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Interfacial phase transitions in imidazolium-based ionic liquids

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Abstract

We report measurements of the surface tension and capillary wave spectra at the liquid/vapour interface of the ionic liquids $[\text{C}_4\text{mim}]^+\text{X}^-$ ($\text{X}^- = \text{Cl}^-, \text{AlCl}_4^-$) and compare these with recent results of $[\text{C}_4\text{mim}]^+\text{PF}_6^-$. Special attention is given to the temperature dependence of the surface dipole moment density $\gamma(T)$, which has been derived from the capillary wave spectra with the aid of the properly extended dispersion relation. For $[\text{C}_4\text{mim}]^+\text{PF}_6^-$ an order-disorder interfacial phase transition with a critical temperature of $T_c = 385$ K is found, which has not been reported before. At higher temperatures a first order ferroelectric surface phase transition is indicated in $\gamma(T)$ of both $[\text{C}_4\text{mim}]^+\text{PF}_6^-$ and $[\text{C}_4\text{mim}]^+\text{Cl}^-$ melts. Increasing the anion size in $[\text{C}_4\text{mim}]^+\text{AlCl}_4^-$, these interfacial phase transitions are suppressed.

1. Introduction

Ionic liquids are typically composed of a molecular cation and an inorganic anion. As such, their physico-chemical properties are influenced by both non-ionic molecular and ionic interactions. This is visible in the microscopic structure [1, 2] and, in particular, is responsible for the low melting points of ionic liquids [3]. This last property together with excellent solubility characteristics and low vapour pressures explains the increasing interest in ionic liquids as new solvents for chemical synthesis. In several applications like multiphase homogeneous catalytic reactions and nanoscale electrodeposition the interfacial properties play an important role, see e.g. [4, 5].

Focusing on the liquid/vapour interface the interplay of molecular and ionic interaction seems to be important for understanding of the interfacial structure and dynamics. Simulation calculations of dimethylimidazolium chloride at 400 and 500 K find an enhanced density near the interface different from the behaviour in molecular liquids or in pure molten salts like the alkali halides [6]. As for the interfacial structure, the atomistic simulation gives the following details: the cations are oriented with their planes perpendicular to the surface and their dipoles in the surface plane. No segregation of cations and anions is found in the surface plane. These results essentially agree with recent direct recoil spectrometric measurements, with one important exception. From the experimental investigation it is

concluded that the dipole vector of the imidazolium cation lies perpendicular to the surface plane [7]. Measurements have been performed for a variety of room-temperature ionic liquids of the type $[C_n\text{mim}]^+X^-$, where $[C_n\text{mim}]^+$ = 1- $C_n\text{H}_{2n+1}$ -3-methyl-imidazolium cation ($n = 4, 8, 12$) and $X^- = \text{Cl}^-, \text{Br}^-, \text{BF}_4^-, \text{PF}_6^-$. Only for the salts with the $[C_{12}\text{mim}]$ cation have measurements at a constant temperature above room temperature been recorded.

In this investigation we are interested in the structural changes at the liquid/vapour interface as a function of temperature for $[C_4\text{mim}]^+X^-$ ionic liquids with $X^- = \text{Cl}^-, \text{AlCl}_4^-$ and PF_6^- . With this aim we have probed the interface by surface light scattering measurements at various temperatures between 300 and 420 K. Attention is focused on the temperature variation of the surface dipole moment density which is determined from the capillary wave spectra together with the proper dispersion relation developed previously [8]. For this evaluation independent measurements of the surface tension are needed which have been obtained by the maximum bubble pressure method.

2. Experimental details

The non-invasive method of capillary wave spectroscopy and the method of maximal bubble pressure were used to investigate the properties of the liquid/vapour interface. The experimental set-up and data evaluation procedure for the capillary wave spectra has been described in detail in [8]. In principle, laser light (10 mW He–Ne laser, TEM₀₀, $\lambda = 632$ nm) is impinging on the liquid surface after passing the lenses–pinhole arrangement and the diffraction grating. Some of the light is specularly reflected and some scattered by the capillary waves. One of the diffracted beams was selected by a pinhole located just before the optical detector and mixed with the scattered light which falls on the same place on the detector surface. The output of the detector is modulated by beats between the diffracted and scattered light. The signal is recorded in the frequency domain with a fast Fourier transform analyser (SR670, Stanford Research Systems). The set-up used for the maximal bubble pressure measurement is similar to the one described previously [8]. Due to the freezing of the compound $[C_4\text{mim}]^+\text{Cl}^-$ at elevated temperatures near 341 K an additional heating element for the capillary was applied. The experiment and data analysis were performed as described previously [8].

