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Excess Magnitudes for Ionic Liquid Binary Mixtures with a Common Ion

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Densities, isobaric thermal expansivities, and excess enthalpies were determined for the binary systems formed by ionic liquids with a common anion, 1-hexyl-3-methylimidazolium tetrafluoroborate + 1-ethyl-3-methylimidazolium tetrafluoroborate, and 1-hexyl-3-methylimidazolium tetrafluoroborate + 1-butyl-3-methylimidazolium tetrafluoroborate, and by those with a common cation, 1-butyl-3-methylimidazolium tetrafluoroborate + 1-butyl-3-methylimidazolium methylsulfate and 1-butyl-3-methylimidazolium tetrafluoroborate + 1-butyl-3-methylimidazolium hexafluorophosphate. Volumetric properties were obtained by means of a vibrating tube densimeter, whereas Calvet microcalorimetry was used to determine the excess enthalpies. Due to the high viscosity of the samples, nonstandard experimental techniques had to be used to obtain the results. The experimental data are interpreted on the basis of the chemical structure of the ionic liquids.

Introduction

In recent years, much attention has been devoted to the study of ionic liquids (ILs). They are salts, usually composed by an organic cation and an organic or inorganic anion, that are liquid at room temperature.[1] These compounds present unique physical and chemical properties such as an extremely low vapor pressure, specific solvent abilities, and a broad liquid temperature range.[2−4] In addition, the actual capability for synthesizing ILs makes it possible to select the appropriate ionic liquid for a specific process by fine-tuning the chemical structure of the cation and anion that constitute the IL. All these characteristics make ILs potential, very specific, environmental-friendly substitutes to the traditional organic solvents in most of the chemical industry processes.[5−9] Therefore, the study of the physical properties of ILs presents great interest from both a fundamental and applied research point of view.

Pure ILs have received great attention in the past years.[2−4,10] Nevertheless, there are few papers[11,12] that discuss the behavior of IL mixtures from a thermophysical point of view. It is worth noting that mixtures of ILs increase enormously the above-cited tuning capability of ILs because there is an unlimited quantity of possible IL binary mixtures. In this context, previous works[11,12] have shown that IL binary mixtures do not deviate in a large amount from the ideal mixture, but these conclusions are solely based on experimental volumetric data. To confirm this near-ideal behavior, the investigation on other kinds of properties would be desirable. This work analyzes the behavior of a set of excess properties, not only volumetric, for four IL binary systems. The selected ILs were three 1-alkyl-3-methylimidazolium tetrafluoroborates ($[C_n\text{mim}][BF_4]$ with $n = 2$, 4, 6), 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4\text{mim}][PF_6]$), and 1-butyl-3-methylimidazolium methylsulfate ($[C_4\text{mim}][MeSO_4]$). To make the analysis easier, this study was limited to binary systems that contain a common ion. To this end, densities and excess enthalpies were experimentally determined over the whole composition range and within the temperature interval (298.15 to 303.15) K for the systems containing a common anion ($([C_2\text{mim}] + [C_6\text{mim}])[BF_4]$ and $([C_4\text{mim}] + [C_6\text{mim}])[BF_4]$ and for those containing a common cation $[C_4\text{mim}]([BF_4]+[MeSO_4])$ and $[C_4\text{mim}]([BF_4]+[PF_6])$. From density data, excess molar volumes were calculated and isobaric thermal expansivities were obtained and compared to the ideal behavior defined by the Benson and Kiyohara[13] criterion. The obtained magnitudes are discussed taking into account the molecular structure of the substances that form the mixture because, for some of the studied systems, the observed behavior was found to be similar to nonelectrolyte binary systems composed by substances that belong to the same homologous series.

Experimental

Materials. All ILs were purchased from Solvent Innovation. They were degassed and dried for 3 days by stirring under a vacuum at moderate temperature (333.15 K). The certified purities for $[C_2\text{mim}][BF_4]$, $[C_4\text{mim}][BF_4]$, $[C_6\text{mim}][BF_4]$, $[C_4\text{mim}][PF_6]$, and $[C_4\text{mim}][MeSO_4]$ were higher than 99.85, 99.0, 99.7, 99.6, and 99.0 %, respectively.

