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Aqueous solutions of tetraalkylammonium halides: ion hydration, dynamics and ion-ion interactions in light of steric effects

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Supporting Information

The Supporting Information includes:

a) Field Parameters

b) Simulated and experimental densities for TMABr and TBABr aqueous solutions

c) Details of water orientation in the hydration shells of cations

d) NMR diffusion measurements by B. Ancian and G. Mériguet

e) Methyl group rotation for TBA^+ and TMA^+

f) X-ray scattering intensity - comparison of experimental and simulated data

a) Field parameters

Table 1: Interaction potentials for TBA$^+$. H_N represents hydrogen atoms closest to the central nitrogen atom.

atom or group (in bold)	atomic charge (e)		
	N	C	H
-**N**-	0.056669		
-N-$\mathbf{CH_2}$-		0.017461	0.053130
-N-$CH_2 - \mathbf{CH_2}$-		-0.002556	0.021844
-N-$CH_2 - CH_2 - \mathbf{CH_2}$-		0.011361	0.020886
-N-$CH_2 - CH_2 - CH_2 - \mathbf{CH_3}$		-0.086548	0.034799

bond elongation harmonic parameters	energy term (kcal/mol/Å^2)	length (Å)
C-H_C	340	1.090
C-H_N	240	1.090
C-C	310	1.526
C-N	367	1.471

bond bending harmonic parameters	energy term (kcal/mol/rad^2)	angle (degree)
H_C-C-H_C	35	109.5
H_N-C-H_N	35	109.5
C-C-H_C	50	109.5
C-C-H_C	50	109.5
C-C-C	40	109.5
C-C-N	80	111.2
H_N-C-N	50	109.5
C-N-C	50	109.5

dihedral interaction	energy term (kcal/mol)	angle (degree)
H_C-C-C-H_C	0.15	0.0
H_C-C-C-C	0.16	0.0
H_C-C-C-H_N	0.15	0.0
H_N-C-C-C	0.16	180.0
C-C-C-C	0.18	0.0
X-C-C-X	0.15	0.0
X-C-N-X	0.15	0.0

LJ parameters	ϵ (kcal/mol)	σ (Å)
H_C	0.0157	1.487
H_N	0.0157	1.100
C	0.1094	1.900
N	0.1700	1.8240

Table 2: Interaction potentials for TMA$^+$.

atom or group (in bold)	atomic charge (e)		
	N	C	H
-N-	0.096521		
-N-$\mathbf{CH_3}$		-0.165381	0.130417

bond elongation harmonic parameters	energy term (kcal/mol/Å^2)	length (Å)
C-H	240	1.090
C-N	367	1.471

bond bending harmonic parameters	energy term (kcal/mol/rad^2)	angle (degree)
H-C-H	35	109.5
H-C-N	50	109.5
C-N-C	50	109.5

dihedral interaction	energy term (kcal/mol)	angle (degree)
X-C-N-X	0.15	0.0

LJ parameters	ϵ (kcal/mol)	σ (Å)
H	0.0157	1.100
C	0.1094	1.900
N	0.1700	1.8240

Table 3: Interaction parameters for monoatomic ions.

