



Electrostatic charge confinement using bulky tetraoctylammonium cation and four anions



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ABSTRACT

Thanks to large opposite electrostatic charges, cations and anions establish strong ionic bonds. However, applications of ionic systems – electrolytes, gas capture, solubilization, etc. – benefit from weaker non-covalent bonds. The common approaches are addition of cosolvents and delocalization of electron charge density via functionalization of ions. We report fine tuning of closest-approach distances, effective radii, and cation geometry by different anions using the semi-empirical molecular dynamics simulations. We found that long fatty acid chains employed in the tetraalkylammonium cation are largely inefficient and new substituents must be developed. The reported results foster progress of task-specific ionic liquids.

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1. Introduction

Room-temperature ionic liquids (RTILs) are organic salts with low melting points (below 100 °C) [1–4]. RTILs comprise bulky organic cations and inorganic or organic anions, both exhibiting principal influence on the physical chemical properties of a liquid. A relatively low melting point, when compared with hardcore ionic compounds, is achieved due to an energetically inefficient cation–anion packing and, therefore, a hindered crystal structure formation. RTILs are applied as reaction medias, catalysts, solvents, charge carriers, gas scavengers, etc. [5–11]. The most currently used RTILs are those, in which the cation–anion attraction is weaker (no particular ion–ion binding site), whereas strongly coordinating ions (e.g. chlorides, acetates) exhibit high viscosity, low self-diffusion, mediocre miscibility with molecular cosolvents, and higher melting points [12–15]. The latter tend to exist as ionic aggregates with an even number of ions, sometimes denoted as liquid ion pairs [16].

The size and the shape of both ions determine a phase behavior of the corresponding RTIL. MacFarlane and coworkers [17] employed crystallographic analysis to demonstrate the dependence of ion sizes on melting point of RTIL: more bulky ions imply smaller melting points. Asymmetry of a cation structure additionally fosters a wider liquid range. The π – π interactions, in

turn, decrease ionic mobility and increase melting points, according to Dupont and coworkers [18]. Effect of alkyl chains on ionic conductivity and shear viscosity in dialkylimidazolium RTILs was thoroughly addressed in a few recent works [19–21]. Well-defined dependences were obtained and different effects of the anions were determined. Large-scale and multi-resolution computer simulations are actively applied for identify various electronic, physical and chemical properties of RTILs [22–25].

A relatively weak cation–anion binding appears particularly beneficial for universality of the solvent, gas capture and mobile ionic subsystem (electrochemical applications). The cations and anions with delocalized charge densities and buried charged centers are expected to exhibit an advanced behavior in this aspect. A positive charge in the tetraalkylammonium and tetraalkylphosphonium cations is centered predominantly on the nitrogen atom, being defended by the alkyl groups. One would anticipate that anions are unable to approach this center and, thus, an electrostatic coupling of the cation and the anion is smaller than in other RTILs. Similar considerations apply to the tetrafluorophenylborate anion, wherein boron is defended by the four fluorinated phenyl rings. It still remains unclear to which extent the positive/negative charge can be confined by means of such functionalization and whether the size and the shape of the attached groups play a significant role.

In the present work, molecular dynamics simulations, which include electronic polarization and quantum effects, were employed to identify the closest-approach distances and relevant ionic structures for RTILs composed of the $(C_8H_{17})_4N$ cation, the

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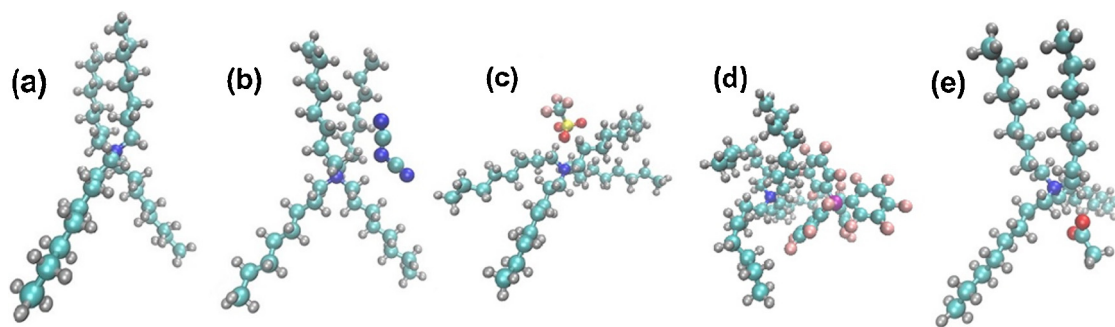


Fig. 1. Optimized geometries of the simulated ions: (a) tetraoctylammonium cation; (b) dicyanamide anion; (c) trifluoromethanesulfonate anion; (d) tetrafluorophenylborate anion; (e) acetate anion. The depicted structures were taken from the equilibrated systems at room conditions, for visualization purposes.

dicyanamide $N(CN)_2$ anion, the trifluoromethanesulfonate CF_3SO_3 anion, the tetrafluorophenylborate $B(C_6F_5)_4$ anion and the acetate CH_3COO anion. The primary goal of this work is to identify to which extent the alkyl chains are able to prevent strong cation–anion coordination.

