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Influence of Typical Impurities on the Surface Tension Measurements of Binary Mixtures of Water and the Ionic Liquids 1-Butyl-3-Methylimidazolium Tetrafluoroborate and Chloride

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The effect of typical chemical impurities on the surface tension of two binary water + ionic liquid (IL) systems was carefully evaluated for 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF_4], and 1-butyl-3-methylimidazolium chloride, [bmim]Cl. The impurities considered were mineral acids and bases, potassium chloride, 1-methylimidazole, acetone, ethanol, vacuum grease, and a nonionic detergent. It is very likely that in particular detergents and/or vacuum grease may have been present in prior reported studies explaining the discrepancies present in the reported values for the particular cases of [bmim][BF_4] and [bmim]Cl in water. As part of the study, the composition-dependent surface tension was remeasured three times for each for these two systems. For both binary water + IL systems, the results could be fitted to an exponential decay function, and the critical aggregation concentrations (CACs) were found to be in mole fraction of IL at 0.026 for [bmim][BF_4] and 0.234 for [bmim]Cl.

Introduction

Room temperature ionic liquids (ILs) are salts that are liquid at ambient conditions. They have attracted an ever-increasing amount of attention as green and/or task-specific designer solvents with a plethora of applications. A Scifinder literature search done in August 2010 revealed about 50 review articles published in 2010 alone covering IL research on topics such as synthesis,[1,2] materials,[3,4] separations,[5,6] catalysis,[7−9] electrochemistry,[10−12] solvation dynamics,[13,14] and physicochemical properties in general.[15−17] In many of the applications the IL is in contact with other solvents including water. However, as Rilo et al. pointed out, reports on measurements of physical properties on binary systems with ILs only became increasingly available since about 2005.[18] Some of the most studied binary systems of water and IL concern ILs based on the 1-alkyl-3-methylimidazolium cation. With respect to composition-dependent surface tension measurements, there are significant data available for the two ILs [bmim][BF_4][18−23] and [bmim]Cl.[19,24−26] However, the disagreement in these reported data is surprisingly large. As undoubtedly many more surface tension measurements on binary IL systems will be made in the future, we deemed it to be important to identify the experimental reasons behind the data disparity. Specifically, we thoroughly investigated the effect of a variety of conceivable impurities on the surface tension measurements in these systems. As impurities we considered the following: a nonionic surfactant as a detergent example as well as 2-propanone (acetone) and ethyl alcohol (ethanol) as common laboratory solvents typically used for cleaning purposes; vacuum grease because ILs are often times exposed to vacuum during purification to remove water and other volatile impurities; 1-methylimidazole as the commonly used starting material for the synthesis of the ILs; mineral acid and base, that is, the effect of the water pH; and the presence of potassium chloride as an exemplary generic salt impurity that could originate for example from ion exchange processes during the IL manufacturing.

Experimental Section

The ILs were supplied by EMD chemicals with the following specifications: [bmim][BF_4] (CAS: 174501-65-6) Lot # S5206849 950, purity > 99 % with mass fraction (w) < 10^{-5} halides and $w < 10^{-5}$ water; [bmim]Cl (CAS: 79917-90-1), Lot # S4968179 005, purity > 98 % with less than 1 % water. The original IL bottles, sealed from manufacturer, were opened and stored under nitrogen atmosphere in a drybox (O_2: $w \leq 2 \cdot 10^{-5}$; H_2O: $w \leq 2 \cdot 10^{-5}$). The water used was double-distilled and further purified by a Barnstead UV purification system. The investigated organic impurities were 99.9 % pure acetone (CAS: 67-64-1) from Pharmco-AAPER, 99.98 % pure ethanol (CAS: 64-17-5) from Pharmco-AAPER, and 99 % pure 1-methylimidazole (CAS: 616-47-7) from Aldrich. The nonionic surfactant used was a polydisperse ethoxylated C_8-C_{10} alcohol mixture from Rhodia (CAS: 68439-45-2), a typical ingredient for home, personal care, and industrial surfactant formulations. In prior work[27] the number of ethoxy units, n, in the surfactant used was chromatographically determined to be 0.75 mole fraction of $n > 3$ with an average value of $n = 5$. The vacuum grease used was a high vacuum silicone grease from Dow Corning. The mineral acid and base used for adjusting pH were solutions made from ACS grade hydrochloric acid (CAS: 7647-01-0) and sodium hydroxide (CAS: 1310-73-2) from Pharmco-AAPER. The potassium chloride (CAS: 7447-40-7) used was of purity > 99.9 % obtained from Fisher Scientific Company. All chemicals were used as received.

