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Measurements of Surface Tension and Chemical Shift on Several Binary Mixtures of Water and Ionic Liquids and Their Comparison for Assessing Aggregation

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Supporting Information

ABSTRACT: Surface tension and proton chemical shift data are presented for aqueous solutions of 1,3-dimethylimidazolium methylsulfate [C1mim][$MeSO_4$], 1-butyl-3-methylimidazolium methanesulfonate [C4mim][$MeSO_3$], and 1-hexyl-3-methylimidazolium chloride [C6mim]Cl, as well as surface tension data for 1-ethyl-3-methylimidazolium methanesulfonate [C2mim][$MeSO_3$]. Even though a wide range of concentrations were investigated, none of the studied ionic liquid solutions displayed a plateau value for the surface tension, and a critical aggregation concentration (CAC) could not be established from the obtained surface tension data. However, further analyses of the chemical shift and surface tension data with the inclusion of additional available data for other ionic liquids revealed why CAC values in the literature may vary widely for principle and experimental reasons that are discussed in detail.

INTRODUCTION

Ionic liquids (ILs) are ionic compounds that are liquid below 100 °C and are by now an established class of neoteric chemical solvents. A recent review on the present situation about the knowledge of thermophysical properties of pure ILs notes that despite a remarkable increase in published articles there still remains a need for additional data.[1] It is probably safe to assume that the same can be said for binary systems involving ILs such as aqueous solutions of ILs. It has become evident that particularly ILs with long carbon side chains show surfactant-like behavior.[2−7] Recently, we noticed that published literature data on the binary IL−water systems involving 1-butyl-3-methylimidazolium tetrafluoroborate ([C4mim][BF_4]) and 1-butyl-3-methylimidazolium chloride ([C4mim]Cl) are in severe disagreement, and after a careful investigation, we came to conclude that contamination with vacuum grease or detergent or a combination of both is the most likely cause for the large scatter in the published data.[8] The CAC value for [C4mim][BF_4] derived from our surface tension data was somewhat higher than the CAC determinations reported and summarized by Singh and Kumar[9] using several other techniques including fluorescence, viscosity, and proton NMR chemical shift measurements, which are all measurements concerning the bulk of the solution. However, for [C4mim] Cl the CAC value from our surface tension data was excessively higher, by about 10 times, than the CAC values obtained from the same other experimental bulk measurements. As we desired to further investigate this apparent discrepancy we embarked in additional composition dependent surface tension and proton chemical shift measurements for several other IL−water binary systems. The ILs 1-hexyl-3-methylimidazolium chloride [C6mim]Cl, 1-butyl-3-methylimidazolium methane sulfonate [C4mim][$MeSO_3$], 1-ethyl-3-methylimidazolium methane sulfonate [C2mim][$MeSO_3$], and 1,3-dimethylimidazolium methane sulfate [C1mim][$MeSO_4$] were chosen to inspect possible effects of side chain length and anion with an initial hypothesis in mind that disparities between surface tension measurements and proton chemical shift measurements would be more likely for ILs with short aliphatic side chains and with "hard", less polarizable anions. The results we report here are also compared to the literature, where available.

EXPERIMENTAL SECTION

The ILs were supplied with the following specifications: [C_4mim][$MeSO_3$] (CAS: 342789-81-5), lot no. G00203.1.2, purity >99% with less than 1% water, supplied by io-li-tec; [C_6mim]Cl (CAS: 171058-17-6), lot no. 99220, purity >99% supplied by solvent innovations; [C_1mim][$MeSO_4$] (CAS:), lot no. 99/0156, purity >99% supplied by solvent innovations. 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. All ILs 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 sample temperature with a resolution of 0.1 K in set time intervals of (1 to 2) s. Approximately 30 to 50 data points were recorded for each measured sample composition, and the average and standard deviations for each of these measurements were calculated. In particular for measurements at elevated temperatures, where the water content reduces over time due to gradual evaporation, a sample was withdrawn after

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each surface tension measurement, and a proton spectrum was obtained on a Bruker Avance 300 instrument at 300.13 MHz to evaluate the sample composition through careful signal integration. The method of using NMR signal integration for composition determination was compared with obtaining solution composition directly from mass measurements. The results indicated that even at room temperature some evaporation of water occurred because the IL molefractions from NMR analysis were generally about 5% higher for the increasingly concentrated solutions toward the end of a measurement series. The reported chemical shift values are relative to the terminal methyl group of the aliphatic side chain of the cation, except for [C1mim]-[MeSO$_4$] where the chemical shifts are reported relative to the methyl group of ethanol that was added in small quantities (~1 vol %) as an internal standard.

