

Evidence of a Phase Transition in Water–1-Butyl-3-methylimidazolium Tetrafluoroborate and Water–1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate Mixtures at 298 K: Determination of the Surface Thermal Coefficient, $b_{T,P}$

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We studied the aggregation behavior of two short-chain room-temperature ionic liquids. Previous surface tension studies have shown that 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄) aggregates in water. We observed the same behavior for another ionic liquid, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (bdmimBF₄). We carried out a thermodynamic study of the mixtures between water and the two butylimidazolium salts to investigate this unusual behavior for cations with short chains by determining the surface thermal coefficient, $b_{T,P}$. Plotting $b_{T,P}$ as a function of the molar fraction (X) of the two salts showed a clear discontinuity at $X = 0.016$ for bmimBF₄ and $X = 0.004$ for bdmimBF₄. This discontinuity could be attributed to a transition such as an aggregation.

Introduction

For more than a decade now, there has been an increasing use of ionic liquids as new solvents in chemistry^{1–5} and biochemistry.^{6–9} Room-temperature or close to room-temperature molten salts are generally composed of an organic cation and an inorganic or organic anion that determines the physicochemical properties of the salt. Thus, for a given cation, the miscibility of the salt with water depends on the choice of the anion. There are many studies on the physicochemical properties of these media.¹⁰ Among these new solvents, salts based on the 1-alkyl-3-methylimidazolium cation have been the most studied. These cations have an amphiphilic character when the alkyl group is a long hydrocarbon chain. Thus, at low concentrations, 1-decyl-3-methylimidazolium bromide forms aggregates in water¹¹ and then self-assembles to form mesophases at higher concentrations.¹² However, recent studies have shown^{13,14} that this characteristic is also sometimes found for cations with short chains. Measurements of the surface tension of aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄) has shown that this salt behaves as a surfactant and forms aggregates when the molar fraction of salt is higher than about 0.016. In a recent thermodynamic study of water–bmimBF₄ mixtures,¹⁵ several excess extents (excess chemical potential, enthalpy, and entropy) were observed. These results showed that, at a molar fraction of 0.015 of the salt, there is change of behavior that can be attributed to self-association of the ionic liquid.

We determined the surface thermal coefficient, $b_{T,P}$, of mixtures between water and two imidazolium salts—1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (bdmimBF₄)—to investigate this unusual behavior for cations with short alkyl chains. In a previous study,¹⁶ we showed that the thermal coefficient, $b_{T,P}$, introduced by Defay and Prigogine,¹⁷ was a

very sensitive variable for studying phase transitions such as micelle formation by surfactants and surface transitions, even for surfactants that are soluble in the considered medium.

Chemicals. Sodium tetrafluoroborate (98%), 1-methylimidazole (99%), 1,2-dimethylimidazole (98%), 1-bromobutane (99%), and acetonitrile (99%) were from Acros Organics. Acetone (Normapur) was from Prolabo, ethyl acetate (purex for analysis), and dichloromethane were from SDS. All mixtures were prepared in ultrapure water (all water used was distilled and then filtered with an ELGA UHQ II system, $\kappa = 18$ M Ω).

All the imidazolium salts were synthesized according to standard methods.¹⁸

Synthesis of 1-Butyl-3-methylimidazolium Bromide (bmimBr) and 1-Butyl-2,3-dimethylimidazolium Bromide (bdmimBr). An excess of 1-bromobutane was slowly added to a stirred solution of 1-methylimidazole (or 1,2-dimethylimidazole) in ethyl acetate. The mixture was then heated at reflux for 24 h. The reaction was stopped when two phases were formed. The top phase, containing unreacted starting material in ethyl acetate, was decanted and discarded. The bottom phase contained the butylimidazolium bromide. For the bmimBr salt, the bottom phase was washed three times with ethyl acetate to remove any unreacted reagents (particularly 1-methylimidazole). Residual ethyl acetate was removed by heating (70 °C) under vacuum (12 h). bmimBr was obtained as a colorless hygroscopic solid. The structure of the resulting salt was confirmed by ¹H NMR spectroscopy (400 MHz, CDCl₃, δ /ppm relative to TMS) = 0.94 (t, NCH₂CH₂CH₂CH₃, $J = 7.4$ Hz); 1.35 (m, NCH₂CH₂CH₂CH₃, $J = 7.5$ Hz); 1.88 (m, NCH₂CH₂CH₂CH₃, $J = 7.6$ Hz); 4.10 (s, NCH₃); 4.31 (t, NCH₂CH₂CH₂CH₃, $J = 7.4$ Hz); 7.41 (s, CH(ring)); 7.52 (s, CH(ring)); 10.38 (s, CH(ring)).

