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Thermodynamic Properties of 1-Butyl-3-methylpyridinium Tetrafluoroborate and Its Mixtures with Water and Alkanols

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In this article, we study the behavior of an ionic liquid (IL) derived from pyridinium, 1-butyl-3-methylpyridinium tetrafluoroborate [b3mpy][BF_4], in mixtures with water and with the first alkanols of the series from methanol to butan-1-ol, at the temperatures of (298.15 and 318.15) K. First, the miscibility regions with the alkanols were established at these two temperatures, determining experimentally the liquid−liquid equilibria and the upper critical solution temperature (UCST) for each binary mixture, confirming the quasiexponential variation of the UCST with the alkanol chain. The enthalpies H_m^E were determined experimentally with a newly designed calorimetric cell, and the excess molar volumes V_m^E were determined from densities, at (298.15 and 318.15) K. In all cases, the H_m^E are positive with $(dH_m^E/dT)_p > 0$, whereas the V_m^E are negative for mixtures with alkanols but positive for the mixture of IL + water. The thermal coefficient $(dV_m^E/dT)_p > 0$ was also positive in all cases. All data were correlated with a suitable polynomial equation, and the area and volume parameters of [b3mpy][BF_4] were calculated. Finally, we give an interpretation of the results and of the behavior of the mixtures.

Introduction

Over the past few years, there has been an incredible increase in the amount of research on solutions containing ionic liquids (ILs), salts that are liquids below approximately 373 K.[1−5] This is reflected in an exponential increase in the number of publications appearing on the properties of these materials. In spite of all this attention, there are still very few known values for the thermophysical properties required to design and develop processes that use ILs and for their applications in engineering processes.[5] Moreover, to expand our knowledge on the molecular structure of these substances, it is necessary to know the degree of miscibility. Usually, one would start with inert substances such as saturated hydrocarbons; however, the existent literature has repeatedly reported a clear immiscibility of the hydrocarbon/IL pair. Hence, Domanska and Mazurowska[6] studied the influence of the type of anion on solubility of imidazolium-based ILs with several solvents. This is one of the objectives of our project but with derivatives of pyridinium instead.

Most previous research has focused on studies of imidazolium-based ILs. However, we have undertaken a research project with ionic liquids formed from pyridinium, consisting of a systematic study starting with 1-butyl-3-methylpyridinium tetrafluoroborate, [b3mpy][BF_4], which is as of yet little characterized, and alkanols, in an attempt to ascertain the effects of the alkanolic chain (methanol to butan-1-ol) in these mixtures. In future studies, we will also analyze the effects of the alkylic portions in the cation and the nature of the anion. Also, owing to the hydrophilic nature of the IL, we considered it appropriate to also study the physical and energetic effects occurring in the mixing processes of the ILs derived from pyridinium with water. For the alkanol mixtures, we first study the liquid−liquid equilibria (LLE), in the temperature range of (275 to 325) K, to establish the miscibility region of these substances. This information can be used to determine the range of measurements of other mixing properties such as excess volumes V_m^E and enthalpies H_m^E, helping to complete the information required to establish the nature of the interactions between the IL ions and the corresponding solvent.

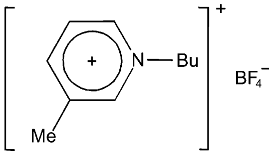

Figure 1. Structure of 1-butyl-3-methylpyridinium tetrafluoroborate [b3mpy]-[BF_4].

As mentioned, there are few data in the literature[7,8] for [b3mpy][BF_4], although Crosthwaite et al.[8] present miscibility data for two of the systems chosen for this work, [b3mpy][BF_4] + propan-1-ol or +butan-1-ol, that will be used as a reference.

Experimental Section

Materials. The alkanols (methanol to butan-1-ol) used in this work supplied by Fluka and Aldrich were of maximum commercial grade. The purity of the alkanols determined by a GC model HP6890 equipped with a FID gave values very similar to those specified by the manufacturer. The IL [b3mpy]-[BF_4] (Figure 1) was provided by Solvent Innovation with a commercial purity of 99 % and a water content < 890 ppm, verified with a Karl Fischer, DHL-48 model, from Mettler.

To prevent contact with the ambient air, materials were stored in a hermetically sealed desiccator placed in a room with continuous dehumidification. Before use, both the IL and alkanols were degasified in an ultrasound bath for several hours, and the alkanols were stored on a previously activated molecular sieve of 0.3 nm from Fluka. The water used for the experiments and for calibration was obtained by bidistillation in our laboratory with a final conductivity < 2 μS.

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Table 1. Physical Properties of Pure Compounds, Thermal Expansion Coefficient α, Density ρ, and Refractive Index n_D

	$10^3\alpha/K^{-1}$			$\rho/(kg\cdot m^{-3})$		n_D	
compound	exptl	lit.	T/K	exptl	lit.	exptl	lit.
$[b3mpy]^+[BF_4]^-$	0.59	−	298.15	1182.19	−	1.4473	−
			318.15	1168.31	−	1.4422	−
methanol	1.21	1.23[b]	298.15	786.44	786.37[a]	1.3268	1.3265[a]
			318.15	768.04	767.85[b]	1.3190	1.3187[b]
ethanol	1.13	1.13[b]	298.15	785.15	784.93[a]	1.3600	1.3594[a]
			318.15	767.57	767.62[b]	1.3548	1.3551[b]
propan-1-ol	1.06	1.05[b]	298.15	799.70	799.96[a]	1.3831	1.3837[a]
			318.15	783.16	783.17[b]	1.3757	1.3750[b]
butan-1-ol	0.98	0.98[b]	298.15	805.95	805.85[a]	1.3968	1.3970[a]
			318.15	790.27	790.20	1.3900	1.3892[b]

[a] Ref 9. [b] Ref 10.