In order to minimize the amount of sample needed during measurements, glass cones obtained from cutting the bottoms off from 2.54 cm (1 in.) 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 solutions inside the conical flask prior to measurement. Stirring was stopped during measurements. For temperature control a water jacket for the glass cone was devised from a 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 desired temperature for measurement, the actual sample temperature would fluctuate during the course of a measurement series, as much as 0.5 K for room temperature measurements and 3 K for measurements performed at the highest temperature of 320 K. For this reason we provide in the Supporting Information in Tables S1 to S4 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.

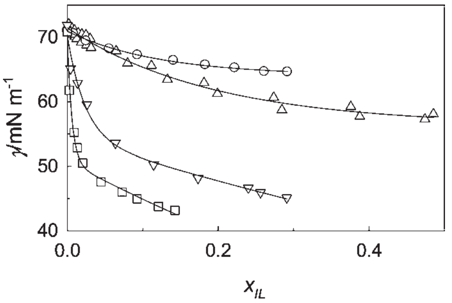

Figure 1. Surface tension, γ, as a function of composition in mole fraction of ionic liquid x_{IL}: [C1mim][MeSO$_4$] at 297.5 K, ○; [C2mim][MeSO$_3$], Δ, at 300.7 K (data points above fit line) and at 302.0 K (data points below fit line); [C4mim][MeSO$_3$] at 297.8 K, ∇; [C6mim]Cl at 297.7 K, □. The full lines are the corresponding best fits according to eq 1 with coefficients listed in Table 1.

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, and surface tension measurements were performed. After measurement, a sample solution was carefully removed for NMR analysis at 298 K. Each addition of IL was thoroughly mixed before measuring the surface tension. Since the ILs were either solid at room temperature or were very viscous liquids, concentrated solutions of IL's in water were made ($x_{\mathrm{IL}} \approx 0.5$) instead of directly adding the IL to water.

RESULTS AND DISCUSSION

Surface Tension. Figure 1 shows the surface tension, γ, for aqueous solutions of the ILs [C1mim][MeSO$_4$], [C2mim]-[MeSO$_3$], [C4mim][MeSO$_3$], and [C6mim]Cl as a function of IL mole fraction, x_{IL}. The data sets shown in Figure 1 are also presented in Tables S1 to S4 in the Supporting Information including the standard deviation for each data point. Kolbeck et al. recently reported on a systematic study of density and surface tension for a large number of neat ILs and could explain structure—property trends for the surface tension data in terms of the strength of present Coulomb and van der Waals interactions in consideration of Langmuir's principle that only the part of the molecule at the outer surface will mainly contribute to the surface tension.[10] For the surface tension of aqueous solutions of ILs there are additional considerations namely the ability of the IL to disrupt the hydrogen bonding interactions of the surface water and the tendency or lack thereof to populate preferentially the surface over the bulk. The surface tension results in Figure 1 are consistent with these considerations as the surface tension systematically decreases with increasing length of the alkyl side chain of the IL cation.

The fit lines to the data sets in Figure 1 were obtained from a four-component exponential decay function shown in eq 1 with the fit parameters a, b, c, and d included in Table 1.

$$\gamma = ae^{-bx_{\mathrm{IL}}} + ce^{-dx_{\mathrm{IL}}} \tag{1}$$

For [C1mim][MeSO$_4$] and [C2mim][MeSO$_3$], the data could be fitted without using the fourth fit-parameter d (i.e., $d = 0$). From our previous study on [C$_4$mim][BF$_4$] and [C$_4$mim][BF$_4$] using the same measurement technique, we concluded an overall measurement uncertainty of ± 0.6 mN·m^{-1} in our surface tension data,[8] which is slightly less than the size of the symbols

Table 1. Fit Coefficients to eq 1 for the Surface Tension, γ, in mN·m^{-1} of Binary Water-IL System As a Function of Mole Fraction of Ionic Liquid, x_{IL}

