Density and Heat Capacity as a Function of Temperature for Binary Mixtures of 1-Butyl-3-methylpyridinium Tetrafluoroborate + Water, + Ethanol, and + Nitromethane

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Experimental measurements of density and isobaric molar heat capacity for the binary systems containing ionic liquid 1-butyl-3-methylpyridinium tetrafluoroborate + water, + ethanol, and + nitromethane are presented within the temperature range (293.15 to 318.15) K at atmospheric pressure. From these data, excess molar volumes and excess molar isobaric heat capacity are calculated and discussed based on arguments often used for the study of liquid mixtures.

Introduction

In recent years, room-temperature ionic liquids (RTILs) have become a major topic of interest in scientific research due to their possible applications in new environmentally friendly industrial processes.[1−10] RTILs are organic molten salts that are liquid at room temperature. The most interesting properties of these compounds are that they have a low vapor pressure and are liquid over a broad temperature and pressure range. Although some works have dealt with the study of the capability of RTILs as solvents,[1,3,4] there are few papers devoted to the study of the thermodynamics of mixtures of RTILs + common solvents, especially with regard to the study of thermal properties such as enthalpy or heat capacity.[8,11−15] It is worth noting that most of these works study imidazolium-based RTILs, whereas there are few papers devoted to other kinds of RTILs. This work focuses on the study of density and heat capacity of binary mixtures of the pyridinium-based RTIL 1-butyl-3-methylpyridinium tetrafluoroborate, [BPyr][BF_4], with three different common solvents: water, ethanol, and nitromethane, compounds that present an evident technological significance and have quite different chemical structures that allow studying different RTIL + solvent interactions. This information can provide an understanding of the thermodynamics of the RTIL + solvent mixtures. Therefore, densities and isobaric heat capacity were measured in the temperature interval from (293.15 to 318.15) K at atmospheric pressure. From these data, excess molar volume and excess molar isobaric heat capacity were calculated, since excess properties indicate how a mixture deviates from ideal behavior and, therefore, can give information about the structure of the mixture.

Table 1. Densities for *x* [bpyr][BF_4] + (1 − *x*) Water at Temperature *T*

	T/K					
x	293.15	298.15	303.15	308.15	313.15	318.15
	ρ/g·cm^{-3}					
0	0.9982	0.9971	0.9957	0.9941	0.9922	0.9902
0.0494	1.0660	1.0633	1.0604	1.0575	1.0545	1.0513
0.0973	1.0959	1.0927	1.0894	1.0860	1.0825	1.0790
0.2312	1.1397	1.1360	1.1323	1.1287	1.1250	1.1212
0.3559	1.1573	1.1536	1.1500	1.1464	1.1427	1.1391
0.4035	1.1618	1.1582	1.1545	1.1509	1.1473	1.1437
0.5195	1.1679	1.1643	1.1608	1.1572	1.1537	1.1502
0.7087	1.1795	1.1760	1.1725	1.1691	1.1656	1.1622
0.7512	1.1812	1.1778	1.1743	1.1708	1.1674	1.1639
0.8838	1.1832	1.1798	1.1763	1.1729	1.1695	1.1661
1	1.1886	1.1852	1.1817	1.1783	1.1749	1.1716

Table 2. Densities for *x* [bpyr][BF_4] + (1 − *x*) Ethanol at Temperature *T*

	T/K					
x	293.15	298.15	303.15	308.15	313.15	318.15
	ρ/g·cm^{-3}					
0	0.7896	0.7853	0.7810	0.7767	0.7723	0.7678
0.0073	0.8005	0.7963	0.7920	0.7876	0.7833	0.7789
0.0126	0.8078	0.8035	0.7993	0.7949	0.7906	0.7862
0.0231	0.8215	0.8173	0.8130	0.8088	0.8045	0.8003
0.0512	0.8551	0.8510	0.8468	0.8426	0.8384	0.8341
0.1003	0.9041	0.9001	0.8960	0.8919	0.8878	0.8837
0.2569	1.0103	1.0064	1.0026	0.9987	0.9948	0.9909
0.3847	1.0654	1.0616	1.0579	1.0542	1.0504	1.0467
0.4841	1.0971	1.0934	1.0897	1.0861	1.0824	1.0787
0.5963	1.1249	1.1213	1.1177	1.1142	1.1106	1.1071
0.7107	1.1480	1.1445	1.1409	1.1374	1.1339	1.1304
0.7966	1.1622	1.1587	1.1552	1.1517	1.1483	1.1448
0.9514	1.1831	1.1796	1.1762	1.1728	1.1694	1.1660
1	1.1886	1.1852	1.1817	1.1783	1.1749	1.1716