Apparatus and Procedures. Densities, ρ, of all samples were determined by means of an Anton Paar DMA 602 densimeter cell coupled to a mPDS 2000 v3 evaluation unit. Ultrapure water and tetrachloroethylene were used as calibration standards. The density data needed for water were taken from the literature,[14] whereas tetrachloroethylene density was supplied by Fitzgerald;[15] this company certifies it from (278.15 to 333.15) K with an uncertainty of $1 \cdot 10^{-5}$ g·cm^{-3}.

Usually, ILs present high viscosities. This becomes an important problem if a vibrating tube densimeter is used[16] because there is an increase of the experimentally determined density due to the damping that the high viscosity of the liquid produces on the tube vibration. This trouble can be circumvented by calibrating the densimeter with liquids with known viscosity and density. These liquids were supplied by Fitzgerald, which also certifies their density from (278.15 to 333.15) K with an uncertainty of $1 \cdot 10^{-5}$ g·cm^{-3}, and cover all the interesting viscosity ranges for the ionic liquids, (10 to 500) mPa·s. The temperature dependence of these standards was taken from a previous work.[17] Therefore, a dependence of the density

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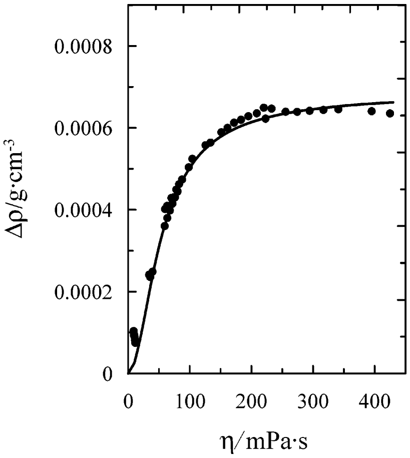

Figure 1. Density correction curve, $\Delta\rho$ (η): ●, experimental data; —, calculated values from eq 1.

correction $\Delta\rho = (\rho_{\mathrm{measured}} - \rho_{\mathrm{reported}})$ on the viscosity was obtained. These data were fitted to a rational equation, and the following expression was obtained

$$\Delta\rho(\eta) = \frac{\eta^2}{1448\cdot\eta^2 + 18\,300\cdot\eta + 3\,587\,000} \qquad (1)$$

These data and the fitting curve are presented in Figure 1. A detailed explanation of this procedure for a very similar apparatus (Anton Paar DSA48 vibrating tube densimeter) is given in a previous work.[17] Therefore, once the viscosity of the sample is known, from the experimentally determined data and by means of eq 1, the corrected value for density can be obtained. Taking into account all the factors involved in the density determination, the estimated uncertainty is $2\cdot10^{-4}$ $\mathrm{g\cdot cm^{-3}}$.

Excess molar enthalpies, H^{E}, were obtained at atmospheric pressure by Calvet microcalorimetry, a technique widely used in H^{E} determination. The apparatus has been described in previous contributions.[18−20] Nevertheless, the design of the cells was changed with regard to the classical arrangement,[20] due to the fact that the high viscosity of the ILs makes them difficult to mix 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. Figure 2 shows a scheme of the experimental cell. The cell, which was partially filled with a known mass of one of the liquids, was screwed into a long PVC pipe by means of a support with a Teflon stopper. It has a small hole where a silicon tablet was fitted and perforated by the needle of the syringe where the other liquid was located. The stopper is crossed by one metallic axis in whose bottom a helix is placed. At its top, there is a hook where a metallic rod can be fitted to join it to a motor placed outside the calorimeter that stirs the mixture. To obtain thermal stability, the experiment was not started until 120 min after the cell was placed into the calorimeter. When thermal equilibrium was reached and checked by the stability of the calorimetric signal (baseline), the experiment was started and the syringe was pumped to introduce the liquid into the cell. After, the syringe was removed from the calorimeter and the rod needed to stir the liquids was fitted to the agitation mechanism. The liquids were vigorously stirred for a time interval programmed by a high-precision digital clock connected to the motor (precision of about 0.1 s). To favor mixing, the rod was raised and dropped manually several times. The required time to stir the sample depends basically on the viscosity and miscibility of the liquids; values from (4 to 15) s were needed. After this, the experiment progressed until it stopped when the baseline was reached again. Therefore, an unknown heat due to the stirring was added to the mixing heat of the liquids. To evaluate it, a new experiment was made for the same sample, in which only the stirring heat was registered because the mixture was already well-mixed. The final heat of mixing was the difference between that obtained from the first experience (mixing heat plus stirring heat) and that from the second one (only stirring heat). From the values for all samples, the relative uncertainty of stirring heat was estimated to be 10 % of their own value. This implies that in the worst case (mixture of the two less-miscible and most viscous liquids) a uncertainty in the mixing heat of 0.5 J was obtained, which is small compared to the typical absolute values obtained in mixing heat experiments (about 15 J). To evaluate the accuracy of this method, excess enthalpies were determined for the cyclohexane + hexane system,[21] which is a standard binary system used to check the accuracy of any method in H^{E} determinations. In spite of the uncertainty that the agitation involves, a mean deviation of