Table 2. Experimental $x_{IL}-T$ Data for x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL}) Alkanol (2)

x_{IL}	T/K	x_{IL}	T/K	x_{IL}	T/K
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Ethanol					
0.045	276.40	0.0924	278.21	0.1294	277.22
0.070	278.00	0.1195	277.57		
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Propan-1-ol					
0.0166	293.82	0.1713	304.18	0.3968	292.52
0.0287	299.20	0.2172	303.21	0.4215	290.13
0.0407	302.04	0.2402	302.48	0.4400	287.07
0.0762	303.83	0.2798	300.68	0.4633	284.65
0.1102	304.42	0.3206	298.41	0.4918	281.71
0.1386	304.55	0.3577	295.55		
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Butan-1-ol					
0.0072	293.72	0.2145	320.35	0.5067	300.56
0.0134	302.81	0.2421	319.51	0.5284	298.22
0.0232	311.12	0.2708	318.01	0.5527	295.25
0.0504	318.28	0.2942	317.17	0.5742	292.90
0.0930	320.78	0.3278	315.40	0.6033	289.48
0.1304	321.58	0.3733	312.80	0.6540	281.22
0.1678	321.34	0.4243	308.86		
0.1814	321.17	0.4633	305.27		

The physical properties density, ρ, and refractive index, n_D, were measured as indicated below for all substances and at two temperatures, and the values are recorded in Table 1, observing for the alkanols a good agreement between our values and those published in the literature. Neither ρ nor n_D data have been found for the IL. Using other density values measured by us but not presented here, we also have calculated the thermal expansion coefficients α, which are shown in Table 1 for all substances, and the concordance with the values from the literature for alkanols was good. Because a value for viscosity of the IL of 177 mPas at 298.15 K was found in the literature,[7] we measured the viscosity for the pure IL obtaining at the same temperature a value of 145 mPas, slightly smaller than that reported in the literature, which is probably due to the higher water content of our IL.

Apparatus and Procedures. Refractive indices for the pure compounds were measured in an Abbe refractometer by Zuzi, model 320, at a wavelength of 5893 Å, with an uncertainty of ± 0.0002 units. The measurement of n_D was verified at each temperature comparing the values with those obtained for pure water and values published in the literature. The equipment was thermostated with water from a Haake external circulation bath, model Phoenix II, that provides a desired temperature controlled to within ± 0.01 K, and this same thermostat was used to maintain a constant temperature in the rotational viscosimeter from the Selecta Co., model ST-1000, equipped with a cell for small volumes with an accuracy of ± 1 % at the lower end of the scale and a reproducibility of 0.2 %. The viscosimeter was calibrated with a reference substance supplied by Brookfield Engineering Laboratories at a temperature of 298.15 K.

The solubilities of the binary systems {x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL}) an alkanol (methanol to butanol)} were determined with a cell for liquid−liquid equilibria (LLE), using a method of continuous dilution with visual detection of turbidity changes. Measurements were carried out in the interval (275 to 325) K and at atmospheric pressure, and the cell was thermostated with the previously indicated system. The transition temperature was measured with an ASL-F25 thermometer with a precision of ± 1 mK, using a PT100 probe submerged in the liquid, with an estimated uncertainty of ± 0.02 K. The measurements were made by starting the experiment with a known quantity of IL that was introduced into the perfectly sealed equilibrium cell. Next, known quantities of the second component (alkanol) were added with a Hamilton 1001-TLL syringe screwed onto a stainless-steel needle fitted with a stop valve to prevent contamination. After adding quantities of the second component, the cell was stirred continually with an electromagnetic stirrer in its interior, slowly heating and cooling the cell until the immiscibility transition was observed. The mole fraction in IL, x_{IL}, calculated in each step of this continuous process, presents a reading error that increases systematically in a quasilinear form in each experiment, the overall uncertainty in the mole fraction x_{IL} being less than $\pm 5\cdot 10^{-4}$. The process is repeated again but in the opposite direction, introducing a known amount of the second component and continually adding the IL.

The densities at the temperatures selected for this work, (298.15 and 318.15) K, were measured in an Anton-Paar oscillating-tube densimeter, model DMA58, with a reading error of ± 0.02 kg·m^{-3}. The working temperatures for the densimeter and its control of ± 0.01 K were obtained with a Peltier effect incorporated in the apparatus. The instruments were calibrated previously at the indicated temperatures with water and nonane, following a standard procedure established in our laboratory.[11] To determine the V_m^E, the mixtures were prepared by weighing them in sealed 5 mL glass vials to minimize the IL/ambient air contact. The mixture was first mixed and homogenized using a magnetic stirrer for (10 to 20) min before being introduced into the densimeter. With the density data for each of the mixtures and for the pure substances, excess volumes were calculated, obtaining the pairs (x_{IL},V_m^E). The uncertainty of the compositions of the directly prepared synthetic mixtures was estimated to be around ± 0.0002 mole fraction in IL, x_{IL}, and that of the V_m^E was $\pm 2\cdot 10^{-9}$ m^3·mol^{-1}.