Experimental Section

Materials. Nitromethane was supplied from Fluka in a purity higher than 98.5 mass %, ethanol from Probus in a purity higher than 99.5 mass %, and [BPyr][BF_4] from Solvent Innovation in a purity higher than 99 mass %. Ethanol and nitromethane were dried over Fluka-type 0.3 nm molecular sieves before use. The ionic liquid was dried in a vacuum at $T = 333.15$ K for 48 h prior to use to eliminate volatile compounds. No decomposition of the RTIL is observed at experimental conditions. The water mass fraction of the dried RTIL was determined by Karl Fisher titration, and it was found to be $< 1.2 \cdot 10^{-3}$. MilliQ water was used, after being degassed.

Apparatus and Procedure. Mixtures were prepared by weighing on a Mettler AE-240 balance, and the uncertainty in the mole fraction was estimated to be $\pm\ 1 \cdot 10^{-4}$. Densities, ρ, were determined using a vibrating tube densimeter (Anton Paar

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Table 3. Densities for x [bpyr][BF4] + (1 − x) Nitromethane at Temperature T

	T/K					
x	293.15	298.15	303.15	308.15	313.15	318.15
	ρ/g·cm^{-3}					
0	1.1402	1.1334	1.1266	1.1197	1.1129	1.1060
0.0517	1.1534	1.1474	1.1413	1.1353	1.1292	1.1231
0.1038	1.1615	1.1560	1.1505	1.1449	1.1394	1.1339
0.1952	1.1703	1.1654	1.1604	1.1555	1.1506	1.1456
0.3078	1.1767	1.1722	1.1678	1.1633	1.1588	1.1544
0.3563	1.1787	1.1743	1.1700	1.1657	1.1614	1.1571
0.3998	1.1801	1.1759	1.1716	1.1674	1.1632	1.1591
0.5121	1.1830	1.1790	1.1750	1.1710	1.1670	1.1631
0.5994	1.1846	1.1807	1.1769	1.1731	1.1692	1.1654
0.6856	1.1858	1.1821	1.1783	1.1746	1.1709	1.1672
0.7863	1.1869	1.1833	1.1797	1.1761	1.1725	1.1690
0.8842	1.1877	1.1842	1.1807	1.1772	1.1737	1.1703
0.9034	1.1879	1.1844	1.1809	1.1774	1.1740	1.1705
0.9410	1.1882	1.1848	1.1813	1.1779	1.1744	1.1710
1	1.1886	1.1852	1.1817	1.1783	1.1749	1.1716

Table 4. Equation 3 Coefficients for V^E

	T	A_1	A_2	A_3	A_4	
	K	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	χ^2
[bpyr][BF$_4$] + water	298.15	2.232	−0.962			0.0007
	308.15	3.095	−1.789			
	318.15	3.889	−2.517			
[bpyr][BF$_4$] + ethanol	298.15	−10.830	29.506	−31.145	11.353	0.0003
	308.15	−11.967	32.282	−33.659	12.077	
	318.15	−13.711	38.068	−41.151	15.486	
[bpyr][BF$_4$] + NM	298.15	−9.873	23.285	−23.119	8.575	0.0001
	308.15	−10.875	25.059	−23.787	8.315	
	318.15	−12.276	28.748	−23.769	9.971	

Table 5. Isobaric Molar Heat Capacities for x [bpyr][BF$_4$] + (1 − x) Water at Temperature T

