Thermodynamic and Thermophysical Properties of Ionic Liquid + Water Systems

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Excess enthalpy measurements on four ionic liquid (1-ethyl-3-methylimidazolium thiocyanate, 1-ethyl-3-methylimidazolium diethylphosphate, ethyl(tributyl)phosphonium diethylphosphate, and 1-hexyl-3-methylimidazolium trifluoromethanesulfonate) + water mixtures are reported. Heat capacities and densities of seven pure ionic liquids were measured. These measurements of imidazolium- and phosphonium-based ionic liquids are compared to our previous physical property measurements.

Introduction

Ionic liquids (ILs) are organic salts that are liquid near room temperature. ILs have a negligible vapor pressure under normal operating conditions and have a large liquid working temperature range. ILs have many favorable properties which make them attractive for a number of applications. In fact, understanding thermodynamic and thermophysical properties of pure ILs and IL mixtures is essential to determine potential applications.

We are interested in excess enthalpies of IL and water mixtures, pure IL heat capacities, and pure IL densities as these properties will be used in a future publication to evaluate IL and water mixtures for absorption refrigeration applications. To evaluate ILs for absorption refrigeration applications, one must be able to calculate the enthalpy of the mixtures as a function of temperature, pressure, and composition. Therefore, the key thermodynamic properties necessary for evaluating ILs for absorption refrigeration applications are pure component heat capacities, excess enthalpies of the water + IL mixtures, and the vapor−liquid equilibrium of the water + IL mixtures (to determine liquid phase nonideality). Density is important for sizing of equipment. Here we will focus on densities, heat capacities, and excess enthalpies. Moreover, these properties are useful for characterizing new ILs and identifying their potential for a wide variety of applications.

Here, we have experimentally measured the excess enthalpy of four IL and water mixtures, 1-ethyl-3-methylimidazolium thiocyanate ([emim][SCN]), 1-ethyl-3-methylimidazolium diethylphosphate ([emim][DEP]), ethyl(tributyl)phosphonium diethylphosphate ([P_{2444}][DEP]), and 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([hmim][OTf]). The heat capacities and densities were measured for these ILs, as well as 1-(2-hydroxyethyl)-3-methylimidazolium trifluoroacetate ([OHemim][TFA]), 1-ethyl-3-methylimidazolium hydrogensulfate ([emim][HSO_4]), 1-ethyl-3-methylimidazolium methylsulfate ([emim][$MeSO_4$]), and 1-ethyl-3-methylimidazolium methanesulfonate ([emim][$MeSO_3$]). The excess enthalpies of the IL systems not reported here have been previously published.[1,2] The structures and abbreviations of all of the ILs are listed in Table 1. The ILs were chosen to systematically vary the substituents (on either the anion or cation) and evaluate the effect on the coefficient of performance. In general we are interested in ILs that are completely miscible with water. Thus, it is important to note that the only IL investigated which is only partially miscible with water is the [hmim][OTf].

Experimental Methods

Chemicals. The ILs were purchased commercially from EMD Chemicals, Inc. ([emim][HSO_4] and [emim][DEP]), Sigma Aldrich ([emim][SCN]), Iolitec ([emim][$MeSO_4$], [emim][$MeSO_3$], and [hmim][OTf]), and Cytec Industries, Inc. ([P_{2444}][DEP]), all which had a purity of ≥ 99 % except for [emim][HSO_4] with ≥ 98 % purity. The samples were used as received except for drying. The [OHemim][TFA] was synthesized in our laboratory, as detailed previously,[1] and had impurity levels (mass fraction) of bromide and silver of less than $50 \cdot 10^{-6}$.

Additionally, high-purity water, deionized through a Milli-Q Water System (>18 MΩ·cm resistivity), was used for all the excess enthalpy experiments. The water content of the ILs was measured with a Karl Fisher Coulometer (Metrohm 831). Each IL had a mass fraction of water less than $200 \cdot 10^{-6}$ prior to experimentation except for the following: [emim][HSO_4] less than $300 \cdot 10^{-6}$ (both ρ and C_p), [P_{2444}][DEP] less than $600 \cdot 10^{-6}$ (ρ only), [emim][DEP] less than $300 \cdot 10^{-6}$ (H^E only), and less than $650 \cdot 10^{-6}$ (both ρ and C_p).