The excess enthalpies, H_m^E, were determined directly by measuring the calorific energy generated in the mixing process. The miscibility diagram for the binary systems IL + alkanol clearly indicates the regions where the measurements can be made at the two temperatures selected, (298.15 and 318.15) K. A Calvet MS80 calorimeter from Setaram was previously calibrated at each temperature with a special cell provided by

Table 3. Excess Molar Enthalpies, H_m^E, for Binaries x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Alkanol or + (1 − x_{IL})Water at T = 298.15 K and T = 318.15 K

x_{IL}	H_m^E J·mol^{-1}	x_{IL}	H_m^E J·mol^{-1}	x_{IL}	H_m^E J·mol^{-1}	x_{IL}	H_m^E J·mol^{-1}
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Water							
T = 298.15 K							
0.0060	78	0.0724	732	0.1713	1362	0.4051	1533
0.0137	167	0.0876	858	0.1993	1465	0.4511	1459
0.0226	266	0.1038	982	0.2307	1555	0.5139	1330
0.0328	374	0.1204	1103	0.2676	1619	0.6139	1093
0.0448	489	0.1234	1123	0.3091	1635	0.7899	631
0.0580	609	0.1415	1248	0.3573	1602		
T = 318.15 K							
0.0058	95	0.0774	927	0.1574	1545	0.3403	2148
0.0136	217	0.0961	1089	0.1845	1681	0.3889	2141
0.0231	352	0.1167	1250	0.2023	1819	0.4492	2064
0.0339	487	0.1225	1280	0.2358	1941	0.5301	1894
0.0459	623	0.1348	1377	0.2685	2041	0.6433	1532
0.0605	769	0.1378	1399	0.3026	2099	0.8206	841
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Methanol							
T = 298.15 K							
0.0057	109	0.1071	991	0.2672	1599	0.7167	1077
0.0149	228	0.1312	1133	0.3069	1617	0.7441	948
0.0279	386	0.1585	1287	0.3541	1604	0.8438	662
0.0440	546	0.1851	1391	0.4100	1578	0.9196	394
0.0635	699	0.2119	1502	0.4816	1512	0.9707	174
0.0842	846	0.2357	1560	0.5621	1379		
T = 318.15 K							
0.0159	246	0.1382	1406	0.2641	2142	0.4391	2253
0.0352	506	0.1674	1631	0.2984	2230	0.5504	1995
0.0581	723	0.1970	1799	0.3343	2276	0.6911	1460
0.0823	939	0.2147	1934	0.3787	2294	0.8526	801
0.1098	1176	0.2317	2043				
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Ethanol							
T = 298.15 K							
0.0052	148	0.1263	1515	0.2305	2070	0.4689	2026
0.0159	414	0.1280	1539	0.2577	2155	0.5396	1777
0.0279	620	0.1450	1656	0.2878	2223	0.6277	1457
0.0457	849	0.1585	1693	0.3217	2275	0.7386	1074
0.0691	1088	0.1639	1748	0.3623	2284	0.8712	584
0.0972	1304	0.1838	1863	0.4085	2205	0.9405	304
0.1132	1413	0.2062	1968				
T = 318.15 K							
0.0123	262	0.1279	1721	0.2681	2531	0.5648	2295
0.0273	540	0.1612	1987	0.3063	2624	0.6576	1889
0.0472	842	0.1789	2127	0.3498	2694	0.7668	1364
0.0704	1125	0.2034	2278	0.4055	2699	0.8810	769
0.0980	1430	0.2335	2416	0.4787	2572		
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Propan-1-ol							
T = 298.15 K							
0.0139	163	0.3707	2345	0.4980	2117	0.7278	1246
0.0242	236	0.4045	2309	0.5458	1965	0.7939	959
0.0278	285	0.4278	2275	0.5983	1741	0.8653	685
0.3397	2341	0.4642	2222	0.6621	1521	0.9335	407
T = 318.15 K							
0.0232	417	0.2044	2311	0.3585	2773	0.6073	2248
0.0520	776	0.2311	2441	0.3982	2777	0.6740	1912
0.0852	1156	0.2591	2557	0.4404	2742	0.7504	1509
0.1233	1552	0.2896	2652	0.4891	2654	0.8323	1053
0.1608	1924	0.3223	2727	0.5441	2502	0.9131	598
0.2011	2235						
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Butan-1-ol							
T = 318.15 K							
0.0098	151	0.3603	2849	0.5101	2726	0.7667	1582
0.0250	286	0.3932	2860	0.5852	2473	0.8531	1104
0.0464	577	0.4450	2832	0.6705	2106	0.9346	521

the manufacturer, applying a Joule effect and using different values of electrical power with the EJ2 unit, also from Setaram. The electrical calibration of the apparatus was verified at the two indicated temperatures with the mixture (propan-1-ol + benzene),[12] giving an overall mean error between our experimental (x, H_m^E) values and those corresponding to the fitting curve presented in the literature[12] of less than 1 % for H_m^E. In this work, the uncertainty in the mole fractions for IL is estimated to be ± 2·10^{-4}. Owing to the special characteristics of the IL, high density, and viscosity in relation to the second component, alkan-1-ol or water, a cell was designed and constructed for the mixtures studied in this work, with the elements included in the diagram of Figure 2, to ensure complete dilution of the compounds. An inverted, empty stainless-steel cylinder was introduced to function as a stirrer, with several holes in its surface to permit better diffusion of the liquids, and was rotated at the moderate speed of 6 rpm. One of the liquids was introduced by means of an 18-gauge stainless-steel needle, which crosses the cylinder, along its axis, connected to a Hamilton syringe (model TLL1000). Before carrying out the

