



Selective cation depletion from an ionic liquid droplet under an electric field



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ARTICLE INFO

Article history:

Received 15 March 2017

Received in revised form 19 August 2017

Accepted 25 August 2017

Available online 1 September 2017

Keywords:

Molecular dynamics

Ionic liquid

Intermolecular interaction

Electrophoresis

Ion depletion

ABSTRACT

We conducted MD simulation to investigate the general electrohydrodynamic behavior of droplets of imidazolium-based ionic liquids composed of 1-ethyl-3-methylimidazolium (EMIM) anion and either bis(trifluoromethylsulfonyl)imide (NTf₂) or ethylsulfate (ES) cation. The cation depletion phenomena observed in the previous work [J. Phys. Chem. Lett. 5 3021 (2014)] is analyzed in detail to clarify its mechanism. Shape deformation due to electric stress and the ion distributions inside the droplet are calculated with 200 ion pairs and the intermolecular interactions between ions are directly analyzed. Together with an analytical interpretation of the conducting droplet in an electric field, we show that the MD simulation successfully explains the mechanism of selective ion depletion of an ionic liquid droplet in an electric field, and the retreating motion of the droplet observed by experiments.

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1. Introduction

Ionic liquids have unique chemical, electrochemical and physical properties, such as negligible vapor pressure, thermal stability, and tunability, and therefore have applications as solvents or electrolytes. Numerical investigation and molecular dynamics (MD) simulation have been used to characterize their electrochemical and physical properties [1–8]. MD simulations to investigate the thermodynamic properties of ionic liquids have shown good agreement with experimental data [2,3]. Furthermore, the predictions of physical and electrochemical properties have suggested ways to formulate new ionic liquids [9]. The understanding of the behaviors of ionic liquids under an external electric field is important in their various applications, including in fuel cells and electrowetting [10–12]. Studies on the electrohydrodynamics of ionic liquid in various situations have shown the possibilities of easy and efficient manipulation of ionic liquid droplets [13–15].

A charged ionic liquid droplet composed of ionic liquid 1-ethyl-3-methylimidazolium (EMIM) cation and bis-(trifluoromethylsulfonyl)imide (NTf₂) anion shows an interesting retreating behavior (Fig. 1a) [13]: Coulomb force under the electric field drives a positively-charged droplet from the positive electrode to the

negative electrode. However, the velocity of the droplet decreases continuously as the strength of the electric field increases, and the droplet returns to the positive electrode, unlike previously-reported back-and-forth bouncing droplet movements under the same experimental setup [14,15]. The droplet shows almost a constantly accelerated motion except for the moment it touches the positive electrode (Fig. 1b). This retreating behavior occurs because NTf₂ ions are depleted from the droplet under the applied electric field. Thus, the interaction between cations and anions is a key parameter in the retreating motion of ionic liquid droplets under an electric field, so the interaction between cations and anions of ionic liquids must be analyzed [16–18]. In droplets with NTf₂ anions, a weaker interaction occurs, that might lead to the retreating motion of the droplet. Although cation depletion has been verified in experiments by FTIR spectroscopy analysis, the behavior of the ions at the interface of the droplet has not been visualized and quantified at the molecular level. Therefore, a direct approach to calculate intermolecular interaction between cations and anions is crucial to fully understand the cation depletion phenomenon.

In this study, we use MD simulation to investigate the general electrohydrodynamic behavior of ionic liquid droplets under an electric field. Many MD studies have discussed the effects of an external electric field on the structure or dynamic properties of ionic liquids [19–21], but the intermolecular behavior and polarization of an ionic liquid droplet in an electric field have not yet been analyzed in detail, as far as we know. Here we focus more on the ion depletion from droplets rather than on the electrophoretic motion of whole droplets. To understand

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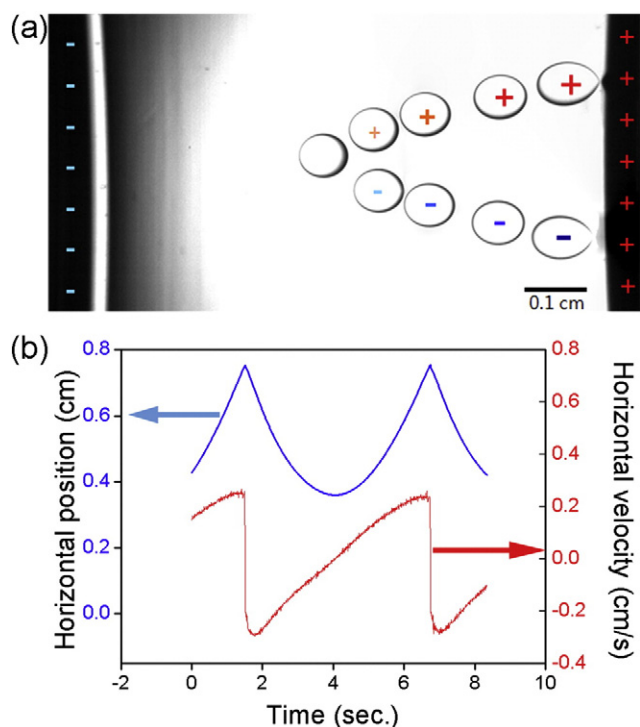


Fig. 1. Experimental results of the retreating behavior of an ionic liquid droplet [13] (a) Sequential images of a 400-nL EMIM-NTf2 droplet motion under 3.0 kV/cm. Symbols in the droplet indicate its net charge. (b) Horizontal position (blue) from the negative electrode and velocity (red) of the droplet.

the motion of ionic liquid molecules under an external electric field with respect to the molecular structure of the anions, the ionic motions in an imidazolium-based ionic liquid droplet with NTf2 anions are compared with those of a droplet of a non-retreating ionic liquid that has EMIM cations and ethylsulfate (ES) anions. The intermolecular interactions between cations and anions are also analyzed to clarify that the main cause of the different molecular behavior of the ionic liquids is due to the interaction between cations and anions. Results from this research may help explain the core mechanism of the retreating motion of an ionic liquid droplet in an electric field (Fig. 1).

