Enthalpy of Solution of 1-Octyl-3-methylimidazolium Tetrafluoroborate in Water and in Aqueous Sodium Fluoride

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An adiabatic calorimeter was used to measure the enthalpy of solution of 1-octyl-3-methylimidazolium tetrafluoroborate (0.0035 mol·kg^{-1} to 0.02 mol·kg^{-1}) in water and in aqueous sodium fluoride of different ionic strengths (0.1 mol·kg^{-1} to 0.43 mol·kg^{-1}) at nominal temperatures of 298 K, 306 K, and 313 K. Two additional measurements of the enthalpy of solution of 1-butyl-3-methylimidazolium tetrafluoroborate (0.013 mol·kg^{-1}) in water at 298 K are also reported. The present results lead to the standard-state changes of enthalpy and heat capacity for the solution process. The contribution of a methylene group to the enthalpy of solution of these ionic liquids was determined from the measurements and is shown to be in agreement with the value obtained from other classes of organic compounds. The enthalpy of solution increment for the methylene group is used to calculate the enthalpy of solution of the series of 1-alkyl-3-methylimidazolium tetrafluoroborates. Calculated standard-state heat capacity values for the aqueous solution process and the aqueous solute are also given. Potential micelle formation of 1-octyl-3-methylimidazolium tetrafluoroborate in water was examined.

Introduction

Materials known as ionic liquids have attracted considerable interest recently as replacements for volatile organic solvents in which synthesis reactions are conducted. These "ionic liquids" are essentially salts in which one or more of the ions is a fairly large organic ion. Several ionic liquids consist of a large organic cation combined with an inorganic anion. These materials indeed show large differences in several of their properties, including aqueous solubility and hygroscopicity. Generally, for a given large organic cation, the aqueous solubilities of the ionic liquids formed with a halide are much greater than those formed with a less well hydrated anion (e.g., tetrafluoroborate or hexafluorophosphate ions). We have begun examinations of the aqueous thermodynamics of ionic liquids. We intend to make use of the additivity of standard-state properties of aqueous ions. For thermodynamic reasons, we initiate our studies with moderately soluble ionic liquids. This group is composed largely of ionic liquids that contain either the hexafluorophosphate ion or the tetrafluoroborate ion.

In particular, tetrafluoroborate ionic liquids and hexafluorophosphate ionic liquids were declared to be "one of the best model systems for predictive methods."[1] Recently, reports have appeared in which were described measurements of various thermodynamic properties of systems containing water and a tetrafluoroborate ionic liquid, examples of which can be found in refs 1−3. At least one study of the tetrafluoroborate ionic liquid + water system attempted a description of molecular-level interactions in aqueous solutions from the measured thermodynamic properties.[2]

However, it has been known for more than 50 years that the tetrafluoroborate and hexafluorophosphate anions decompose, or hydrolyze, to some extent in water. For example, at equilibrium and at room temperature almost 14 % of the tetrafluoroborate ions in a solution of HBF$_4$ will have hydrolyzed to BF$_3$OH$^-$(aq).[4] One of the reaction products—for both of the anions in question, tetrafluoroborate and hexafluorophosphate—is hydrogen fluoride. The presence of aqueous hydrogen fluoride as a decomposition product makes it an easy matter to determine qualitatively whether the solution measured has undergone decomposition during the time scale of the thermodynamic measurement. One needs only to check the pH of the solution after completion of the measurements. None of the cited references that detailed measurements on the tetrafluoroborate ionic liquids in water described the simple determination of the pH value of the solutions either during or after the measurements. The decomposition of the anion of the ionic liquid does not necessarily invalidate a thermodynamic measurement, per se. In other words, the vapor pressure of water over the equilibrated solution may be measured correctly even if the solute has decomposed; what is in question is the composition of the solution to which that vapor pressure corresponds. The hydrolysis reaction products introduce additional species into the solution that, in turn, may invalidate the application of thermodynamic relations if the additional species have not been properly and/or explicitly recognized. For example, the use of the Gibbs−Duhem relation and the vapor pressure of water in the solutions, as a function of stoichiometric composition, would introduce error into the calculation of the activity coefficient of a hydrolyzing tetrafluoroborate ionic liquid solute in just the same way that it does for a solute containing a hydrolyzing carbonate anion or a hydrolyzing ammonium cation; the latter cases have been discussed previously and so should not have to be repeated here. Also

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potentially corrupted by the anion decomposition reactions would be the calculation of temperature and pressure dependences of molar thermodynamic properties. Those calculations would be compromised on two potential grounds. First, consider the case where the measurement can be completed before the system reaches equilibrium. Then, at different temperatures, the extent of the reaction present at that particular time will be different because the reaction rate is different at the different temperatures. An alternate case is that the system reaches equilibrium and that the measurement is for the fully equilibrated system. Because the reaction quotient is most probably a function of temperature, the solutions would have different extents of reaction at the different temperatures, even if the stoichiometric composition would have been the same at the two temperatures. Finally, measured heat capacities of the hydrolyzing solution will contain a component of the heat capacity that is due to the temperature dependence of the hydrolysis equilibrium. As before, this effect from the hydrolysis reaction, when not explicitly recognized, does not make the heat capacity measurement erroneous but rather makes erroneous the apportionment of the heat capacity among the incorrectly assumed species in the solution.

Quite clearly, the attribution of molecular-level interactions on the basis of the values of higher-order composition and temperature derivatives of the Gibbs energy is dubious when the decomposition/hydrolysis products and reactions have been neglected.