	T/K					
x	293.15	298.15	303.15	308.15	313.15	318.15
	C_p/J·mol^{-1}·K^{-1}					
0	75.4	75.3	75.3	75.2	75.2	75.3
0.0015	76.7	76.7	76.8	76.9	77.0	77.1
0.0020	77.4	77.4	77.5	77.6	77.6	77.7
0.0027	77.7	77.7	77.7	77.8	77.9	78.0
0.0036	78.1	78.2	78.2	78.3	78.4	78.4
0.0102	81.0	81.1	81.2	81.3	81.5	81.7
0.0938	112.7	113.1	113.4	113.8	114.2	114.7
0.1885	142.4	143.1	143.8	144.5	145.2	146.0
0.2704	167.0	167.8	168.6	169.5	170.4	171.4
0.3620	193.8	195.0	196.1	197.3	198.4	199.5
0.4454	218.2	219.3	220.5	221.7	222.8	224.0
0.6432	275.2	276.9	278.6	280.3	282.1	283.8
0.8094	325.2	327.3	329.5	331.7	334.0	336.3
0.8791	346.0	348.3	350.8	353.3	355.8	358.5
0.9468	367.8	370.4	373.0	375.7	378.4	381.3
1	385.8	387.7	390.1	392.8	395.9	399.3

Table 6. Isobaric Molar Heat Capacities for x [bpyr][BF$_4$] + (1 − x) Ethanol at Temperature T

	T/K					
x	293.15	298.15	303.15	308.15	313.15	318.15
	C_p/J·mol^{-1}·K^{-1}					
0	111.3	113.3	115.3	117.5	119.7	122.1
0.0073	113.6	115.4	117.3	119.5	121.7	124.1
0.0126	115.2	117.1	119.1	121.2	123.3	125.6
0.0231	119.1	120.9	122.7	124.7	126.7	128.8
0.0512	129.4	131.0	132.6	134.3	136.0	137.9
0.1003	146.4	147.5	148.7	150.1	151.6	153.2
0.2569	190.3	191.3	192.4	193.6	194.9	196.2
0.3847	223.7	224.8	226.0	227.2	228.5	229.8
0.5031	252.6	254.2	255.7	257.3	258.9	260.4
0.5963	276.9	278.5	280.1	281.8	283.5	285.3
0.6919	301.6	303.4	305.3	307.3	309.4	311.5
0.7784	324.5	326.6	328.9	331.1	333.5	335.9
0.8711	350.0	352.1	354.4	356.9	359.5	362.2
0.8923	355.9	358.1	360.5	363.0	365.7	368.5
0.9514	372.8	375.1	377.4	379.7	382.0	384.4
1	385.8	387.7	390.1	392.8	395.9	399.3

Table 7. Isobaric Molar Heat Capacities for x [bpyr][BF$_4$] + (1 − x) Nitromethane at Temperature T

	T/K					
x	293.15	298.15	303.15	308.15	313.15	318.15
	C_p/J·mol^{-1}·K^{-1}					
0	106.6	106.9	107.3	107.7	108.2	108.6
0.0517	120.3	120.5	120.9	121.3	121.9	122.4
0.1038	134.2	134.7	135.2	135.7	136.4	137.1
0.1952	159.9	160.4	161.0	161.8	162.5	163.5
0.3563	205.2	206.0	206.9	208.0	209.2	210.6
0.3998	217.4	218.3	219.3	220.5	221.9	223.5
0.5121	249.2	250.2	251.4	252.8	254.4	256.3
0.5994	273.7	274.8	276.2	277.9	279.8	281.9
0.6856	297.7	299.0	300.6	302.5	304.6	307.0
0.7863	326.4	327.8	329.6	331.7	334.1	336.8
0.8842	353.6	355.3	357.3	359.7	362.4	365.5
0.9034	359.1	360.8	362.9	365.3	368.1	371.1
0.9410	369.8	371.6	373.7	376.2	379.0	382.3
1	385.8	387.7	390.1	392.8	395.9	399.3