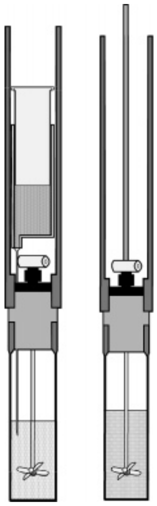

Figure 2. Scheme of the experimental cell.

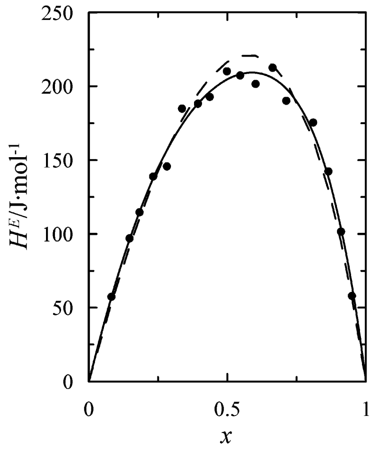

Figure 3. Excess molar enthalpies for x cyclohexane + (1−x) hexane at T = 298.15 K: ●, experimental data; —, calculated values from eq 3; ----, data obtained from the literature.[21]

Table 1. Densities of Binary Mixtures Containing Two ILs with Common Anion [BF_4]

	ρ/g·cm^{-3}								
x	T/K = 298.15	T/K = 299.15	T/K = 301.15	T/K = 302.15	T/K = 303.15	T/K = 304.15	T/K = 305.15	T/K = 307.15	T/K = 308.15
				x [C_6mim][BF_4] + (1−x) [C_2mim][BF_4]					
0	1.2796	1.2788	1.2772	1.2765	1.2757	1.2749	1.2742	1.2727	1.2719
0.0978	1.2616	1.2608	1.2593	1.2586	1.2579	1.2571	1.2564	1.2549	1.2542
0.1484	1.2533	1.2525	1.2510	1.2511	1.2495	1.2488	1.2480	1.2465	1.2458
0.2070	1.2437	1.2430	1.2415	1.2407	1.2400	1.2392	1.2385	1.2370	1.2363
0.2941	1.2303	1.2296	1.2281	1.2274	1.2266	1.2259	1.2252	1.2237	1.2230
0.3994	1.2151	1.2144	1.2129	1.2122	1.2114	1.2107	1.2100	1.2085	1.2078
0.4474	1.2082	1.2075	1.2061	1.2054	1.2047	1.2040	1.2033	1.2018	1.2011
0.5062	1.2006	1.1999	1.1984	1.1977	1.1970	1.1963	1.1956	1.1942	1.1934
0.5540	1.1944	1.1937	1.1923	1.1916	1.1909	1.1902	1.1895	1.1881	1.1874
0.5939	1.1895	1.1888	1.1874	1.1867	1.1860	1.1853	1.1846	1.1832	1.1825
0.6855	1.1784	1.1776	1.1763	1.1756	1.1749	1.1742	1.1735	1.1721	1.1714
0.8197	1.1636	1.1629	1.1614	1.1607	1.1600	1.1593	1.1586	1.1572	1.1565
0.8804	1.1572	1.1566	1.1552	1.1545	1.1538	1.1531	1.1524	1.1510	1.1503
0.9455	1.1508	1.1501	1.1487	1.1481	1.1473	1.1466	1.1459	1.1445	1.1438
1	1.1458	1.1451	1.1437	1.1430	1.1423	1.1415	1.1408	1.1395	1.1388
				x [C_4mim][BF_4] + (1−x) [C_6mim][BF_4]					
0	1.2017	1.2008	1.1994	1.1987	1.1980	1.1973	1.1966	1.1952	1.1945
0.1083	1.1946	1.1937	1.1923	1.1916	1.1909	1.1903	1.1896	1.1882	1.1875
0.1910	1.1895	1.1887	1.1873	1.1866	1.1859	1.1852	1.1845	1.1831	1.1824
0.4020	1.1770	1.1761	1.1747	1.1740	1.1733	1.1726	1.1719	1.1705	1.1698
0.4450	1.1746	1.1738	1.1724	1.1717	1.1710	1.1703	1.1696	1.1682	1.1675
0.4953	1.1717	1.1709	1.1695	1.1688	1.1681	1.1674	1.1667	1.1653	1.1646
0.5617	1.1680	1.1671	1.1657	1.1650	1.1643	1.1636	1.1629	1.1615	1.1608
0.6398	1.1636	1.1628	1.1614	1.1607	1.1600	1.1594	1.1587	1.1573	1.1566
0.7924	1.1559	1.1550	1.1536	1.1529	1.1522	1.1516	1.1509	1.1495	1.1488
0.8970	1.1506	1.1498	1.1484	1.1477	1.1470	1.1463	1.1457	1.1443	1.1436
0.9460	1.1481	1.1473	1.1459	1.1452	1.1445	1.1438	1.1432	1.1418	1.1411
1	1.1453	1.1445	1.1431	1.1424	1.1417	1.1411	1.1404	1.1390	1.1383