We report here measurements of the enthalpies of solution of two ionic liquids. The two ionic liquids, 1-octyl-3-methylimidazolium tetrafluoroborate (herein [C8mim]-BF$_4$) and 1-butyl-3-methylimidazolium tetrafluoroborate (herein [C4mim]BF$_4$), are soluble in water. The solubility of [C8mim]BF$_4$ in water was reported to be 0.065 mol·kg^{-1} at room temperature.[3] [C4mim]BF$_4$ is miscible with water at room temperature.[5] In aqueous solution, the BF$_4^-$(aq) anion hydrolyzes, forming the fluoride ion. To suppress the hydrolysis reaction, we also conducted measurements of the enthalpy of solution of [C8mim]BF$_4$ in aqueous sodium fluoride in addition to the measurements made with pure water as a solvent.

For our measurements that led to the standard-state properties of [C8mim]BF$_4$, we suppressed hydrolysis by adding various amounts of sodium fluoride to some of the measured solutions. At higher concentrations of [C8mim]-BF$_4$, different self-associating behavior of the ionic-liquid solute might be observed in aqueous sodium fluoride than might be observed in water. Therefore, we also explored the behavior of the aqueous [C8mim]BF$_4$ solute at higher concentrations in the absence of sodium fluoride. Although these solutions will allow the hydrolysis of the anion to proceed to some small extent, these conditions would be more like the conditions encountered by a real system during processing or accidents.

Experimental Section

A sample of 1-octyl-3-methylimidazolium tetrafluoroborate, [C8mim]BF$_4$, was obtained from Solvent Innovation (purum, ≥98 %). The [C8mim]BF$_4$ was transferred into a vacuum flask containing a Teflon-coated stir bar. Volatile impurities, including water, were removed from the ionic liquid by attaching the flask to a vacuum line consisting of a mechanical pump and a liquid-nitrogen trap. The sample was evacuated with stirring and gentle heating (~318 K) for 2 days. Following purification, the [C8mim]-BF$_4$ was stored in the Teflon-stoppered vacuum flask to prevent the adsorption of atmospheric moisture. For the purified material, coulometric Karl Fischer titration indicated a mass fraction water content of 50×10^{-6} (50 ppm). Proton nuclear magnetic resonance (NMR) indicated a mole fraction purity of 0.995. Fluorine NMR showed no visible impurity, corresponding to an impurity level of <0.2 %. A chloride-selective electrode indicated chloride content of 360 $\times 10^{-6}$ mass fraction (360 ppm). The material was liquid at room temperature and was orange in color. The color indicates the presence of a colored impurity because the ionic liquid itself is expected to be colorless. Even though such colored impurities are common in ionic liquid chemistry, their nature is not known because they occur in such trace quantities that they have been detected only by UV–visible spectroscopy. (It has not been possible to detect them by NMR, for example.[6]) We assumed that the low level of impurity that colors the sample would not affect the measurements described herein.

We also made use of two preliminary measurements of the enthalpy of solution of 1-butyl-3-methylimidazolium tetrafluoroborate. This material was analyzed for water content, by Karl Fischer titration, and was found to contain about 0.5 % water by weight.

Sodium fluoride, 99 %, was obtained from Aldrich. Sodium fluoride solutions were prepared gravimetrically. The purity of sodium fluoride was not very critical because its role was to provide an ionic strength medium that was capable of suppressing the potential hydrolysis of the tetrafluoroborate ion. Water was purified by reverse osmosis and deionized. All weighings were corrected for buoyancy.

The adiabatic solution calorimeter was described previously.[7] The high accuracy of the calorimeter was demonstrated in ref 7. The calorimeter's thermometer was calibrated on the International Temperature Scale of 1990 at NIST. All other measurement instruments had calibrations that were performed at NIST or that were traceable to NIST. Electrical calibrations of the calorimeter, including its contents, were made both before and after each mixing experiment. At the onset of mixing in the calorimeter, a controlled amount of electrical energy that is converted to heat is introduced into the calorimeter through the calibration heater. The observed temperature change in the calorimeter during the mixing measurement results from the known input of electrically generated heat, the mixing enthalpy, and some much smaller sources such as the vaporization of water into the free space in the sample cell, shield imbalance at the onset of the mixing process, and changes in vapor pressure due to changes in the temperature of the calorimeter during the electrical calibrations and the mixing experiment.[7] The enthalpy of the dissolution process is calculated from the observed temperature change, which is converted to an enthalpy change through the electrical calibration of the calorimeter, combined with the amount of electrical energy converted to heat in the calorimeter, and corrected for the additional small energy effects.

Upon disassembly of the calorimeter after each measurement using [C8mim]BF$_4$, the calorimetric solution had a visible inhomogeneity that was manifested as pearlescence on the surface of the fluid. The dilute solutions also supported some foaming upon agitation. Both effects are consistent with [C8mim]BF$_4$ possessing surfactant qualities. As a result, we conducted a series of measurements at higher concentration of [C8mim]BF$_4$ but without the added NaF(aq).
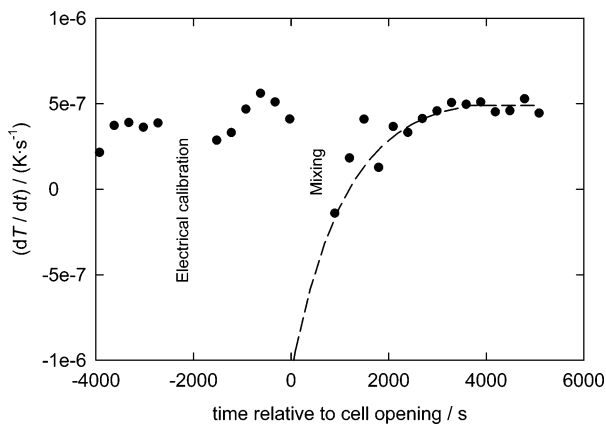
Figure 1. Values of dT/dt for the calorimeter and its contents during the progress of a measurement.