IL	T/K	a/ mN·m^{-1}	b	c/ mN·m^{-1}	d	R^2	σ/ mN·m^{-1}
[C1mim][MeSO4]	297.5	6.87 ± 0.25	8.22 ± 0.83	64.08 ± 0.27	0	0.996	0.16
[C2mim][MeSO3]	301.4	15.15 ± 0.68	5.17 ± 0.55	56.32 ± 0.67	0	0.986	0.60
[C4mim][MeSO3]	297.8	15.82 ± 2.00	42.75 ± 11.57	54.50 ± 1.92	0.66 ± 0.16	0.989	0.80
[C4mim][MeSO3]	305.0	13.23 ± 2.01	53.05 ± 5.85	57.01 ± 0.77	1.01 ± 0.10	0.998	0.34
[C4mim][MeSO3]	312.5	12.50 ± 0.97	53.55 ± 8.51	56.41 ± 0.97	0.92 ± 0.13	0.997	0.42
[C4mim][MeSO3]	320.1	14.84 ± 0.89	39.78 ± 4.73	52.84 ± 0.86	0.55 ± 0.07	0.998	0.41
[C6mim]Cl	297.7	19.56 ± 0.96	163.08 ± 20.1	50.75 ± 0.79	1.22 ± 0.17	0.996	0.99

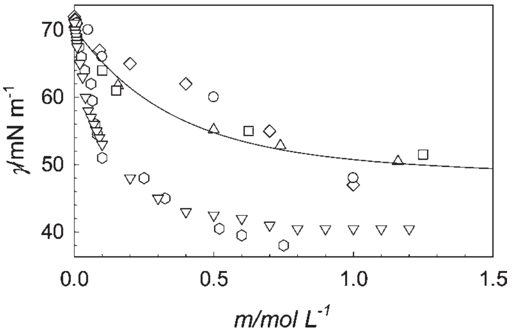

Figure 2. Surface tension of [C6mim]Cl as a function of concentration in water at room temperature: ◇, ref 5; ○, ref 12; □, ref 11; Δ with fit line, this work; ∇, ref 14; ⬡, ref 13.

used in Figure 1. In this study, we did one reproducibility check for [C2mim][MeSO$_3$] for which are two data sets shown in Figure 1, and the reproducibility is consistent with our previously determined measurement uncertainty. However, we note that in Table 1 the standard deviations of the data sets in Figure 1 to their fit lines exceed a value of 0.6 mN·m^{-1} for [C4mim][MeSO$_3$] at 297.8 K and for [C6mim]Cl, despite R^2 values of 0.989 and 0.996, respectively. The data points contributing most to the large standard deviation are the ones at the lowest IL concentration. Indeed, a study by Jungnickel et al. shows that the surface tension of aqueous solution of [C6mim]Cl stays essentially that of pure water for very low concentration up to about 0.01 mol·L^{-1} of added [C6mim]Cl, and then surface tension gradually starts to decline upon further addition of [C6mim]Cl. This behavior at very low IL concentration is not captured in eq 1, and thus the data points at the lowest concentrations contribute the most and significantly to the overall standard deviation of the data sets to the fit lines.

Although we are not aware of literature data for surface tension measurements of binary water−IL mixtures with [C1mim][MeSO$_4$], [C2mim][MeSO$_3$], and [C4mim][MeSO$_4$], there are several surface tension data sets available in the literature for aqueous solutions of [C6mim]Cl. In Figure 2 we are comparing our results for [C6mim]Cl with the literature data that were read off from the reported graphs as accurately as possible. Since we did not measure densities for our solutions, we can only report our concentrations in molality units, which we approximated to be equal to molarity units in Figure 2. Our data set is in good agreement with the results by Pan et al.[11] and in reasonable agreement with the results by Blesic et al.[5] and Jungnickel et al.[12] The data sets by Ghasemein et al.[13] and by Vaghela[14] et al. are apparently not reliable, probably due to the presence of vacuum grease and/or detergent impurities in their samples as we previously investigated these to be the primary common impurities causing lower surface tension measurements in aqueous IL solutions.[8]

Surface tension values at (20 or 25) °C for the neat ILs used in this study are also reported in the literature. For [C1mim][MeSO$_4$][15−18] they are reported near 60 mN·m^{-1}, which is about 5 mN·m^{-1} lower than the lowest surface tension value at the largest IL concentration in Figure 1 indicating that the surface tension would further decrease at higher [C1mim][MeSO$_4$] concentration. Similar can be said for [C2mim][MeSO$_3$] where the surface tension of the neat IL is reported as (50.7 and 49.9) mN·m^{-1}.[19,20] For [C6mim]Cl Ghatee and Zolghadr report a surface tension value of 41.8 mN·m^{-1},[21] which is only slightly lower than our lowest measured value of 43.2 mN·m^{-1} at the highest concentrated solution. The IL [C4mim][MeSO$_3$] melts according to the manufacturer at 75 °C and is thus a solid at room temperature. The [C2mim][MeSO$_3$] should actually also be a solid at room temperature with a melting point of 35 °C according to the manufacturer but tends to form a subcooled melt. The surface tension values for [C2mim][MeSO$_3$] reported in the literature are thus for the metastable liquid state.