The ionic liquid $[C_4\text{mim}]^+\text{Cl}^-$ and its mixtures with 50 at.% AlCl_3 and 40 at.% AlCl_3 , respectively, were used for the experiments. The 1-butyl-3-methyl-imidazolium chloride was synthesized using the procedure described in [9]. Two components, 1-methylimidazolium (Merck, purity of >99%) and 1-chlorbutan (Merck, purity of >99.6%) were used for the synthesis. For the cleaning of the product by the method of recrystallization acetonitrile (Merck, purity of >99.8%) was employed. All components were distilled before use. To remove adsorbed water the ionic liquids or their mixtures before the measurements were dried in vacuum (residual pressure $\sim 10^{-8}$ mbar) at 333 K for 24 h. The AlCl_3 (Merck, purity of >98%) was cleaned before use three times by vacuum distillation. All manipulations for the sample preparation were performed in an Ar glove box ($\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm).

3. Results

Figure 1 shows the temperature dependence of the surface tension σ obtained by the maximum bubble pressure method. Plotted are the results for the pure component $[C_4\text{mim}]^+\text{Cl}^-$ above its melting point of 341 K and for its mixture with 50 at.% AlCl_3 . Within experimental errors a linear dependence of σ on temperature is observed. Adding 50 at.% of AlCl_3 to the pure $[C_4\text{mim}]^+\text{Cl}^-$ ionic liquid the surface tension is reduced by roughly 10%, which implies that AlCl_3 acts as a surfactant. At the same time the temperature coefficient of σ is increased by

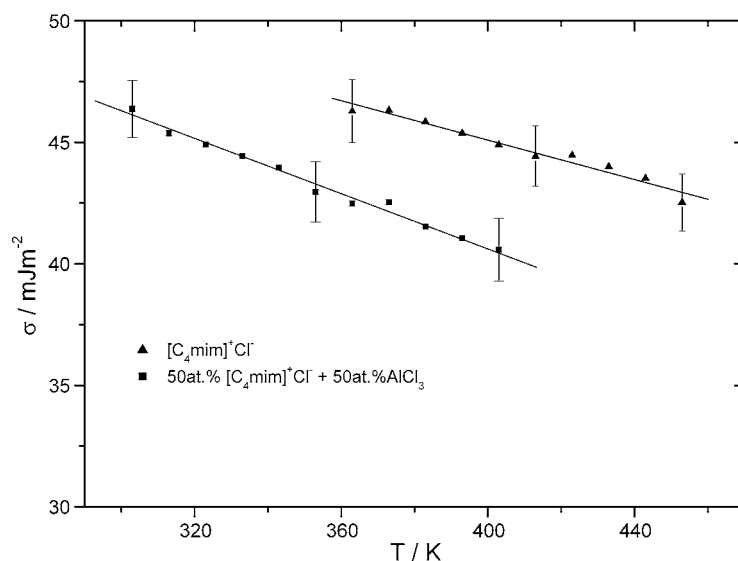


Figure 1. Surface tension σ of liquid $[\text{C}_4\text{mim}]^+\text{Cl}^-$ (▲) and a mixture with 50 at.% AlCl_3 (■) versus temperature T .

nearly 40%, indicating an increase of the surface excess entropy. Since the mixture is a neutral melt, i.e. one where the mole ratio of $[\text{C}_4\text{mim}]^+\text{Cl}^-$ and AlCl_3 is 1:1, the only anionic species is AlCl_4^- [10]. However, the acidity of this melt changes sharply with reference to the 1:1 composition and for $x_{\text{Al}} > 0.5$ species like Al_2Cl_7^- form [10].

In figure 2 we show the experimental peak frequencies ω_m of the capillary wave spectra of pure $[\text{C}_4\text{mim}]^+\text{Cl}^-$ and of two mixtures with 50 and 40 at.% AlCl_3 , respectively. The symbols give the experimental results as a function of temperature at constant wavenumber q ; the respective curves refer to model calculations; see below. The experimental points have been obtained in separate runs at different cooling rates of 5 and 2.5 K h^{-1} . Qualitatively, the temperature dependence of ω_m resembles that of $[\text{C}_4\text{mim}]^+\text{PF}_6^-$ [8].

