high charge density, dielectric friction forces acting on the ion are not negligible,[40] therefore the hydrodynamic radius must be corrected by a term resulting from dielectric friction:[31]

$$r_{ion} = \frac{kT}{4\pi\eta D_{ion}} + 0.0103\varepsilon \qquad (8)$$

R$_4$N$^+$ ions are, however, more 'apolar' than 'ionic',[16–18] thus the hydrodynamic radius, computed from eqn. (7) without any correction, might be treated as the size of the solvated ion. The iodide ion is considered as 'ionic' and its hydrodynamic radius is usually corrected with the dielectric term, according to eqn. (8). Sizes of I$^-$ and Me$_4$N$^+$ in the crystal are, however, not very different, 0.22 and 0.28 nm,[34] respectively. Similar charge densities of these ions suggest that their hydration is also similar. MD simulation studies[17,19,41] have confirmed this supposition, showing that in aqueous solution the iodide ion behaves as an 'apolar' species and water molecules in the coordination shell of I$^-$ do not exhibit any preferred orientation. Therefore the radii of Me$_4$N$^+$ and I$^-$ were computed from both eqn. (7) and (8). Variations of all ionic radii with the mole fraction of t-BuOH are shown in Fig. 4.

In aqueous solution the radii of the iodide ion, both the hydrodynamic $r_{hydr} \cong 0.18$ nm, and the corrected, $r_{ion} \cong 0.25$ nm, ones are close to its radius in crystal. This leads to the conclusion that motions of the iodide ions and coordinated water molecules are independent and the hydration shell is transient, because its lifetime, about 11 ps, is shorter than the characteristic time of the anion translations, about 30 ps.[41] Addition of alcohol reduces the I$^-$ radius and even the corrected value, r_{ion}, becomes smaller than the crystallographic radius. Such a feature, observed previously for iodide ions in aqueous solutions of methanol and propanols, reflects probably a fast exchange of the molecules between the coordination shells and the bulk.[20,41]

In aqueous solution the hydrodynamic radius of Me$_4$N$^+$ ions, about 0.35 nm, exceeds its size in crystal. This suggests that the lifetime of the water structure around this ion is longer than the time of ion translations. The corrected radius of Me$_4$N$^+$ is about 0.43 nm and is close to the ion–oxygen distance found in MD simulation. The first maximum of the $g_{ion-O}(r)$ function was noticed at 0.5 nm for the Me$_4$N$^+$ ion 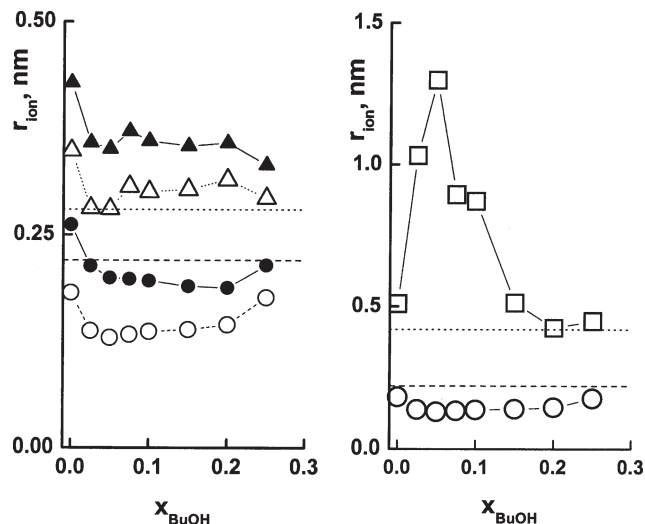considered as the charged sphere,[19] whereas for flexible, five-site model of Me$_4$N$^+$, a shorter distance, about 0.45 nm, between nitrogen and oxygen was found.[42]

Considering ions and water molecules as spheres one can obtain a number of water molecules n_W in the vicinity of the ion:

$$n_W = \frac{r_{ion}^3 - r_{cryst}^3}{r_W^3} \qquad (9)$$

r_{ion} denotes the radius of the ion in solution, calculated from either eqns. (7) or (8), r_{cryst} is the ion radius in crystal and r_W is the size of water molecule. We assumed $r_W = 0.145$ nm, half of the distance between two oxygen atoms in water structure.