2. Methodology

The results were obtained using semi-empirical molecular dynamics simulations, PM7-MD [26–31]. The method employs immediate forces on every atom of the simulated system from the PM7 Hamiltonian to propagate Newton equations-of-motion with a given integration time-step.

Unlike classical MD, PM7-MD allows to capture quantum effects, such as chemical bonding, electronic polarization, tunneling and so on. Validation and application of PM6 and PM7 to manifold systems of physical and chemical interest are described elsewhere [26,31,32].

Simulations of the systems (Fig. 1) were carried out at 300 K and this constant temperature was maintained by the Andersen thermostat [33]. Each system was sampled during 200 ps with a time-step of 1.0 fs. The coordinate frames were saved every 5.0 fs, whereas the energy components were saved every 50.0 fs. Equilibration was controlled in terms of the thermodynamic quantities evolution.

The analysis was done in terms of distance probabilities (pair correlation functions) upon thermal motion and distribution of selected angles. The atoms with the largest positive or negative point charges on them belonging to the cation (nitrogen) and the anions (oxygen, sulfur, boron, nitrogen) were used to investigate the closest-approach distance.

Visual Molecular Dynamics (VMD)[34] and Gabedit [35] front-ends were used to prepare the MD systems and analyze the results.

3. Results and discussion

Fig. 1 depicts optimized ionic configurations of the simulated species. The tetraoctylammonium, $(C_8H_{17})_4N$, cation is analogous to the tetraethylammonium and tetrabutylammonium cations, which constitute the basis of many commercially applied electrolyte solutions. The nitrogen atom of the X_4N^+ cations, where $N=2, 4, 6, 8$, is buried relatively far from the surface formed by hydrophobic groups. The positive charge (electron deficiency) is concentrated at the geometric center of the cation. One believes that the anions are unable to tightly approach this electron deficient center, and therefore, the cation–anion Coulombic attraction gets problematic, when compared with other cation structures. Weakening electrostatic interactions is favorable for numerous applications, since it promotes boosts properties of the

corresponding system and increases solubility/miscibility in molecular solvents.

Equilibration of the simulated systems is exemplified in Fig. 2 in terms of potential energy. An average equilibration time at 300 K is 10 ps, after which no drift was observed. These first 10 ps of the trajectory were disregarded and the analysis was performed on the remaining 190 ps. The potential energy was defined as heat of formation, as defined in PM7 [36], of the heated (i.e. non-equilibrated) ionic configuration and, thus, allows to compare thermodynamic stabilities of the ions in relation to the corresponding simple substances. Note that the depicted potential energy of the $N(C_8H_{17})_4$ cation was taken from the simulation of the isolated cation, whereas the potential energies of the other systems correspond to the neutral ion pairs. In this context, it can be understood why this heat of formation is least favorable. Ions are less favorable than neutral species (e.g. ion pairs).

The closest-approach distance (Fig. 3) is strongly dependent on the anion. The distances were derived from thermal motion,

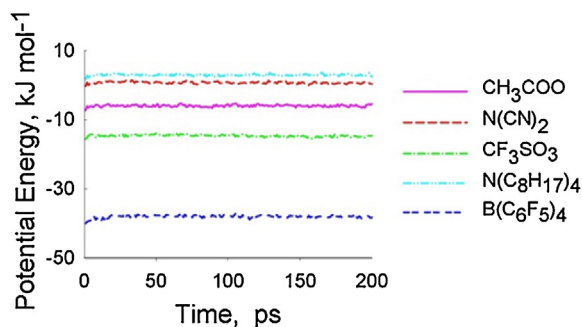


Fig. 2. Evolution of potential energies in the course of simulations.

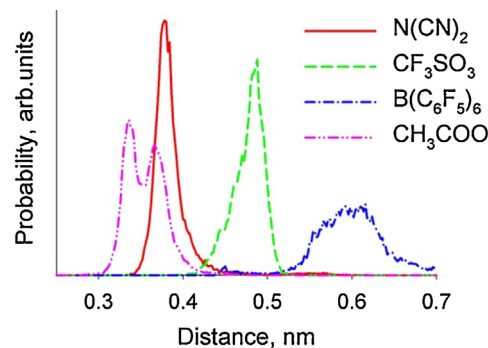


Fig. 3. Probabilities of the inter-ionic separations implemented during thermal motion at room conditions. The depicted distances are between the most electron deficient atom of the cation (N) and the representative atom of the anion: central N for $N(CN)_2$, S for CF_3SO_3 , B for $B(C_6F_5)_6$, O for CH_3COO .

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