4. Analysis of capillary wave spectra

In a previous paper [8] we derived the dispersion relation of capillary waves propagating on an ionic liquid/vapour interface

$$D(\omega, q) = (2\eta q^2/\rho)^2 \sqrt{1 + i\omega\rho/\eta q^2} - (i\omega + 2\eta q^2/\rho)^2 - (\sigma - \gamma^2 q/\varepsilon_0) q^3/\rho \quad (1)$$

where q and ω are the wavevector and frequency, ρ and η are the mass density and viscosity of the ionic liquid, and σ and γ are the surface tension and the dipole moment density at the ionic liquid/vacuum interface. The presence of the surface dipole moment is reflected in a potential difference between the vacuum and the ionic liquid, which is of the order of 1 V according to molecular dynamics simulations [11]. In the same paper [8] we have also derived an expression

$$\omega_m^2 = \omega_0^2 - \kappa^2 - \Delta^2 \{ \partial_q (\omega_0^2 - \kappa^2) \partial_q \ln [(\sigma - \gamma^2 q/\varepsilon_0) q^2 \kappa^3 \omega_0^4 / (\omega_0^2 + \kappa^2)] - \partial_q^2 (\omega_0^2 - \kappa^2) / 2 \} \quad (2)$$

where ω_0 and κ are the real and imaginary parts of the roots of the dispersion relation (1) satisfying the expression $D(\omega_0 + i\kappa, q) = 0$ and Δ is a wavevector deviation due to the

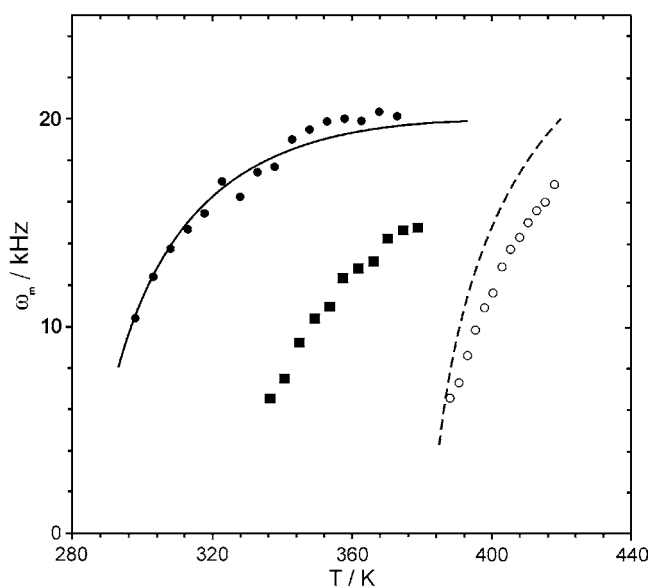


Figure 2. Temperature dependence of the capillary wave peak frequency ω_m : \circ , pure $[\text{C}_4\text{mim}]^+\text{Cl}^-$ and $q = 247 \text{ cm}^{-1}$; \blacksquare , 60% $[\text{C}_4\text{mim}]^+\text{Cl}^- + 40\% \text{ AlCl}_3$ mixture and $q = 224 \text{ cm}^{-1}$; \bullet , 50% $[\text{C}_4\text{mim}]^+\text{Cl}^- + 50\% \text{ AlCl}_3$ mixture and $q = 242 \text{ cm}^{-1}$; the dashed and solid lines correspond to $\omega_m(q, \Delta, \rho, \eta, \sigma, \gamma = 0)$ for pure $[\text{C}_4\text{mim}]^+\text{Cl}^-$ ($q = 247 \text{ cm}^{-1}$) and 50% $[\text{C}_4\text{mim}]^+\text{Cl}^- + 50\% \text{ AlCl}_3$ mixture ($q = 242 \text{ cm}^{-1}$), respectively.

instrumental broadening. For the present set-up the value of $\Delta = 15.7 \text{ cm}^{-1}$ is estimated from the diameter of the experimental spot being of the order of 0.2 cm.