Table 8. Equation 3 Coefficients for C_p^E

	T	A_1	A_2	A_3	A_4	
	K	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	χ^2
[bpyr][BF$_4$] + water	298.15	330.63	−1102.82	1371.32	−626.34	0.5
	308.15	335.43	−1079.99	1282.89	−558.74	
	318.15	357.61	−1169.31	1405.35	−622.02	
[bpyr][BF$_4$] + ethanol	298.15	49.24	246.41	−743.13	453.16	0.1
	308.15	23.71	269.26	−728.29	439.89	
	318.15	11.10	201.50	−539.78	318.07	
[bpyr][BF$_4$] + NM	298.15	−18.43	21.86			0.06
	308.15	−19.80	21.91			
	318.15	−20.95	21.67			

DMA5000): this apparatus performs an automatic viscosity correction when working with high viscosity liquids such as some RTILs. MilliQ water and dry air were used as standard liquids, and the uncertainty of the measurement is estimated to be ± 1·10^{-4} g·cm^{-3}. Further experimental details can be found in the literature.[9] Isobaric molar heat capacities, C_p, were obtained from the densities and isobaric heat capacity per unit volume, C_pV^{-1}, measured in a Setaram Micro DSCIII differential scanning calorimeter. Water and toluene were used as C_pV^{-1} standards, and their densities and molar heat capacities were obtained from the literature.[16−19] The uncertainty of the measurement is estimated to be 0.3 %. Detailed information about this instrument can be found elsewhere.[20−21] Temperature uncertainty is estimated in 0.01 K for both instruments.

Results and Discussion

Tables 1 to 3 and 5 to 7 present the densities and isobaric molar heat capacities for the studied systems. Because the measured properties are density and isobaric heat capacity per unit volume, it is necessary to calculate the molar isobaric heat capacity. This we obtained from the measured properties and the molecular weight, M_W, using the equation

$$C_p = \frac{(C_pV^{-1})M_W}{\rho} \qquad (1)$$

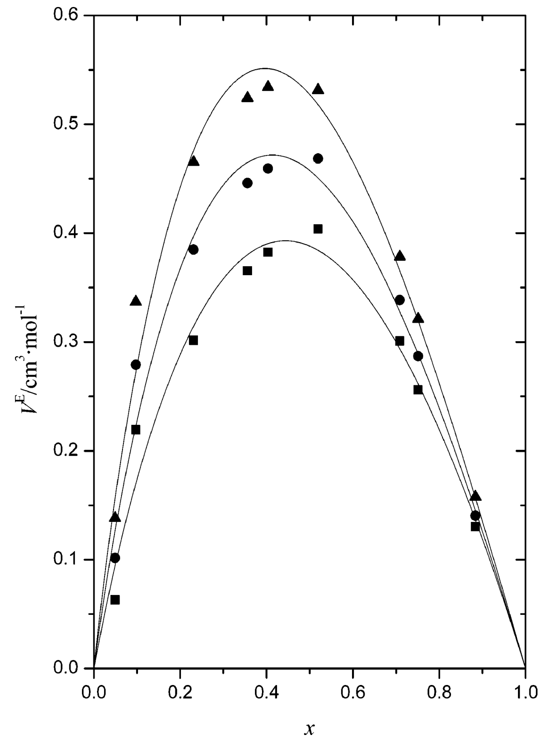

Figure 1. Excess molar volume for x [bpyr][BF$_4$] + (1 − x) water at: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K; −, eq 3 at each temperature.

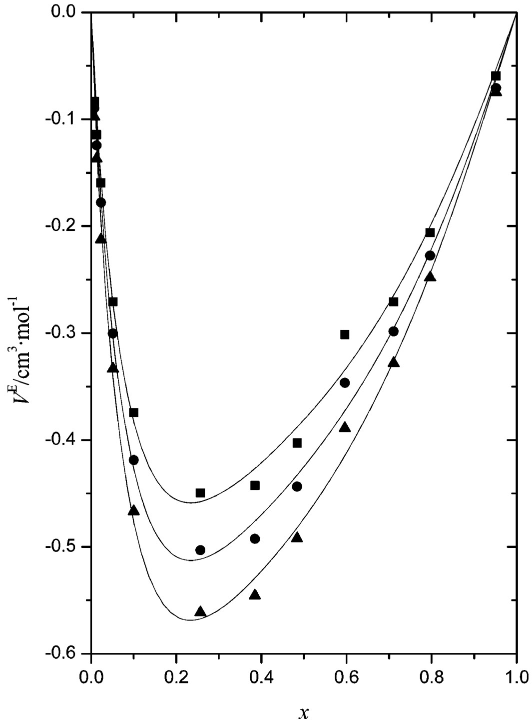

Figure 2. Excess molar volume for x [bpyr][BF$_4$] + (1 − x) ethanol at: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K; −, eq 3 at each temperature.

