Densities and Excess Enthalpies for Ionic Liquids + Ethanol or + Nitromethane

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Density in the temperature interval (293.15 to 323.15) K and excess enthalpy at 303.15 K are determined for 1-butyl-3-methylimidazolium tetrafluoroborate $[BMIM][BF_4]$ + ethanol or + nitromethane and 1-butyl-3-methylimidazolium methylsulfate $[BMIM][MeSO_4]$ + ethanol or + nitromethane. Excess molar volumes are calculated at several temperatures from density data. Both excess properties are fitted to a Redlich−Kister-based equation, and results are discussed in terms of the chemical nature of the compounds that form the mixtures.

Introduction

Room-temperature ionic liquids (RTILs) have been the object of attention due to their unique physical and chemical properties: extremely low vapor pressure (almost negligible), specific solvent abilities, high thermal stability, high electrical conductivity, and nonflammability.[1–4] All these characteristics make them potential, environmentally friendly substitutes to common organic solvents in most industrial processes. In fact, RTILs have been successfully used as solvents in catalysis,[5] chemical processing,[6] liquid−liquid separations,[7,8] and vapor−liquid equilibria,[9] as the basis of electrochemical applications (batteries, capacitors, photoelectrical cells), as thermal fluids, and as lubricants.[10] In this context, with a view on a proper design of the industrial processes, the precise determination of their physical properties is revealed as an essential task.[11–18]

In recent years, there has been a considerable amount of work devoted to the study of physical properties of pure RTILs and their mixtures with common solvents. However, concerning thermal properties, such as enthalpy or heat capacity, little work has been done.[19–21] This paper reports the excess enthalpy and excess volume behavior for two RTILs + organic solvent binary systems. Excess volume in the temperature interval (293.15 to 323.15) K and excess enthalpy at 303.15 K were determined for the systems 1-butyl-3-methylimidazolium tetrafluoroborate $[BMIM][BF_4]$ + ethanol or + nitromethane and 1-butyl-3-methylimidazolium methylsulfate $[BMIM][MeSO_4]$ + ethanol or + nitromethane. The excess functions are discussed in terms of molecular interactions.

Experimental

Materials. 1-Butyl-3-methylimidazolium tetrafluoroborate $[BMIM][BF_4]$ and 1-butyl-3-methylimidazolium methylsulfate $[BMIM][MeSO_4]$ were supplied by Solvent Innovation with a certified mass fraction greater than 99.8 %. Ethanol with mass fraction greater than 99.5 % was supplied by Probus, and nitromethane was supplied by Fluka, with a mass fraction greater than 98.5 %. In order to reduce the water content and other volatile compounds, a vacuum at 333.15 K was applied for 48 h to the RTILs before measurements were started. Ethanol and nitromethane were dried over Fluka 0.3 nm molecular sieves before use. The water content of the RTILs was measured by Karl Fischer titration. Mass fractions of 0.08 % for $[BMIM][BF_4]$ and 0.12 % for $[BMIM][MeSO_4]$ were obtained.

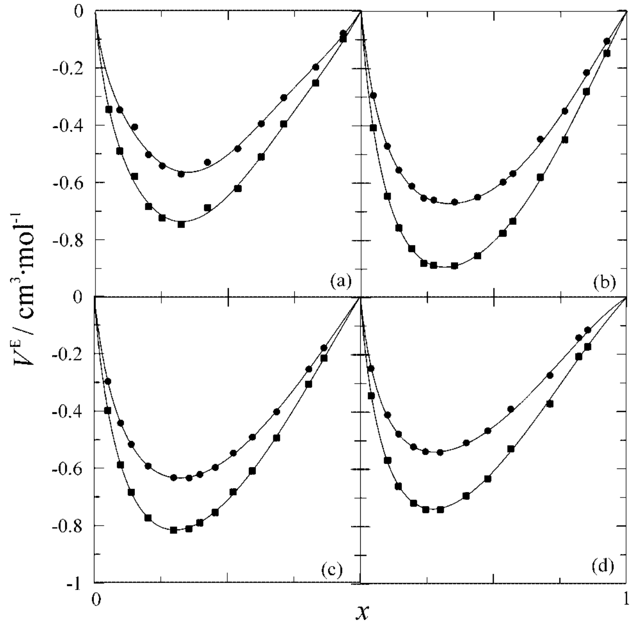

Figure 1. Excess molar volume at ●, T = 293.15 K and ■, T = 323.15 K of the binary systems (a) x $[BMIM][BF_4]$ + $(1-x)$ ethanol, (b) x $[BMIM][MeSO_4]$ + $(1-x)$ ethanol, (c) x $[BMIM][BF_4]$ + $(1-x)$ nitromethane, and (d) x $[BMIM][MeSO_4]$ + $(1-x)$ nitromethane. Solid line, fitted by eq 2.