As is seen in figure 2, addition of AlCl_3 substantially affects the value of ω_m . The lines in figure 2 correspond to values calculated from equation (2) in the case of absence of interfacial polarization, i.e. $\omega_m(q, \Delta, \rho, \eta, \sigma, \gamma = 0)$. The required temperature dependences of the surface tension are estimated from figure 1 while those of the mass density and viscosity are taken from the literature [12, 13]: $\sigma = 61.1 - 0.04T \text{ mN m}^{-1}$, $\rho = 1297.4 - 0.6032T \text{ kg m}^{-3}$ and $\eta = \sqrt{T} \exp[2232/(T - 163) - 9.4849] \text{ cP}$ for $[\text{C}_4\text{mim}]^+\text{Cl}^-$ and $\sigma = 63.1 - 0.056T \text{ mN m}^{-1}$, $\rho = 1465.1 - 0.7623T \text{ kg m}^{-3}$ and $\eta = \sqrt{T} \exp[484/(T - 184.5) - 3.819] \text{ cP}$ for a 50 at.% $[\text{C}_4\text{mim}]^+\text{Cl}^- - 50 \text{ at.}\% \text{ AlCl}_3$ mixture. The necessary density and viscosity data for the mixture with 40 at.% AlCl_3 are not available. As is seen, the prediction describes well the experimental observations for the mixture with 50 at.% AlCl_3 but it deviates substantially in the case of pure $[\text{C}_4\text{mim}]^+\text{Cl}^-$. This means that, similar to $[\text{C}_4\text{mim}]^+\text{PF}_6^-$, the $[\text{C}_4\text{mim}]^+\text{Cl}^-$ liquid/vapour interface is also polarized. However, addition of AlCl_3 obviously completely destroys the interfacial polarization. This effect should also be reflected in an increase of the surface entropy, which manifests itself in a stronger temperature dependence of the surface tension of the mixture compared to the pure liquid (see figure 1).

5. Discussion and conclusion

The comparison of the experimental values with $\omega_m(q, \Delta, \rho, \eta, \sigma, \gamma = 0)$ for pure $[\text{C}_4\text{mim}]^+\text{Cl}^-$ shows that their discrepancy increases with increase of the temperature. Treating the surface dipole moment density γ as an adjustable parameter we can estimate its temperature dependence from the experimental points in figure 2 and the result is presented in figure 3.

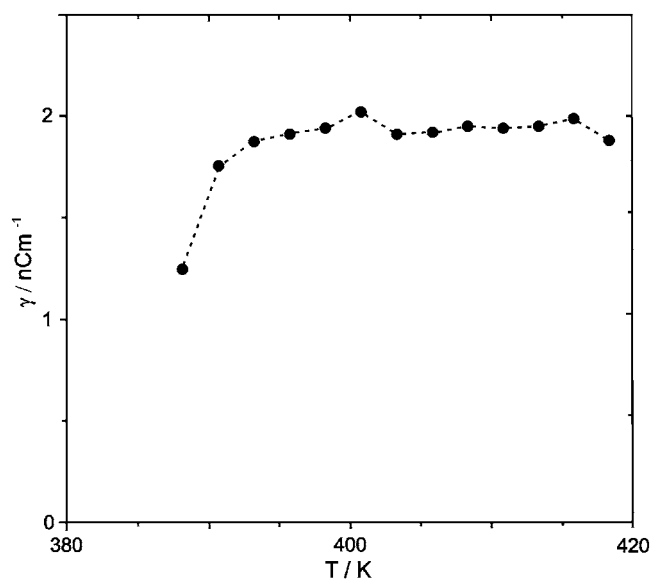


Figure 3. Temperature dependence of the surface dipole moment density at the $[\text{C}_4\text{mim}]^+\text{Cl}^-$ liquid/vapour interface.

As is seen γ remains nearly constant in the considered temperature range but drops abruptly at a temperature of about 385 K. This is indicative of a first order ferroelectric phase transition at this temperature. It is interesting to note that the magnitude of $\gamma \sim 1 \text{ nC m}^{-1}$ in the ferroelectric phase is comparable to an estimated value of $\sim 0.5 \text{ nC m}^{-1}$ taking the *ab initio* value of the cation dipole moment of 4.3 D [2] and an area of the cation of $\sim 2.5 \text{ \AA}^2$. Unfortunately, the viscosity of $[\text{C}_4\text{mim}]^+\text{Cl}^-$ is too high below 385 K and the surface waves become overdamped with a maximum of the spectral density at $\omega_m = 0$. Hence, it is impossible to perform our analysis using equation (2) for temperatures below 385 K. To elucidate better the nature of this phase transition we have analysed the temperature dependence of γ for pure $[\text{C}_4\text{mim}]^+\text{PF}_6^-$ measured in the same manner as before [8]. This is presented in figure 4. As seen at higher temperatures the surface dipole moment density is again more or less constant and drops at $T = 385 \text{ K}$. Hence, the first order phase transition is also present at the $[\text{C}_4\text{mim}]^+\text{PF}_6^-$ liquid/vapour interface. The fact that the transition temperatures in both liquids coincide suggests the important role of the $[\text{C}_4\text{mim}]^+$ cations. Due to the lower viscosity of $[\text{C}_4\text{mim}]^+\text{PF}_6^-$, however, we are able to measure γ at temperatures below 385 K. This dependence presented in figure 4 suggests another ferroelectric phase transition. Indeed, the mean field approximation

