

Structural and Dynamic Properties of Tetra-alkyl Ammonium Bromide

aqueous solutions: A Molecular Dynamics Simulation Study Using a

Polarizable Force Filed

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Force Field. The potential forms utilized in the development of our force field are given as following. The total potential energy $U^{tot}(\mathbf{r})$, given in equation (1), is composed of two main contributions: non-bonded potentials $U^{NB}(\mathbf{r})$ and bond-based potentials. In this study, all bonds were constrained by SHAKE algorithm. In the potential form of bend, θ_{ijk} and θ_{ijk} denotes instantaneous bend formed by atoms i, j and k , where the force constant is given by $k_{\alpha\beta\gamma}^{bend}$. The atom types α, β and γ are given as subscripts. In the dihedral potential the angle is formed by atoms i, j, k and l and is denoted as ϕ_{ijkl} , with force constant $k_{\alpha\beta\gamma\delta n}^{dihedral}$ s, where n is the fold number of cosine series and $\alpha, \beta, \gamma, \delta$ define the atom types comprising the dihedral.

$$U^{tot}(\mathbf{r}) = U^{bend}(\mathbf{r}) + U^{dihedral}(\mathbf{r}) + U^{NB}(\mathbf{r}) \quad (1)$$

$$U^{bend} = \frac{1}{2} k_{\alpha\beta\gamma}^{bend} (\theta_{ijk} - \theta_{ijk}^0)^2 \quad (2)$$

$$U^{dihedral} = \sum_n \frac{1}{2} k_{\alpha\beta\gamma\delta n}^{dihedral} (1 - \cos(n\phi_{ijkl})) \quad (3)$$

The non-bond potential form is given in equation (4). To capture the repulsion-dispersion(RD) interaction $U^{RD}(\mathbf{r})$ we use exponential-6 form of the potential where $A_{\alpha\beta}$ and $B_{\alpha\beta}$ are repulsion parameters and $C_{\alpha\beta}$ corresponds to attraction part. The term D is utilized to adjust the repulsion-dispersion making the repulsion the dominant at close i - j distance ($r_{ij} < 1.0$ Å). The classical electrostatic potential form is utilized for the interaction between fixed charge. Simultaneously, polarization energy between induced dipoles and induced dipoles with fixed charges is calculated, where $\vec{\mu}_i = \alpha_i \vec{E}_i^{tot}$ is the induced dipole on atom i , $\vec{E}_i^0$ denotes the electric field induced by fixed charge only, $\vec{E}_i^{tot}$ is the total electrostatic field. To avoid the ‘polarization catastrophe’, the Thole screening was utilized to smear the induced dipoles at short distances.¹

$$U^{BN}(\mathbf{r}) = U^{RD}(\mathbf{r}) + U^{coul}(\mathbf{r}) + U^{pol}(\mathbf{r}) =$$

$$\sum_{i>j} (A_{\alpha\beta} \exp(-B_{\alpha\beta} r_{ij}) - C_{\alpha\beta} r_{ij}^{-6} + D (\frac{12}{B_{\alpha\beta}})^{12}) + \sum_{i>j} \left(\frac{q_i q_j}{4\pi \epsilon_0 r_{ij}} \right) - \frac{1}{2} \sum_i \vec{\mu}_i \cdot \vec{E}_i^0. \quad (4)$$

Parameters for the FF-orig used in this work for TMA system are given in Table S1. Additionally, parameters for cross-terms for repulsion-dispersion interactions in TMA systems are given in Table S2.