Surface tension measurements were performed using a pocket dyne tensiometer manufactured by Krüss, which measures the force needed to push a gas bubble out of a Teflon capillary of defined radius. The tensiometer was interfaced with a computer that recorded concurrently surface tension with a resolution of 0.1 $mN \cdot m^{-1}$ and the sample temperature with a resolution of 0.1 K in set time intervals of (1 to 2) s. Approximately (30 to

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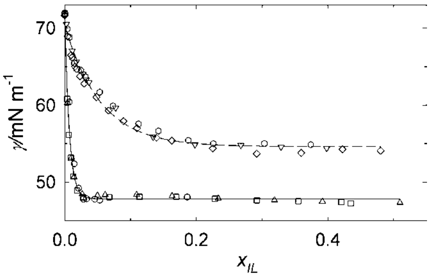

Figure 1. Surface tension, γ, as a function of composition in mole fraction of the IL, x_{IL}: [bmim]Cl at ⬡, 300.3 K; ▽, 300.1 K; ◇, 298.7 K; and [bmim][BF$_4$] at △, 298.9 K; ○, 298.6 K; □, 298.1 K. The dashed and full lines are the corresponding best fits according to eq 1 with coefficients listed in Table 1.

50) data points were recorded for each measured sample composition, and the average and standard deviation for each of these measurements were calculated. To minimize the amount of sample needed during measurements, glass cones obtained from cutting the bottoms off from 2.54 cm (one inch) diameter test tubes were used. Prior to using these cones, they were placed overnight in a muffle oven at a temperature of 600 °C to remove any organic contamination. A clean and dry Teflon coated stir bar was used for mixing the solution inside the glass cone prior to measurement. Stirring was stopped during measurements. For temperature control a water jacket for the glass cone was devised from a poly(vinyl chloride) (PVC) tubing adaptor with an end-cap, in which the glass cone was placed and the seal was made by a rubber O-ring. Despite the use of a Lauda K-2 RD refrigerated circulator bath, set to a temperature of 25 °C, the actual sample temperature would fluctuate by as much as 1.5 K over the course of a measurement series. For this reason we provide in the Supporting Information the data tables with the measured temperature of each individual data point (along with standard deviations directly obtained from the (30 to 50) recordings), while we indicate in the figure captions in this report the average temperature of each measurement series.

In a typical experiment, surface tension measurements were started with pure water for calibration purposes. A new, unused Teflon capillary was used for each measurement series. Aliquots of IL were added to the water by mass difference (Mettler Toledo A6104 balance to a precision of ± 0.0001 g). If the glass cone became too full, sample solution was carefully removed. The amount of removed material was determined by mass difference of pipet and waste container before and after removal. Each addition of IL was thoroughly mixed before measuring the surface tension. Since [bmim]Cl is a solid at room temperature, concentrated solutions of [bmim]Cl in water were made ($x_{\mathrm{IL}} \approx 0.5$) instead of directly adding the IL to water. Additional details concerning the impurities studied are provided where appropriate in the Results and Discussion Section.