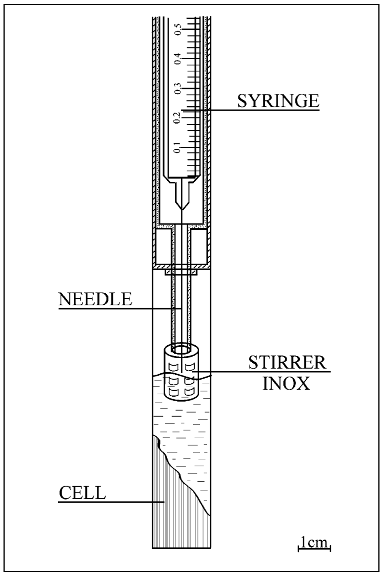

Figure 2. Diagram of experimental cell used for H_m^E measurements.

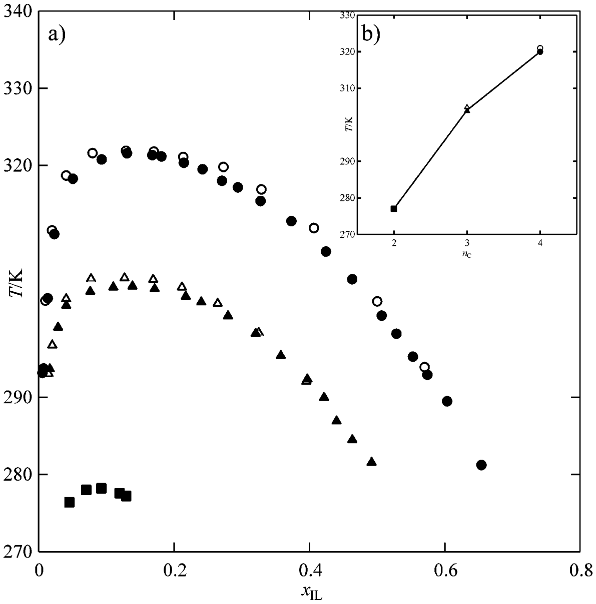

Figure 3. Plots of T vs x_{IL} for binaries [b3mpy][BF$_4$] (IL) + alkanols. ■, ethanol; ▲, propan-1-ol; ●, butan-1-ol. Comparison with literature values from ref 8 for: Δ, propan-1-ol, and ○, butan-1-ol. Inset represents the upper critical solution temperature (UCST) vs the number of alkanol carbon atoms n_C.

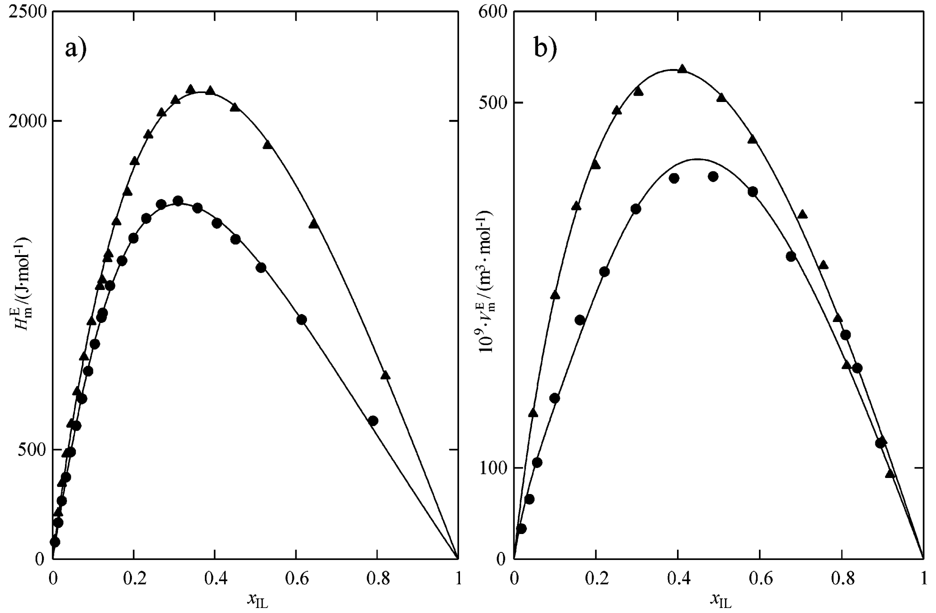

Figure 4. Plots of experimental values and correlation curves for excess properties for binaries [b3mpy][BF$_4$] (IL) + water at: ●, $T = 298.15$ K; ▲, $T = 318.15$ K. (a) For H^E_m vs x_{IL}. (b) For V^E_m vs x_{IL}.

experiments, an experiment was carried out in blank to establish the thermogram corresponding to mild agitation. In most cases, owing to the high enthalpic values for the mixtures studied here, the thermogram for the stirring was negligible and thus had little influence on the final result.

