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Influence of ion size asymmetry on the properties of ionic liquid–vapour interfaces

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Abstract

The influence of ion size asymmetry on the properties of ionic liquid–vapour interfaces is investigated using molecular dynamics simulations of the soft primitive model. Ion size asymmetry results in charge separation at the liquid–vapour interface and therefore in a local violation of the electroneutrality condition. For moderate size asymmetries the electrostatic potential at the interface can reach values of the order of 0.1 V. Size asymmetry plays a very important role in determining ion adsorption at the liquid–vapour interface of ionic mixtures. The interfacial adsorption of the bigger component results in an increase of the electrostatic potential, and a reduction of the interfacial surface tension. Our results show that ionic mixtures provide a very efficient way to tune the electrostatics and surface properties of ionic liquid–vapour interfaces.

1. Introduction

The investigation of interfacial properties of ionic liquids is of relevance to understand fundamental questions concerned with phase equilibria and critical phenomena [1–4], wetting phenomena of ionic surfaces [5], or double-layer effects at molten salt interfaces [6]. An understanding of the structure of ionic liquid interfaces is essential to advance in the description of interfaces between immiscible electrolyte solutions (ITIES), and the charge transfer occurring between them [7]. On the practical side, an understanding of the interfacial properties of ionic liquids is relevant to technological applications of these systems as environmentally friendly solvents [8, 9].

Computer simulations provide a means to obtain detailed quantitative information on the structure and thermodynamics of ionic interfaces. Recently, using hybrid molecular dynamics, canonical molecular dynamics and Monte Carlo simulations, we investigated the liquid–vapour interface of size symmetric and size asymmetric ionic liquids. We computed the surface tension

of the restricted primitive model (RPM) [1, 2]. The simulated surface tensions have served as a benchmark to test the accuracy of earlier theoretical calculations [10, 11].

The RPM provides the simplest representation of an ionic liquid. Despite its simplicity, it is accurate in predicting several properties of real molten salts [12, 1, 2]. The RPM predicts a very rich physical behaviour: ion association [13], cavity nucleation and surface drying [14], and solid–solid and order–disorder transitions [15–17]. Several of these observations, particularly the existence of cavities and the structure of the solid phases, are consistent with recent experimental observations [8, 18, 24].

In this paper we consider simulations of size asymmetric ionic liquids and ionic liquid mixtures. Size asymmetry has a dramatic effect on the phase diagram of ionic liquids. A decrease in the critical temperature [3, 4, 2] that conflicts with predictions from mean field theories is observed. Also the surface tensions of size-asymmetric ionic liquids do not conform to a simple corresponding states law [2]. In this work we investigate using computer simulations two important consequences of size asymmetry: firstly charge separation at the ionic-liquid vapour interface, and secondly ion adsorption at the liquid–vapour interface of ionic liquid mixtures. Our results show that relatively small differences in ion diameter can play an important role in determining the electrostatics of the liquid–vapour interface and ion surface activity.

2. Models and simulation details

We consider an ionic liquid consisting of spherical rigid ions interacting through the so-called ‘soft primitive model’ (SPM) [1, 2]. The SPM is closely connected to the RPM, the main difference being that the RPM hard core repulsion is replaced by a soft repulsive interaction. The potential is defined as

$$u_{ij}(r) = A \left(\frac{\sigma_{ij}}{r} \right)^n + \frac{z_i z_j e^2}{4\pi \epsilon_0 r} \quad (1)$$

where r is the distance between two ions, e is the electronic charge, z_i is the valence of the ion i , and ϵ_0 is the vacuum permittivity. The exponent $n = 225$ [1, 2] defines the ‘hardness’ of the repulsive interaction. The effective diameter, $\sigma_{ij} = 0.5(\sigma_i + \sigma_j)$, is defined in terms of the ion diameters. The constant $A = \frac{|z_i z_j| e^2}{4\pi \epsilon_0 \sigma_{+-}}$ follows from the condition $u_{+-}(\sigma_{+-}) = 0$, i.e., the potential between unlike charged ions is zero at $r = \sigma_{+-}$.