Results and Discussion

Figure 1 shows the results for surface tension, γ, as each of the two investigated ILs [bmim]Cl and [bmim][BF$_4$] is incrementally added to water resulting in compositions expressed in the mole fraction of IL, x_{IL}. A total of three measurement series are shown for each IL. The standard deviation of each individual data point (see table material in Supporting Information) was directly evaluated from the (30 to 50) sample repetitions and is generally much smaller than 1.0 mN·m^{-1}, typically less than 0.5 mN·m^{-1}. However, the actual scatter in the data shown in Figure 1 for any particular composition is within 0.5 mN·m^{-1} for the [bmim][BF$_4$] data and within 1.2 mN·m^{-1} for the [bmim]Cl data, and the overall uncertainty of the data may thus be set as ± 0.6 mN·m^{-1}. Part of the larger scatter could be due to the sample temperature instability mentioned in the Experimental Section. However, on the basis of reports in the literature, a temperature difference of 2 °C would cause a decrease of the surface tension by 0.3 mN·m^{-1} for pure water[28] and by 0.1 mN·m^{-1} for either of the neat IL,[29−31] which is less than the observed overall measurement uncertainty of the data sets.

Table 1. Fit Coefficients to Equation 1 for the Surface Tension, γ, in mN·m^{-1} of Binary Water−IL Systems as a Function of Mole Fraction of the IL, x_{IL}

	y_0	a			σ
IL	mN·m^{-1}	mN·m^{-1}	b	R^2	mN·m^{-1}
[emim]Cl	54.6 ± 0.2	$15.7_7 \pm 0.3_2$	18.3 ± 1.0	0.983	0.70
[emim][BF$_4$]	47.8 ± 0.2	$23.9_0 \pm 0.4_8$	145.3 ± 6.3	0.987	0.80

The addition of either IL to water causes first an exponential decline of the solution surface tension and eventually results in a flat plateau. For [bmim]Cl the plateau value is reached at much larger x_{IL} (approximately above $x_{\mathrm{IL}} = 0.35$), compared to [bmim][BF$_4$] (approximately above $x_{\mathrm{IL}} = 0.05$). Each of the combined data sets could thus be fit to the exponential decay function shown in eq 1

$$\gamma(x_{\mathrm{IL}}) = y_0 + ae^{-bx_{\mathrm{IL}}} \tag{1}$$

where Table 1 lists the values for the fit coefficients y_0, a, and b. The R^2-values of the fits are provided as well in Table 1 and are both greater than 0.98. The effect of the anion on the binary water + IL surface tension values has previously been explained by Freire et al. in terms of the increased ability of the smaller anions to undergo hydrogen bonding with the cation.[31]

In Figure 2 we show a comparison of our results with those reported in the literature to date. For clarity, we display the best fit lines for our results from eq 1 and the coefficients in Table 1. The literature results were read off from the reported graphs as accurately as possible. For the case of [bmim]Cl (Figure 2a) our data agrees very well with Liu et al.[19] up to $x_{\mathrm{IL}} = 0.1$. At higher x_{IL} their data continues to decrease while our data approaches a plateau. The data by Blesic[25] et al.[24] were

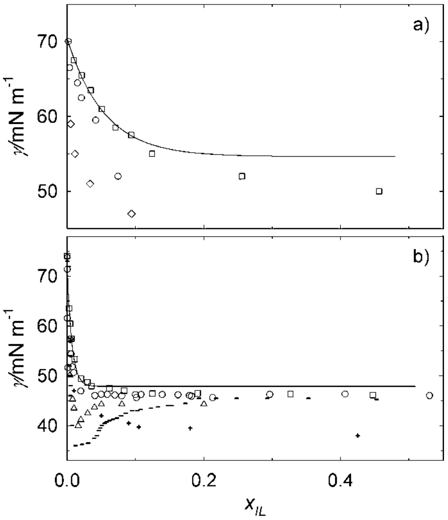

Figure 2. Surface tension, γ, as a function of composition in mole fraction of the IL, x_{IL}, for (a) [bmim]Cl; —, this work; □, ref 19; ○, ref 25; ◇, ref 24; (b) [bmim][BF$_4$]; —, this work; □, ref 20; ○, Rilo ref 18; △, ref 22; -, ref 23; +, Ries ref 21.