Table S1. Parameters of force field for each atom type

Label	A/(kcal/mol)	B($\text{\AA}^{-1}$)	C/(kcal/mol* $\text{\AA}^{-6}$)	Charge/e	Induced polarizability/ (kcal/(mol* $\text{\AA}^{-3}$))
N+	39091.80	4.56720	122.04	0.1484	1.7000
Cm	108283.00	3.64050	560.53	0.0491	1.0000
H	5352.30	4.36460	22.59	0.0546	0.3500
Br	2233701.8	3.75000	5053.18	-1.0000	2.6000
Hw	0.0000	0.0000	0.0000	0.5537	0.0000
Ow	880783.40	0.00000	851.26	0.0000	1.0425
Lp	0.00	0.00	0.00	-1.1074	0.0000

Table S2. Parameters for cross terms and valence interactions

Cross-term repulsion-dispersion parameters			
RD pair	A/(kcal/mol)	B/($\text{\AA}^{-1}$)	C/(kcal/mol* $\text{\AA}^{-6}$)
N+ Cm	52447.87	3.93375	261.55
N+ H	14331.84	4.45788	52.51
N+ Br	250410.9	4.02584	785.3
N+ Hw	17036.14	5.12627	0
N+ Ow	16377.93	3.57842	352.74
N+ Lp	0	0	0
Cm H	20901.72	3.89336	112.53
Cm Br	489867.5	3.69241	1682.99
Cm Hw	14362.57	4.08627	0
Cm Ow	40307.17	3.41006	755.97
Cm Lp	0	0	0
H Br	98910.11	3.97861	337.86
H Hw	5501.88	4.89892	0
H Ow	6701.35	3.55728	151.76
H Lp	0	0	0
Br Hw	71296.68	4.20917	0
Br Ow	177247.3	3.44237	2269.81
Br Lp	0	0	0
Hw Ow	0	0	0
Hw Lp	0	0	0
Ow Lp	0	0	0

Constrained bonds	
Bond pair	Bond length/($\text{\AA}$)

Cm N+	1.500
H Cm	1.100
Hw Ow	0.957
Hw Hw	1.514
Ow Lp	0.238

Bending potential		
Bond pair	$k_{\alpha\beta\gamma}^{\text{bend}}$ (kcal/mol)	Bend angle
Cm N+ Cm	140.000	109.3
H Cm N+	70.000	102.0
H Cm H	77.000	109.3
Hw Ow Hw	0.00	104.52

Dihedral					
$\alpha \beta \gamma \delta$	n	K0/(kcal/mol)	K1/(kcal/mol)	K2/(kcal/mol)	K3/(kcal/mol)
H Cm N+ Cm	4	0.00	0.00	0.00	-0.21

Geometries from QC Calculations. The binding energies obtained from quantum chemistry (QC) calculations were utilized as benchmarks in the development of our force field. In this study, the M05-2X or MP2 level of theory and aug-cc-pVDZ or and aug-cc-pVTZ basis sets were used for the QC calculation. Optimized geometries of TMA-H₂O, TMA-Br and Br-H₂O obtained using M05-2X/aug-cc-pVDZ are shown in Table S3-S5, respectively, while binding energies from different combinations of QC setting are given in Table S6. The geometries are shown in Cartesian coordinates in Å units.

Table S3. Optimized TMA-H₂O geometry

Atom	X	Y	Z
N	0.70943	-0.00061	0
C	0.17174	-0.68206	-1.21562
H	-0.91638	-0.59572	-1.19579
H	0.48146	-1.72883	-1.19091
H	0.58281	-0.18868	-2.09871
C	2.19778	-0.07174	0.00091
H	2.57243	0.42332	-0.89733
H	2.49708	-1.12185	0.00617
H	2.57167	0.43216	0.89456
C	0.27174	1.42602	-0.00675
H	0.66495	1.90699	-0.90461
H	0.66324	1.91506	0.88751
H	-0.81919	1.44075	-0.00787
C	0.17089	-0.67092	1.22145
H	0.48122	-1.71769	1.20684
H	-0.91725	-0.58534	1.1997
H	0.58088	-0.16899	2.10026
Ow	-2.91004	-0.00097	-0.00018
Hw	-3.50398	0.75569	0.00098

Hw	-3.4976	-0.76265	0.00068
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Table S4. Optimized TMA-Br geometry