Throughout the paper we use reduced units. The length is reduced by the effective diameter, σ_{+-} , and the energy by the minimum of the potential between unlike ions, $\epsilon = u_{+-}(r_{\min}) = |A[n^{n/(1-n)} - n^{1/(1-n)}]|$, where the bars indicate absolute value, and $r_{\min} = n^{1/(n-1)}\sigma_{+-}$ defines the location of the minimum of the potential energy curve. We have shown in our previous work [1, 2] that the SPM model predicts interfacial properties in excellent agreement with those of the RPM.

The interface was modelled as a liquid slab in a rectangular box. The box length in the direction perpendicular to the liquid vapour interface, L_z , was at least four times longer than in x and y directions. Full periodic boundary conditions were used in all three directions. The Coulombic interactions were computed using the Ewald summation method [19, 2]. The molecular dynamics simulations were performed at constant temperature [20]. The trajectories involved 10^6 time steps, the time step being $\delta t^* = \delta t \sqrt{\epsilon / (m \sigma_{+-}^2)} = 0.0002$ – 0.0004 . Cations and anions were assigned the same mass. All the simulations reported below were performed using 3000 ions at the reduced temperature $T^* = k_B T / \epsilon = 0.03$. Averages were obtained over five independent trajectories.

Table 1. Interfacial properties of ionic liquids and ionic liquid mixtures for a representative reduced temperature, $T^* = k_B T / \epsilon = 0.03$. σ_+ and σ_- represent the cation and anion diameters respectively. In the case of mixtures (system 3) σ_b is the diameter of the bigger anion. $x_i = N_i / N$ represents the number fraction of ions of species i . N is the total number of ions. $\rho^* = (N/V)\sigma_{+-}^3$ is the reduced density. $\gamma^* = \gamma\sigma_{+-}^2/\epsilon$ is the reduced surface tension, and ϕ is the electrostatic potential. The numbers in parenthesis indicate the error associated with the data, e.g., 0.0057(7) means 0.0057 ± 0.0007 .

System	$[\sigma_+/\sigma_-, \sigma_b/\sigma_-]$	$[x_+, x_-, x_b]$	ρ_l^*	ρ_v^*	γ^*	ϕ (V)
1	[0.5, —]	[0.5, 0.5, —]	0.415(3)	...	0.0057(7)	0.09
2	[0.25, —]	[0.5, 0.5, —]	0.254(1)	0.0001(1)	0.0023(3)	0.15
3	[1, 2]	[0.5, 0.492, 0.008]	0.467(3)	...	0.0059(12)	0.30

The surface tension of the liquid–vapour interface was computed using the pressure tensor route,

$$\gamma = L_z [P_{zz} - \frac{1}{2}(P_{xx} + P_{yy})] \quad (2)$$

where $P_{\alpha\beta}$ are the pressure components, which were computed from the virial expressions (see for instance [2]).

We have recently shown that equation (2) can give erroneous surface tensions when the interfacial area is small [2]. This is a finite size effect (‘periodic error’) that is connected to the use of periodic boundary conditions. This effect becomes important when the interfacial area is small, typically $A = (L_x \times L_y) < (10\sigma)^2$, where σ is the diameter of the biggest species in the simulation box. All our simulations were performed using large interfacial areas in order to avoid the periodic error.

3. Results

3.1. Electrostatic potential of ionic liquid–vapour interfaces

Table 1 summarizes the systems simulated in this work. The pure ionic liquids (systems 1 and 2 in table 1) consisted of an equimolar mixture of cations and anions of unequal diameter. The surface tension and coexistence densities obtained in the present work were in excellent agreement with our previous results for these systems [2].