Apparatus and Procedure. Samples were prepared using a Mettler AE 240 balance, with an uncertainty of $\pm\ 5\cdot10^{-5}$ g, calculating the composition by mass difference. The uncertainty of mole fraction was estimated in $\pm\ 1\cdot10^{-4}$. Density was measured with an Anton Paar DMA-5000 vibrating-tube densimeter, calibrated with ultrapure water and dry air. Due to the high viscosity of RTILs, the standard procedure used for vibrating-tube densimeters was not valid and density must be corrected.[22] DMA-5000 performs this correction automatically. Densities of the samples were measured within the temperature range (293.15 to 323.15) K at atmospheric pressure, with steps of 10 K. Uncertainty is estimated in $1\cdot10^{-4}$ g·cm^{-3} for density and 0.01 K for temperature. Details about the experimental procedure can be found elsewhere.[13]

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Excess molar enthalpies were obtained by Calvet microcalorimetry[23] following the basic procedure described in previous contributions.[24,25] However, the design of the cells was changed with regard to the classical arrangement because the high viscosity of the samples makes them not mix spontaneously in the calorimeter cell, a problem that usually did not take place with the organic liquids studied in previous works. The modifications involve mainly the introduction of elements that allow the mixture to be stirred and thus well-mixed. Therefore, an unknown heat due to the stirring is added to the mixing heat of the liquids that can be evaluated from a new experiment with the same sample, in which only the stirring heat is registered since the mixture is now well-mixed. Consequently, the stirring procedure increases the uncertainty of the experimental excess enthalpy: it was estimated to be about 4 %. As for temperature uncertainty, it is estimated to be ± 0.05 K. Details about the experimental procedure can be found elsewhere.[26]

Results and Discussion

Table 1 shows all experimental density data. Excess molar volume V^E was calculated from these data according to

$$V^{E}=\frac{xM_{1}+(1-x)M_{2}}{\rho}-\left[x\frac{M_{1}}{\rho_{1}}+(1-x)\frac{M_{2}}{\rho_{2}}\right] \quad (1)$$

where x is the mole fraction of compound 1; M is the molecular weight; ρ is the density; and subscripts denote pure-product properties. These values were fitted to the equation[27]

$$V^{E}/\mathrm{cm}^{3}\cdot\mathrm{mol}^{-1}=x(1-x)\sum_{i=1}^{5}\sum_{j=1}^{3}A_{ij}\,(x^{1/2})^{i-1}\,(T/\mathrm{K}-T_{0}/\mathrm{K})^{j-1} \quad (2)$$

where $T_0 = 298.15$ K. Figure 1 shows the excess molar volumes for the four studied systems. V^E values are negative and decrease as temperature is increased for all studied systems.

Excess enthalpies H^E were determined over the whole composition range at 303.15 K for all the studied systems. Experimental data, shown in Table 2, were fitted to the next equation

$$H^{E}/\mathrm{J}\cdot\mathrm{mol}^{-1}=x(1-x)\sum_{i=1}^{3}B_{i}\,(2x-1)^{i-1} \quad (3)$$

Figure 2 shows the experimental H^E data and curve fits for the studied systems. Excess enthalpy is positive for ethanol systems, whereas it is negative for the nitromethane systems.

Standard deviation was calculated from

$$\sigma(Y)=\left[\sum\frac{(Y_{\mathrm{calcd}}-Y_{\mathrm{exptl}})^{2}}{n-m}\right]^{1/2} \quad (4)$$

where n is the total number of experimental values; m is the number of parameters; and $Y = V^E$ or H^E. Tables 3 and 4 list fitting parameters A_{ij} and B_i and standard deviations for eqs 2 and 3, respectively. The optimum number of fitting parameters A_{ij} and B_i were determined by means of an F-Test.

Negative values and negative temperature dependence of V^E are often observed for ionic liquid + polar compound systems.[11–14] They can be interpreted based on the fact that interactions between the ions of ionic liquids are Coulombic, much stronger than those that exist between molecules of organic solvents. Therefore, and with a view on the difference between molar mass of the components of the mixtures, excess volume results would suggest that ions are surrounded by molecules of the organic solvent, reducing the free volume of the mixture. Even though the chemical nature of both the ionic liquids and organic solvents is quite different, there are not important differences in V^E for all studied systems.