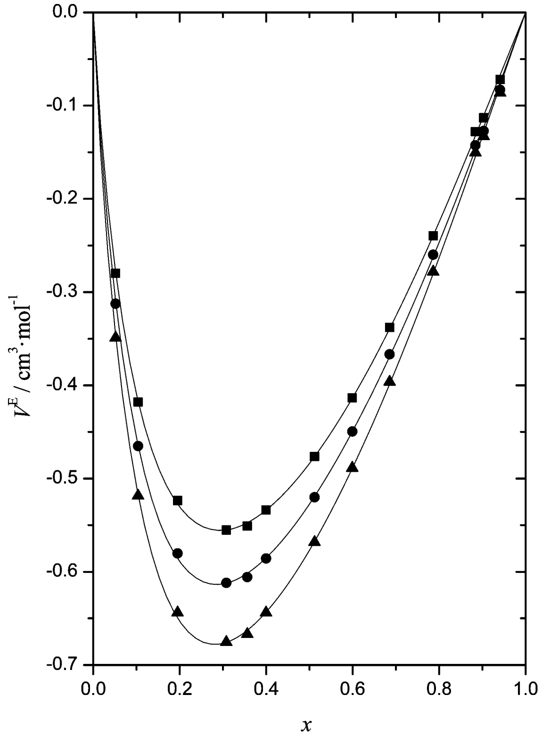

Figure 3. Excess molar volume for x [bpyr][BF$_4$] + (1 − x) nitromethane at: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K; −, eq 3 at each temperature.

Experimental data were used to calculate excess molar properties, defined as follows

$$Y^{\mathrm{E}} = Y^{\mathrm{M}} - \sum_{i=1}^{2} x_i Y_i^0 \qquad (2)$$

where Y is the thermodynamic property, in this case V and C_p; M is the mixture property; and 0 corresponds to the pure compound, being x_i, the mole fraction of component i.

The excess properties were fitted to an equation of the form

$$Y_{\mathrm{m}}^{\mathrm{E}} = x(1 - x) \sum_{i=0}^{n} A_i (x^{1/2})^i \qquad (3)$$

The coefficients obtained from fitting are presented in Tables 4 and 8, for excess molar volume and excess molar isobaric heat capacity, respectively. The fitting process for each system was based on the optimization of χ^2 (presented in Tables 4 and 8), which is defined as the sum of the squares of the deviations of experimental data from the fitting curve, divided by the number of experimental points minus the number of parameters used in the fitting equation. An F-test was used to obtain the optimum number of parameters.

Excess Molar Volumes. V^{E} can give information about the net destruction of interactions and packing phenomena that appears in the mixing process.[22] Figures 1 to 3 show the obtained V^{E} results. As for the system [bpyr][BF$_4$] + water, the excess molar volume is positive, having a maximum at mole fraction $x = 0.4$ (about 0.4 cm^3·mol^{-1} at $T = 298.15$ K), and V^{E} increases as the temperature is raised. For the system [bpyr][BF$_4$] + ethanol, V^{E} presents a negative parabolic dependence against composition, with a minimum at the mole fraction $x = 0.25$ (about −0.45 cm^3·mol^{-1} at $T = 298.15$ K), and as temperature increases, the values become more negative. This behavior is similar to that found for V^{E} of the system [bpyr][BF$_4$] + nitromethane, in which negative parabolic curves with a minimum in mole fraction of $x = 0.3$ (about −0.55 cm^3·mol^{-1} at $T = 298.15$ K) were obtained. Also, as temperature increases, V^{E} decreases for this system. These tendencies were often obtained for IL + organic compound systems; therefore, the system that presents an unusual V^{E} behavior is the [bpyr][BF$_4$] + water system.[14,24−28]