Results

LLE Data. Table 2 shows the experimental results for *temperature concentration* of the mixtures of [b3mpy][BF$_4$] with the alkanols, from ethanol to butan-1-ol, as a function of the mole fraction of the IL. All the systems present asymmetric binodal curves with the upper critical solution temperature (UCST) shifted toward low mole fractions of the IL (Figure 3). Table 2 clearly shows the value of the point of separation of the phases for each of the different systems. The comparison between the values determined here and those published in the literature[8] for the systems [b3mpy][BF$_4$] + propan-1-ol or + butan-1-ol is shown graphically in Figure 3. Our values are slightly lower in the region of the UCST possibly due to the slightly higher water content in our samples, with differences ranging from 0.3 °C for the system with butan-1-ol to 1 °C for the system with propan-1-ol. These observations are consistent with other systems with ILs, of imidazolium or pyridinium, reported in the literature and for both primary and secondary alkanols. The inset graph shows the quasiexponential variation between the UCST of these mixtures and the alkan-1-ol chain, giving a value of 329 K for the upper critical limit of the system [b3mpy][BF$_4$] + pentan-1-ol that will be studied in future works. It is only logical that the reduction in the polar character of the alkanol with increasing chain length increases the tendency toward immiscibility in mixtures with the IL.

Excess Properties. Tables 3 and 4 present, respectively, the excess quantities, H^E_m and V^E_m, for all the mixtures studied in this work, all with the common compound [b3mpy][BF$_4$], as a function of the mole fraction of this compound. For the first time, working with excess properties of solutions containing ionic liquids, we have carried out the correlation of data with a polynomial equation used frequently by our group,[13] expressed for a generic excess quantity $Y^E_m/(J\cdot mol^{-1}$ or $m^3\cdot mol^{-1})$, as a function of the active fraction of IL, z_{IL}, as follows

$$Y^E_m = z_{IL}(1 - z_{IL})\sum_{i=0} A_i z^i_{IL} \quad \text{being} \quad z_{IL} = \frac{x_{IL}}{x_{IL} + k(1 - x_{IL})} \tag{1}$$

Depending on the correlation that is carried out, it is necessary to stipulate how to estimate the parameter k. This parameter is identified with the molar volume ratio when the pairs (x_{IL},V^E_m) are fitted; in other words

$$k_v(p,T) = \frac{V^o_i(p,T)}{V^o_{IL}(p,T)} = \frac{M_i}{M_{IL}}\frac{\rho_{IL(p,T)}}{\rho_i(p,T)} \tag{2}$$

It is clear that this quotient is almost the same as that for the volume parameters of the substances, r_{IL}/r_i. However, it is preferable to calculate $k_v(p,T)$ using eq 2, which contains the dependence on pressure and temperature. For treatment of the pairs (x_{IL},H^E_m), the k parameter should be calculated as indicated in a previous paper,[13] which for the mixtures containing ILs would be

$$k_h = \frac{S^o_i}{S^o_{IL}} = \left(\frac{q_i}{q_{IL}}\right)\left(\frac{r_{IL}}{r_i}\right)^{2/3}\left(\frac{V^o_i}{V^o_{IL}}\right)^{2/3} = k_q\left(\frac{k_v}{k_r}\right)^{2/3} \tag{3}$$

The area and volume group parameters are determined from the corresponding weighted contributions of the Van der Waals parameters (see ref 14). In the literature,[6] there are some approximate empirical expressions that can be used to obtain values of r_{IL} and q_{IL}. However, because here we are dealing with binary systems, we have preferred to use the relationships established with eqs 2 and 3, which have already been described in detail. In other words, for an IL, the volume parameter can be calculated by referring to that of another substance, for which the values can be determined from the relationship

$$r_{IL} = \frac{V^o_{IL}}{V^o_i}r_i = \frac{r_i}{k_v} \tag{4}$$

Table 4. Excess Molar Volumes, V_m^E, for Binaries x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Alkanol or + (1 − x_{IL})Water at T = 298.15 K and T = 318.15 K