Results

Measured Enthalpies of Solution. Dissolution of the [C8mim]BF$_4$ usually required less than an hour to reach equilibrium in the calorimeter. The time at which dissolution was complete was obvious from examining the time derivative of the temperature of the calorimeter. An example of some of the temperature drift values for a measurement is shown in Figure 1. Each point in the Figure is a calorimeter drift rate calculated from a first-order representation of 300 temperatures obtained at a 1 s^{-1} sampling rate. Drift rates prior to and following the first electrical calibration are shown, as are drift rates following the mixing experiment. As can be seen, the return to the normal drift characteristics of the calorimeter is quite obvious, and for that particular measurement, complete dissolution required about 3000 s at 298 K. Dissolution was faster either at higher temperature or with sodium fluoride present.
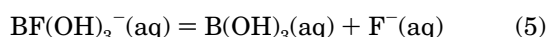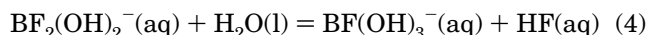
The pH values of the aqueous solutions of [C8mim]BF$_4$ formed in the calorimeter were determined after disassembly of the calorimeter vessel. For dissolutions of [C8mim]BF$_4$ into water, the pH values were acidic. For example, for measurements made at 313 K, the pH values fell between 4.5 and 5.5. For dissolution into aqueous sodium fluoride, the pH values were weakly basic, with pH values ranging from 7.5 to 8.5. The acidic pH values resulted from the slow hydrolysis of the tetrafluoroborate anion:

$$BF_4^-(aq) + H_2O(l) = BF_3OH^-(aq) + HF(aq) \quad (1)$$
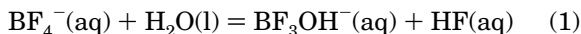
The equilibrium constant for reaction 1, in dilute solution, can be approximated from Wamser's[4] measurements for the reaction

$$HBF_4(aq) + H_2O(l) = HBF_3OH(aq) + HF(aq) \quad (2)$$

Wamser found, at equilibrium and 298.15 K, that 13.7 % hydrolysis occurred for reaction 2. Additional hydrolysis reactions follow the first step of reaction 1:

$$BF_3OH^-(aq) + H_2O(l) = BF_2(OH)_2^-(aq) + HF(aq) \quad (3)$$

$$BF_2(OH)_2^-(aq) + H_2O(l) = BF(OH)_3^-(aq) + HF(aq) \quad (4)$$

$$BF(OH)_3^-(aq) = B(OH)_3(aq) + F^-(aq) \quad (5)$$

Mesmer et al.[8] quantified equilibrium quotients for the subsequent hydrolysis reactions (eqs 3–5). Platford[9] ex-

amined the effect of aging of aqueous solutions of sodium tetrafluoroborate and potassium tetrafluoroborate. Platford[9] advised that the half-life for hydrolysis equilibrium of 0.01 mol·kg^{-1} NaBF$_4$ and KBF$_4$ is 250 h at 298.15 K.

The enthalpy of reaction 1 is small. Using values of enthalpies of formation given by Devina et al.,[10] the standard-state enthalpy of reaction 1 is +0.9 kJ·mol^{-1}. If one accepts that the standard-state apparent molar heat capacity of BF$_3$OH$^-$(aq) is somewhat similar to that of BF$_4^-$(aq), then the standard-state heat capacity of reaction 1 will be on the order of $(-150$ to $-200)$ J·K^{-1}·mol^{-1}. A heat capacity of reaction of that magnitude implies a standard-state enthalpy of reaction of -2 kJ·mol^{-1} at 313.15 K. These enthalpy of reaction values are an order of magnitude smaller than the enthalpies of solution of the ionic liquids, which are on the order of (15 to 25) kJ·mol^{-1}. As such, accepting these values and accepting a 15 % extent of reaction for reaction 1, the error that could occur from ignoring the first hydrolysis reaction upon reaching full equilibrium would be on the order of (1 to 1.5) %. We extrapolated the observed drift temperatures, after dissolution was complete, to the time at which the cell was opened. This practice should eliminate enthalpy effects from the slow hydrolysis reactions and their small enthalpies of reaction. The experimental values of the enthalpy of solution determinations for [C8mim]BF$_4$, the temperatures of the mixing process, and the final solution compositions are given in Table 1. The experimental quantities for [C4mim]BF$_4$ are given in Table 2.