Size asymmetry has an important effect on the ion distribution at the liquid–vapour interface. The different chemical potentials of small and big ions result in charge separation at the interface, leading to a local violation of the electroneutrality condition. This issue has been investigated in the case of molten salts using the gradient expansion theory [6]. The electrostatic field, E_z , originated by the charge separation at the interface can be computed using Gauss’s theorem,

$$E_z(z) = -\frac{d\phi}{dz} = \frac{1}{\epsilon_0} \int_{-\infty}^z \rho_q(z') dz', \quad (3)$$

where ϕ is the electrostatic potential and $\rho_q(z)$ is the charge density at the position z . The charge density was computed by dividing the simulation cell into layers parallel to the liquid–vapour interface, and computing the local charge density in each layer. Figure 1(a) shows the electrostatic field for two representative size asymmetric ionic liquids (systems 1 and 2 in table 1). The charge separation at the interface results in electrostatic fields of the order of 10^8 V m^{-1} . We note that the sign of the field is consistent with the fact there is a small excess of the bigger ions, anions in our case, in the vapour region of the interface. This observation is consistent with earlier theoretical investigations [6]. The increase in size asymmetry enhances the effect of charge separation, and as a consequence the electrostatic

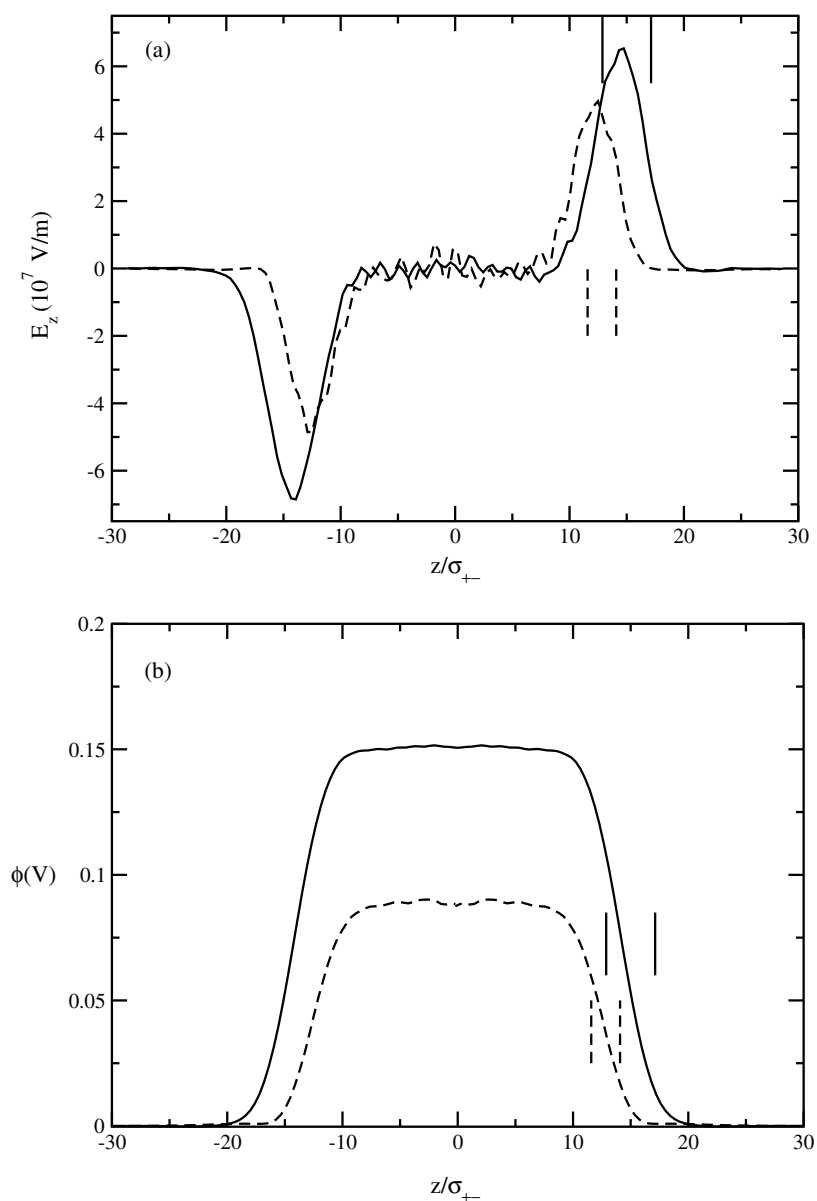


Figure 1. (a) Electrostatic field and (b) electrostatic potential, for ionic liquids with size asymmetries, $\sigma_+/\sigma_- = 0.5$ (dashed lines) and 0.25 (full line). The vertical lines represent the width of the corresponding liquid–vapour interface. The width was estimated by fitting the density profiles to a hyperbolic tangent function (see [22]). The electrostatic potentials correspond to an average using both liquid–vapour interfaces.

field increases in magnitude (cf figure 1(a)). Our results show that the electrostatic field extends slightly beyond the interfacial width. The latter was computed from a fitting of our density profiles to a hyperbolic tangent function [22].

The electrostatic potential provides a quantitative measurement of the magnitude of the charge separation at the interface. For the ionic liquids considered in this work we obtain

electrostatic potentials of the order of 0.1 V (cf figure 1(b)), and as suggested by the electrostatic field an increase in size asymmetry results in an increase of the potential. These potentials are of the same order of magnitude as the ones observed in ionic Newton Black films [23] for instance, but smaller than the ones reported in simulation studies of imidazolium ionic liquids [21]. We note nonetheless that a proper comparison between our results and those of imidazolium salts requires a careful choice of the thermodynamic conditions. In this way it should be possible to address the effect that the molecular structure of the ions has on the magnitude of the electrostatic potential.