only measured to compositions of less than $x_{\mathrm{IL}} = 0.1$ but nevertheless clearly reveal large discrepancies to our data and the data by Liu et al. since they are grossly lower in value. Jungnickel et al. also studied the surface tension of a series of chloride ILs including [bmim]Cl.[26] Unfortunately, their corresponding data graph is not labeled. However, on the basis of other graphical presentations in their report, it appears that at their measured surface tension value at the most IL-rich composition of $x_{\mathrm{IL}} \approx 0.125$ is about 53.6 $\mathrm{mN \cdot m^{-1}}$, which would be slightly lower than our data and the data by Liu et al.

For the case of [bmim][$\mathrm{BF_4}$] (Figure 2b) the reported data in the literature are not only quantitatively in disagreement, but also the shape of the curve varies dramatically. The data by Rilo et al.[18] and Liu et al.[20] are in good agreement to our data except that their surface tension data plateaus at a value slightly lower than ours, lower by about 1.5 $\mathrm{mN \cdot m^{-1}}$. The data by Ries et al.[21] are systematically lower than ours and that of Rilo et al. and Liu et al. but qualitatively also show a continuous decline upon the addition of [bmim][$\mathrm{BF_4}$]. In contrast, the data by Sung et al.[22] and Malham et al.[23] display a minimum in surface tension near a composition of about $x_{\mathrm{IL}} = 0.01$. Sung et al. attributed the minimum to structural changes or changes of the chemical composition at the surface. Malham even used the surface tension data to evaluate the surface thermal coefficient. Similar minima were also observed for 1-decyl-3-methylimidazolium chloride[26] and 1-octyl-3-methylimidazolium chloride.[32] Blesic noted the minimum in the data by Bowers et al. as well and hints at contaminations as the cause of the minimum. To discern if such minimum is indeed absent and to elucidate the cause of the sometimes observed surface tension minimum has been one major motivation of our study. Since it is known that surface tension can be very sensitive to impurities, we systematically investigated the effect of those impurities that could likely be present in the ILs or in the water.

ILs are frequently exposed to vacuum to remove volatile impurities including water, and we thus considered vacuum grease as one possible contaminant. We observed that at best only minimal amounts of vacuum grease would dissolve in either IL. We therefore attempted to add vacuum grease to the ILs by adding an excess amount of vacuum grease to a clean vial and stir bar. The IL was then added to the vial and stirred for over an hour. Figure 3a and b shows the effect of prior vacuum grease exposure on the surface tension for [bmim]Cl and [bmim][$\mathrm{BF_4}$], respectively. For comparison, the fit lines to our data (eq 1 and the entries in Table 1) are shown. For [bmim]Cl the surface tension is systematically lower after exposure to vacuum grease. Since no significant effect of vacuum grease is observed for the case of [bmim][$\mathrm{BF_4}$], it is quite possible that no vacuum grease at all dissolved into [bmim][$\mathrm{BF_4}$].