Excess Enthalpy Measurements. The excess enthalpy measurements were made with a Setaram C80 calorimeter which has been described in detail previously.[1,2] The amount of sample in the batch mixing vessels was determined by mass ($\pm 1 \cdot 10^{-5}$ g). The water was placed in the bottom section of the vessel and the IL in the top. A stainless steel lid sits on top of the bottom section, and mercury was used to completely separate the two liquids prior to mixing. Each IL was saturated with mercury prior to experimentation by mixing at an elevated temperature (323 K). The mass fraction of mercury in the IL was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) and was found to be less than $50 \cdot 10^{-6}$. The mixing of the water + IL occurred by continuously rotating the entire calorimeter by 180°. The uncertainty associated with these measurements is 2 %.

Heat Capacity Measurements. The heat capacity measurements were performed using a Mettler Toledo DSC822^e using STAR^e software data collection which has been described in detail previously.[2] A (20 to 40) mg IL sample was placed in an aluminum crucible and hermetically sealed. The heat capacities were determined using the sapphire method, which requires a

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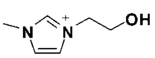
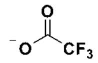
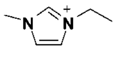
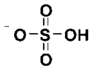
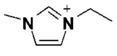
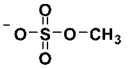
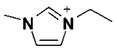
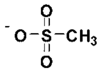
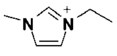
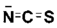
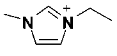
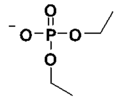
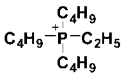
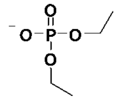
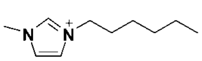
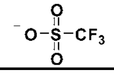
10.1021/je100522z

Table 1. IL Structures and Abbreviations

Cation	*Anion*	*Abbreviation*	*Name*
		[OHemim][TFA]	1-(2-Hydroxyethyl)-3-methylimidazolium Trifluoroacetate
		[emim][HSO_4]	1-Ethyl-3-methylimidazolium Hydrogensulfate
		[emim][$MeSO_4$]	1-Ethyl-3-methylimidazolium Methylsulfate
		[emim][$MeSO_3$]	1-Ethyl-3-methylimidazolium Methanesulfonate
		[emim][SCN]	1-Ethyl-3-methylimidazolium Thiocyanate
		[emim][DEP]	1-Ethyl-3-methylimidazolium Diethylphosphate
		[P_{2444}][DEP]	Ethyl(tributyl)phosphonium Diethylphosphate
		[hmim][OTf]	1-Hexyl-3-methylimidazolium Trifluoromethanesulfonate

minimum of three experimental runs: the blank, the sapphire, and the sample. The uncertainty associated with these measurements is estimated to be 4 %.

Density Measurements. The density measurements were performed on an Anton Paar DMA 4500 density meter at atmospheric pressure which utilizes Anton Paar's vibrating U-tube technology to provide measurement reproducibility of 10^{-5} $g \cdot cm^{-3}$. This instrument has an operating temperature range of (273.15 to 363.15) K. The internal temperature is measured within ± 0.01 K using integrated Pt 100 thermometers. The instrument is adjusted using two known standards: air and water. The uncertainty associated with these measurements is estimated to be $\pm\ 5 \cdot 10^{-5}$ $g \cdot cm^{-3}$.

Results and Discussion

Experimental Excess Enthalpies. The excess enthalpies (H^E) of four new IL and water systems are presented in Figures 1 to 4 at temperatures between (313 and 348) K. The solid curves correspond to the experimental data correlated with a Redlich−Kister type equation used to guide the eye. The experimental raw data for the excess enthalpies can be found in Tables S1 to S4, and fit parameters and absolute average relative deviations for the excess enthalpies can be found in Table S5 in the Supporting Information.

The water + [emim][SCN] system, shown in Figure 1, is a very interesting system in that it has both exothermic and endothermic behavior over the composition range investigated.

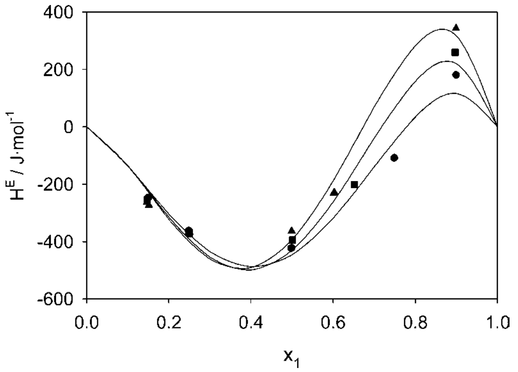


Figure 1. Excess enthalpy, H^E, for the binary system water (1) + [emim][SCN] (2) as a function of mole fraction of water, at different temperatures: ●, 313.14 K; ■, 333.14 K; ▲, 348.13 K. Empirical correlations are plotted as solid lines.