Table 2. Densities of Binary Mixtures Containing Two ILs with Common Cation [C_4mim]

	ρ/g·cm^{-3}								
x	T/K = 298.15	T/K = 299.15	T/K = 301.15	T/K = 302.15	T/K = 303.15	T/K = 304.15	T/K = 305.15	T/K = 307.15	T/K = 308.15
				x [C_4mim][BF_4] + (1−x) [C_4mim][$MeSO_4$]					
0	1.2079	1.2073	1.2060	1.2053	1.2046	1.2040	1.2033	1.2020	1.2014
0.1209	1.2074	1.2067	1.2054	1.2047	1.2040	1.2034	1.2027	1.2013	1.2006
0.2166	1.2069	1.2063	1.2049	1.2042	1.2036	1.2029	1.2022	1.2008	1.2001
0.3057	1.2064	1.2057	1.2043	1.2037	1.2030	1.2023	1.2016	1.2003	1.1996
0.4060	1.2058	1.2051	1.2038	1.2031	1.2024	1.2017	1.2010	1.1997	1.1990
0.4358	1.2056	1.2050	1.2036	1.2029	1.2022	1.2015	1.2009	1.1995	1.1988
0.5118	1.2052	1.2045	1.2031	1.2024	1.2017	1.2011	1.2004	1.1990	1.1983
0.5412	1.2050	1.2043	1.2029	1.2022	1.2015	1.2009	1.2002	1.1988	1.1981
0.6026	1.2045	1.2039	1.2025	1.2018	1.2011	1.2004	1.1997	1.1983	1.1976
0.6480	1.2044	1.2036	1.2022	1.2015	1.2008	1.2001	1.1994	1.1981	1.1973
0.6934	1.2038	1.2031	1.2017	1.2011	1.2004	1.1997	1.1990	1.1976	1.1969
0.7813	1.2032	1.2025	1.2011	1.2004	1.1998	1.1991	1.1984	1.1970	1.1963
0.9005	1.2022	1.2016	1.2002	1.1995	1.1988	1.1981	1.1974	1.1960	1.1953
0.9363	1.2020	1.2012	1.1998	1.1991	1.1984	1.1977	1.1971	1.1957	1.1950
0.9683	1.2019	1.2011	1.1997	1.1990	1.1983	1.1976	1.1969	1.1957	1.1948
1	1.2014	1.2007	1.1993	1.1986	1.1979	1.1972	1.1966	1.1952	1.1945
				x [C_4mim][PF_6] + (1−x) [C_4mim][BF_4]					
0	1.2014	1.2006	1.1993	1.1987	1.1981	1.1973	1.1966	1.1952	1.1946
0.0568	1.2116	1.2109	1.2095	1.2089	1.2082	1.2075	1.2068	1.2053	1.2046
0.1034	1.2202	1.2195	1.2181	1.2174	1.2167	1.2159	1.2152	1.2138	1.2131
0.2095	1.2391	1.2383	1.2369	1.2362	1.2355	1.2347	1.2340	1.2326	1.2318
0.3012	1.2548	1.2540	1.2526	1.2519	1.2512	1.2504	1.2497	1.2482	1.2475
0.3825	1.2687	1.2679	1.2665	1.2657	1.2650	1.2642	1.2635	1.2620	1.2612
0.4647	1.2826	1.2817	1.2803	1.2796	1.2789	1.2781	1.2773	1.2758	1.2750
0.4999	1.2883	1.2875	1.2861	1.2853	1.2846	1.2838	1.2830	1.2815	1.2807
0.5974	1.3045	1.3035	1.3021	1.3014	1.3006	1.2998	1.2990	1.2975	1.2967
0.6928	1.3198	1.3189	1.3174	1.3166	1.3159	1.3150	1.3142	1.3126	1.3119
0.8330	1.3423	1.3414	1.3399	1.3391	1.3383	1.3375	1.3366	1.3350	1.3342
0.8877	1.3507	1.3497	1.3482	1.3474	1.3466	1.3458	1.3450	1.3433	1.3425
0.9450	1.3594	1.3585	1.3570	1.3562	1.3554	1.3545	1.3537	1.3521	1.3512
1	1.3679	1.3669	1.3654	1.3647	1.3639	1.3630	1.3622	1.3605	1.3597