x_{IL}	$\frac{\rho}{\mathrm{kg\cdot m^{-3}}}$	$\frac{10^9 V_m^E}{\mathrm{m^3\cdot mol^{-1}}}$	x_{IL}	$\frac{\rho}{\mathrm{kg\cdot m^{-3}}}$	$\frac{10^9 V_m^E}{\mathrm{m^3\cdot mol^{-1}}}$	x_{IL}	$\frac{\rho}{\mathrm{kg\cdot m^{-3}}}$	$\frac{10^9 V_m^E}{\mathrm{m^3\cdot mol^{-1}}}$
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Water								
T = 298.15 K								
0.0182	1027.1	33	0.2208	1131.4	315	0.6761	1171.8	332
0.0376	1050.3	66	0.2975	1143.6	384	0.8091	1176.6	246
0.0567	1067.1	106	0.3909	1154.0	417	0.8376	1177.6	209
0.0995	1093.7	176	0.4861	1161.5	419	0.8942	1179.4	127
0.1608	1116.8	262	0.5827	1167.2	403			
T = 318.15 K								
0.0466	1046.8	161	0.3038	1130.2	513	0.7551	1160.9	323
0.1004	1080.4	290	0.4108	1141.5	537	0.7904	1162.3	265
0.1523	1099.8	388	0.5062	1148.8	506	0.8123	1163.2	213
0.1991	1112.4	432	0.5822	1153.3	460	0.8988	1165.7	131
0.2510	1122.2	492	0.7042	1158.9	378	0.9180	1166.3	94
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Methanol								
T = 298.15 K								
0.0493	873.4	−366	0.2007	1014.7	−699	0.6009	1138.7	−485
0.0629	893.1	−482	0.2956	1061.6	−732	0.6913	1151.7	−377
0.0986	934.4	−580	0.4052	1098.2	−700	0.7611	1159.7	−241
0.1499	979.6	−629	0.5128	1122.8	−549			
T = 318.15 K								
0.0557	865.7	−515	0.3016	1048.4	−802	0.7088	1139.8	−354
0.1052	924.3	−697	0.3944	1079.5	−714	0.8550	1156.2	−202
0.1493	964.0	−814	0.4970	1104.7	−597	0.9465	1164.4	−91
0.2479	1025.1	−854	0.5868	1121.6	−476			
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Ethanol								
T = 298.15 K								
0.0518	851.1	−268	0.2539	1006.2	−715	0.5895	1118.0	−391
0.0719	872.9	−369	0.3000	1028.2	−700	0.6640	1133.0	−271
0.1054	905.6	−526	0.4054	1068.6	−617	0.7275	1144.5	−212
0.1999	975.5	−668	0.5082	1098.9	−516	0.7682	1151.0	−149
T = 318.15 K								
0.0401	821.1	−317	0.2531	989.5	−776	0.5998	1106.3	−527
0.0671	851.0	−414	0.3062	1015.1	−772	0.6632	1118.8	−389
0.0992	882.7	−542	0.4041	1053.0	−715	0.7118	1127.7	−320
0.1497	924.5	−653	0.5002	1082.2	−645	0.7904	1141.0	−278
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Propan-1-ol								
T = 298.15 K								
0.0160	816.7	−111	0.5959	1106.9	−308	0.7993	1150.4	−169
0.4528	1066.5	−442	0.6934	1129.5	−250	0.8582	1160.4	−88
0.4940	1079.3	−408	0.7543	1141.9	−197	0.8962	1166.6	−54
0.5262	1088.6	−379						
T = 318.15 K								
0.0143	798.4	−67	0.2295	957.5	−496	0.6072	1095.8	−441
0.0249	808.8	−100	0.3112	997.8	−566	0.6405	1103.5	−359
0.0477	830.6	−212	0.4002	1033.6	−550	0.7096	1118.9	−326
0.1003	873.4	−239	0.4285	1043.6	−544	0.8001	1136.9	−272
0.1222	890.6	−375	0.4635	1055.3	−526	0.8522	1145.7	−169
0.1492	909.3	−417	0.5638	1084.7	−470	0.9028	1154.2	−157
0.2000	940.8	−455						
x_{IL}[b3mpy][BF$_4$] + (1 − x_{IL})Butan-1-ol								
T = 298.15 K								
0.0166	819.7	−46	0.8166	1147.7	−109	0.9040	1165.1	−67
0.7641	1136.6	−170	0.8558	1155.7	−76			
T = 318.15 K								
0.0191	805.5	−2	0.7777	1125.9	−265	0.9084	1152.1	−108
0.6961	1107.5	−411	0.8535	1141.6	−177	0.9479	1159.4	−75

Doing this calculation for the mixtures considered here, a mean value of 7.29 is obtained for the volume parameter.

We can propose a similar relationship for the value of k_h from eq 3, which, modified for a binary solution of an IL + a second component, would produce the following equation

$$q_{IL} = q_i\left(\frac{S^o_{IL}}{S^o_i}\right)\left(\frac{r_{IL}V^o_i}{r_iV^o_{IL}}\right)^{2/3} = q_i\left(\frac{S^o_{IL}}{S^o_i}\right)\left(\frac{k_v}{k_r}\right)^{2/3} \qquad (5)$$

but if we consider the hypothesis established for eq 4, eq 5 is reduced to its original definition as the quotient of areas because the bracketed term with the power of (2/3) would be equal to the unity. This would also give rise to a practical, but not rigorous, estimation of the value of q_{IL}, an identical form to that presented by eq 4 for the r_{IL}. To determine the quotient of the areas, we have used an empirical method, with the advantage that the quotient would eliminate any possible errors common to both surfaces. Using for this case the commercial software