In aqueous solution the number of the water molecules around Me$_4$N$^+$ is either 6 for the hydrodynamic radius obtained from eqn. (7) or 20 for the corrected radius, calculated from eqn. (8). The latter value better fits results of MD simulation,[17–19] between 20 and 30 molecules, and neutron scattering experiments,[16] about 20 molecules. The higher hydration number seems to be unrealistic, because of two reasons. First, because both techniques, the MD simulation and neutron scattering, give the 'static' hydration number whereas the self-diffusion experiment shows the 'dynamic' hydration number. The dynamic number is usually smaller because it represents only the molecules moving with the ion. These molecules must stay in the coordination shell longer than the characteristic time of the Me$_4$N$^+$ translations. This time is about 50 ps,[19] but the residence time, computed in MD simulation, is noticeably shorter, about 10 ps.[19] Moreover the existence of the long-lived coordination shell of the Me$_4$N$^+$ ion, containing 20 water molecules, should affect noticeably the translations of the water molecules, similar to that observed previously for sodium ions.[20] However self-diffusion coefficients of water (Fig. 2) do not support such hypothesis.

To deduce the influence of ions on the solvent structure we introduced[43] the 'structure coefficient' $F_{solvent}$, for all component of the solvent. This represents the ratio of the hydrodynamic radii of the diffusion unit of the solvent component in the salt free solvent $(r_{solvent})_{mix}$ and in the electrolyte solution $(r_{solvent})_{salt}$:

$$F_{solvent} = \frac{(r_{solvent})_{mix}}{(r_{solvent})_{salt}} \equiv \frac{(D_{solvent}\eta)_{salt}}{(D_{solvent}\eta)_{mix}} \qquad (10)$$

The $F_{solvent}$ coefficient is calculated as the ratio of the products of the self-diffusion coefficient and viscosity, measured for electrolyte solution $(D_{solvent}\eta)_{salt}$ and for the salt free solvent $(D_{solvent}\eta)_{mix}$, reported previously.[25] As seen from Fig. 2 the F_W coefficient is close to unity over the whole range of x_{BuOH}. This suggests that addition of Me_4NI does not affect the water motions noticeably. Thus the hydrodynamic radius, calculated from eqn. (7) reflects the real size of the hydrated ion, what means that dielectric friction forces can be neglected. This demonstrates the 'apolar' character of the Me_4N^+ ion.

In the t-BuOH–water mixture the hydrodynamic radius of Me_4N^+ decreases rapidly with increasing x_{BuOH} and reaches its size in the crystal, about 0.28 nm. Similar behaviour has been noticed previously for Et_4N^+ ions in aqueous solutions of n-propanol.[44] The observed destruction of the Me_4N^+ shell may suggest that water prefers to hydrate alcohol clusters or, possibly, alcohol monomers. The question is whether clathrate-like aggregates of t-BuOH, observed in aqueous solution,[25,26] exist in presence of the apolar Me_4N^+ ions. In Me_4NI solution the F_{BuOH} coefficients are close to unity, over the whole range of the studied x_{BuOH} (see Fig. 2). This means that the presence of Me_4N^+ does not affect the size of the alcohol diffusion units. Comparison of the changes of the hydrodynamic radii of Me_4N^+ and t-BuOH in ternary systems leads to the conclusion that the Me_4N^+ ion is 'less' hydrophobic than t-BuOH, because alcohol molecules win the competition for water molecules and the Me_4N^+ ions lose their hydration shells.

In aqueous solution the hydrodynamic radius of the Bu_4N^+ ion is about 0.51 nm and exceeds the radius in crystal, 0.42 nm.[34] The number of water molecules around the cation, estimated from eqn. (9), is about 20. Molecular volume[45] and dielectric spectroscopy[10] yield greater hydrophobic hydration numbers, about 46 and 36, respectively. The latter result is consistent with the structure of stable clathrate $Bu_4NBr\cdot36H_2O$ observed in the solid state,[46] but the 'dynamic' hydration number is smaller, as might be expected.