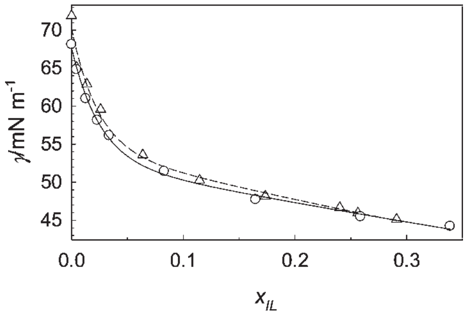

Figure 3. Surface tension of [C4mim][MeSO$_3$] as a function of concentration in water at: Δ, 297.8 K; ○, 320.1 K.

While there are a number of studies measuring the temperature dependence of the surface tension for neat ILs we are not aware of any such temperature dependent surface tension measurements for aqueous IL solutions. Therefore, we desired to at least check for one IL if temperature would significantly alter the surface tension concentration dependence of the aqueous IL solution. In Figure 3 we show for [C4mim][MeSO$_3$] the surface tensions results of the lowest and highest measured temperatures at (297.8 and 320.1) K, respectively. We also measured the surface tension at (305.0 and 312.5) K, and the results are presented in Table S4 in the Supporting Information. Although there is slight systematic decrease in surface tension with increasing temperature, it is evident from Figure 3 that the decrease is minimal, and the observed change in surface tension with temperature is barely reaching the magnitude of our measurement uncertainty. These temperature dependent data sets were also fitted to eq 1, and the resulting fit parameters are included in Table 1. Because of the minimal temperature dependence of the surface tension of aqueous [C4mim][MeSO$_3$] no additional temperature dependent surface tension measurements were attempted for the other studied aqueous IL solutions.

Chemical Shift. Table 2 shows the chemical shift results for aqueous solutions of [C1mim][MeSO$_4$], [C4mim][MeSO$_3$], and [C6mim]Cl. We have already reported similar chemical shift data for aqueous solutions of [C2mim][MeSO$_3$] in an unrelated study.[22] The chemical shift values in Table 2 are reported against the methyl group of the alkyl side chain, except for [C1mim][MeSO$_4$] where we used the methyl group of ethanol that we dissolved in small amounts as internal chemical shift standard. The aromatic protons are denoted in Table 2 as H2, H4, and H5, and the protons of the aliphatic side chain are labeled according to their closeness to the aromatic ring. In Figure 4 we show [C4mim][MeSO$_3$] as one example graph of chemical shift as a function of solution composition in terms of ionic mole fraction x_{IL}. The qualitative trends are similar for [C1mim][MeSO$_4$] and [C6mim]Cl. As IL concentration increases the chemical shift values for water, and where available, the anion protons decrease (more shielded) while the chemical shift values of the cation protons increase (less shielded). We also

Table 2. Proton Chemical Shift in ppm for Aqueous Solutions of Ionic Liquids at 298 K

					[C1mim][MeSO$_4$]		
x_{IL}	m/ kg·mol^{-1}	water	anion	H2	H4	H5	NCH$_3$
0.008	0.460	3.507	2.435	7.394	6.135	6.135	2.601
0.025	1.411	3.490	2.434	7.369	6.165	6.165	2.632
0.055	3.259	3.436	2.431	7.403	6.206	6.206	2.664
0.093	5.679	3.371	2.430	7.443	6.248	6.248	2.691
0.141	9.079	3.304	2.431	7.490	6.296	6.296	2.717
0.183	12.411	3.247	2.433	7.530	6.332	6.332	2.736
0.222	15.816	3.203	2.436	7.563	6.361	6.361	2.752
0.261	19.605	3.162	2.438	7.593	6.388	6.388	2.766
0.292	22.870	3.134	2.439	7.614	6.406	6.406	2.775