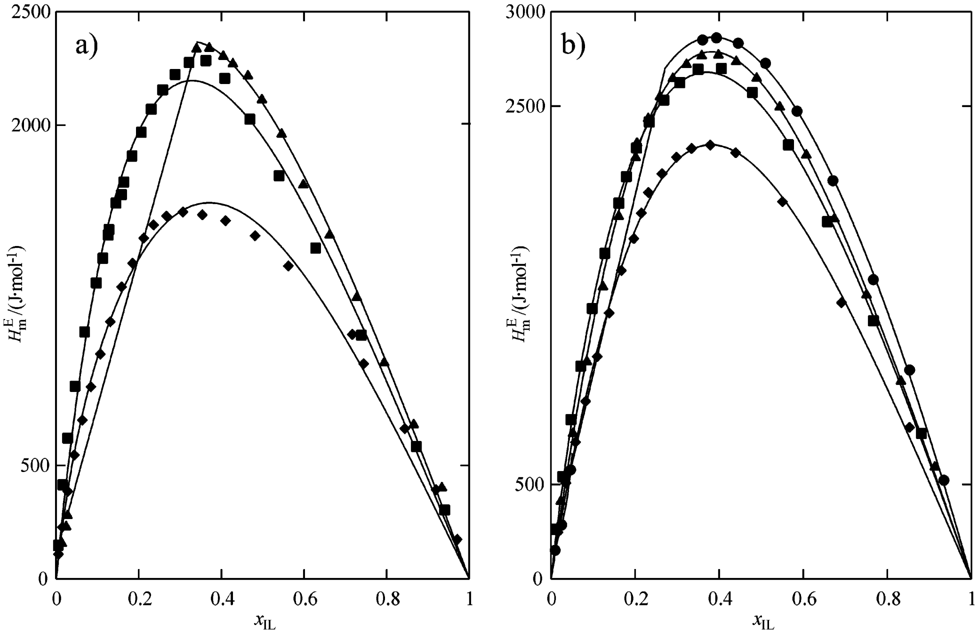

Figure 5. Plots of experimental values and correlation curves of H_m^E vs x_{IL} for binaries [b3mpy][BF$_4$] (IL) + alkanols: ◆, methanol; ■, ethanol; ▲, propan-1-ol; ●, butan-1-ol. (a) At $T = 298.15$ K. (b) At $T = 318.15$ K. Straight lines correspond to immiscibility zones.

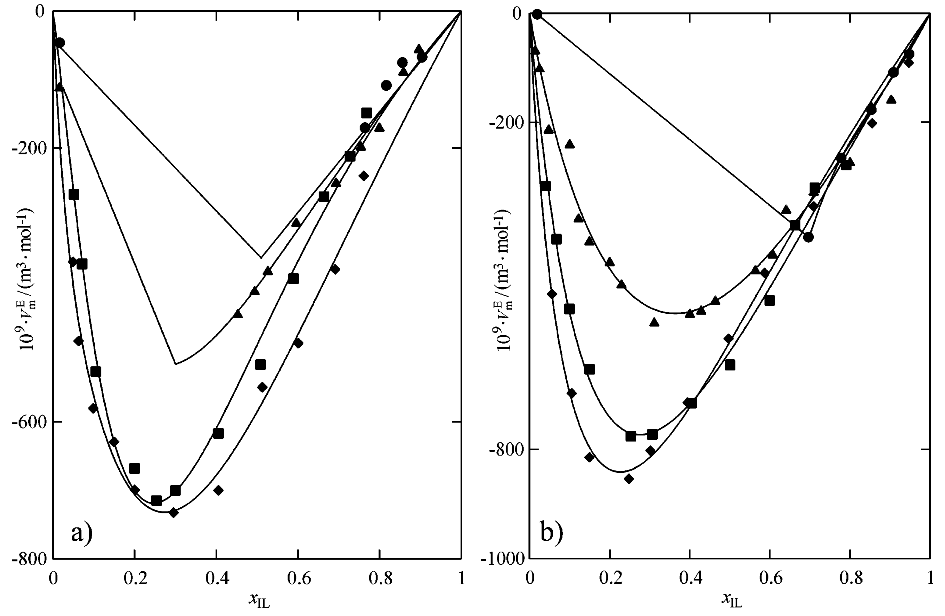

Figure 6. Plots of experimental values and correlation curves of V_m^E vs x_{IL} for binaries [b3mpy][BF$_4$] (IL) + alkanols: ◆, methanol; ■, ethanol; ▲, propan-1-ol; ●, butan-1-ol. (a) At $T = 298.15$ K. (b) At $T = 318.15$ K. Straight lines correspond to immiscibility zones.

PCMODEL, the corresponding areas were determined for the substances studied in this work, producing a mean value for all the mixtures of the surface parameter of $q_{IL} = 6.69$. With these values, experimental data were treated by applying eq 1.

IL + Water Binary Mixtures. The binary mixture [b3mpy]-[BF$_4$] + water is completely soluble at the temperatures selected for this work. The numerical values are presented in Table 3 for (x_{IL},H_m^E) and in Table 4 for (x_{IL},V_m^E). The pairs were correlated with eq 1 by the procedure indicated previously to estimate the parameter *k* and using a least-squares procedure to obtain the coefficients A_i. The values obtained and the standard deviations $s(Y_m^E)$ of the data for each excess property are recorded in Table 5. It can be observed that the correlations obtained are not very good, giving place to global average errors close to 5 % in some cases. Certain dispersion in experimental values because of the difficulty of handling of ILs and that the *k* parameter is considered fixed can be two of the reasons. If *k* was considered variable and obtained by trial in the same optimization process, the fitting curve would be very good. However, we are trying to analyze the utility of eq 1 in the mixtures with ILs and check the regularity of the parameters A_i for a same family of compounds, which will be an objective in future works. Graphical representations are shown in Figure 4, where a positive effect can be observed for both mixing quantities: an expansion in the final volume and endothermicity. Further, these effects increase with the temperature leading to positive thermal coefficients for both excess quantities; i.e, $(dH_m^E/dT)_p > 0$ and $(dV_m^E/dT)_p > 0$. The curves are asymmetric

Table 5. Coefficients A_i and k and Standard Deviation $s(Y^E_m)$ Obtained for Equation 1[a]