atom	LJ ϵ (kcal/mol)	LJ σ (Å)	charge (e)
Na	0.1	2.583	+1.0
Br	0.1	4.54	-1.0

b) Simulated and experimental densities for TMABr and TBABr aqueous solutions

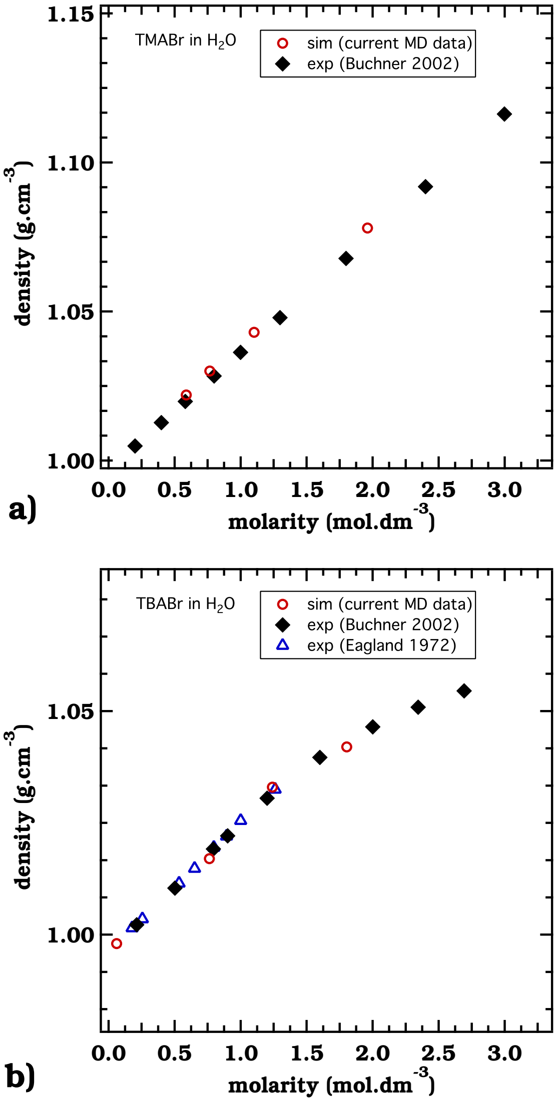

Figure 1: Simulated and experimental densities for a) TMABr aqueous solutions and b) TBABr aqueous solutions, as a function of concentration. Experimental data is taken from *R. Buchner, C. Holzl, J. Stauber and J. Barthel, Phys. Chem. Chem. Phys., 2002, 4, 2169 - 2179 and D. Eagland and G. Pilling, J. Phys. Chem., 1972, 76, 1902 - 1906.*