We next tested the effect of detergent as a possible contaminant. We chose as a representative detergent a commercial, polydisperse nonionic surfactant since it is a common ingredient in household cleaning agents, and we had it previously characterized.[27] As evident in Figure 3a, the addition of 0.009 mass fraction of nonionic surfactant into [bmim]Cl causes a systematic decrease in surface tension over the measured composition range, and a minimum in surface tension is observed near $x_{\mathrm{IL}} = 0.1$. Contamination of nonionic surfactant by 0.015 mass fraction in [bmim]Cl causes an even more severe overall decrease in surface tension, and the minimum shifts toward $x_{\mathrm{IL}} = 0.05$. In the case of [bmim][$\mathrm{BF_4}$] (Figure 3b) we added $w = 0.045$ of surfactant to the IL, and the effect is similar as observed for [bmim]Cl where surface tension decreases drastically; a minimum is observed in this case near $x_{\mathrm{IL}} = 0.01$. We also checked if vacuum grease could dissolve more significantly into the IL when contaminated with surfactant. Indeed, as evident in Figure 3a, the presence of 0.009 mass fraction of nonionic surfactant in the IL increased the uptake of vacuum grease as the resulting surface tension values are significantly lower than when only the surfactant is present as contaminant. In the case of [bmim][$\mathrm{BF_4}$] shown in Figure 3b, the resulting composition-dependent surface tension displays a shape with a minimum that is qualitatively very similar to the reported graphs by Sung et al.[22] and Malham et al.[23] We therefore believe that it is quite likely that traces of vacuum grease with detergent were the cause of their observed surface tension minimum in their data. Sung et al. state that they obtained the IL from a Korean supplier and used it as received. Malham et al. synthesized the IL themselves.

In Figure 4 we show the effect of water pH (addition of mineral acid or base) and the presence of salt on the composition-dependent surface tension measurements. In this case the

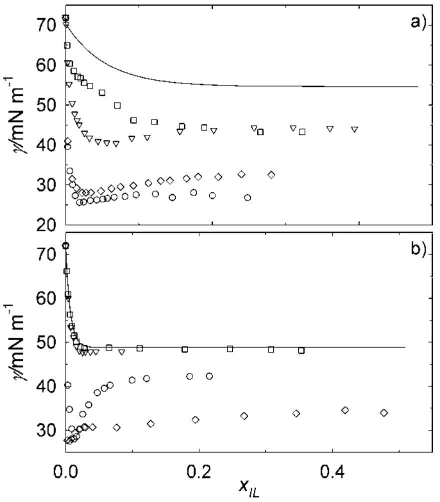

Figure 3. Surface tension, γ, as a function of composition in mole fraction of the contaminated IL, x_{IL}. (a) [bmim]Cl; □, at 299.8 K, prior exposure to vacuum grease; ▽, at 297.9 K, contaminated with 0.009 mass fraction of nonionic surfactant; ◇, at 299.0 K, contaminated with 0.014 mass fraction of nonionic surfactant; ○, at 299.6 K, contaminated with 0.011 mass fraction of nonionic surfactant and prior exposure to vacuum grease. (b) [bmim][$\mathrm{BF_4}$]; □ and ▽, prior exposure to vacuum grease (repeated trials at (298.8 and 298.6) K, respectively); ◇, at 297.9 K, contaminated with 0.046 mass fraction of nonionic surfactant; ○, at 297.9 K, contaminated with 0.009 mass fraction of nonionic surfactant and prior exposure to vacuum grease. The fit lines are the best fits (eq 1, Table 1) from the data in Figure 1.

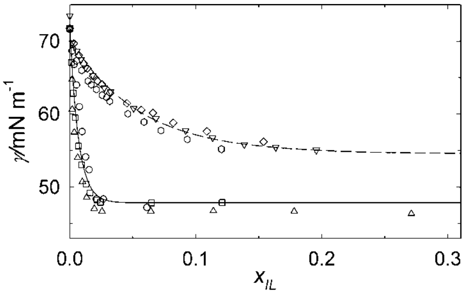

Figure 4. Surface tension, γ, as a function of composition in mole fraction of the IL, x_{IL}; ◇, [bmim]Cl at 299.5 K with water at pH 11; ▽, [bmim]Cl at 298.8 K, aqueous solution of 0.4 molar KCl; ⬡, [bmim]Cl at 299.4 K with water at pH 3; □, [bmim][$\mathrm{BF_4}$] at 299.6 K with water at pH 11; ○, [bmim][$\mathrm{BF_4}$] at 300.4 K, aqueous solution of 0.4 $\mathrm{mol \cdot L^{-1}}$ KCl; △, [bmim][$\mathrm{BF_4}$] at 299.5 K with water at pH 3. The dashed and full lines are the corresponding best fits according to eq 1 with coefficients listed in Table 1.