4 % was obtained, which is in the same order as that usuallyobtained for these calorimeters (1 to 2 %),[22] a fact that confirms the suitability of the proposed methodology for H^E measurements. Figure 3 shows these results.

Results and Discussion

Volumetric Properties. Density data were obtained in the temperature interval (298.15 to 308.15) K over the whole

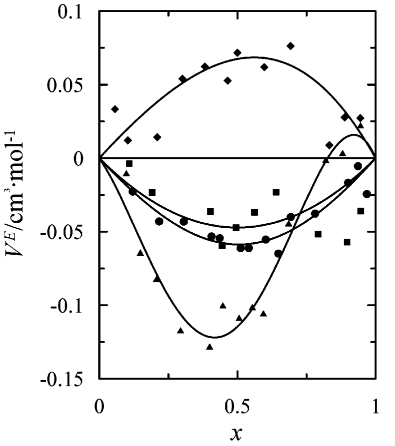

Figure 4. Excess molar volume as a function of composition at $T = 303.15$ K: ▲, x [C$_6$mim][BF$_4$] + (1−x) [C$_2$mim][BF$_4$]; ■, x [C$_4$mim][BF$_4$] + (1−x) [C$_6$mim][BF$_4$]; ◆, x [C$_4$mim][PF$_6$] + (1−x) [C$_4$mim][BF$_4$]; ●, x [C$_4$mim][BF$_4$] + (1−x) [C$_4$mim][MeSO$_4$]; —, calculated values from eq 3.

Table 3. Fitting Coefficients B_i and Standard Deviation s of Equation 3 for Excess Molar Volume and Excess Enthalpy at T = 303.15 K of the Studied Systems

	B_i	
	V^E/cm^3·mol^{-1}	H^E/J·mol^{-1}
	x [C$_6$mim][BF$_4$] + (1−x) [C$_2$mim][BF$_4$]	
$i = 1$	−0.4582	1187
$i = 2$	0.3505	−249
$i = 3$	0.5377	−380
s	0.013	18
	x [C$_4$mim][BF$_4$] + (1−x) [C$_6$mim][BF$_4$]	
$i = 1$	−0.189	263
$i = 2$	–	−76
s	0.02	4
	x [C$_4$mim][BF$_4$] + (1−x) [C$_4$mim][MeSO$_4$]	
$i = 1$	−0.2347	−1425
$i = 2$	−0.0052	−83
$i = 3$	0.0345	578
s	0.008	12
	x [C$_4$mim][PF$_6$] + (1−x) [C$_4$mim][BF$_4$]	
$i = 1$	0.2698	−487
$i = 2$	0.0676	−119
$i = 3$	–	270
s	0.019	13