For bdmimBr, the bottom phase was recrystallized three times in ethyl acetate/acetonitrile (3:2 v/v) to remove any unreacted reagents (particularly 1,2-dimethylimidazole). Residual solvents were removed under vacuum in the presence of P₂O₅ (24 h). bdmimBr was obtained as a white hygroscopic solid. The structure of the resulting salt was confirmed by ¹H NMR

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spectroscopy (300 MHz, CDCl₃, δ /ppm relative to TMS) = 0.91 [t, J = 7.3 Hz, NCH₂CH₂CH₂CH₃]; 1.32 [m, J = 7.6 Hz, NCH₂CH₂CH₂CH₃]; 1.75 [m, J = 7.5 Hz, NCH₂CH₂CH₂CH₃]; 2.77 [s, CCH₃]; 4.00 [s, NCH₃]; 4.18 [t, J = 7.2 Hz, NCH₂CH₂CH₂CH₃]; 7.50 [dd, CH(ring)]; 7.79 [dd, CH(ring)].

Synthesis of 1-Butyl-3-methylimidazolium Tetrafluoroborate (bmimBF₄) and 1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate (bdmimBF₄). A solution of NaBF₄ in acetone was slowly added to a rapidly stirred solution of the appropriate imidazolium (bmimBr or bdmimBr). The mixture was stirred at room temperature for 4 days and then filtered through Celite. The acetone was removed on the rotary evaporator. The resultant viscous liquid was dissolved in dichloromethane (CH₂Cl₂) and washed with small volumes of distilled water (3:1 v/v) until no precipitation of AgBr occurred in the aqueous phase on addition of a concentrated AgNO₃ solution. The CH₂Cl₂ was then evaporated. Traces of water and other volatile solvents were removed by freeze-drying just before starting the experiment. bmimBF₄ and bdmimBF₄ were obtained as colorless, very viscous, hydrophilic liquids. The structures were confirmed by ¹H and ¹³C NMR spectroscopy. For bmimBF₄: ¹H NMR spectroscopy (400 MHz, D₂O, δ /ppm relative to TMS) = 0.83 [t, J = 7.4 Hz, NCH₂CH₂CH₂CH₃]; 1.23 [m, J = 7.5 Hz, NCH₂CH₂CH₂CH₃]; 1.76 [m, J = 7.6 Hz, NCH₂CH₂CH₂CH₃]; 3.79 [s, NCH₃]; 4.10 [t, J = 7.4 Hz, NCH₂CH₂CH₂CH₃]; 7.35 [d, J = 1.8 Hz, CH(ring)]; 7.36 [s, CH(ring)]; 8.60 [s, CH(ring)]. ¹³C NMR spectroscopy (300 MHz, D₂O, δ /ppm relative to TMS) = 15.37 [NCH₂CH₂CH₂CH₃]; 21.52 [NCH₂CH₂CH₂CH₃]; 34.04 [NCH₂CH₂CH₂CH₃]; 38.35 [NCH₃]; 52.04 [NCH₂CH₂CH₂CH₃]; 124.97 [C(ring)]; 126.25 [C(ring)]; 138.60 [C(ring)]. ElectroSpray mass spectrometry (ESI positive): bmimBF₄, m/z = 139.04 (bmim⁺). For bdmimBF₄: ¹H NMR spectroscopy (400 MHz, D₂O, δ /ppm relative to TMS) = 0.83 [t, J = 7.39 Hz, NCH₂CH₂CH₂CH₃]; 1.24 [m, J = 7.6 Hz, NCH₂CH₂CH₂CH₃]; 1.69 [m, J = 7.5 Hz, NCH₂CH₂CH₂CH₃]; 2.49 [s, CCH₃]; 3.67 [s, NCH₃]; 4.01 [t, J = 7.3 Hz, NCH₂CH₂CH₂CH₃]; 7.21 [dd, CH(ring)]; 7.25 [dd, CH(ring)]. ¹³C NMR spectroscopy (400 MHz, D₂O, δ /ppm relative to TMS) = 8.67 [NCH₂CH₂CH₂CH₃]; 12.86 [NCH₂CH₂CH₂CH₃]; 18.99 [NCH₂CH₂CH₂CH₃]; 31.14 [C(ring)CH₃]; 34.45 [NCH₃]; 47.96 [NCH₂CH₂CH₂CH₃]; 120.73 [C(ring)]; 122.12 [C(ring)]; 144.26 [C(ring)-CH₃]. ElectroSpray mass spectrometry (ESI positive): bdmimBF₄, m/z = 152.89 (bdmim⁺).

