Thermodynamic Properties of Ionic Liquids in Organic Solvents from (293.15 to 303.15) K

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Densities, speeds of sound, and refractive indices of the binary mixtures of BMIM PF_6 (1-butyl-3-methyl imidazolium hexafluorophosphate), HMIM PF_6 (1-hexyl-3-methylimidazolium hexafluorophosphate), OMIM PF_6 (1-methyl-3-octylimidazolium hexafluorophosphate), and MMIM CH_3SO_4 (1,3-dimethylimidazolium methyl sulfate) with 2-butanone, ethylacetate, and 2-propanol were determined from (293.15 to 303.15) K. Excess molar volumes, changes of refractive index on mixing, and deviations in isentropic compressibility were calculated for the above systems. The liquid−liquid equilibrium data of the binary mixtures ionic liquid + 2-propanol were carried out, and they were compared with the correlated values obtained by means of the NRTL and UNIQUAC equations.

Introduction

Ionic liquids (ILs) are a group of organic salts that result from the combination of several organic cations and inorganic anions, and they may be liquid at room temperature. The most commonly studied ILs contain the imidazolium cation with varying heteroatom functionality. In this paper, we have considered the use of the following ILs formed by 1-alkyl-3-methylimidazolium (C_nMMIM) as cation and hexafluorophosphate (PF_6^-) and methyl sulfate ($CH_3SO_4^-$) as anions. The ILs based on the (PF_6^-) anion are considered historically the most important and commonly investigated, despite that this anion can undergo hydrolysis producing HF in contact with water[1] and at high temperatures;[2] however, the $CH_3SO_4^-$ anion ILs represent halogen-free and relatively hydrolysis-stable[3] compunds. They could be an interesting alternative for industrial application due to the fact that they avoid the liberation of toxic and corrosive HF into the environment.

This paper is a continuation of the thermodynamic study of ILs with imidazolium cation in the physical properties on mixing[4−7] with organic solvents and their dependency with the temperature since they are necessary to determine the liquid−liquid equilibria (LLE) and then designing extractive process involving ILs on an industrial scale for azeotropic mixtures. As the ILs are relatively new, experimental measurements of physical properties are extremely scarce but clearly needed.

In this paper, the densities, refractive indices, and speeds of sound of the binary mixtures BMIM PF_6 or MMIM CH_3SO_4 + 2-butanone or ethylacetate or 2-propanol, HMIM PF_6 + 2-propanol, and OMIM PF_6 + ethylacetate from (293.15 to 303.15) K and atmospheric pressure were measured. Excess and derived properties have been calculated from the experimental data. A function of the mole fraction and temperature polynomial equation[8] was used to fit these quantities. The standard deviations between experimental and calculated values are shown. LLE data of the binary mixtures BMIM PF_6 or HMINPF_6 + 2-propanol in the range from (278.15 to 343.15) K and from (278.15 to 328.15) K were determined, respectively. The LLE for the binary mixture BMINPF_6 + 2-propanol was determined until 343.15 K in order to prevent hydrolysis. Moreover, the experimentally obtained LLE data were correlated by applying the NRTL[9] and UNIQUAC[10] equations.

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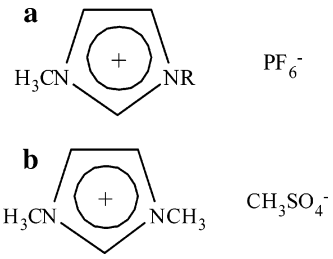

Figure 1. Schematic structures of MMIM CH_3SO_4 and RMIM PF_6 where R can be B (butyl), H (hexyl), or O (octyl).

Table 1. Density ρ and Refractive Index n_D for Pure Components at 298.15 K and Comparison with Literature Data

	ρ/g·cm^{-3}		n_D	
component	exptl	lit	exptl	lit
2-butanone	0.7997	0.79974[a]	1.37618	1.37685[b]
ethylacetate	0.8944	0.8940[c]	1.36977	1.3704[c]
2-propanol	0.7810	0.7810[d]	1.37496	1.3752[d]
BMIM PF_6	1.3673	1.36745[e] 1.36788[f]	1.40937	na[m]
HMIM PF_6	1.2937	1.2935[g]	1.41787	na
OMIM PF_6	1.2357	1.23684[h] 1.2245[j]	1.42302	1.423[i]
MMIM CH_3SO_4	1.3272	1.3290[k] 1.328[l]	1.48270	na

[a] Ref 11. [b] Ref 12. [c] Ref 13. [d] Ref 14. [e] Ref 15. [f] Ref 16. [g] Ref 17. [h] Ref 18. [i] Ref 19. [j] Ref 20. [k] Ref 21. [l] Ref 22. [m] na, not applicable.