The characteristic time of the Bu_4N^+ translations was estimated from the Einstein formula, assuming the shortest hopping distance equal to the hydrodynamic radius of the ion,[38] i.e. about 0.51 nm. The self-diffusion coefficient, 4.3×10^{-10} $m^2 s^{-1}$ (see Table 1) yields the characteristic time of Bu_4N^+ translations about 100 ps. Such long residence time leads to the conclusion that the hydrodynamic radius may reflect only the water molecules located between alkyl chains of the cation.[21]

The influence of t-BuOH on the Bu_4N^+ ions is not the same as that found for Me_4N^+ and I^- ions. Addition of t-BuOH causes a significant increase of the Bu_4N^+ radius. The largest radius, about 1.2 nm, is observed at $x_{BuOH} = 0.05$. It is worth stressing that this is the composition with the highest concentration of the alcohol aggregates.[25]

The observed increase of the Bu_4N^+ radius might be due to one of the following phenomena: (i) strong hydrophobic hydration which causes an 'iceberg' formation around the cation, (ii) incorporation of the $tert$-butanol molecules in the coordination shell of the cation and (iii) hydrophobic association of the cations. Both the 'iceberg' formation and the incorporation of the alcohol molecules in the cation shell should retard significantly translations of the solvent molecules, either water or alcohol. In consequence we should notice significant changes either for F_W or for F_{BuOH}. However, both F_W and F_{BuOH} coefficients, as seen from Fig. 2, do not deviate noticeably from unity, which means that the structure of the solvent remains unaffected and neither 'iceberg' formation nor solvation of the Bu_4N^+ ion by alcohol molecules occurs. Thus the increase of the Bu_4N^+ radius must reflect aggregation of cations. Association of cations was noted in aqueous solution of Pr_4NBr. MC simulation and neutron diffraction experiments have shown that the Pr_4N^+ ions 'can come into close

contact',[21] without any water molecules between them. The most probable separation between nitrogen atoms of Pr_4N^+ ions was about 1.0 nm. For Bu_4N^+ ions this distance should be slightly longer and the hydrodynamic radius of about 1.2 nm may reflect the size of Bu_4N^+ aggregate. The hydrodynamic radius of Bu_4N^+ ions decreases rapidly when alcohol content increases and reaches the same size as in crystal. This means that in more concentrated solutions of t-BuOH the aggregation of Bu_4N^+ ions vanishes. It is worth stressing that in such mixtures the cluster-like structure around alcohol molecules also vanishes.[25,26]

Self-diffusion coefficients of R_4N^+ cations in 0.5 M aqueous solution of urea were computed from eqn. (6) using the limiting self-diffusion coefficient of the iodide ions, $D_I^\infty = 2.10 \times 10^{-9}$ $m^2 s^{-1}$, determined previously as a function of urea concentration.[47] The self-diffusion coefficients, the hydrodynamic radii and the dynamic hydration numbers of R_4N^+ ions in aqueous and 0.5 M urea solutions are summarized in Table 4. As mentioned above the hydrodynamic radii of small ions, Me_4N^+ and Et_4N^+, were computed for the perfect slipping conditions and $\alpha = 4$, whereas for bigger Pr_4N^+ and Bu_4N^+ ions the perfect sticking conditions, with $\alpha = 6$, were assumed.