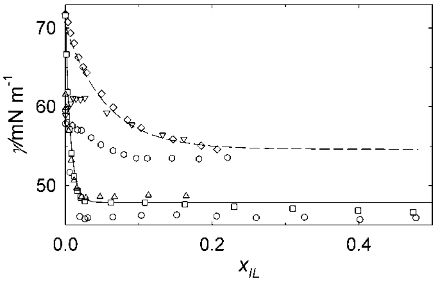

Figure 5. Surface tension, γ, as a function of composition in mole fraction of IL x_{IL} in the presence of contaminates; ◇, [bmim]Cl at 299.1 K with 0.043 mass fraction of 1-methylimidazole in IL; ▽, [bmim]Cl at 298.6 K, with 0.045 mass fraction of acetone in water; ⬡, [bmim]Cl at 300.0 K with 0.039 mass fraction of ethanol in water; △, [bmim][BF$_4$] at 299.6 K with 0.037 mass fraction of ethanol in water; □, [bmim][BF$_4$] at 300.3 K with 0.028 mass fraction of 1-methylimidazole in IL; ○, [bmim][BF$_4$] at 298.4 K with 0.040 mass fraction of acetone in water. The dashed and full lines are the corresponding best fits according to eq 1 with coefficients listed in Table 1.

impurities were added to the water rather then into the IL. As evident in Figure 4, the effect of pH is minimal at best for both ILs, as the deviation from the best fit lines obtained from the (uncontaminated) data in Figure 1 are within the overall uncertainty of ± 0.6 mN·m^{-1}. Nevertheless, we note that the data in Figure 4 for pH 3 are for both ILs consistently lower than the data for pH 11. Because of the near absence of any pH effects, we dissolved a very high quantity of KCl salt in water, that is, 0.4 mol·L^{-1}. Still, even at that high concentration of salt the observed composition-dependent surface tension in Figure 4 is essentially unchanged from the data in Figure 1. It seems therefore safe to say that pH and salt impurities do not play a significant role in affecting the outcome for the composition-dependent surface tension measurements of binary water + IL systems, at least for the two ILs studied here.

In Figure 5 we show the effect of conceivable organic impurities on the surface tension measurements. While 1-imidazole was added to the IL, acetone and ethanol were added to the water prior to measurements. Again, for comparison to the data in Figure 1, we show the corresponding fit lines for [bmim]Cl and [bmim][BF$_4$]. It is evident in Figure 5 that 1-methylimidazole can also be discounted as a significant source for deviations in reported surface tension data, as the corresponding [bmim]Cl data in Figure 5 is essentially unchanged from the data in Figure 1, and only a relatively small decrease in surface tension is observed for the corresponding [bmim][BF$_4$] data in Figure 5. Since ethanol and acetone were each already present in the water, the values at $x_{\mathrm{IL}} = 0$ are substantially less than the value for pure water. For [bmim]Cl the initial amounts of acetone and ethanol in water were in mass fractions of 0.045 and 0.039, resulting in initial surface tension values of (58.9 and 57.8) mN·m^{-1}, respectively. The addition of [bmim]Cl leads actually to an initial slight increase of surface tension in the case of present acetone as apparently the IL replaces the acetone on the solution surface. After a maximum near $x_{\mathrm{IL}} = 0.05$ is reached, the surface tension values gradually decrease and approach closely the dashed fit line representing the data in Figure 1. The surface tension in the presence of ethanol continuously decreases upon addition of [bmim]Cl, and the values are overall significantly lower than the data in Figure 1.