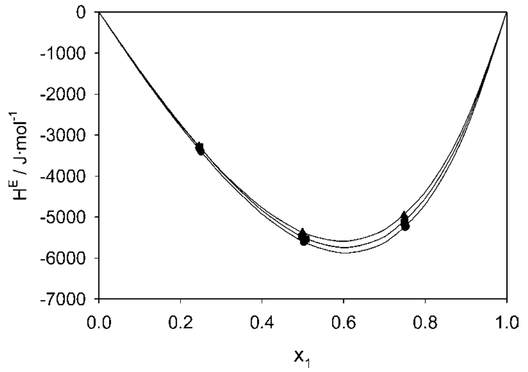


Figure 2. Excess enthalpy, H^E, for the binary system water (1) + [emim][DEP] (2) as a function of mole fraction of water, at different temperatures: ●, 313.13 K; ■, 333.13 K; ▲, 348.12 K. Empirical correlations are plotted as solid lines.

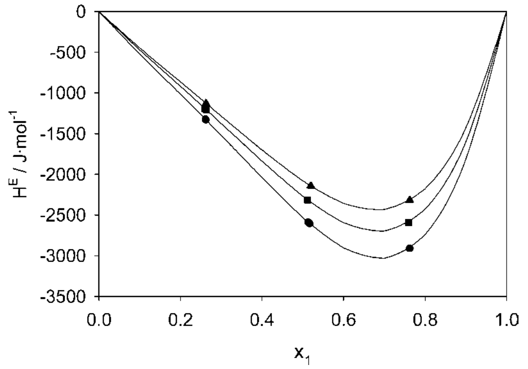


Figure 3. Excess enthalpy, H^E, for the binary system water (1) + [P_{2444}][DEP] (2) as a function of mole fraction of water, at different temperatures: ●, 313.11 K; ■, 333.11 K; ▲, 348.11 K. Empirical correlations are plotted as solid lines.

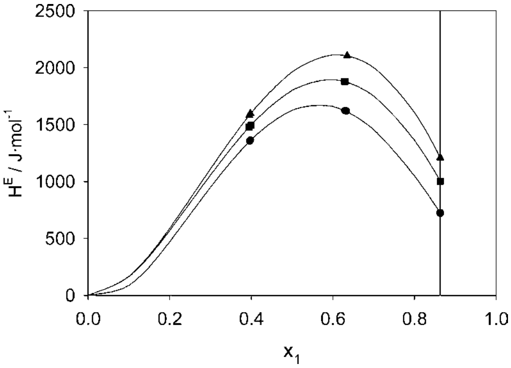


Figure 4. Excess enthalpy, H^E, for the binary system water (1) + [hmim][OTf] (2) as a function of mole fraction of water, at different temperatures: ●, 313.12 K; ■, 333.12 K; ▲, 347.85 K. Empirical correlations are plotted as solid lines. The vertical line represents the solubility of water in the IL at 295 K.

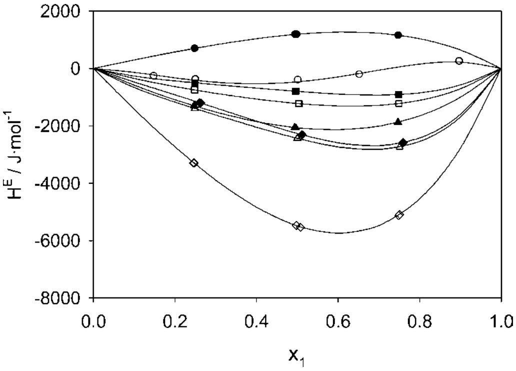


Figure 5. Excess enthalpy, H^E, for the binary systems water (1) + IL (2) as a function of mole fraction of water, at 333.15 K. ILs: ●, [emim][OTf];[2] ○, [emim][SCN]; ■, [emim][EtSO$_4$];[2] □, [OHemim][TFA];[1] ▲, [emim]-[TFA];[2] △, [emim][MeSO$_3$];[1] ♦, [P$_{2444}$][DEP]; ◇, [emim][DEP]. The solid curves represent Redlich−Kister model correlations to guide the eye.