3.2. Ion adsorption at ionic liquid–vapour interfaces

In this section we analyse the interfacial properties of a representative mixture of ionic liquids. The mixture consists of cations and anions of the same size, and a small fraction of anions of bigger size. The exact number fractions used in this investigation are reported in table 1 (system 3).

Figure 2(a) represents a typical snapshot of the ionic mixture, which clearly shows that the bigger ions preferentially adsorb at the interface. The adsorption can be quantified by computing the density profile (cf figure 2(b)), which exhibits a maximum at the interface. Integration of the density profile indicates that about 70% of the bigger ions are adsorbed at the interface. The accumulation of the bigger negative ion at the interface is followed by a depletion of the smaller negative ion. This depletion can be easily seen in a molar fraction density profile (not shown), which for the smaller anion shows a clear minimum at the interface. Our simulations show that the introduction of a third species in the ionic liquid results in charge separation at the interface. Interestingly, the simulations show that the electrostatic potential for this mixture is larger than the potential of the equimolar mixtures (systems 1 and 2 in table 1). Taking into account that the big ions only represent 1% of the total number of particles, our result points out the sensitivity of the interfacial properties of ionic mixtures to ion size asymmetry.

We have also investigated the effect of ion adsorption on the surface tension of the liquid–vapour interface. The resulting surface tension is smaller than the surface tension of the equimolar-equisized system. We obtain $\gamma^* = 0.0057$ versus $\gamma^* = 0.007$ (see table 1 and data reported in [2]), which represents about a 20% reduction in the surface tension. In fact the surface tension for the mixture is of the same order as the one we obtained above for system 1 (see table 1). We note that the latter system corresponds to an ionic liquid where the smaller anion has been completely replaced by the bigger anion.

4. Conclusions

In this paper we have investigated the implications of ion size asymmetry on charge separation and ion adsorption at the ionic liquid–vapour interface. It is clear that size asymmetry results in a local violation of the electroneutrality condition at the interface, i.e., charge separation. In agreement with theoretical studies on molten salts we observe that there is a small excess of the bigger ions on the vapour side of the ionic interface. The charge separation and the associated interfacial electrostatic potential increase with size asymmetry. We have found that the electrostatic potentials can be quite significant, ~ 0.1 V, for relatively small ion size asymmetries. These potentials are of the same order of magnitude than those computed in ionic Newton Black films [23].