Figure 2 shows values of $\Delta_{sol}H_m - \nu z_M z_X A_H \ln[1+bI^{1/2}]/2b$ from the present results for [C8mim]BF$_4$ for nominal temperatures of 298.15 K, 306.15 K, and 313.15 K and against ionic strength, where the second term in the quantity is a Debye−Hückel limiting term for the relative apparent molar enthalpy. The symbols are the following: ν is the number of particles into which the solute dissociates ($\nu = 2$); z_M and z_X are the charges of the cation and the anion, respectively; b is a constant, chosen to be 1.2 kg$^{1/2}$·mol$^{-1/2}$; I is ionic strength; and A_H is the Debye−Hückel coefficient for the apparent molar enthalpy. The Debye−Hückel coefficients used in the present work were calculated from the equation of state for water from Hill[11] and the dielectric-constant equation from Archer and Wang.[12]

Standard-State Properties of the Solution Process. The standard-state enthalpy and heat capacity of solution were extracted from the measured enthalpies of solution. Complete dissociation of the dissolved ionic liquids and sodium fluoride was assumed. The following function was fit to those measured enthalpies of solution that were unaffected by micellization

$$\Delta_{sol}H_m - \frac{\nu z_M z_X A_H \ln(1+bI^{1/2})}{2b} =$$
$$\Delta_{sol}H_m°(T_r) + \Delta_{sol}C_p°(T_r)(T - T_r) - \frac{T^2(dB/dT)IH°}{T°m°} \quad (6)$$

where $\Delta_{sol}H_m$ is the observed enthalpy of solution, $T°$ is 1 K, $H°$ is 1 J·mol^{-1}, and $m°$ is 1 mol·kg^{-1}. $\Delta_{sol}H_m°(T_r)$ and $\Delta_{sol}C_p°(T_r)$ are the standard-state enthalpy and heat capacity at temperature T_r, the last of which was chosen to be 298.15 K. The parameter dB/dT is the coefficient of an ionic strength dependence term. We have not used the ion-interaction model here because there are not available sufficient ion-interaction terms to model the process and

Table 1. Enthalpy of Solution of [C8mim]BF₄(l) in Water and in Aqueous Sodium Fluoride

T(ITS-90)	m([C8mim]BF₄)	m(NaF)	$\Delta_{sol}H_m$(obsd)	T(ITS-90)	m([C8mim]BF₄)	m(NaF)	$\Delta_{sol}H_m$(obsd)
K	mol·kg⁻¹	mol·kg⁻¹	J·mol⁻¹	K	mol·kg⁻¹	mol·kg⁻¹	J·mol⁻¹
298.1665	0.006299	0	18.984	298.1356	0.007627	0.0997	19.332
298.0039	0.006865	0	19.197	298.1653	0.007533	0.428	19.012
298.1145	0.006116	0	19.195	313.1897	0.007502	0.428	24.988
298.1187	0.008176	0	19.306	298.1428	0.020143	0	19.677
313.1184	0.007541	0	24.465	313.1041	0.013047	0	24.289
306.3284	0.007579	0	22.094	298.1556	0.013073	0	19.610
313.1934	0.006719	0	24.543	298.1537	0.009834	0	19.476
305.6972	0.007651	0.0994	22.087	313.1480	0.006089	0	24.767
313.1846	0.007351	0.400	24.871	313.1497	0.004742	0	24.969
298.1202	0.008066	0.400	19.064	313.1484	0.004139	0	25.148
306.6591	0.007688	0.400	22.580	313.1236	0.003378	0	25.116
298.1329	0.007836	0.250	19.480	313.1483	0.004706	0	25.173
305.7345	0.007881	0.250	21.848	313.1452	0.005341	0	24.823
313.1866	0.007827	0.250	25.203	298.1583	0.003953	0	19.089
298.6747	0.007380	0.0997	19.124	313.1501	0.016696	0	24.148
313.1784	0.007416	0.0997	24.975				

Table 2. Enthalpy of Solution of [C4mim]BF₄(l) in Water

T(ITS-90)	m([C4mim]BF₄)	m(NaF)	$\Delta_{sol}H_m$(obsd)
K	mol·kg⁻¹	mol·kg⁻¹	J·mol⁻¹
298.1496	0.01257	0	15.325
298.1576	0.01349	0	15.136
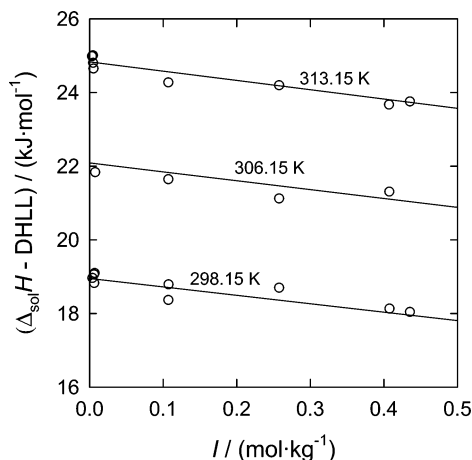
Figure 2. Values of the enthalpy of solution of [C8mim]BF₄, less a Debye−Hückel contribution to the enthalpy, against the stoichiometric ionic strength of the final solution for temperatures of 298.15 K, 306.15 K, and 313.15 K.

Table 3. Thermodynamic Properties of the Aqueous Solution Process for [C8mim]BF₄(l) at 298.15 K

$\Delta_{sol}H°$	(18.97 ± 0.15) kJ·mol⁻¹
$\Delta_{sol}C_p°$	(392 ± 14) J·K⁻¹·mol⁻¹
dB/dT	(−2.50 ± 0.57) × 10⁻⁵

the present data are not sufficient to determine all, or even most, of the ion-interaction terms required. The fitted parameters, and their 95 % confidence intervals within this model, are given in Table 3. The root-mean-square error for the fitted measurements was ±170 J·mol⁻¹, which corresponds to a root-mean-square error of approximately ±2.0 × 10⁻⁴ K in the observed temperature rise for the measurement.