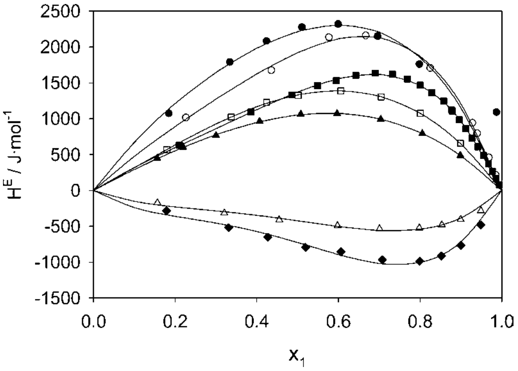


Figure 6. Excess enthalpy, H^E, from the literature for the binary systems water (1) + IL (2) as a function of mole fraction of water with solid lines to guide the eye: ●, [bmpy][BF$_4$] at 303.15 K;[4] ○, [bmim][BF$_4$];[6] ■, [bmpy][BF$_4$] at 298.15 K;[5] □, [bmim][OTf];[4] ▲, [emim][OTf];[4] △, [bmim][MeSO$_4$];[4] ♦, [emim][EtSO$_4$].[4]

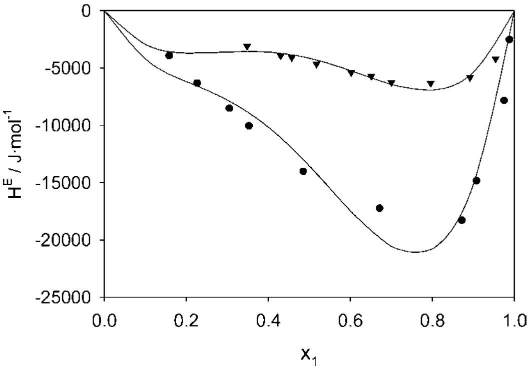


Figure 7. Excess enthalpy, H^E, from the literature for the binary systems water (1) + IL (2) as a function of mole fraction of water with solid lines to guide the eye: ▼, [choline][glycolate][8] and ●, [choline][lactate].[8]

It is important to note that the excess enthalpies for this system are small in magnitude, between (400 and −600) J·mol^{-1}.

The excess enthalpy of the water + [emim][DEP] mixture, shown in Figure 2, is exothermic and increases with increasing temperature. The [emim][DEP] system is the most exothermic system measured indicating strong IL/water interactions.

The water + [P$_{2444}$][DEP] system is exothermic and has increasing excess enthalpy with increasing temperature, as shown in Figure 3. Despite the alkyl chains on the ethyl(tributyl)phosphonium cation, the exothermic excess enthalpy shows that this system has strong IL/water interactions.

The excess enthalpy of water (1) + [hmim][OTf] (2) was thoroughly investigated over the miscible range of composition ($x_1 < 0.86$). This IL was chosen due to the fact that infinite dilution activity coefficients exist in the literature, which is useful for modeling purposes. The vertical solid line in Figure 4 represents the solubility of water in the IL at 295 K, which is $x_1 = 0.86$.[3] Since this is a partially miscible system, it is not surprising that the excess enthalpies are positive. As shown in Figure 4, the excess enthalpy increases with increasing temperature.

In addition to these four new systems, we have previously reported H^E values for other 1-ethyl-3-methylimidazolium-based ILs with water.[1,2] The excess enthalpies for the ILs which are completely miscible with water at 333.15 K are shown in Figure 5, comparing the new systems presented here with our previous work. [emim][OTf] is the only IL that is completely miscible with water and that has a completely endothermic excess enthalpy. The [emim][SCN] has a partially exothermic and partially endothermic excess enthalpy, and the IL with the most negative excess enthalpy is [emim][DEP].

Several groups have reported excess enthalpies of water + IL systems which have been thoroughly investigated for the entire composition range and one or more temperatures: [bmpy][BF$_4$],[4,5] [bmim][BF$_4$],[6,7] [bmim][OTf],[4] [emim][OTf],[4] [bmim][MeSO$_4$],[4] [emim][EtSO$_4$],[4] [choline][lactate],[8] and [choline][glycolate].[8] Figures 6 and 7 show the excess enthalpies for each of the water + IL systems mentioned in the literature. In Figure 6, the water + IL systems with the most endothermic excess enthalpy contain the [BF$_4$]$^-$ anion, followed by the [OTf]$^-$ anion. The literature water + IL systems with exothermic excess enthalpies contain sulfate anions. The [choline]$^+$-based ILs are shown in Figure 7 due to the difference in magnitude of the excess enthalpies compared to those in Figure 6. The [choline][lactate] has the most exothermic excess enthalpy of all of the water + IL systems published to date.