Techniques. Surface tensions were measured using a Krüss tensiometer (K10T model) by the Wilhelmy plate method. The solutions were maintained at a constant temperature (± 0.1 °C) in a circulating water–ethylene glycol bath.

Surface tensions were measured every 2 K between 279 and 294 K. Each surface tension value was the average of three to five measurements, for which the maximum deviation from the average value was always <0.4%.

Recalls of Thermodynamic Relationships. We have previously published the full thermodynamic relationships relating to the surface thermal coefficients¹⁶ and will only highlight those relationships necessary for understanding the present work. Water–molten salt mixtures, at equilibrium and in contact with atmospheric air, contain n_1 moles of water (1) and n_2 moles of the nonvolatile salt (2). We assume that the amount of 1 and 2 in the vapor phase are negligible compared to the amounts in the solution. The interface is taken as being planar. Taking into account an interfacial energy in the internal energy gives

$$dU = T dS - P dV + \mu_1 dn_1 + \mu_2 dn_2 + \gamma dA \quad (1)$$

where γ is the interfacial tension associated with an area A and

μ_i is the chemical potential of the species i at a temperature T and pressure P .

U is a homogeneous first-order function of the extensity variables, and thus the integral equation can then be written

$$U = TS - PV + \mu_1 n_1 + \mu_2 n_2 + \gamma A \quad (2)$$

and by coherence

$$0 = S dT - V dP + n_1 d\mu_1 + n_2 d\mu_2 + A d\gamma \quad (3)$$

The evolution of a system at controlled temperature and pressure is usually characterized in terms of the enthalpy, H ; thus,

$$H = U + PV \quad (4)$$

in which the variations in enthalpy can be expressed from the thermal coefficients in a reversible transformation. When the system involves an area variable, Defay and Prigogine¹⁷ proposed introducing a surface thermal coefficient, $b_{T,P}$ (corresponding to the heat of the reversible extension of the surface at T and P), in the expression of the reversible heat. Taking the area variable into account gives

$$\delta Q_{\text{rev}} = C_p dT + h dP + b_{T,P} dA \quad (5)$$

where C_p , h , and $b_{T,P}$ are thermal coefficients. This last equation leads to the following expression for changes in enthalpy:

$$dH = C_p dT + (h + V) dP + (b_{T,P} + \gamma) dA \quad (6)$$

The derivative of the entropy is then

$$dS = \frac{\delta Q_{\text{rev}}}{T} = \frac{C_p}{T} dT + \frac{h}{T} dP + \frac{b_{T,P}}{T} dA \quad (7)$$

In this case, the surface thermal coefficient, $b_{T,P}$, plays the same role as the isobaric heat capacities, C_p , to which it is linked by the relation

$$\left(\frac{\partial(C_p/T)}{\partial A} \right)_{T,P} = \left(\frac{\partial(b_{T,P}/T)}{\partial T} \right)_{P,A} \quad (8)$$

As for C_p , this surface thermal coefficient may become discontinuous when a transition occurs in the system. We have previously shown this in a study of the behavior of nonionic surfactants in water.¹⁶ When a surfactant was added to the solvent, we observed a surface transition at low concentrations, with the water being excluded from the surface layer, and then the formation of micelles at higher concentrations.