Atom	X	Y	Z
N	-1.68296	-0.00003	0.00014
C	-1.17463	-0.47108	1.32537
H	-0.07772	-0.45646	1.27819
H	-1.55321	-1.4824	1.49185
H	-1.55015	0.20933	2.09317
C	-3.16464	0.00244	0.0011
H	-3.51627	0.34794	-0.97345
H	-3.51748	-1.01388	0.18985
H	-3.51467	0.67436	0.78786
C	-1.17726	-0.91384	-1.07025
H	-0.0804	-0.88644	-1.03269
H	-1.55205	-0.55111	-2.03014
H	-1.55845	-1.91724	-0.86612
C	-1.1735	1.38249	-0.25599
H	-1.55156	2.03458	0.53496
H	-1.5481	1.70549	-1.23007
H	-0.07678	1.33419	-0.24539
Br	2.05765	0.00005	-0.00001

Table S5. Optimized Br-H₂O geometry

Atom	X	Y	Z
Hw	-1.65565	-0.30953	0.00025
Ow	-2.60738	-0.0805	-0.00003
Hw	-2.55911	0.87766	0.00007
Br	0.7164	0.00217	-.00000

Table S6. Dimer binding energies calculated at various levels of theory and basis sets.

Binding pair	TMA-H ₂ O/(kcal/mol)	TMA-Br/(kcal/mol)	Br-H ₂ O/(kcal/mol)
M05-2X/aug-cc-pVDZ	-10.62	-91.57	-13.23
M05-2X/aug-cc-pVTZ	-10.37	-91.53	-13.38
MP2/aug-cc-pVDZ	-10.84	-94.37	-12.24
MP2/aug-cc-pVTZ	-10.46	-96.37	-12.83

Binding Energy Paths. The binding energy paths were calculated by fixing a series of distance between cationic nitrogen and Br anion (for TMA-Br dimer) and between Br and water oxygen (for Br-water). Thereafter, for each separation r , the dimer geometry was optimized keeping the separation constrained. Br-water and TMA-Br binding energy paths obtained from *ab initio* calculation using M05-2X/aug-cc-pVDZ are shown in Figure S1 where they are compared with FF-orig and FF-fit predictions. Since only TMA-water interactions were adjusted in the FF-fit, the two force fields predict identical values for the Br-water and TMA-Br dimers.

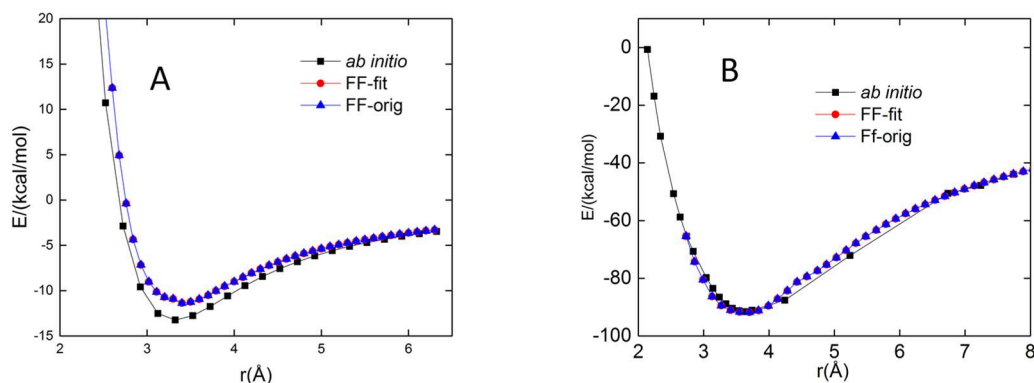


Figure S1. Comparison of Br-H₂O binding energy (A) and TMA-Br binding energy(B) between QC calculations using M05-2X/aug-cc-pVDZ and force field predictions.

Simulation trajectory lengths. The equilibration time and trajectory length for each simulated system are given in Table S7. All systems had an equilibration period over 3 ns or longer while trajectory length for production runs were longer than 20ns.