2. Material and methods

MD simulations of ionic liquid droplets were conducted with EMIM-NTf2 and EMIM-ES (Fig. 2a). An EMIM-NTf2 molecule was parameterized using the force field model for ionic liquids that is based on the OPLS-AA/AMBER framework [22] (Fig. 2b), and an EMIM-ES molecule was parameterized using an OPLS-AA force field. The force-field information of ionic liquids includes intramolecular parameters such as bond stretching, angle bending, dihedral torsion, and partial charges of atoms, as well as force parameters related to van der Waals or Coulomb forces. The Packmol [23] program was used to obtain the initial coordinates of the molecules, and the open source software Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [24] was used for MD calculation. The pair potentials between molecules were calculated using a combination of the Lennard-Jones and Coulombic potentials with cutoff distances of 10 and 50 Å respectively, and the interaction potential parameters were calculated by geometric coupling where $\sigma_{ij} = (\sigma_i \times \sigma_j)^{0.5}$ and $\epsilon_{ij} = (\epsilon_i \times \epsilon_j)^{0.5}$. The long-range Coulombic interactions were computed by a particle-particle particle-mesh solver [25]; the time step of computation was 1 fs.

For the initial condition, we needed the stabilized equilibrium state of an ionic liquid droplet without an electric field, presumably with a spherical configuration at a given temperature. Initially, 200 cations

and 200 anions were randomly packed in a cubic box with periodic boundary conditions (Fig. 2c). The simulation box was large enough ($100 \times 100 \times 100$ Å) to exclude the effects of periodic conditions and to allow formation of a droplet of the liquid. The simulation domain was large enough to exclude the influences of neighboring cells (Supplementary material). The ions were simulated in a vacuum environment. In the first step, the energy of the system was minimized with a conjugate gradient algorithm to remove the effects of bad configurations from the random initial distribution. Then MD computation was conducted with a microcanonical ensemble (NVE ensemble) but we wanted our system temperature to be ~ 300 K to match the experimental condition. While the NVE ensemble was used, a geometrical instability caused by the randomly-packed initial configuration imparted additional energy to the system. This summative energy increased the kinetic energy to the equilibration process, coarsened the equilibrated shape, and increased the temperature.

To remove this additional energy, we used a simple velocity rescaling method that is typically used with an NVT ensemble [26]. The velocities of each atom were generated using a random number generator with the specified temperature (300 K) initially; the temperature increased over time due to the remaining excess energy stored in the initial configuration. Thereafter, the computation was restarted with the previous positions of the atoms, but with new velocity ensembles generated at 300 K. This velocity rescaling was repeated until the temperature converged to 300 K, and the simulation result was the same as obtained using the Nose-Hoover thermostat with an NVT ensemble. Physically, this process represents the energy dissipation from a high energy state in a cubic configuration to a low energy state in a spherical one. The equilibration runs took 15 ns, which seems sufficient for a system of 200 ion pairs [17,27–30], then the canonical ensemble was subject to a 3-ns dynamic simulation in which the external electric field was applied. After MD computation, LAMMPS tools and a Visual Molecular Dynamics (VMD) [31] package were used for analysis and visualization. At the equilibrium, the droplet became spherical (Fig. 2c).

We postulated that the bouncing motion (Fig. 1a) of a positively-charged ionic liquid droplet was due to the continuous loss of positive charges of the droplet. Therefore, the purpose of this research was to use MD simulation to quantify the cation depletion phenomenon under an external electric field. As in Fig. 1a, the neutral ionic liquid droplet also lost positive ions even when it was far from the electrode. Thus, we assumed the total charge inside the ionic liquid droplet could not affect the cation depletion phenomenon, but that the external electric field could affect it. For that reason, we simulated with a neutral droplet. Further, the neutral droplet did not interact with the electrode, so we neglected the interactions between the ionic liquid droplet and each electrode atom. Thus, in this MD simulation only the external electric field was applied to charged atoms.

3. Results and discussion

Before the electric field was applied, the density and structure of the ionic liquid droplet were analyzed to verify the equilibrium state of the droplet. To observe the time evolution of the density of an EMIM-NTf2 droplet during equilibration (Fig. 3a), the density was calculated from 0 to 1 ns in increments 0.01 ns, then from 1 ns to 15 ns in increments of 0.1 ns, and plotted as averages and standard deviations. The density stabilized after 2 ns and remained almost constant at ~ 1.54 g/cm³, which agrees well with the experimental value (1.519 g/cm³). This result confirms that the equilibration time (15 ns) is sufficient that the system can reach equilibrium.

The site-site intermolecular radial distribution functions in the ionic liquid droplet were also calculated (Fig. 3b). The (C-A) distribution function between the C₂ carbon atom of the EMIM cation (C) and the nitrogen atoms of the NTf2 anion (A) had a peak of ~ 5 Å. The distribution functions of C-C and A-A first peaked at ~ 8 Å, and those distribution functions show opposite tendencies to the distribution function of

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