					[C4mim][MeSO$_3$]					
								aliphatic side chain		
x_{IL}	m/ kg·mol^{-1}	water	anion	H2	H4	H5	NCH$_3$	C1	C2	C3
0.003	0.190	3.885	1.882	7.782	6.555	6.507	2.968	3.272	0.926	0.395
0.005	0.287	3.884	1.879	7.784	6.558	6.510	2.970	3.273	0.926	0.395
0.009	0.482	3.877	1.872	7.791	6.566	6.518	2.975	3.277	0.929	0.397
0.011	0.620	3.872	1.869	7.796	6.569	6.521	2.977	3.278	0.929	0.396
0.015	0.837	3.865	1.864	7.805	6.579	6.531	2.984	3.283	0.931	0.400
0.017	0.981	3.871	1.862	7.810	6.584	6.535	2.986	3.285	0.932	0.399
0.026	1.470	3.849	1.855	7.829	6.602	6.553	2.998	3.294	0.936	0.402
0.027	1.513	3.844	1.855	7.829	6.602	6.554	2.998	3.294	0.936	0.402
0.051	3.012	3.791	1.846	7.896	6.657	6.609	3.032	3.323	0.949	0.410
0.052	3.042	3.803	1.846	7.892	6.655	6.606	3.030	3.321	0.947	0.408
0.080	4.805	3.745	1.842	7.969	6.714	6.666	3.065	3.352	0.959	0.413
0.096	5.893	3.712	1.841	8.017	6.752	6.702	3.084	3.371	0.965	0.416
0.109	6.817	3.699	1.841	8.042	6.770	6.720	3.094	3.380	0.969	0.417
0.141	9.108	3.657	1.838	8.116	6.826	6.772	3.120	3.407	0.978	0.422
0.146	9.455	3.647	1.837	8.135	6.841	6.786	3.127	3.414	0.980	0.420
0.160	10.598	3.627	1.835	8.169	6.866	6.809	3.137	3.425	0.983	0.424
0.177	11.918	3.608	1.834	8.202	6.891	6.832	3.148	3.436	0.987	0.426
0.199	13.805	3.581	1.831	8.244	6.924	6.861	3.161	3.451	0.991	0.429
0.239	17.431	3.528	1.825	8.320	6.982	6.914	3.183	3.474	0.997	0.432

					[C6mim]Cl					
								aliphatic side chain		
x_{IL}	m/ kg·mol^{-1}	water	anion	H2	H4	H5	NCH$_3$	C1	C2	C3−C5
0.003	0.157	3.953		7.861	6.628	6.583	3.042	3.339	1.011	0.443
0.009	0.499	3.949		7.897	6.654	6.611	3.061	3.356	1.020	0.446
0.013	0.739	3.950		7.926	6.672	6.631	3.075	3.368	1.025	0.448
0.020	1.160	3.949		7.974	6.702	6.666	3.096	3.388	1.036	0.451
0.045	2.608	3.918		8.117	6.775	6.775	3.154	3.448	1.062	0.462
0.073	4.361	3.892		8.238	6.844	6.844	3.194	3.494	1.081	0.472
0.092	5.652	3.872		8.310	6.886	6.886	3.214	3.519	1.091	0.475
0.121	7.632	3.857		8.409	6.944	6.944	3.238	3.556	1.103	0.478
0.143	9.233	3.844		8.481	6.987	6.987	3.256	3.576	1.111	0.479

observed this behavior for [C2mim][MeSO$_3$] and were able to explain this behavior by a competition between the anion and water to interact through Coulomb forces and hydrogen bonding with the cation.[22] The contribution from hydrogen bonding may vary significantly depending on the hydrogen bond basicity of anion and the alkyl chain length. For example, the chemical shift of the aromatic protons increase much less with increasing IL concentration for [C4mim]Cl compared to [C6mim]Cl and even decrease with increasing IL concentration for [C4mim]-[BF$_4$].[9] The interested reader is referred to a recent study of a