Table S7. Detailed equilibration time and trajectory length

System	Equilibration time/ns	Production run/ns
TMA-1:10	3.0	24
TMA-1:20	3.0	20
TMA-1:30	3.0	23
TMA-1:63	5.0	27
TMA-1:500	3.0	24
TBA-1:10	3.0	27
TBA-1:20	3.0	27
TBA-1:30	3.0	25
TBA-1:63	5.0	32
TBA-1:500	3.0	25

Coordination numbers and cation distribution. Coordination number (CN) of water molecules within the first hydration shell of cation is illustrated in Figure S2, showing prominent concentration dependence. At dilute concentration of 1:500, the CN of water around TMA was 33.7. As the concentration of TMA increased to 1:10 the CN decreased to 21.75. The CN in the TBA systems is also shown in Figure S2, which ranged between 25.91 in dilute solution to 10.42 at 1:10 composition.

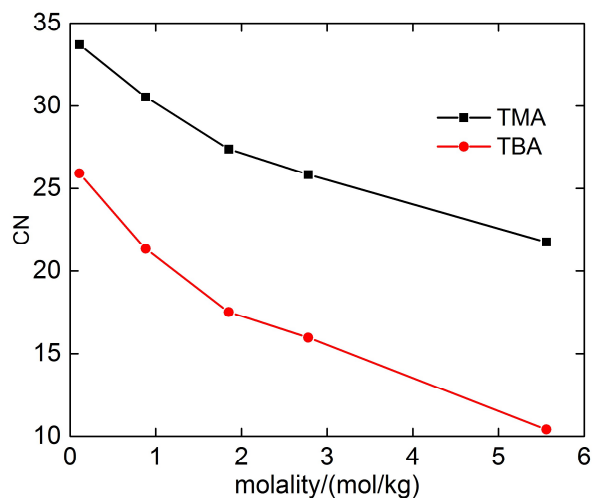


Figure S2 Coordination number of water molecule within the first hydration shell of TAA ions.

A snapshot illustrating the spatial distribution of nitrogen atoms for 1:20 compositions of TMA and TBA-based systems is given in Figure S3. As can be seen from Figure S3(A), TMA cations are uniformly distributed in the simulation box. Fig. S3(B) shows that though the TBA cations form an inter-penetrating structure, their centers remain uniformly distributed at this composition.

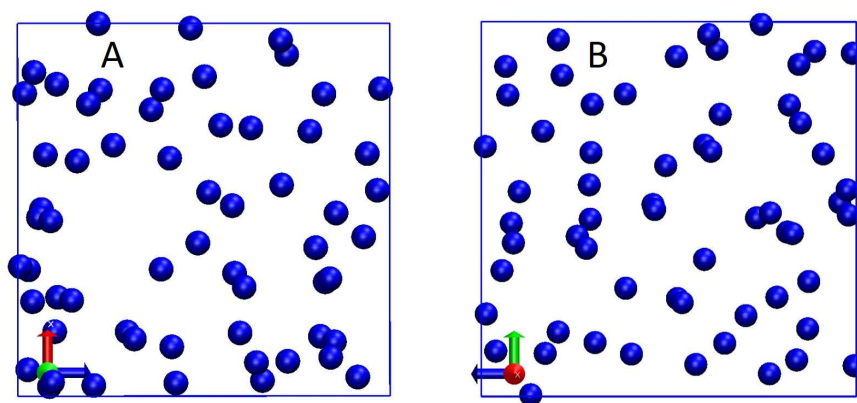


Figure S3: Snapshot of spatial distribution of nitrogens at 1:20 composition: A) TMA and B) TBA.

Residence times. The autocorrelation functions (ACF) obtained from our analysis of water residence near TAA cations and the corresponding fits with the KWW function are shown in Figure S4.