The standard-state enthalpy of solution of [C4mim]BF₄ was calculated from the average of the values in Table 2, from which had been subtracted a Debye−Hückel contribution for the ionic strength. The value thus obtained was $\Delta_{sol}H_m°(T_r)$ = 15.02 kJ·mol⁻¹. We take the uncertainty in this value to be the same as that calculated for the [C8mim]-BF₄ enthalpy of solution, namely, ±150 J·mol⁻¹, consistent with a 95 % confidence interval.

Discussion

Standard-State Properties. Group additivity schemes can be used to calculate standard-state thermodynamic properties of many processes for many compounds for which measurement data do not exist, provided that sufficient data exist for the "groups" that can be used to describe the compounds. We begin work on establishing these group properties for ionic liquids herein.

Using the standard-state enthalpies of solution at 298.15 K for [C8mim]BF₄ and [C4mim]BF₄, one can calculate an enthalpy of solution value for a methylene group, $\Delta_{sol}H°$-(CH₂). That value is 1.0 kJ·mol⁻¹ per CH₂ group; $\Delta_{sol}H°$-(CH₂) = 1.0 kJ·mol⁻¹. This quantity, which could be used in group additivity schemes for ionic liquids, refers to the methylene in the ionic liquid, and we compared it to the value obtained for nonionic liquids in order to determine the closeness of this value to that for a methylene group in nonionic liquids. If the two are similar, then one may have some confidence in using additivity values for other groups, determined from nonionic liquid materials, in group additivity schemes for ionic liquids. From Plyasunov and Shock's[13,14] studies of group additivity parameters for hydrocarbons and alkanols, the value $\Delta_{hyd}H°$(CH₂) = (−3.76 ± 0.22) kJ·mol⁻¹ was obtained, where the uncertainty was a 95 % confidence interval within the context of their model. Plyasunov and Shock's enthalpy of hydration is related to the enthalpy of solution by

$$\Delta_{hyd}H° = \Delta_{sol}H° - \Delta_{vap}H° \qquad (7)$$

We obtained an estimate of $\Delta_{vap}H°$(CH₂) from the enthalpy of vaporization values tabulated by Majer and Sovoboda[15] for the series of homologous normal alkanes (pentane through octane, $\Delta_{vap}H°$(CH₂) = 4.93 kJ·mol⁻¹) and normal 1-alkanols (methanol through 1-octanol, $\Delta_{vap}H°$-(CH₂) = 4.77 kJ·mol⁻¹). We took the average of these two values, $\Delta_{vap}H°$(CH₂) = (4.85 ± 0.1) kJ·mol⁻¹. A combination of the vaporization and the hydration group additivity values gives the group additivity value for the enthalpy of solution, $\Delta_{sol}H°$(CH₂) = (1.09 ± 0.24) kJ·mol⁻¹. The group additivity value obtained from the measurements for the two ionic liquids is in excellent agreement with the value obtained from the linear alkanes and linear 1-alkanols. This agreement indicates that the ionic nature of the ionic liquid appears to have little effect on the enthalpy of transfer of the hydrocarbon portion of the molecule from the ionic liquid to the aqueous solution.

Using the group additivity value determined above for the enthalpy of solution of the methylene group, one can

Table 4. Thermodynamic Properties for Aqueous Homologous 1-Alkyl-3-methylimidazolium Tetrafluoroborates at 298.15 K

alkyl	$\Delta_{sol}H°$ kJ·mol^{-1}	$C_{p,\phi}°([Cxmim]BF_4(aq))$ J·K^{-1}·mol^{-1}	$C_{p,\phi}°([Cxmim]^+(aq))$ J·K^{-1}·mol^{-1}	$C_{p,1}°$ J·K^{-1}·mol^{-1}	$\Delta_{sol}C_p°$ J·K^{-1}·mol^{-1}
C10	21.0	1044	1094	532	512
C9	20.0	954	1004	502	452
C8	(19.0 ± 0.15)	(864 ± 18)	(914 ± 25)	472	(392 ± 14)
C7	18.0	774	824	442	332
C6	17.0	684	734	412	272
C5	16.0	594	644	382	212
C4	(15.0 ± 0.15)	504	554	(351.5 ± 12)	152
C3	14.0	414	464	322	92
C2	13.0	324	374	292	32
C1	12.0	234	284	262	-28

calculate a group additivity value for the enthalpy of solution of the group (1-methyl-3-methylimidazolium tetrafluoroborate). That value is $\Delta_{sol}H° = 12$ kJ·mol^{-1}. We do not yet have sufficient information to separate the tetrafluoroborate ion contribution from that group additivity value.