Experimental Section

Chemicals. The chemicals were supplied by Merck for 2-butanone and 2-propanol (99.5 % and 99.7 % mass fraction, respectively), by Fluka for ethylacetate (99.8 % mass fraction), and by Green Solutions Chemicals S. L. the ILs with a certified purity higher than 98 % mass fraction. Chromatographic tests of the organic solvents showed purities that fulfilled purchaser specifications. Before using, the reagents were degassed ultrasonically, dried over freshly activated molecular sieves (types

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Table 2. Density ρ, Excess Molar Volume V_m^E, Refractive Index n_D, Changes of Refractive Index on Mixing Δn_D, Speed of Sound u, Isentropic Compressibility κ_s, and Deviation in Isentropic Compressibility $\Delta\kappa_s$ for the Binary Mixtures at (293.15, 298.15 and 303.15) K

x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol	n_D	Δn_D	u / m·s^{-1}	κ_S / T·Pa^{-1}	$\Delta\kappa_S$ / T·Pa^{-1}	x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol	n_D	Δn_D	u / m·s^{-1}	κ_S / T·Pa^{-1}	$\Delta\kappa_S$ / T·Pa^{-1}
BMIM PF_6 (1) + 2-Butanone (2)															
T = 293.15 K															
0	0.8056	0	1.37879	0	1212	845	0	0.5943	1.2541	−1.456	1.40795	0.0102	1399	407	−140
0.0533	0.8777	−0.742	1.38660	0.0061	1242	739	−80	0.7085	1.2939	−1.036	1.40900	0.0076	1418	385	−106
0.1058	0.9388	−1.249	1.39154	0.0094	1265	666	−126	0.8093	1.3239	−0.647	1.40971	0.0051	1433	368	−72
0.2081	1.0362	−1.816	1.39807	0.0126	1301	570	−171	0.9013	1.3483	−0.333	1.41019	0.0026	1444	356	−38
0.2992	1.1045 <	−1.984	1.40183	0.0135	1331	511	−184	0.9491	1.3597	−0.141	1.41042	0.0014	1449	350	−20
0.4044	1.1679	−1.929	1.40475	0.0131	1360	463	−180	1	1.3716	0	1.41069	0	1455	344	0
0.4926	1.2116	−1.742	1.40661	0.0121	1380	433	−165								
T = 298.15 K															
0	0.7997	0	1.37618	0	1192	880	0	0.5943	1.2501	−1.603	1.40645	0.0105	1390	414	−152
0.0533	0.8726	−0.846	1.38487	0.0069	1224	765	−87	0.7085	1.2898	−1.140	1.40757	0.0079	1408	391	−114
0.1058	0.9340	−1.390	1.39004	0.0103	1248	687	−136	0.8093	1.3198	−0.723	1.40833	0.0053	1421	375	−77
0.2081	1.0313	−1.940	1.39642	0.0133	1286	586	−184	0.9013	1.3440	−0.356	1.40888	0.0028	1433	362	−41
0.2992	1.0995	−2.082	1.39987	0.0138	1317	524	−197	0.9491	1.3555	−0.165	1.40911	0.0014	1438	357	−22
0.4044	1.1632	−2.038	1.40296	0.0134	1348	473	−193	1	1.3673	0	1.40937	0	1443	351	0
0.4926	1.2073	−1.877	1.40505	0.0125	1369	442	−177								
T = 303.15 K															
0	0.7949	0	1.37355	0	1163	931	0	0.5943	1.2457	−1.650	1.40517	0.0111	1374	426	−165
0.0533	0.8676	−0.845	1.38273	0.0073	1195	807	−93	0.7085	1.2855	−1.183	1.40617	0.0082	1393	401	−124