c) Details of water orientation in the hydration shells of cations

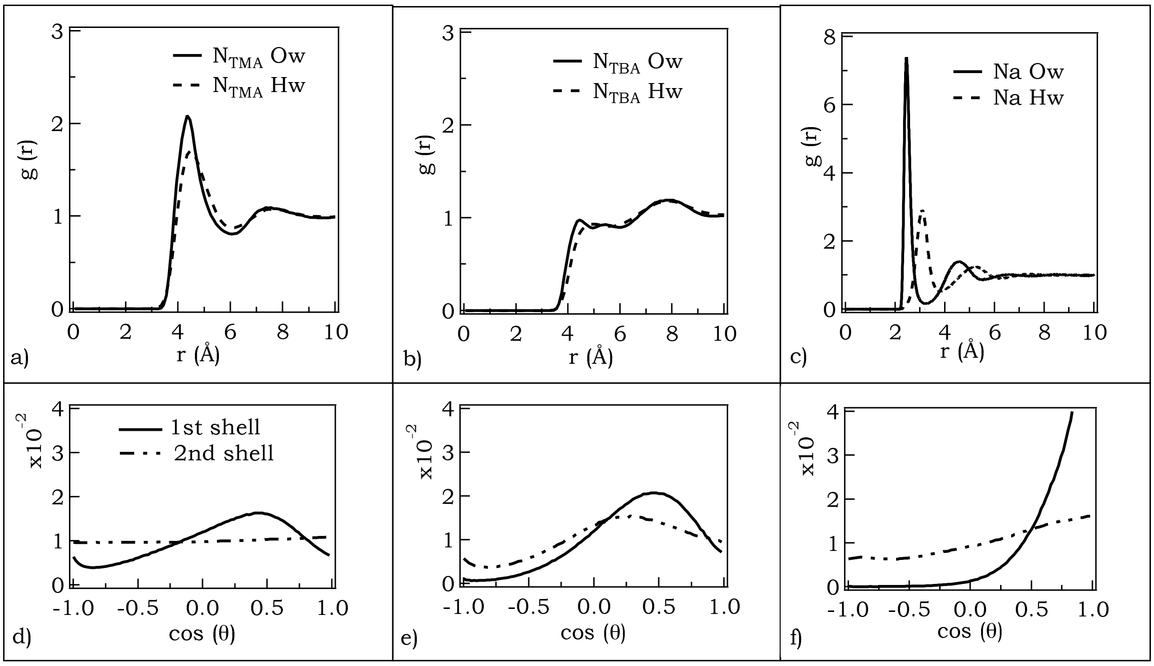

Figure 2: Details of water orientation around cations for TMABr, TBABr and NaBr solutions, all at 1m concentration: a) to c) Radial distribution functions between cations (central N atom or Na) and oxygen/hydrogen (Ow/Hw) atoms of surrounding water molecules; d) to f) Angular distribution of water molecules surrounding the cations, with θ representing the angle between the cation-Ow vector and the dipole moment vector of the water molecule. In the case of TMA^+ and TBA^+, the most probable values of θ are around 60°, which is a close to tangential orientation of the water molecules with respect to the central N atom of the cations. We see that this preferential orientation is lost in the second hydration shell of TMA^+, while it is retained in case of TBA^+. The distinction between the first and second shell in case of TBA^+ is taken as below or above N–O_w distance of 6.2 Å

d) NMR diffusion measurements by B. Ancian and G. Mériguet

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All diffusion experiments were recorded at 298 K using a $^{1}H/^{13}C/^{15}N$ TXI inverse probe on a Bruker Avance DRX 500 NMR spectrometer operating at 499.76 MHz for ^{1}H using the so-called bipolar pulse pair longitudinal eddy current delay sequence (BPP-LED) (*Johnson CS (1999) Diffusion ordered nuclear magnetic resonance spectroscopy: principles and applications. Prog NMR Spectrosc 34:203-256*). The ^{1}H nominal 90° pulse was around 10 μs and measured systematically on the actual sample. The maximum value of the gradient (56.5 G cm^{-1}) has been calibrated with the value of the self-diffusion coefficient of HOD in D_2O.

For each sample, a series of 32 spectra with increasing gradient value (from 0 to 56 % of the maximum value) were recorded. The data were analysed using the NMRPipe processing software package (*Delaglio F, Grzesiek S, Vuister GW, Zhu G, Pfeifer J, Bax A 736 (1995) NMRPipe: a multidimensional spectral processing system based on UNIX pipes. J Biomol NMR 6:277-293*). Rectangular gradients of constant duration (3 ms) were chosen for encoding and decoding, whereas the spoil gradient (2 ms) was sine-shaped. The LED was kept at a value of 10 ms in all the experiments. Each diffusion constant has been obtained using at least three diffusion times, Δ, from 25 to 500 ms.