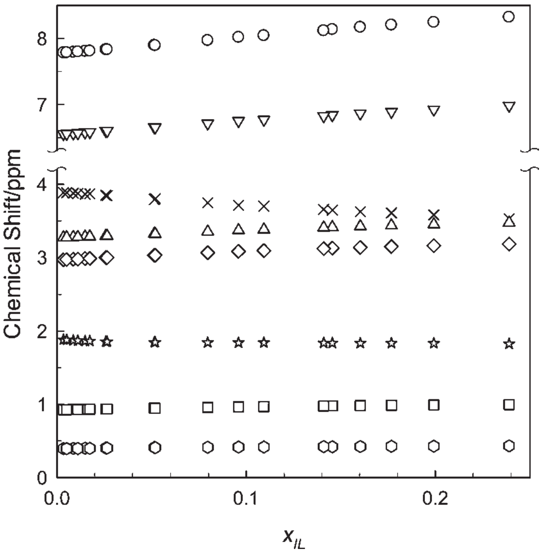

Figure 4. Proton chemical shift values for [C4mim][$MeSO_3$] in water as a function of ionic liquid mol fraction, x_{IL}: ○, H2; ∇, H4; ×, water; Δ, C1; ◊, NCH_3; *, anion; □, C2; ⬡, C3.

large number of ILs dissolved in ethanol where the observed chemical shift trends could be correlated to the anion-dependent hydrogen bond acceptor properties.[23]

With respect to comparison of our chemical shift measurements with available literature data, we are only aware of the very recent study by Vaghela et al. we already mentioned for the surface tension measurements of [C6mim]Cl.[14] Although we found their surface tension data to be inconsistent with our data and data published by others, the chemical shift values for aqueous IL solutions are much less prone to error due to the presence of small amounts of impurities. Indeed, their chemical shift values reported for concentrations of aqueous solutions of [C6mim]Cl up to 1 M are in excellent agreement to our data listed in Table 2. Specifically, once we adjust our chemical shift data by the chemical shift value for the methyl protons of the hexyl side chain, they agree within 0.005 ppm to the chemical shifts reported by Vaghela et al. except for the less defined signal for C3−C5 where agreement is within 0.02 ppm.

Critical Aggregation Concentration. We now turn to the discussion of the apparent inconsistencies of reported CAC's from surface tension measurements and bulk property measurements such as proton chemical shifts. Typically, researchers would plot chemical shift data as a function of inverse concentration such as inverse molarity and then determine the CAC as the intersection point from the linear extrapolations of the low and high concentration data. In Figure 5a−d, we show such inverse concentration plots for our H2-proton chemical shift data (triangle symbols). On first sight, it appears to be a valid method to determine CAC values from the chemical shift data by finding the intersection point of linear extrapolations of the data at low and high concentrations. We do not show such graphical analysis in Figure 5, but the analysis would result in intersection points near 0.2 inverse molality, i.e., 5 $mol \cdot kg^{-1}$ for [C2mim][$MeSO_3$] and [C4mim][$MeSO_3$], and 0.4 inverse molality or 2.5 $mol \cdot kg^{-1}$ for [C6mim]Cl. These would be very large CAC values, for [C6mim]Cl much larger than the reported CAC value of about 0.9 $mol \cdot L^{-1}$.[5,14] However, we remind that in Figure 1 none of the corresponding surface tension data has reached yet a plateau value with increasing IL concentration. Therefore, none of the surface tension data sets can be used to obtain a CAC value. Or, if there is indeed a CAC for any of the ILs in Figure 1, then its value would be larger than the largest measured concentration according to the surface tension data. In an attempt to reconcile this discrepancy it is instructive to also plot the surface tension as a function of inverse concentration, as we have done as well in Figure 5. Specifically, we have scaled the surface tension and chemical shift y axes such that the largest and lowest values of each property match up at the respective inverse concentration x-axis value. We also include in Figure 5, panels e and f, additional data for [C4mim][BF_4] and [C4mim]Cl for which CAC values have been reported.[7−9,24] Specifically, the chemical shift data for Figure 5, panels e and f, were taken from Singh and Kumar,[9] and the surface tension data from our prior work.[8] Several important observations can be made.

First, the surface tension data generally follow the qualitative trend of the chemical shift data but always fall below the chemical shift curves resulting in less sharply bend curves then for the chemical shift graphs, especially in the case of [C6mim]Cl.

Second, for [C4mim][BF_4] the plateau region in the surface tension measurements at high concentration, i.e., low inverse concentration, is clearly visible in Figure 5e. At even higher concentrations the surface tension eventually begins to decrease further. The concentration range of the corresponding chemical shift data in Figure 5e just barely reaches the plateau region. For [C4mim]Cl, while the surface tension data in Figure 5f just reaches a plateau value that is at significantly higher concentration (lower inverse concentration) compared to [C4mim][BF_4], the chemical shift data is clearly far from that region.