Excess Molar Isobaric Heat Capacity. C_p^{E} is a quantity which has been shown to be a useful indicator of changes in liquid order during the mixing process.[22] The results for C_p^{E} for these systems are presented in Figures 4 to 6. In all cases,

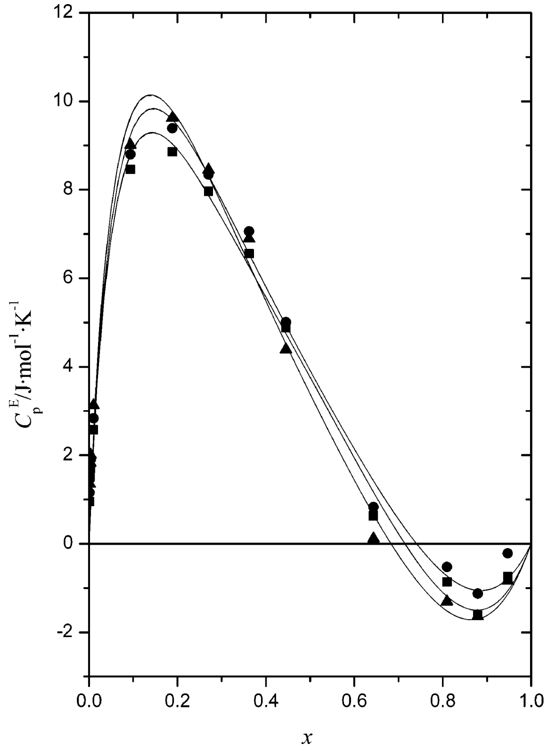

Figure 4. Excess molar isobaric heat capacity for x [bpyr][BF$_4$] + (1 − x) water at: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K; −, eq 3 at each temperature.

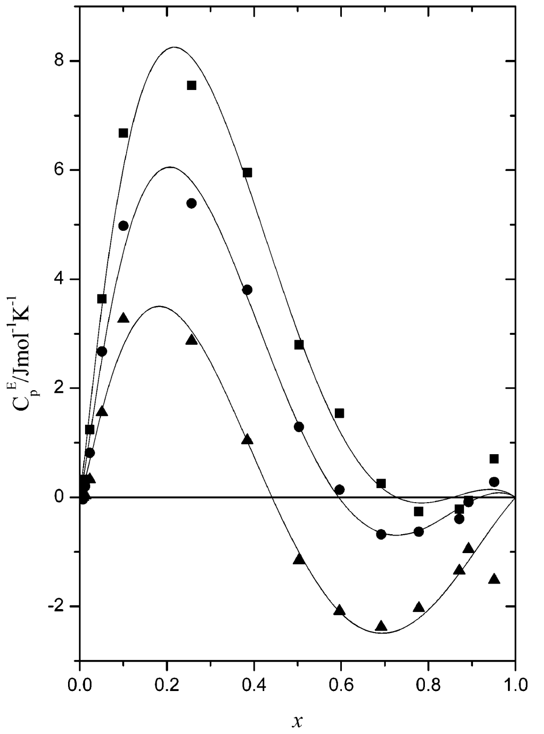

Figure 5. Excess molar isobaric heat capacity for x [bpyr][BF$_4$] + (1 − x) ethanol at: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K; −, eq 3 at each temperature.