Table 4. Isobaric Thermal Expansivity α_p for the Studied IL Binary Mixtures at T = 303.15 K

x	α_p/kK^{-1}	x	α_p/kK^{-1}
	x [C$_6$mim][BF$_4$] + (1−x) [C$_2$mim][BF$_4$]		
0	0.5996	0.5540	0.5897
0.0978	0.5865	0.5939	0.5920
0.1484	0.5978	0.6855	0.5921
0.2070	0.5996	0.8197	0.6125
0.2941	0.6004	0.8804	0.6051
0.3994	0.6013	0.9455	0.6153
0.4474	0.5904	1	0.6161
0.5062	0.5967	–	–
	x [C$_4$mim][BF$_4$] + (1−x) [C$_6$mim][BF$_4$]		
0	0.5937	0.5617	0.6076
0.1083	0.5888	0.6398	0.5955
0.1910	0.5957	0.7924	0.6106
0.4020	0.6027	0.8970	0.6070
0.4450	0.6015	0.9460	0.6059
0.4953	0.6027	1	0.6035
	x [C$_4$mim][BF$_4$] + (1−x) [C$_4$mim][MeSO$_4$]		
0	0.5454	0.6026	0.5755
0.1209	0.5610	0.6480	0.5811
0.2142	0.5657	0.6934	0.5723
0.3057	0.5623	0.7813	0.5745
0.4060	0.5691	0.9005	0.5823
0.4358	0.5714	0.9363	0.5828
0.5118	0.5710	0.9683	0.5817
0.5412	0.5769	1	0.5762
	x [C$_4$mim][PF$_6$] + (1−x) [C$_4$mim][BF$_4$]		
0	0.5686	0.4999	0.5921
0.0568	0.5775	0.5974	0.5922
0.1034	0.5859	0.6928	0.5971
0.2095	0.5848	0.8330	0.6059
0.3012	0.5827	0.8877	0.6031
0.3825	0.5881	0.9450	0.6026
0.4647	0.5910	1	0.6012

composition range at atmospheric pressure. To derive the isobaric thermal expansivity, densities for all mixtures were determined for, at least, nine temperatures, as shown in Tables 1 and 2. The viscosities of each sample, needed to obtain the corrected density, were obtained from ref 23. From density data at $T = 303.15$ K, excess molar volumes V^E were obtained from

$$V^E = (xM_1 + (1 - x)M_2)/\rho - (M_1/\rho_1 + M_2/\rho_2) \qquad (2)$$

where M is the molar mass and the subscripts denote pure compounds. The uncertainty in this magnitude for the measurements of this work was quoted in 0.03 cm^3·mol^{-1}. The obtained values were fitted to a Redlich−Kister polynomial of the form

$$X^E = x(1 - x)\sum_{i=1}^{n} B_i(2x - 1)^i \qquad (3)$$

The B_i coefficients are listed in Table 3. Figure 4 shows the V^E values for the binary systems at $T = 303.15$ K. All systems have very small V^E values. This fact corroborates the previous studies[11] that mention the ideal character of these mixtures. Positive V^E values were found for the [C$_4$mim] ([BF$_4$] + [PF$_6$]) system, whereas $V^E < 0$ for the other systems. The results for [C$_4$mim] ([BF$_4$] + [PF$_6$]) are in good agreement with the data from the literature; in fact, at $x = 0.5$, in this work, a V^E value of (0.08 ± 0.03) cm^3·mol^{-1} was obtained, whereas that reported in the literature is (0.12 ± 0.02) cm^3·mol^{-1}. On the other hand, although the results for ([C$_4$mim] + [C$_6$mim])([BF$_4$]) and ([C$_4$mim] + [C$_6$mim])([BF$_4$]) are negative and contradict the predictions of ref 11, it must be noted that, although cations present the same nature (alkylmethylimidazolium), the common anion is not the same (NTf$_2$, abbreviation of bis(trifluoromethylsulfonyl)imide, in ref 11). The differences probably come from the fact that the density of BF$_4$-based ILs is considerably lower than that of NTf$_2$-based ones, a fact that makes the available free volume increase; therefore, packing phenomena could appear more easily, which explains the observed negative V^E. At last, it must be noted that V^E for the studied systems is not affected by viscosity correction. Differences between noncorrected V^E data and corrected data are much smaller than the experimental uncertainty in density.