$Y^E_m = H^E_m/(J\cdot mol^{-1})$					
mixture	k	A_0	A_1	A_2	$s(Y^E_m)$
x_{IL}[b3mpy][BF$_4$] +					
$T = 298.15$ K					
$(1 - x_{IL})$water (2)	0.308	3534	5370		14
$(1 - x_{IL})$methanol (2)	0.219	4843	−8090	18154	74
$(1 - x_{IL})$ethanol (2)	0.297	6622	−1844	9986	60
$(1 - x_{IL})$propan-1-ol (2)	0.371	3550	12439	−3568	37
$T = 318.15$ K					
$(1 - x_{IL})$water (2)	0.269	4716	−1498	13410	14
$(1 - x_{IL})$methanol (2)	0.222	4889	−8060	24038	35
$(1 - x_{IL})$ethanol (2)	0.300	6923	−2312	15285	20
$(1 - x_{IL})$propan-1-ol (2)	0.371	5849	6547	4998	27
$(1 - x_{IL})$butan-1-ol (2)	0.449	5592	10007	848	34

$Y^E_m = 10^9 V^E_m/(m^3\cdot mol^{-1})$					
mixture	k	A_0	A_1	A_2	$s(Y^E_m)$
x_{IL}[b3mpy][BF$_4$] (1) +					
$T = 298.15$ K					
$(1 - x_{IL})$water (2)	0.802	1627	133	1	8
$(1 - x_{IL})$methanol (2)	0.203	−2655	2453	−5138	32
$(1 - x_{IL})$ethanol (2)	0.293	−1318	−5265	4359	24
$(1 - x_{IL})$propan-1-ol (2)	0.375	−2843	1597	−652	14
$(1 - x_{IL})$butan-1-ol (2)	0.459	−1184	−4749	4999	15
$T = 318.15$ K					
$(1 - x_{IL})$water (2)	0.374	1617	−435	2428	12
$(1 - x_{IL})$methanol (2)	0.206	−3098	1220	−3153	24
$(1 - x_{IL})$ethanol (2)	0.296	−2573	−420	−1043	26
$(1 - x_{IL})$propan-1-ol (2)	0.378	−1616	−310	−1365	28
$(1 - x_{IL})$butan-1-ol (2)	0.462	341	−10176	7573	15

[a] The k parameters are identified with k_h for H^E_m and with k_v for V^E_m.

with peaks in the low x_{IL} because the water mole fraction in this region has a greater contribution to interactional effects between both compounds.

IL + Alkanol Binary Mixtures. From the solubility curves shown in Figure 3, the working regions can be conveniently chosen for each property. It is observed that the miscibility is complete at the two working temperatures, in mixtures of IL with methanol and ethanol. However, with propan-1-ol, immiscibility appears at 298.15 K in the interval of x_{IL} from 0.028 to 0.324, with butan-1-ol at 298.15 K in the interval from 0.0150 to 0.528, and in the range of x_{IL} from 0.0501 to 0.2719 at 318.15 K. These data established the ranges of mole fractions where the liquids were miscible and thus where the excess properties could be determined. The values recorded in Tables 3 and 4 were correlated with eq 1, applying the previously described method. The optimum coefficients are shown in Table 5, and the graphical representation of the experimental data and the curves at the two temperatures are shown in Figures 5 and 6. The comments made above regarding the goodness of the correlations are also valid here. The H^E_m values for IL + alkanol mixtures are all endothermic, and the effect increases regularly with chain length of the alkanol and with temperature. In particular, the results of H^E_m for mixtures of IL with water and with methanol are very similar. However, excess volumes with alkanol present effects opposite to mixtures with water, i.e., contraction with $V^E_m < 0$, which becomes increasingly negative with increasing temperature. The contraction effect becomes less as the alkanol chain length increases, obeying for V^E_m the following order: methanol < ethanol < propan-1-ol < butan-1-ol. The minimum value for the mixture with methanol at 298.15 K is similar to that reported by Heintz et al.,[15] for the mixture with the isomeric IL 1-butyl-4-methylpyridinium tetrafluoroborate [b4mpyBF$_4$].

Discussion

From the results obtained for the mixtures [b3mpy][BF$_4$] + H_2O or + $C_nH_{2n+1}(OH)$, it can be deduced that several effects, some of which are opposing, are involved in the mixing process. Some are positive due to the splitting of hydrogen bonds in the molecules, of both the alkanol and the water, and to the reduction of Coulombic interactions by increasing the dipolar distance. Other effects are negative due to the interactions of very different molecules, especially the interaction of the −OH group of the alkanol and the pyridinium cation, supported by dipole−dipole interactions between alkanol or water and the IL. In addition to the interactional effects, it is also worth mentioning the existence of purely physical effects. One example of these is IL + alkanol contraction, owing to the large difference between the molecular volumes, helping the small alkanol molecules to occupy the empty spaces between the larger volumes of the IL constituents. Therefore, the most likely cause of contraction of the final volume is the tighter packing of the final mixture compared with the initial components. This difference could also explain the greater asymmetry of the curves, which becomes less pronounced as the presence of the IL increases in the solution and also with increasing chain length of the alkanol. The opposite volumetric effect, expansion of the IL + water mixture, indicates that the packing is not as favorable in this case. The rise in temperature appears to have a greater influence in the first alkanols, and the differences between the expansion coefficients, which become smaller with increasing alkanol chain length, also contribute to this.

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