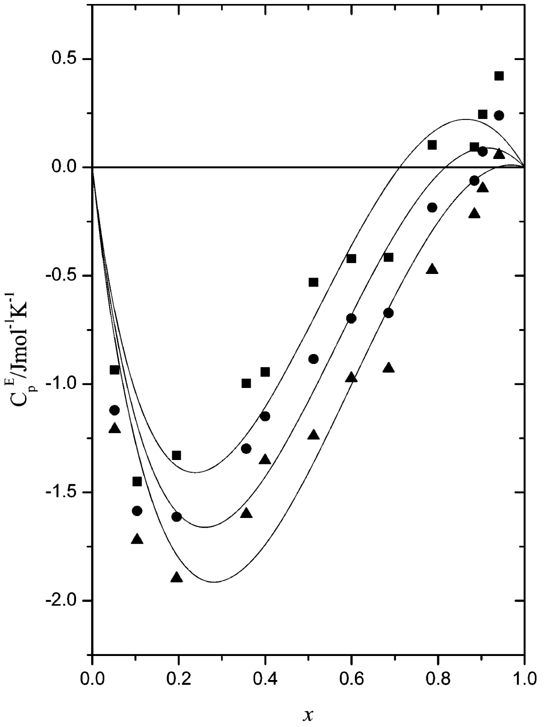

Figure 6. Excess molar isobaric heat capacity for x [bpyr][BF$_4$] + (1 − x) nitromethane at: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K; −, eq 3 at each temperature.

S-shaped curves against composition are found. As a rule, accuracy is worse at a high mole fraction. This can be explained by the difference in molecular weight of RTIL and solvent: at high x values, a very small amount of solvent is required, a fact that makes significantly higher the uncertainty in mole fraction. For binary mixtures with water and ethanol, the results are similar in qualitative comparison: at low mole fraction, the C_p^E is positive with a maximum around $x = 0.2$, and at high mole fraction, the curves exhibit a minimum with negative values. At lower temperature, values are quite significant: their maxima are about (10 and 8) J·mol^{-1}·K^{-1}, while their minima is around −2 J·mol^{-1}·K^{-1}. Concerning the C_p^E behavior against temperature, a weak dependence was found for the water system, whereas the [bpyr][BF$_4$] + ethanol system shows a significant, negative change in C_p^E as temperature is increased (about 4 J·mol^{-1}·K^{-1} in a 20 K interval). Often this strong temperature dependence of C_p^E is associated to the nearness of a liquid−liquid critical point, since concentration fluctuations at conditions close to critical values cause C_p^E to increase strongly.[23] To find out if the proximity of a critical point explained the observed C_p^E curves, a sample of mole fraction $x = 0.153$ was cooled in the calorimeter, and a characteristic curve associated to the critical behavior (λ-curve) was found. The observed transition temperature of this sample, which must be essentially the UCST for this system, was $T_c = 277.5$ K. These data were confirmed visually from the observation of the phase separation through cooling the sample on a borosilicate cell. On the other hand, no liquid−liquid equilibria were observed for the [bpyr][BF$_4$] + water system. This system undergoes a solid−liquid transition before any liquid−liquid-phase separation can be observed. As for the [bpyr][BF$_4$] + nitromethane system, the composition dependence is the opposite for the other systems: at low composition, C_p^E is negative going to a minimum at a mole fraction around $x = 0.25$, and then it shows a positive maximum at high composition. The values are significantly smaller, having a maximum of 0.25 J·mol^{-1}·K^{-1}and a minimum of −1.5 J·mol^{-1}·K^{-1} and a small negative temperature dependence. It is remarkable that although the [bpyr][BF$_4$] + water and [bpyr][BF$_4$] + ethanol systems seem to have a similar C_p^E behavior at low temperature, at high temperature the maximum at a small ionic liquid mole fraction is lowered and the C_p^E curves of the [bpyr][BF$_4$] + ethanol system tend to be similar to those of [bpyr][BF$_4$] + nitromethane. This is a clear effect of the critical C_p^E enhancement present in [bpyr][BF$_4$] + ethanol. Therefore, from this point of view, and if critical phenomena are neglected, the [bpyr][BF_4] + water is the system that exhibits a different C_p^E behavior. This fact agrees with the arguments exposed in the discussion of the V^E results. In this context, a previous thermodynamic study of the [bmim][BF_4] + water system,[8] in which, besides V^E and C_p^E, excess enthalpies and liquid−liquid equilibria were reported, revealed that this system is dominated by the fall of the anion−cation electrostatic interaction in water solutions due to the high, unusual value of the dielectric permittivity of water. Bearing in mind that the results for V^E and C_p^E from this work and those reported in that paper are very similar, those arguments can also be applied to explain the observed different V^E and C_p^E behavior for the [bpyr][BF_4] + water system.

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