In aqueous solution the self-diffusion coefficient of R_4N^+ decreases monotonously with increasing number of carbon atoms in the alkyl chain. Such dependence yields, as expected, an increase of the hydrodynamic radius. Results summarized in Table 4 confirm that perfect slipping conditions are more appropriate for Et_4N^+ ions. Similar dynamic hydration numbers observed for Et_4N^+ and Bu_4N^+ ions suggest that penetration of water molecules inside the R_4N^+ cation is limited to external groups of the alkyl chains. The hydrodynamic radius of the Pr_4N^+ ions was computed both for perfect slipping and for perfect sticking conditions. The radius computed for the slipping conditions yields about 70 water molecules around the ion, whereas that for sticking conditions gives only 8 water molecules in the vicinity of the cation. Both results do not fit numbers obtained for Et_4N^+ and Bu_4N^+ ions. This means that neither slipping nor sticking conditions describe translations of Pr_4N^+.

Addition of urea does not affect the translations of Me_4N^+ ions, but accelerates motions of Pr_4N^+ and Bu_4N^+. Thus the hydrodynamic radius and the hydration number of Me_4N^+ in urea solution are similar to those in water. The hydration numbers of Pr_4N^+ and Bu_4N^+ ions in urea solutions are significantly reduced, which might suggest that penetration of water molecules in alkyl chains does not occur. The influence of urea on Et_4N^+ ions is different. Translations of Et_4N^+ are slowed down. As a consequence its hydrodynamic radius and dynamic hydration number are greater than in aqueous solution. Such a feature might reflect either a stabilization of the clathrate-like structure around the ion or incorporation of the urea

Table 4 Limiting self-diffusion coefficients of R_4N^+ ions ($m^2 s^{-1}$), the hydrodynamic radii r_{hydr} (nm), computed from eqn. (7), and the hydration numbers n_W calculated from eqn. (10) in aqueous and 0.5 M urea solutions at 298 K. The radii in crystals, r_{cryst} (nm) are taken from ref. 34

Ion	Aqueous solution			0.5 M urea solution			
	$10^9 D$	r_{hydr}	n_W	$10^9 D$	r_{hydr}	n_W	r_{cryst}
Me_4N^+	1.15 ± 0.03	0.35^a	6	1.13 ± 0.03	0.36^a	7	0.28
Et_4N^+	0.82 ± 0.04	0.47^a	21	0.67 ± 0.05	0.55^a	42	0.34
		0.32^b	–		0.37^b	4	
Pr_4N^+	0.57 ± 0.03	0.64^a	68	0.80 ± 0.04	0.46^a	14	0.38
		0.43^b	8		0.31^b	—	
Bu_4N^+	0.47 ± 0.04	0.51^b	21	0.56 ± 0.04	0.44^b	5	0.41

^{a} Calculated for perfect slipping conditions with $\alpha = 4$. ^{b} Calculated for perfect sticking conditions with $\alpha = 6$.

molecules in the ionic shells. Further investigation of the self-diffusion, particularly of urea and Et_4N^+, with the cation labelled with radioactive tracer, should be done to explain the different behaviour of this ion.

Conclusions

Association of opposite ions in aqueous, aqueous urea and aqueous t-BuOH solutions of R_4NI is weak, but contact ion pairs are observed instead of solvent separated ones. This suggests an important influence of the solvent structure, but in aqueous t-BuOH solutions the association constant of tetraalkylammonium iodides increases with decreasing static dielectric constant of the solvent.

In aqueous solutions the hydrodynamic radii of the R_4N^+ ions exceed their radii in crystal. Thus motions of the ions and a few water molecules are correlated. The hydrodynamic radii yield the hydration numbers of these ions, which are noticeably smaller that the static hydration numbers derived from neutron diffraction and computer simulation. These dynamic hydration numbers represent the water molecules which stay around the ions longer than 50 ps. This leads to the conclusion that dynamic hydration number shows only the molecules located between the alkyl chains. Addition of t-BuOH reduces noticeably the number of water molecules around the Me_4N^+ and Bu_4N^+ ions, but only Bu_4N^+ ions aggregate. The presence of R_4N^+ ions does not affect the clathrate-like structure around the t-BuOH molecule. This leads to the conclusion that ternary system, water + t-BuOH + Bu_4NI, can serve as a model system to study both hydrophobic phenomena, the hydrophobic hydration of t-BuOH molecules and the hydrophobic association of Bu_4N^+ ions.

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