In addition, we have investigated the effect of ion size asymmetry on ion adsorption at the liquid–vapour interface of ionic liquid mixtures. Our simulations show that the bigger component strongly adsorbs at the interface. In fact, small amounts of the bigger ion result in

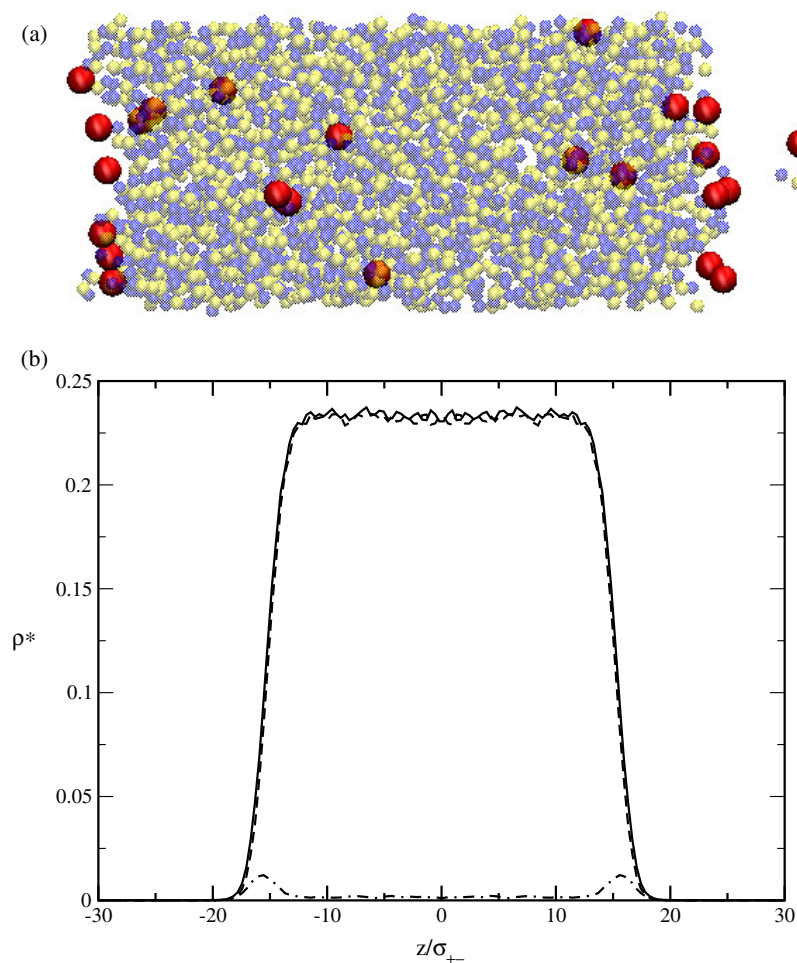


Figure 2. (a) Representative snapshot of an ionic liquid mixture (system 3 in table 1). Small cations and anions are shown as translucent spheres. A neutral cluster is shown in the vapour phase. (b) Density profiles for the ionic liquid mixture. All the densities are in reduced units, $\rho_i^* = (N_i/V)\sigma_{+-}^3$, where σ_{+-} is the effective diameter of the small ions. Full lines represent the density profile of the small cations, dashed lines small anions, dashed-dotted lines big anions. The density profile correspond to an average using both liquid–vapour interfaces.

(This figure is in colour only in the electronic version)

significant electrostatic potentials and a drastic reduction of the interfacial surface tension. These results suggest that ionic liquid mixtures provide a very efficient way to tune the electrostatic properties and surface tensions of ionic liquid–vapour interfaces. Future work will include further extensions of the ideas presented in this paper.

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