The standard-state molar heat capacity of solution of the [C8mim]BF$_4$ solute was calculated from the present measurements to be $\Delta_{sol}C_p° = 392$ J·K^{-1}·mol^{-1}. Strictly speaking, this value is for $T = 305.65$ K, the midpoint of the temperature region considered here, even though we crafted the equations to yield the heat capacity for 298.15 K. However, the change in heat capacity from 305.65 K to 298.15 K is not very large, as we demonstrate with the following estimation. Through heat capacity measurements on aqueous surfactants, Archer[16,17] showed that the heat capacity for an aqueous methylene group decreased with temperature, with $dC_p°/dT = -0.4$ J·K^{-2}·mol^{-1} per CH$_2$ group. Countering this 24 J·K^{-1}·mol^{-1} increase in the 298.15 K apparent molar heat capacity due to the alkyl chain portion of the solute would be a decrease in the standard-state heat capacity that would attend the ionic portion of the solute as temperature is changed from 305.65 K to 298.15 K. We do not currently have highly precise information on that contribution, although it might be expected to be on the order of about -5 J·K^{-1}·mol^{-1} if one uses sodium chloride as a surrogate. Also increasing $\Delta_{sol}C_p°$ for the decrease in temperature from 305.65 K to 298.15 K would be the increase in the heat capacity with respect to temperature for the neat ionic liquid. We estimated that quantity from the sum of values from two sources: from the equation given by Fredlake et al.[18] for the heat capacity of [C4mim]BF$_4$, we calculated the temperature dependence of the molar heat capacity to be 0.261 J·K^{-2}·mol^{-1}, and from the equations given by Messerly et al.[19] for the heat capacity of hydrocarbons pentane to nonane, we obtained an increment for the four additional methylene units, $dC_p°/dT = 0.12$ J·K^{-2}·mol^{-1}. Those two quantities taken together yield $dC_p°/dT = 0.38$ J·K^{-2}·mol^{-1} for [C8mim]BF$_4$, which in turn yields an adjustment of +2.8 J·K^{-1}·mol^{-1}. These three quantities taken together would imply that the 298.15 K standard-state heat capacity should be about 22 J·K^{-1}·mol^{-1} larger than the midpoint value and that the standard-state heat capacity for 313 K would be about 22 J·K^{-1}·mol^{-1} smaller than that for the midpoint of the temperature interval.

The standard-state heat capacity of solution of [C8mim]BF$_4$ could be combined with the heat capacity of the neat ionic liquid to obtain the standard-state heat capacity of aqueous [C8mim]BF$_4$. However, as far as we are aware, reliable values of the heat capacity of liquid [C8mim]BF$_4$ have not yet been published. We estimated this quantity in the following way. We took the 298.15 K heat capacity

of [C4mim]BF$_4$, from Fredlake et al.[18] ($C_{p,1}° = (351.5 ± 12)$ J·K^{-1}·mol^{-1}). To that quantity, we added a contribution for the four methylene groups required to bring the butyl side chain to an octyl side chain. The increment for the methylene group ($C_{p,1}°(CH_2) = 30$ J·K^{-1}·mol^{-1}) was obtained from the data for the hydrocarbons summarized by Messerly et al.[19] The result was ($C_{p,1}°([C8mim]BF_4) = (472 ± 15)$ J·K^{-1}·mol^{-1}). A combination of that value with the heat capacity of solution obtained here, as in

$$\Delta_{sol}C_p° = C_{p,\phi}° - C_{p,1}° \tag{8}$$

gave ($C_{p,\phi}°([C8mim]BF_4) = (890 ± 30)$ J·K^{-1}·mol^{-1}). This quantity can be combined with the standard-state heat capacity of an aqueous methylene unit $C_p°(CH_2(aq)) = 90$ J·K^{-1}·mol^{-1},[20] to obtain $C_{p,\phi}°$ for other ionic liquids containing the 1-alkyl-3-methylimidazolium tetrafluoroborate moiety. In this way, we estimated the standard-state heat capacity of aqueous 1-methyl-3-methylimidazolium tetrafluoroborate to be $C_p°([C1mim]BF_4^-(aq)) = (260 ± 30)$ J·K^{-1}·mol^{-1}. In previous work, we obtained the standard-state heat capacity of the aqueous tetrafluoroborate ion, $C_p°(BF_4^-(aq)) = (-50 ± 18)$ J·K^{-1}·mol^{-1}.[21] This value can be subtracted from $C_p°([Cxmim]BF_4^-(aq))$ to obtain the standard-state heat capacity for the aqueous organic cation. Thermodynamic properties of ionic liquids calculated from these group additivity relations are given in Table 4.

Micellization Behavior. We noted above that during the course of measurements we observed behavior of the solutions consistent with [C8mim]BF$_4$ possessing surfactant properties. The characteristic properties of a surfactant are (1) accumulation at a water interface, where it lowers the interfacial tension between the solution and the second surface when compared to the interfacial tension of pure water with the surface and (2) formation of self-assembled structures in solution that can lead to detergency—the increase of solubility of an organic material by deposition into emulsified or microemulsified structures. We explored the thermodynamics of solutions with concentrations of [C8mim]BF$_4$ larger than those required for the determination of the standard-state properties to attempt to explore the surfactant behavior in more detail.

The enthalpy of solution of [C8mim]BF$_4$ in water as a function of molality is shown in Figure 3. At very low concentrations, the enthalpy of solution is a slowly varying function of ionic strength. In a higher, but narrow, range of concentration, the enthalpy of solution varies more prominently with respect to concentration, and then at yet higher concentrations, it again becomes a slowly varying function of ionic strength. The results in Figure 3 are consistent with the usual appearance of the apparent molar enthalpy changes that arise from micellization as a function of concentration and temperature.[22–24] For the dilute
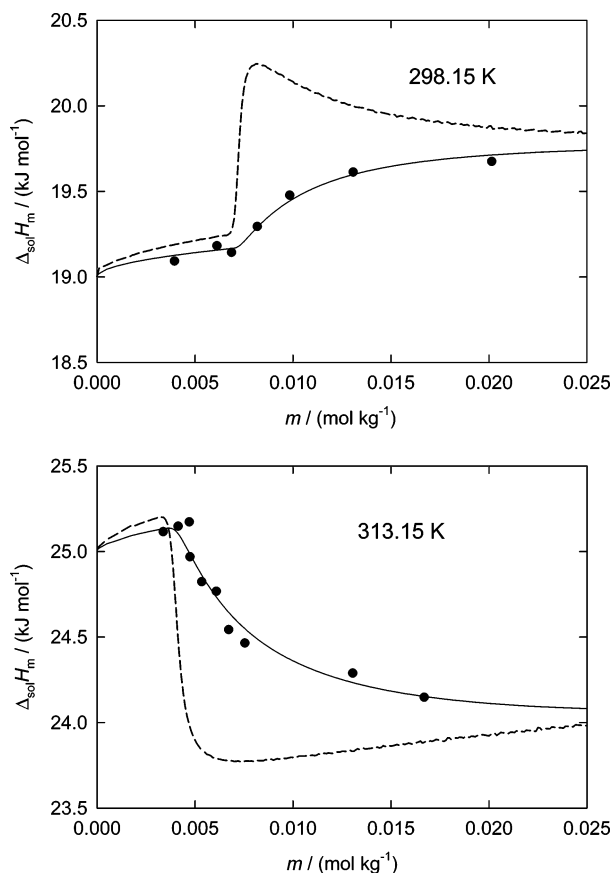
Figure 3. Values of the apparent molar enthalpy of solution and partial molar enthalpy of solution against molality at 298.15 K and 313.15 K. The symbols are measured enthalpies of solution. The solid lines are the apparent molar enthalpy of solution, and the dashed lines are the partial molar enthalpy of solution.