Third, none of the graphs in Figure 5 show the distinct and abrupt change in slopes between clearly linear relations at low and high concentrations as is typical for traditional aqueous surfactant solutions and aqueous IL solutions with long aliphatic side chains. As a recent example, we point to the study by Shi et al.[3] for aqueous solutions of *N*-aryl imidazolium bromide of alkyl chain length of 10 carbon atoms and longer. Here, the chemical shift value of the terminal alkyl protons plotted against inverse molarity shows clear linear relations above and below the CAC, and the CAC value obtained from the chemical shift analysis coincides with the concentration value at which the surface tension reaches a plateau value. The closest to such behavior can be observed in Figure 5, panels b and d, for [C2mim][$MeSO_3$] and [C4mim][$MeSO_3$], but even here and certainly for the remaining graphs in Figure 5 the changes with concentration are never truly linear.

From these three observations we can now begin to see the principle reasons why there is much discrepancy in the literature for establishing CAC values for aqueous solutions of short chained ILs. The more gradual property changes from low to high concentrations indicate that unlike for conventional surfactant molecules, short chained ILs do not abruptly form aggregates beyond a critical concentration value. This is not to say that aggregation does not occur for ILs in aqueous solutions. To the contrary, for [C2mim][$MeSO_3$] we could clearly show that the principle structural architecture of the neat ILs remains intact upon addition of water even up to water mole fractions of 0.9 (i.e., $x_{IL} = 0.1$).[22] There is also increasing evidence from other experimental and theoretical studies that aggregation structures are present in neat ionic liquids[25−28] as well as in aqueous solutions.[29−31] However, structural changes for ILs in aqueous solutions may occur more gradual with increasing IL concentration,