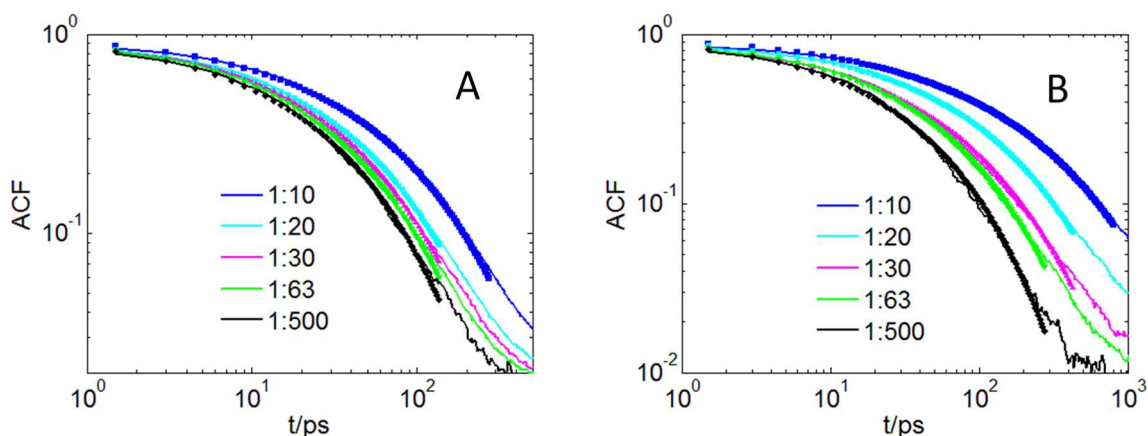


Figure S4. Residence ACFs (lines) and corresponding fits using the KWW function (symbols) for (A) TMA-water and (B) TBA-water

Concentration dependence of dynamic characteristics. To compare the relative effect of concentration and cation structure in Figure S5 we examine several dynamic characteristics. In Figure S5(A) the self-diffusion of Br anion is shown for TMA and TBA-based systems as a function of composition. The self-diffusion coefficient of Br decreases with increasing concentration and Br anions showing a noticeably slower mobility in the TBA-based system than in TMA-based one. In Figure S5(B) we plot the normalized diffusion coefficient of water in the

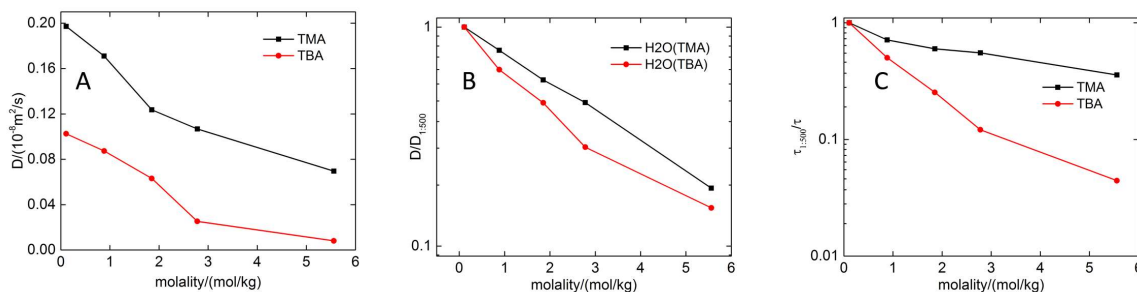


Figure S5. A) Concentration dependence of Br anion self-diffusion in TMA and TBA-based systems. B) Normalized (by the corresponding value at 1:500 concentration) the self-diffusion coefficient of water and C) the residence time of water near TAA.

two systems. Here we normalized the self-coefficient coefficients by the corresponding diffusivity at 1:500 composition. Figure S5(B) shows that diffusivity of water has a similar concentration dependence in both systems. In Figure S5(C) we plot the normalized characteristic residence times of water near cations. For this dynamic characteristic we see that the characteristic residence times of water in TBA have significantly stronger concentration dependence than in TMA-based system.

While in the TMA-based system the residence time of water changes about factor of two over the concentration range investigated, in the TBA-based system the concentration effect is an order of magnitude larger.

References

[1] Borodin, O., Grant D. S., and Peng F. Molecular dynamics simulations of lithium alkyl carbonates. *J. Phys. Chem. B* **2006**, *110*, 22773-22779.