Rebelo et al. presented results on variations in the excess molar isobaric heat capacities of water–bmimBF₄ mixtures.¹⁹ Thus, we tried to confirm this type of behavior by $b_{T,P}$ measurements as this can be easily calculated. Indeed, comparison of the cross-differentiations of eqs 6 and 7 leads to

$$b_{T,P} = -T \left(\frac{\partial \gamma}{\partial T} \right)_{P,A} = - \left(\frac{\partial \gamma}{\partial \ln T} \right)_{P,A} \quad (9)$$

The $b_{T,P}$ coefficient can be determined from variations in the surface tension with respect to the logarithm of the temperature for a given molality of solute. Thus, we determined the surface

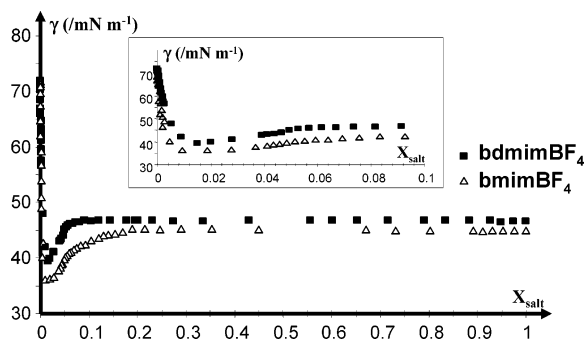


Figure 1. Variations in surface tension depending on the molar fraction of the two butylimidazolium salts at 298.15 K.

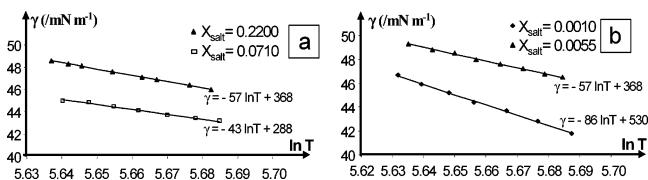


Figure 2. Variations in the surface tension with respect to temperature for water–butylimidazolium salt mixtures of a given composition: (a) water–bmimBF₄; (b) water–bdmimBF₄. The slope of the straight line gives the surface thermal coefficient, $b_{T,P}$.

thermal coefficient for different water–bmimBF₄ and water–bdmimBF₄ mixtures.

Results

The variations in the surface tension with respect to the molar fraction of either bmimBF₄ or bdmimBF₄ in pure water at 298 K are shown in Figure 1. The surface tension values were accurate to within 0.1 mN m⁻¹. For water–bmimBF₄ mixtures, our results are consistent with those recently published by Sung et al.¹⁴ The surface tension decreased to a minimum as the salt content decreased, and then increased to reach a plateau for both salts (Figure 1).

The variation of surface tension of water with the molar fraction of bdmimBF₄ has never been described before. The shape of the curve is similar to that for bmimBF₄; however, the surface tension values are slightly higher. We determined the surface thermal coefficients for the more salt dilute solutions by measuring the surface tension of these solutions at different temperatures. Some of our results are shown in Figure 2. We obtained straight line fits by plotting the surface tension against the logarithm of the temperature, allowing the surface thermal coefficient to be calculated.

We plotted the variations in $b_{T,P}$ against the molar fraction of the salt (Figure 3). For the two butylimidazolium salts, a discontinuity is evident. For bdmimBF₄ salt, the discontinuity appears between a molar fraction of 0.0035 and 0.0047 and for the bmimBF₄ between 0.015 and 0.017. Thus, there is a surface transition at a molar fraction of 0.016 for the bmimBF₄ and 0.004 for the bdmimBF₄. The former value is comparable to those calculated from the excess C_p variations reported by Rebelo et al.¹⁹

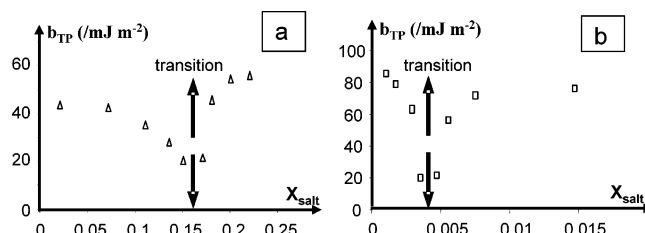


Figure 3. Variations of $b_{T,P}$ with (a) X_{bmimBF_4} and (b) X_{bdmimBF_4} .

Conclusion

Our study confirms the existence of a transition for bmimBF₄ in water, which probably corresponds to aggregation of the electrolyte. We have also shown that the same behavior occurs for bdmimBF₄ in water. Unlike that observed for nonionic surfactants, we observed no visible surface transition before aggregation.

The study of surface thermal coefficients for the systems involving surfactants is interesting as it allows phase or interface transition phenomena to be characterized using a simple approach. This study is complementary to C_p measurements.

References and Notes

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