For [bmim][BF$_4$] the initial amounts of acetone and ethanol in water were in mass fractions of 0.040 and 0.037, leading to initial surface tension values of (59.5 and 61.5) mN·m^{-1}, respectively. In the case of present ethanol impurity addition of [bmim][BF$_4$] the decrease in surface tension follows otherwise closely as the data in Figure 1. In the case of present acetone impurity, surface tension decreases upon the addition of [bmim][BF$_4$] in a similar fashion as the solid fit line from the data in Figure 1, but the surface tension values are all consistently lower by (3 to 4) mN·m^{-1}.

Overall, it is evident that the addition of any of the tested impurities tends to either decrease or have essentially no effect on the surface tension but never causes an increase in surface tension, which is not surprising since water has one of the highest surface tension among all common liquids. In this respect, we were wondering why our plateau value of 47.8 mN·m^{-1} for [bmim][BF$_4$] at high x_{IL} is slightly larger than that of Rilo et al. and Liu et al. While Liu et al. were synthesizing the IL, Rilo et al. were purchasing the IL from essentially the same vendor. (Solvent Innovation was bought by Merck who currently distributes their ILs in the United States through EMD chemicals.) Likewise for [bmim]Cl we have obtained the thus far largest reported surface tension values for concentrations exceeding $x_{\mathrm{IL}} = 0.1$. We therefore checked surface tension against neat cyclohexanol as a more viscous standard to ensure that there are no systematic measurement errors due to larger medium viscosity. Changing three times back and forward between a sample of cyclohexanol standard and a sample of [bmim]Cl solution of $x_{\mathrm{IL}} = 0.54$ led to surface tension values consistent with the literature value for cyclohexanol ($\gamma = 32.92$ mN·m^{-1})[28] and our data reported in Figure 1. The only step in our experimental procedure that appears to be different from the experimental methods generally reported is that we placed our glass sample holders in a muffle oven at 600 °C overnight to remove any organic contaminants. Perhaps the presences of traces of detergent or other organic material is the cause of the slight data disagreement.

We also note that the presence of contaminant traces of detergent and/or vacuum grease may be the principle reason for the scatter present in the surface tension data for neat ILs. For [bmim][BF$_4$] these range[18,20,29−31,33] between (43.6 and 46.6) mN·m^{-1} except for an apparently unreliable value of 36.4 mN·m^{-1} reported by Ries et al.[21] All of these values are lower than our plateau value of 47.8 mN·m^{-1}. However, it cannot be concluded from the present data that the surface tension of binary water + [bmim][BF$_4$] is constant beyond $x_{\mathrm{IL}} \approx 0.5$. In fact, Freire et al. show that for 1-butyl-3-methylimidazolium hexafluorophosphate and 1-octyl-3-methylimidazolium hexaflourophosphate surface tension is going through a minimum near $x_{\mathrm{IL}} = 0.92$.[31] For neat [bmim]Cl it is suspicious that Ghatee and Zolghadr[29] and Guerrero-Sanchez et al.[24] report a surface tension value even though at ambient conditions [bmim]Cl is a solid.

Finally, to obtain the critical aggregation concentration (CAC) from our data in Figure 1, we plotted as shown in Figure 6 surface tension versus log(x_{IL}) for the range of data where the surface tension exponentially declines, that is, the data range $0.005 < x_{\mathrm{IL}} < 0.25$ and $0.004 < x_{\mathrm{IL}} < 0.03$ for [bmim]Cl and [bmim][BF$_4$], respectively. These data points were each fitted to a linear fit function, that is, $\gamma = a \log(x_{\mathrm{IL}}) + \beta$, and the CACs were then obtained from the intersection with the y_0 values (i.e., the value for which we observe the surface tension to level out) listed in Table 1. The slopes, a, intercepts, β, and the CACs in terms of mole fraction of the IL, x_{CAC}, are summarized in Table 2. The uncertainties of the listed x_{CAC} were evaluated from the uncertainties of slope and intercept of the least linear fits.