Experimental Heat Capacities. The heat capacity is the ability of the IL to store heat. The experimental molar heat capacities (C_p) are reported in Table 2 from (283 to 343) K and plotted as a function of temperature in Figure 8. For each IL, there is a slight increase in heat capacity with increasing temperature. The solid lines in Figure 8 are used to guide the eye and were calculated according to the equation

$$C_p = a + \frac{b}{T} \tag{1}$$

Table 2. Experimental Molar Heat Capacity, C_p, for the Pure ILs at Selected Temperatures

IL	C_p/J·mol^{-1}·K^{-1} 283.15 K	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K
[OHemim][TFA]	362	367	371	376	381	387	394
[emim][HSO_4]	290	294	297	302	306	313	324
[emim][$MeSO_4$]	324	330	332	337	343	347	354
[emim][$MeSO_3$]	327	327	330	334	339	344	350
[emim][SCN]	285	287	288	290	293	296	300
[emim][DEP]	517	528	533	540	545	547	557
[P_{2444}][DEP]	683	706	716	728	739	753	768
[hmim][OTf]	484	493	500	506	513	516	522

The fit parameters and absolute average relative deviations for the heat capacities can be found in Table S6 of the Supporting Information.

The [P_{2444}][DEP] has the highest heat capacity followed by the [emim][DEP] and [hmim][OTf]. All of the other ILs have heat capacities between (280 and 380) J·mol^{-1}·K^{-1}. To the best of our knowledge, the heat capacity for the ILs mentioned here have not been previously reported except for [hmim][OTf].[9] Diedrichs et al. report the heat capacity for [hmim][OTf] using three different methods, two different DSCs and a modulated-temperature DSC, all of which provide heat capacities in agreement with our measurements within experimental uncertainty.

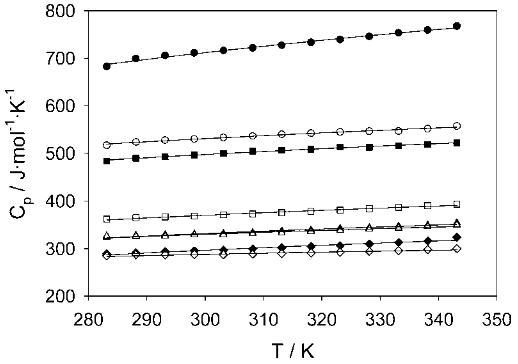


Figure 8. Molar heat capacity, C_p, of the pure ILs as a function of temperature. ILs: ●, [P_{2444}][DEP]; ○, [emim][DEP]; ■, [hmim][OTf]; □, [OHemim][TFA]; ▲, [emim][$MeSO_4$]; Δ, [emim][$MeSO_3$]; ♦, [emim]-[HSO_4]; ◇, [emim][SCN]. Empirical correlations are plotted as solid lines.

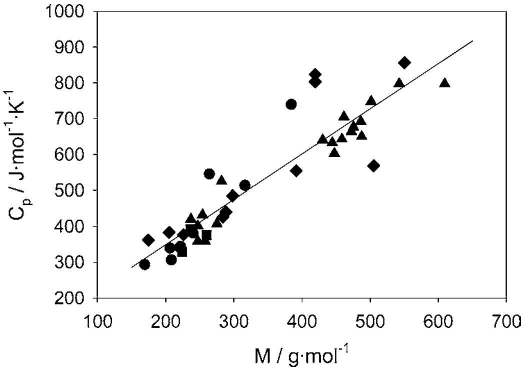


Figure 9. Molar heat capacities, C_p, of pure ILs at 323.15 K as a function of molar mass, M: ●, this work; ■, Ficke et al.;[2] ▲, Crosthwaite et al.;[10] ♦, Fedlake et al.[11]

Our group has published a number of heat capacities previously.[2,10,11] In a plot of heat capacity as a function of molar mass, Figure 9 demonstrates that the new data presented here fall in line with all of the other imidazolium- and pyridinium-based ILs measured previously at 323.15 K. As expected, the ILs with a higher molecular weight generally have a higher heat capacity because more atoms correspond to more bonds in which to store energy.