compositions, the solute dissolves entirely, or almost entirely, as monomers, perhaps with some small number of aggregates with small aggregation numbers also forming. In the region of rapid change in the enthalpy of solution, some of the solute dissolves as monomers, and some of the solute forms larger aggregates or micelles. At yet higher concentration, the solute dissolves primarily in the form of micelles, resulting in the smaller concentration dependence of the enthalpy of solution. The results in Figure 3 are consistent with this picture.

Micelles of ionic surfactants are small aggregates, where small means anything on the order of about 5 to 100, the formation of which depends on the length of the hydrocarbon portion of the surfactant, the structure of the ionic headgroup, and the favorability of hydrolysis of the counterion. Micelles often have a particular small range of geometries, which approximate a spherical arrangement in which the ionic groups are oriented toward the water interface and the hydrocarbon parts of the surfactant molecules associate in the inside of the structure, forming an internal environment like that of a neat hydrocarbon or a wet hydrocarbon.

There are two common methods of treating the thermodynamic properties of the micellization process. One method is the monodisperse micelle model, and the other is the pseudophase transition model. The former treats the micelles as being monodisperse (i.e., all micelles have exactly the same aggregation number), and the thermodynamic properties are fit with a model that contains a single equilibrium constant for the micellar aggregates. The pseudophase transition model essentially ignores the near

monodispersity of the micellar aggregates (i.e., it fails to account for the thermodynamics that cause a preferred narrow band of stoichiometries for the micellar reactions) and treats the properties of the micellar solution as though a phase transition occurred at the critical micelle concentration. The simplicity of both models is so great that it invalidates the models. Both models give model behavior that diverges obviously from the behavior observed over wide ranges of independent variables and also diverges from the better of the available thermodynamic measurements.

Micelles often have nearly monodisperse distributions of aggregation numbers. However, they cannot be monodisperse because we know that average aggregation numbers change dramatically with temperature.[22,25] If micelles were monodisperse, with an aggregation number that changed with temperature, then the thermodynamic properties such as entropy and enthalpy would have to be discontinuous functions of temperature, a phenomenon that we can intuitively dismiss because it is simply implausible.[24]

Specifically, in a model that contains a narrow distribution of highly populated aggregation numbers, and for the case where the average aggregation number decreases with increasing temperature, micelles with aggregation numbers somewhat below the average form with positive changes in enthalpy, and those that form with aggregation numbers at and above the average form with negative changes in enthalpy.[24] That observation means that it is fruitless to try to infer molecular-level interactions from the average thermodynamic property change because the average is obtained from such a wide range of individual-reaction properties. There is usually not enough information regarding the distribution of stoichiometries, particularly as functions of the independent variables, with which to build a realistic thermodynamic model. Thus, one can refer only to average thermodynamic properties of micelle formation, and they become, like the critical micelle concentration, only an operational definition without much basis in the reality of the micellar solution.

The pseudophase transition model predicts a discontinuity in partial molar thermodynamic quantities at the critical micelle concentration. However, careful measurement shows that the properties are not discontinuous at the critical micelle concentration and that, in fact, the critical micelle concentration is not critical at all in the sense that there is not a real discontinuity in the slope of the measured property at the critical micelle concentration. This effect was seen most obviously when the thermodynamic properties of aqueous surfactants were measured over a wide range of temperature. Those measurements showed that the critical micelle concentration was really a region of concentration that became more diffuse with increasing temperature as the average aggregation number of the micelle decreased with increasing temperature.