e) Methyl group rotation for TBA$^+$ and TMA$^+$

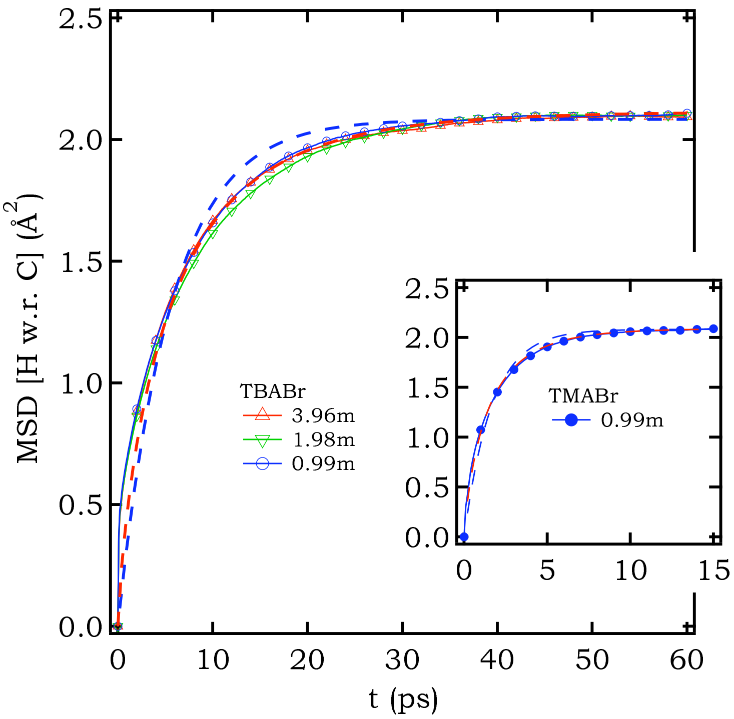

Figure 3: Investigation of methyl group rotation for TBA$^+$ and TMA$^+$: Mean square displacement (MSD) for H atoms of terminal methyl groups with respect to the adjacent C atoms, versus time, for TBA$^+$ in selected TBABr solutions; inset features the same type of data for TMA$^+$ in 0.99m TMABr solution. Dashed lines represent the fits of data with Equation 3 of the main article or its extension, which uses the same values of $b_{\mathrm{C-H}}$ and ϕ, but allows a range of characteristic rotational times (these are distributed according to a Gaussian function truncated at zero to avoid non-physical negative characteristic times). The obtained spread (standard deviation) of characteristic rotational times is significant, of the order of the mean value, i.e. 3-5 ps for TBA$^+$ and 2 ps for TMA$^+$.

f) X-ray scattering intensity - comparison of experimental and simulated data

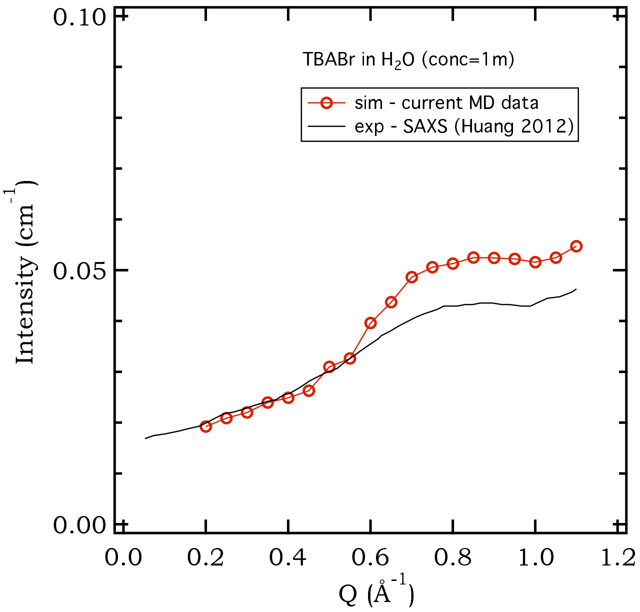

Figure 4: X-ray scattering intensity (in cm^{-1}) versus wave-vector, Q, for TBABr solution in H_2O at 1m concentration determined experimentally in ref *N. Huang, D. Schlesinger, D. Nordlund, C. Huang, T. Tyliszczak, T. M. Weiss, Y. Acremann, L. G. M. Pettersson and A. Nilsson, J. Chem. Phys., 2012, 136, 074507.* and calculated from the current MD simulations using the nMoldyn package. The principal difference between the calculation of X-ray and neutron coherent scattering signal is the use of a Q dependent X-ray scattering length for each atom in the former, instead of the Q-independent coherent neutron scattering length/cross-section for each atom in the latter. The Q-dependent X-ray scattering length was calculated using the D. Cromer and J. Mann formula from *D. Waasmaier and A. Kirfel, New Analytical Scattering-Factor Functions for Free Atoms and Ions, Acta Cryst. (1995). A51,416-43.*