Isobaric thermal expansivity, α_p, was determined from density using

$$\alpha_p = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \qquad (4)$$

From the accuracy achieved in the density determination, the α_p uncertainty is estimated in 0.015 kK^{-1}. α_p at 303.15 K is shown in Table 4. With regard to the ideal behavior, the Benson and Kiyohara criterion,[13] which is the most rigorous and commonly used, is applied. It defines the ideal isobaric thermal expansivity as follows

$$\alpha_p^{id} = \phi\alpha_1 + (1 - \phi)\alpha_2 \qquad (5)$$

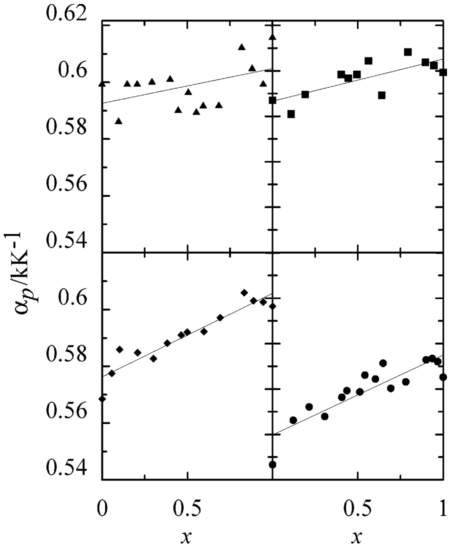

Figure 5. Isobaric thermal expansivity as a function of composition at T = 303.15 K: ▲, x [C$_6$mim][BF$_4$] + (1−x) [C$_2$mim][BF$_4$]; ■, x [C$_4$mim][BF$_4$] + (1−x) [C$_6$mim][BF$_4$]; ◆, x [C$_4$mim][PF$_6$] + (1−x) [C$_4$mim][BF$_4$]; ●, x [C$_4$mim][BF$_4$] + (1−x) [C$_4$mim][MeSO$_4$]; —, calculated values from eq 5.

Table 5. Fitting Coefficients α_{pi} of Equation 5 and Standard Deviation s for the Studied Systems at T = 303.15 K

α_{p1}/kK^{-1}	α_{p2}/kK^{-1}	s/kK^{-1}
	x [C$_6$mim][BF$_4$] + (1−x) [C$_2$mim][BF$_4$]	
0.607	0.591	0.008
	x [C$_4$mim][BF$_4$] + (1−x) [C$_6$mim][BF$_4$]	
0.608	0.593	0.004
	x [C$_4$mim][BF$_4$] + (1−x) [C$_4$mim][MeSO$_4$]	
0.584	0.557	0.005
	x [C$_4$mim][BF$_4$] + (1−x) [C$_4$mim][BF$_4$]	
0.576	0.605	0.004

where the subscripts denote pure compounds and ϕ is the volume fraction defined as

$$\phi = xV_1/(xV_1 + (1 - x)V_2) \tag{6}$$

The α_p data at 303.15 K were fitted to eq 5 taking the α_p values of pure compounds as the fitting parameters (Table 5). Figure 5 shows the fitting curve as well as the experimental values. As has been obtained in previous studies of α_p for ILs, values are significantly lower compared with those obtained for molecular liquids.[17] With regard to composition dependence, experimental results do not deviate systematically from the ideal curve, and they show a random distribution around ideal behavior. Therefore, within the experimental uncertainty, it can be concluded that α_p presents ideal behavior for these IL mixtures.