Our obtained x_{CAC} for [bmim][BF$_4$] translates to a molality of 1.47 mol·kg^{-1}, which is about 50 % higher than previously reported values that range from (0.71 to 1.00) mol·kg^{-1}.[21,34,35]

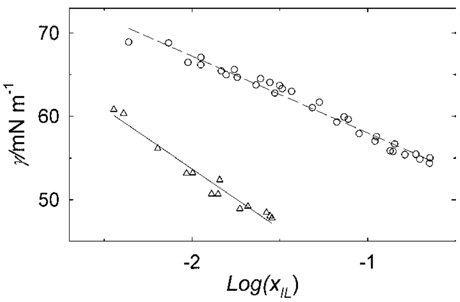

Figure 6. Surface tension, γ, against mole fraction of the IL on a logarithmic scale over the concentration range of; ○, $0.005 < x_{\mathrm{IL}} < 0.25$ for [bmim]Cl in water with dashed linear fit line, and; △, $0.004 < x_{\mathrm{IL}} < 0.03$ for [bmim][BF_4] in water with solid linear fit line.

Table 2. Fit Coefficients for the Surface Tension, γ, in mN·m^{-1} to $\gamma = a \log(x_{\mathrm{IL}}) + \beta$ and Critical Aggregation Concentrations (CACs) for the Binary Water−IL System

	a	β		σ	
IL	mN·m^{-1}	mN·m^{-1}	R^2	mN·m^{-1}	x_{CAC}
[emim]Cl	−9.24 ± 0.26	48.8 ± 0.4	0.977	0.69	0.23 ± 0.02
[emim][BF_4]	−14.38 ± 0.86	25.0 ± 1.7	0.962	0.86	0.026 ± 0.002

In the case of [bmim]Cl, Singh and Kumar report, besides CACs for [bmim][BF_4], also CACs for [emim]Cl from three different measurement methods, namely, the refractive index, fluorescence, and proton NMR chemical shift.[34] The CACs for [bmim]Cl were listed between (0.800 to 0.948) mol·kg^{-1}, which are more than an order of magnitude smaller than our CAC values obtained from surface tension measurements but are actually very similar to their obtained CACs for [bmim][BF_4]. The measurements of refraction, fluorescence, and chemical shift are all reflective of the bulk of the sample. Apparently, in contrast to [bmim][BF_4], aggregates of [bmim]Cl form in water in the bulk of the aqueous solution and penetrate into the solution surface only at sufficiently high concentrations. Chloride is certainly a smaller anion than BF_4^- and interacts more strongly with water. If this interpretation is indeed correct, surface tension measurements may not be an appropriate method to obtain reliable CACs for some of the short-chained ILs. It would be interesting to investigate this aspect further by comparing for a series of short-chained hydrophilic ILs CACs obtained from surface tension measurements with CACs obtained from bulk measurements.

Conclusions

The effect of a number of conceivable impurities on the surface tension of aqueous solutions of the ILs [bmim]Cl and [bmim][BF_4] was investigated. The solution pH, the presence of salt, and the presence of 1-methylimidazolium have no or only a very small effect on the solution surface tension. Ethanol or acetone impurities lead to moderately lower surface tension values. Impurities of detergent especially combined with traces of vacuum grease may lead to drastically changed composition-dependent surface tension traces and may also lead to an apparent false minimum in the composition-dependent surface tension. It is suspected that combined detergent/vacuum grease impurities may have been the leading cause for the large scatter in composition-dependent surface tension data previously reported, in particular for those reports that show a false minimum in the composition-dependent surface tension data. Researchers working with ILs and manufacturers of ILs are cautioned not to inadvertently introduce impurities, that is, detergents, when handling ILs in laboratory glassware and when handling vacuum grease during vacuum drying or other procedures requiring reduced pressure.

Supporting Information Available:

Experimental data shown in Figures 1 and 3 to 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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