Table 1. Experimental Densities from Binary Systems x [BMIM][BF$_4$] + (1−x) Ethanol or + (1−x) Nitromethane and x [BMIM][MeSO$_4$] + (1−x) Ethanol or (1−x) Nitromethane

	T/K			
x	293.15	303.15	313.15	323.15
	ρ/g·cm^{-3}			
	[BMIM][BF$_4$] + ethanol			
0	0.78938	0.78078	0.77204	0.76314
0.0517	0.85459	0.84627	0.83783	0.82927
0.0918	0.89567	0.88754	0.87927	0.87090
0.1479	0.94311	0.93512	0.92702	0.91884
0.1995	0.98007	0.97215	0.96415	0.95611
0.2518	1.01133	1.00346	0.99556	0.98764
0.3228	1.04679	1.03901	1.03122	1.02346
0.4219	1.08581	1.07814	1.07051	1.06291
0.5356	1.12088	1.11335	1.10588	1.09846
0.6244	1.14266	1.13523	1.12786	1.12054
0.7090	1.16024	1.15289	1.14559	1.13837
0.8295	1.18136	1.17412	1.16693	1.15980
0.9327	1.19633	1.18916	1.18204	1.17497
1	1.20493	1.19783	1.19074	1.18372
	[BMIM][BF$_4$] + nitromethane			
0	1.13798	1.12439	1.11068	1.09688
0.0512	1.15427	1.14208	1.12984	1.11757
0.0991	1.16429	1.15298	1.14166	1.13032
0.1392	1.17056	1.15982	1.14908	1.13835
0.2026	1.17815	1.16809	1.15806	1.14805
0.2986	1.18608	1.17678	1.16752	1.15831
0.3565	1.18962	1.18067	1.17176	1.16290
0.3972	1.19164	1.18290	1.17420	1.16555
0.4553	1.19413	1.18565	1.17721	1.16883
0.5231	1.19642	1.18818	1.17999	1.17187
0.5949	1.19848	1.19048	1.18253	1.17465
0.6863	1.20057	1.19282	1.18511	1.17748
0.8073	1.20260	1.19513	1.18769	1.18033
0.8634	1.20337	1.19601	1.18869	1.18143
1	1.20499	1.19789	1.19081	1.18378
	[BMIM][MeSO$_4$] + ethanol			
0	0.78953	0.78094	0.77220	0.76328
0.0459	0.85475	0.84648	0.83814	0.82969
0.0987	0.91325	0.90523	0.89717	0.88906
0.1420	0.95200	0.94414	0.93626	0.92836
0.1905	0.98820	0.98049	0.97279	0.96508
0.2357	1.01676	1.00919	1.00163	0.99407
0.2733	1.03727	1.02980	1.02232	1.01488
0.3516	1.07329	1.06597	1.05867	1.05141
0.4381	1.10490	1.09771	1.09057	1.08348
0.5335	1.13261	1.12556	1.11855	1.11160
0.5712	1.14196	1.13495	1.12799	1.12109
0.6742	1.16383	1.15695	1.15010	1.14331
0.7665	1.18016	1.17337	1.16661	1.15990
0.8482	1.19227	1.18555	1.17885	1.17221
0.9248	1.20235	1.19572	1.18908	1.18249
1	1.21117	1.20448	1.19792	1.19139
	[BMIM][MeSO$_4$] + nitromethane			
0	1.13792	1.12432	1.11062	1.09682
0.0398	1.15279	1.14052	1.12819	1.11581
0.1021	1.16713	1.15618	1.14520	1.13422
0.1433	1.17403	1.16371	1.15339	1.14309
0.1988	1.18104	1.17138	1.16173	1.15211
0.2444	1.18556	1.17634	1.16713	1.15797
0.2998	1.18998	1.18118	1.17241	1.16368
0.3979	1.19581	1.18757	1.17937	1.17123
0.4786	1.19941	1.19153	1.18369	1.17591
0.5652	1.20231	1.19473	1.18719	1.17971
0.7127	1.20624	1.19908	1.19195	1.18488
0.8212	1.20819	1.20128	1.19438	1.18753
0.8546	1.20881	1.20197	1.19514	1.18836
1	1.21116	1.20445	1.19788	1.19135

As for H^E values, the obtained positive values for ethanol systems can be mainly ascribed to the destruction of hydrogen

Table 2. Excess Enthalpies from Binary Systems x [BMIM][BF$_4$] + (1−x) Ethanol or (1−x) Nitromethane and x [BMIM][MeSO$_4$] + (1−x) Ethanol or (1−x) Nitromethane