Excess Enthalpies. H^E was determined over the whole composition range at 303.15 K for all systems. These data are presented in Table 6 and shown in Figure 6, and they were fitted to eq 3 (see fitting coefficients in Table 3). As a rule, they are small (absolute values less than 500 J·mol^{-1}). A variety of behaviors are observed: systems with a common anion present a positive H^E, whereas those with a common cation show a negative H^E. Excess enthalpy is related to the net destruction of interactions in the mixing process.[24] Positive H^E values indicate that interactions between unlike compounds are weaker than between like ones, whereas negative values point to the opposite. Thus, a positive H^E implies a net destruction of the interactions between the constituents of the mixture, whereas a negative H^E indicates net creation of interactions. Therefore, from the results, it can be concluded that interactions between unlike cations are weaker than those between like ones, and the opposite is found for anions. Cation structure is varied only on the length of the alkyl chain at position 1 of the imidazolium; therefore, only the dispersive part of the interaction potential is changed. As a consequence, forces between the cations with a longer alkyl chain are stronger than those between the unlike cations, whereas the latter are roughly the same for the shorter cations. Therefore, mixing results in a net interaction destruction between the ions that form the liquid, a fact that explains the positive enthalpies. Clearly, as the alkyl chain difference increases, higher H^E values are expected, as the experimental results show. This effect is well-known, and it has been observed for binary mixtures composed by two liquids that belong to the same homologous series.[25−27] With regard to common cation mixtures, from the obtained negative H^E values, we deduced that interactions between unlike anions are stronger than those between like ones. Following the arguments given for the

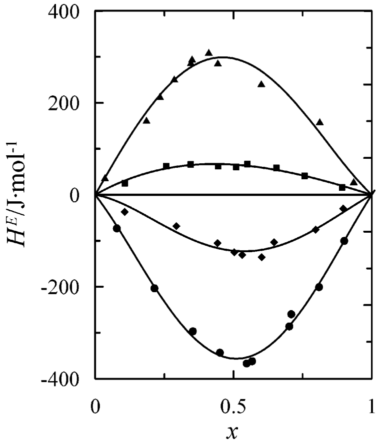

Figure 6. Excess molar enthalpies as a function of composition at T = 303.15 K: ▲, x [C$_6$mim][BF$_4$] + (1−x) [C$_2$mim][BF$_4$]; ■, x [C$_4$mim][BF$_4$] + (1−x) [C$_6$mim][BF$_4$]; ◆, x [C$_4$mim][PF$_6$] + (1−x) [C$_4$mim][BF$_4$]; ●, x [C$_4$mim][BF$_4$] + (1−x) [C$_4$mim][MeSO$_4$]; —, calculated values from eq 3.

Table 6. Excess Molar Enthalpies at T = 303.15 K for the Studied Systems

x	H^E/J·mol^{-1}	x	H^E/J·mol^{-1}
	x [C$_6$mim][BF$_4$] + (1−x) [C$_2$mim][BF$_4$]		
0.0352	37	0.4106	310
0.1856	162	0.4433	287
0.2339	214	0.6006	242
0.2862	252	0.8121	159
0.3459	288	0.9348	28
0.3504	295	–	–
	x [C$_4$mim][BF$_4$] + (1−x) [C$_6$mim][BF$_4$]		
0.1071	17	0.5499	67
0.2572	62	0.6548	58
0.3454	66	0.7573	41
0.4453	62	0.8925	16
0.5099	61	–	–
	x [C$_4$mim][BF$_4$] + (1−x) [C$_4$mim][BF$_4$]		
0.0780	−73	0.5475	−367
0.2142	−203	0.7088	−260
0.3533	−297	0.7019	−286
0.4511	−343	0.8096	−201
0.5674	−362	0.9006	−100
	x [C$_4$mim][BF$_4$] + (1−x) [C$_4$mim][BF$_4$]		
0.1066	−37	0.6024	−136
0.2935	−68	0.6470	−103
0.4424	−105	0.7973	−76
0.5030	−125	0.8968	−30
0.5316	−131	–	–

explanation for systems that contain a common anion, to understand these results, it will be very useful to know H^E data for binary systems that contain these functional groups. Unfortunately, there have been no studies reported, and because these anions are composed by groups that could present specific and complex interactions between them, there is not any simple model that could relate the observed results to any microscopic mechanism.

Conclusion

The experimental results confirm the fact that, as a rule, binary mixtures formed by ionic liquids have small excess properties. This implies that the ideal mixture is a model that fits reasonably well the behavior of this kind of system, and therefore, their physical properties can be accurately predicted using pure compound properties and the ideal mixture model.

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