Both the monodisperse mass-action model and the pseudophase separation model relate the changes in critical micelle concentration with respect to the independent variables of temperature and pressure to the enthalpy of micellization and the volume of micellization, respectively. When analyzing only the dependence of the critical micelle concentration on the temperature or pressure to obtain the enthalpy of micellization or the volume of micellization, there can be no inherent inconsistency. However, when one extracts the enthalpy of micellization from calorimetric results or extracts the volume of micellization from volumetric results and compares those with the quantity

extracted from the temperature or pressure dependence of the critical micelle concentration, then the opportunity for thermodynamic inconsistency arises. If the inconsistency were to arise from experimental uncertainties for any one or each particular surfactant, then one might expect that the differences obtained between the volumes or enthalpies of micellization would be randomly distributed. Such a hypothesis, recast as a null hypothesis, can be, and has been,[26] checked with the customary normal-plot analysis. An examination of volumes of micellization, obtained from the variation of critical micelle concentration with respect to pressure, on one hand, and obtained from measurements of the densities, or specific volumes, of surfactant solution, on the other hand, was conducted for 10 different surfactants.[26] That examination found that 16 of 18 determinations of the volumes of micellization using density data were greater than the volumes of micellization obtained from the variation of critical micelle concentrations with pressure for the same surfactant. That comparison indicated a statistically significant difference between the two different ways of obtaining the volume of micellization, which cannot be attributed to random uncertainties in the measurements. The more probable explanation is that discrepancies between the results from different kinds of measurements reflect limitations that arise from the simplistic assumptions inherent in the monodisperse mass action and pseudophase separation models. In other words, the statistically significant differences may reflect the presence of the variation in distribution of stoichiometries, which is assumed not to exist in the monodisperse mass-action model and the pseudophase separation models. A similar inconsistency for enthalpies of micellization was also observed.[24]

Thus, we come to the assessment that the thermodynamic quantities of micellization reactions, including the critical micelle concentration, are only operationally defined and thermodynamic relationships among them often break down when examined closely enough. Even though these properties are only operational definitions, they still enjoy some practical applicability. For example, the critical micelle concentration, being the concentration at which micelles begin to form in significant numbers with increasing surfactant concentration, gives a lower concentration limit at which one might first encounter increased solubilization of material that is hardly soluble in water, for example, an oil.

If one defines operationally the critical micelle concentration (herein cmc) as the first concentration region at which the enthalpy first noticeably diverges from the slowly varying region that corresponds to premicellar concentrations, then the cmc of [C8mim]BF$_4$ at 298.15 K would be 0.007 mol·kg^{-1} based on Figure 3. This value of the cmc is significantly smaller than the cmc reported for [C10mim]-Br (cmc = 0.04 mol·L^{-1})[27] and for both [C8mim]Cl(aq) and [C8mim]I(aq), namely, cmc = 0.1 mol·kg^{-1}.[28] Bowers et al.[28] observed two break points in their plots of electrical conductivity for [C8mim]Cl(aq) and [C8mim]I(aq). The first and more pronounced of the breaks occurred near 4×10^{-4} and 3×10^{-4} mol·L^{-1}, respectively. Those concentrations are an order of magnitude smaller than the concentrations that we have observed here for the cmc. A comparison of the present hypothesized cmc value with the figure containing the surface tension data from Bowers et al. (their Figure 2) shows that our concentration corresponds to the concentration at which a significant decrease in surface tension occurs. Miskolczy et al.[29] have also examined the behavior of [C8mim]Cl in aqueous solution. They measured

the turbidity of the solution of [C8mim]Cl and found that it became "cloudy" above 0.005 mol·L^{-1} concentration. They concluded that [C8mim]Cl does not micellize but instead forms an inhomogeneous solution containing larger aggregates. This is a remarkably different result from that obtained by Bowers et al. using small-angle neutron scattering (SANS). They interpreted their SANS data as indicating the presence of micelles with mean aggregation numbers of 30 to 45. The concentration that Miskolczy et al. reported from their turbidity study is in good agreement with the value we obtain from the enthalpy of solution data, albeit the two studies utilized a different counterion with the [C8mim] cation. However, we can consider the enthalpic effect that would result from incomplete dissolution, a potential source of turbidity. Incomplete dissolution leads to an apparent molar enthalpy of solution whose absolute value decreases with increasing concentration. The measured data show the opposite behavior at 298.15 K (Figure 3). At 313.15 K, the enthalpy of solution does decrease with increasing concentration of [C8mim]BF$_4$, but the concentration dependence of the decrease is not mathematically consistent with incomplete dissolution. Last, the magnitude of the enthalpy of solution of the inhomogeneous aggregates would have to be very nearly that of the dissolved [C8mim]-BF$_4$ to be in accord with the measured enthalpy of solution. Thus, the presently reported data seem not to support a picture of incomplete dissolution above 0.005 mol·L^{-1}.

The average enthalpy change due to the hypothesized micellization changes sign between 298.15 K and 313.15 K. This is consistent with behavior observed for other cationic surfactants. For example, the average enthalpy of micelle formation of decyltrimethylammonium bromide passes through zero near 298 K.[22]

Conclusions

We have provided here new thermodynamic measurements for aqueous solutions of [C8mim]BF$_4$ and [C4mim]-BF$_4$. From those measurements, we extracted a group additivity parameter for the enthalpy of solution and showed it to be similar to values for other organic liquids. We calculated the standard-state enthalpy of solution, the standard-state heat capacity of solution, the standard-state heat capacity of the homologous series of aqueous 1-alkyl-3-methylimidazolium tetrafluoroborates, and the standard-state heat capacity of the aqueous 1-alkyl-3-methylimidazolium cations.

We observed surfactant-like behavior in the very dilute aqueous solutions of 1-octyl-3-methylimidazolium tetrafluoroborate. We cannot be sure of the critical micelle concentration from either our present measurements or from the results reported in the literature, which are in disagreement. Regardless, the potential micellization of the hydrophobic ionic liquids carries ramifications for their potential industrial use in that they will probably be capable of increasing the apparent solubility of hydrophobic materials in the event of accidental discharge. This effect accompanies the hydrolytic instability of the tetrafluoroborate and hexafluorophosphate ionic liquids, which can liberate hydrogen fluoride in the event of accidental discharge into a water-containing environment.

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