$$\gamma/\gamma_0 = \tanh(T_c\gamma/\gamma_0T) \quad (3)$$

describes well the experimental results with parameters $\gamma_0 = 4.95 \text{ nC m}^{-1}$ and $T_c = 385 \text{ K}$. Hence, the temperature 385 K appears also to be a critical one for this order–disorder phase transition of the surface dipole moments. The fact that the mean field theory describes our observations better than some rigorous lattice calculations of the Ising model [14] is probably due to the liquid nature of the considered interface. Possibly, the low value of T_c reflects the interaction between the alkane chains. Since the addition of AlCl_3 leads to an increase of the volume of the anions— AlCl_4^- in comparison with PF_6^- —it will lead also to an increase of the distance between the cations on the surface. As a result the interaction between them will

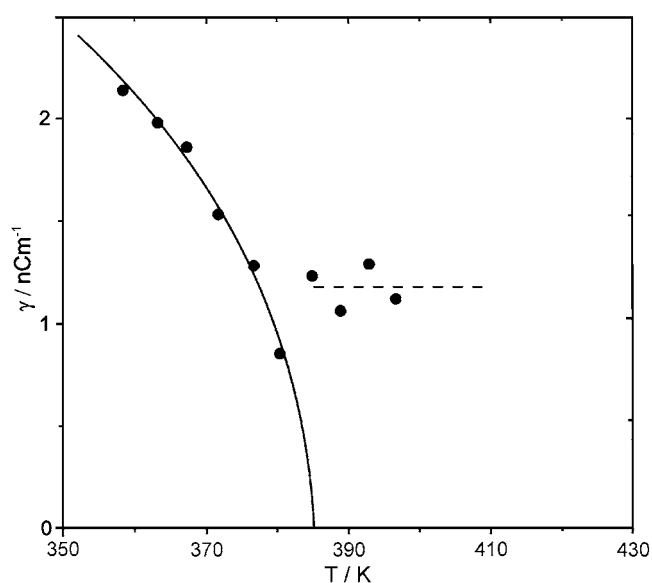


Figure 4. Temperature dependence of the surface dipole moment density of the $[\text{C}_4\text{mim}]^+\text{PF}_6^-$ liquid/vapour interface. The solid line corresponds to the fit by equation (3).

be weaker and the corresponding critical temperature will drop far below 385 K. Hence, our measurements of 50 at.% $[\text{C}_4\text{mim}]^+\text{Cl}^-$ + 50 at.% AlCl_3 mixture are presumably above the critical temperature and for this reason no surface polarization is detected.

In conclusion, we have studied by surface light scattering the temperature variation of the surface dipole moment density γ of various ionic liquids of the type $[\text{C}_4\text{mim}]^+\text{X}^-$ with $\text{X}^- = \text{Cl}^-, \text{PF}_6^-, \text{AlCl}_4^-$. We found that the temperature dependence of γ in the $[\text{C}_4\text{mim}]^+\text{PF}_6^-$ melt can be described by an interfacial order–disorder transition with a critical temperature of $T_c = 385$ K. Above this temperature γ exhibits a distinct increase to values of ~ 1 nC m⁻¹ in both PF_6^- and Cl^- containing melts. We think that this is indicative of a ferroelectric transition at the interface. The magnitude of γ in the ferroelectric state is consistent with a surface potential drop of $\Delta\phi \sim 1$ V, which was predicted by simulation calculations [14]. For this aim, the dielectric constant ϵ of the ionic liquid interface has to be taken into account, i.e. $\gamma = \epsilon\epsilon_0\Delta\phi$. Estimating the dipole coupling energy from $kT_c \cdot (\gamma/\gamma_0)^2$ it is understandable that this small contribution to the surface free energy cannot be resolved within the experimental errors of σ in figure 1. So we do not see a change in slope or a discontinuity in the surface tension at the temperature where a ferroelectric transition is indicated in $\gamma(T)$.

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