Experimental Densities. The densities of all of the pure ILs were measured as a function of temperature as listed in Table 3 from (293 to 343) K. The fit parameters and absolute average relative deviations for the densities can be found in Table S7 of the Supporting Information. In Figure 10, the densities were correlated with a second-order polynomial. The densities of the ILs are all above the density of water except for the [P_{2444}][DEP] which has a density similar to that of pure water. The density decreases with increasing temperature for all of the ILs. Densities for the ILs presented here have not been reported previously.

Adding a hydroxyl group to the [emim][TFA] increases the density. In comparison with our previously published densities,[11,12] there are a number of clear trends. Fluorinated ILs, such as ILs with the trifluoroacetate ([TFA]$^-$), bis(trifluoromethylsulfonyl)imide ([Tf_2N]$^-$), tris(trifluoromethylsulfonyl)methide, or trifluoromethanesulfonate ([OTf]$^-$) anions, have higher densities than nonfluorinated ILs. Additionally, increasing the alkyl chain on the cation or anion decreases the density. For example, the density of [emim][$EtSO_4$] is less than the density of [emim]-[HSO_4], and the density of [bmim][Tf_2N] is lower than the density of [emim][Tf_2N]. Phosphonium-based ILs have lower densities than imidazolium-based ILs; [P_{2444}][DEP] has the lowest density of all of the ILs measured in our laboratory.

Conclusions

Excess enthalpies were reported for four new water + IL mixtures. The systems include those with partial miscibility and

Table 3. Experimental Density, ρ, for the Pure ILs at Selected Temperatures

IL	ρ/g·cm^{-3} 293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K
[OHemim][TFA]	1.37039	1.36636	1.36251	1.35480	1.34698	1.33946	1.33198
[emim][HSO_4]	1.36928	1.36579	1.36263	1.35627	1.35014	1.34438	1.33846
[emim][$MeSO_4$]	1.29115	1.28775	1.28437	1.27761	1.27087	1.26422	1.25772
[emim][$MeSO_3$]	1.24731	1.24383	1.24045	1.23348	1.22703	1.22033	1.21379
[hmim][OTf]	1.23889	1.23513	1.23136	1.22382	1.21631	1.20883	1.20141
[emim][DEP]	1.14892	1.14547	1.14203	1.13519	1.12857	1.12194	1.11536
[emim][SCN]	1.11902	1.11596	1.11291	1.10685	1.10085	1.09491	1.08906
[P_{2444}][DEP]	1.01074	1.00743	1.00410	0.99742	0.99087	0.98433	0.97779

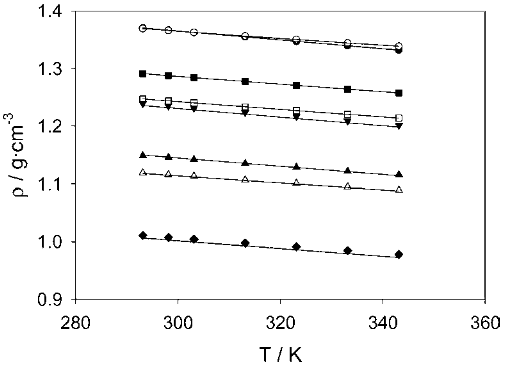


Figure 10. Density, ρ, of pure ILs as a function of temperature. ILs: ●, [OHemim][TFA]; ○, [emim][HSO_4]; ■, [emim][$MeSO_4$]; □, [emim]-[$MeSO_3$]; ▼, [hmim][OTf]; ▲, [emim][DEP]; Δ, [emim][SCN]; ♦, [P_{2444}][DEP]. Polynomial correlations are plotted as solid lines.

positive excess enthalpies ([hmim][OTf]), both positive and negative excess enthalpies ([emim][SCN]), and ones with strong interactions with water so that they exhibit large negative excess enthalpies (ILs with the $[DEP]^-$ anion). Experimental data for IL mixtures with water are important, in general, due to the hygroscopic nature of ILs. We will use this information in a future publication for the evaluation of water + IL systems for absorption refrigeration applications. Heat capacities and densities are also reported for the pure imidazolium- and phosphonium-based ILs.

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Supporting Information Available:

Experimental excess enthalpies of the water + IL systems (Tables S1 to S4); excess enthalpy fit parameters and absolute average relative deviations (Table S5); heat capacity fit parameters and absolute average relative deviations (Table S6); and density fit parameters and absolute average relative deviations (Table S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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