[BMIM][BF$_4$] +				[BMIM][MeSO$_4$] +			
Ethanol		Nitromethane		Ethanol		Nitromethane	
x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}
0.0201	360	0.0016	−7	0.016	211	0.0804	−159
0.0573	852	0.0273	−92	0.0338	368	0.1617	−285
0.1005	1285	0.0558	−182	0.1032	862	0.2832	−396
0.1962	1956	0.1131	−287	0.1897	1157	0.3940	−466
0.3371	2472	0.202	−406	0.2821	1323	0.4351	−451
0.4225	2609	0.3621	−487	0.3379	1277	0.5566	−418
0.5001	2509	0.5067	−452	0.5068	1070	0.6675	−370
0.5874	2279	0.6037	−409	0.5946	958	0.7671	−273
0.6333	2049	0.7226	−316	0.7119	696	0.8761	−130
0.7422	1668	0.8827	−159	0.7889	510		
0.8291	1159			0.9083	220		
0.9257	625						

bonding of alcohol molecules in the mixing process. On the other hand, the negative values for nitromethane systems can be explained from the fact that RTILs present in solution a structure similar to polar compounds,[28,29] which make the interactions RTIL + nitromethane stronger than for the ideal mixture. There are much more important differences for ethanol systems than for nitromethane ones. These tendencies can be interpreted from the a priori higher ability of [BMIM][MeSO$_4$] as a proton acceptor: interactions [BMIM][MeSO$_4$] + ethanol are more favorable than those for [BMIM][BF$_4$] + ethanol, and therefore, H^E is lower. This poor capability of [BMIM][BF$_4$] to form hydrogen bonds is confirmed by previous results for [BMIM][BF$_4$] + water: H^E for this system is also very high, and the system undergoes a liquid − liquid phase transition with an UCST located at 277.6 K.[30]

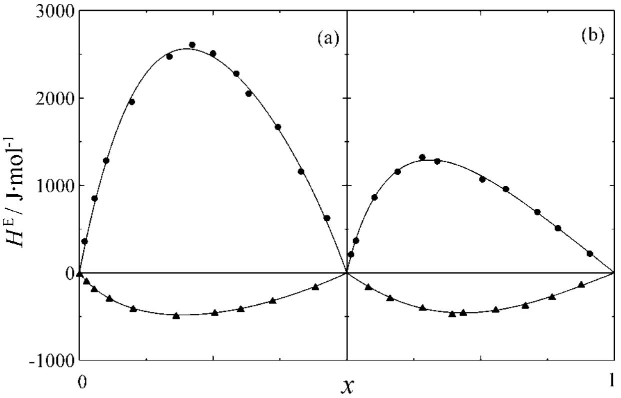

Figure 2. Excess molar enthalpies at T = 303.15 K of the binary systems (a) x [BMIM][BF$_4$] + ●, (1−x) ethanol; ▲, (1−x) nitromethane, and (b) x [BMIM][MeSO$_4$] + ●, (1−x) ethanol; ▲, (1−x) nitromethane. Solid line, fitted by eq 3.

Table 3. Fitting Parameters and Standard Deviations for Equation 2 (T_0 = 298.15 K)

	[BMIM][BF$_4$] +		[BMIM][MeSO$_4$] +	
	ethanol	nitromethane	ethanol	nitromethane
A_{11}	−12.0603	−11.2304	−12.0671	−11.8585
A_{12}	−0.0739	−0.1142	−0.1569	−0.1531
A_{13}	−0.0014	−0.0009	−0.0003	−0.0001
A_{21}	48.2550	28.2497	29.3266	33.6983
A_{22}	−0.0701	0.3138	0.6020	0.5892
A_{23}	0.0094	0.0030	−0.0054	−0.0039
A_{31}	−104.0755	−34.5886	−30.6232	−44.7672
A_{32}	0.7543	−0.3985	−1.2307	−1.1942
A_{33}	−0.0258	−0.0044	0.0247	0.0169
A_{41}	109.0969	20.7316	10.6385	28.7035
A_{42}	−1.1110	0.2629	1.3111	1.2696
A_{43}	0.0293	0.0030	−0.0364	−0.0250
A_{51}	−42.6841	−4.5122	1.2307	−6.5268
A_{52}	0.4976	−0.0691	−0.5513	−0.5371
A_{53}	−0.0118	−0.0007	0.0181	0.0126
σ/g·cm^{-3}	0.012	0.003	0.006	0.007

Table 4. Fitting Parameters and Standard Deviations from Equation 3

	[BMIM][BF$_4$] +		[BMIM][MeSO$_4$] +	
	ethanol	nitromethane	ethanol	nitromethane
B_1	9880	−4454.7	15339	−1946.0
B_2	−3553	5346.6	−21542	−1066.4
B_3	2080	−2326.8	8700	1813.5
σ/J·mol^{-1}	53	6	21	12

Conclusion

Excess volumes and excess enthalpies for the binary systems [BMIM][BF$_4$] + ethanol or + nitromethane and [BMIM][MeSO$_4$] + ethanol or + nitromethane were reported. Negative excess molar volumes were obtained for all systems, whereas excess enthalpies were positive for ethanol systems and negative for nitromethane ones. Large differences in H^E were observed in ethanol mixtures but not for nitromethane. These results can be explained by the differences such as proton acceptor between both RTILs, [BMIM][MeSO$_4$] being the most capable to interact with ethanol through hydrogen bonds.

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