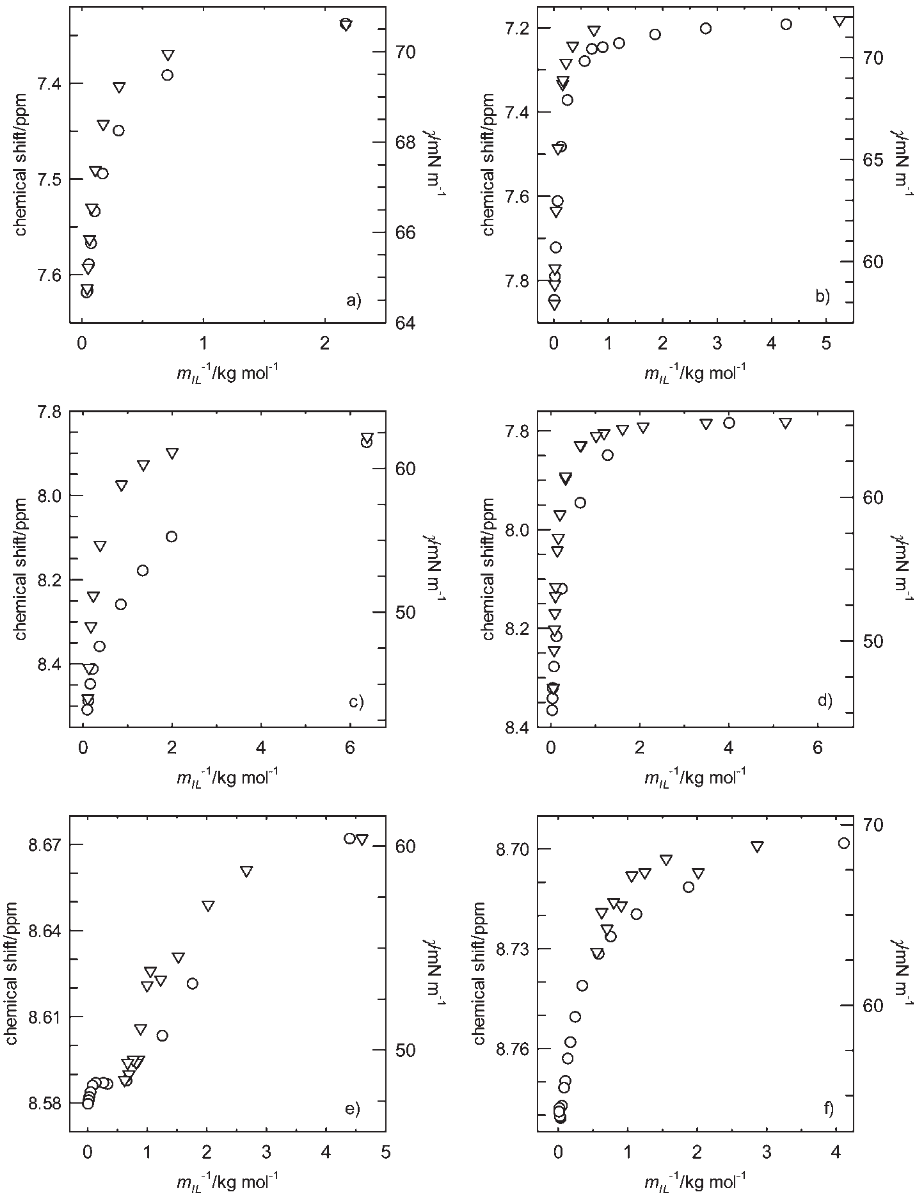

Figure 5. Surface tension, γ (○), and chemical shift of the H2 protons (▽) plotted against inverse molality for (a) [C1mim][MeSO$_4$], b) [C2mim][MeSO$_3$], (c) [C6mim]Cl, (d) [C4mim][MeSO$_3$], (e) [C4mim][BF$_4$], and (f) [C4mim]Cl. Chemical shift data for panel c were taken from ref 22 and for panels e and f from ref 9. Surface tension data for panels e and f were taken from ref 8.

perhaps forming aggregates not well-defined in size and shape that are gradually increasing with increasing IL concentration. At least for [C4mim][BF$_4$] and [C4mim]Cl there appears to be a concentration upon which this structural transformation is completed based on the concentration at which the surface tension plateaus. One could refer to such concentration as the CAC, but one could also refer to some "mid-point" concentration as the CAC. The latter appears to be the result of analyzing concentration dependent data of bulk properties using either inverse concentration graphs as shown in Figure 5 or, as also commonly done, by determining the concentration with maximum gradient change.[12] Indeed, from our surface tension data for aqueous solutions of [C4mim][BF$_4$] we obtained a CAC value of 1.47 mol·kg^{-1}, which is close to the concentration where the plateau value is reached in Figure 5b, whereas CAC values for the same system from bulk property measurements ranged from (0.7 to 1.0) mol·kg^{-1}, which is more aligned with the largest gradient change in the region between (0.7 and 5) kg·mol^{-1}. We would like to refrain on discussing which of these concentrations may be physically more relevant or meaningful and should be used as CAC. Rather, we simply desire to point out the ambiguity in aggregation behavior of short-chained ILs and that in any case CAC values for these systems do not imply a swift change in structure (dissociated to aggregated) as it is known to occur for conventional surfactants.

Beyond the principle ambiguity in assigning CAC values to aqueous solutions of short-chained ILs, there are a couple of additional important considerations. Generally, one can say from inspecting the graphs in Figure 5 that a very large range of concentration needs to be measured. For example, it seems evident that measurements of chemical shifts to higher concentrations of [C4mim]Cl would have resulted in a higher CAC value for this system using the same analysis method.[9] One might also caution for short-chained ILs that the concentration dependence of the surface tension may not report adequately on (all) the structural changes that the IL may undergo in the bulk. We have already mentioned the more gradual nature of structural changes with increasing IL concentration. In addition, short-chained ILs may undergo structural arrangements in the bulk that differ from that of the IL molecules populating the air−liquid interface. In this respect, we refer the reader to the insightful surface spectroscopic studies by the Baldelli group.[18,32−34] Finally, we reiterate that concentration dependent surface tension measurements are very susceptible to impurities from vacuum grease and cleaning agents. Even some of the most recently published surface tension data on aqueous IL solutions[14] are evidently plagued by these impurities.

■ CONCLUSIONS

New surface tension data were provided for aqueous solutions of several short-chained ILs as a function of solution concentration. A comparison with corresponding chemical shift data and with additional data sets for other ILs revealed that the typical definitions and methods of finding CAC values may not apply for aqueous solutions of short-chained ILs. Such ILs may form aggregates of less defined size and shape and in more gradual concentration dependent transitions than is known to occur for surfactant molecules that spontaneously form aggregates of typically well-understood micellar structure at the CAC. As a result, great care is required to obtain meaningful CAC values, if even applicable, from concentration dependent property measurements of aqueous solutions with ILs having short aliphatic side chains.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Tables of all experimental surface tension data. This material is available free of charge via the Internet at http://pubs.acs.org.

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