0.1058	0.9291	−1.412	1.38810	0.0109	1220	724	−147	0.8093	1.3156	−0.764	1.40668	0.0052	1408	384	−84
0.2081	1.0268	−2.013	1.39466	0.0139	1260	614	−198	0.9013	1.3397	−0.367	1.40753	0.0029	1419	370	−44
0.2992	1.0953	−2.185	1.39814	0.0143	1292	547	−212	0.9491	1.3512	−0.168	1.40779	0.0015	1425	364	−23
0.4044	1.1590	−2.133	1.40149	0.0140	1322	494	−206	1	1.3630	0	1.40808	0	1431	358	0
0.4926	1.2030	−1.950	1.40357	0.0130	1349	457	−192								
BMIM PF_6 (1) + Ethylacetate (2)															
T = 293.15 K															
0	0.9005	0	1.37241	0	1162	822	0	0.5936	1.2687	−1.567	1.40599	0.0109	1379	414	−124
0.0520	0.9563	−0.734	1.37948	0.0051	1182	749	−49	0.7000	1.3010	−1.171	1.40788	0.0087	1399	393	−95
0.0979	0.9990	−1.134	1.38419	0.0080	1200	695	−80	0.8146	1.3309	−0.710	1.40911	0.0055	1421	372	−61
0.1980	1.0776	−1.702	1.39206	0.0121	1240	603	−124	0.8997	1.3506	−0.379	1.40991	0.0031	1438	358	−34
0.2939	1.1382	−1.944	1.39736	0.0137	1280	536	−145	0.9499	1.3615	−0.206	1.41046	0.0017	1447	351	−17
0.3968	1.1914	−1.980	1.40129	0.0137	1319	482	−150	1	1.3716	0	1.41069	0	1455	344	0
0.4883	1.2307	−1.853	1.40391	0.0128	1350	446	−143								
T = 298.15 K															
0	0.8944	0	1.36977	0	1141	859	0	0.5936	1.2647	−1.712	1.40451	0.0112	1366	424	−134
0.0520	0.9506	−0.783	1.37726	0.0054	1162	780	−53	0.7000	1.2970	−1.290	1.40638	0.0089	1391	399	−105
0.0979	0.9934	−1.193	1.38208	0.0084	1180	723	−86	0.8146	1.3266	−0.757	1.40768	0.0057	1412	378	−67
0.1980	1.0722	−1.772	1.39005	0.0124	1228	618	−140	0.8997	1.3463	−0.402	1.40855	0.0032	1427	365	−37
0.2939	1.1331	−2.029	1.39538	0.0140	1272	545	−164	0.9499	1.3573	−0.229	1.40915	0.0018	1436	358	−19
0.3968	1.1868	−2.099	1.39946	0.0140	1310	491	−166	1	1.3673	0	1.40937	0	1443	351	0
0.4883	1.2266	−2.011	1.40230	0.0132	1338	455	−156								
T = 303.15 K															
0	0.8882	0	1.36712	0	1111	912	0	0.5936	1.2603	−1.812	1.40301	0.0116	1354	433	−151
0.0520	0.9446	−0.812	1.37520	0.0059	1137	819	−64	0.7000	1.2926	−1.360	1.40490	0.0091	1378	407	−117
0.0979	0.9877	−1.254	1.38016	0.0090	1160	752	−106	0.8146	1.3222	−0.792	1.40632	0.0058	1401	386	−76
0.1980	1.0670	−1.875	1.38819	0.0130	1207	643	−159	0.8997	1.3420	−0.427	1.40723	0.0033	1415	372	−42
0.2939	1.1280	−2.124	1.39346	0.0143	1247	570	−180	0.9499	1.3529	−0.224	1.40793	0.0019	1420	367	−20
0.3968	1.1820	−2.204	1.39774	0.0144	1291	508	−185	1	1.3630	0	1.40808	0	1431	358	0
0.4883	1.2220	−2.116	1.40065	0.0135	1323	468	−174								
BMIM PF_6 (1) + 2-Propanol (2)															
T = 293.15 K															
0	0.7850	0	1.37707	0	1156	953	0	0.8175	1.3282	−0.183	1.40833	0.0038	1429	369	−86
0.0008	0.7863	−0.004	1.37717	0.0001	1156	951	−1	0.8945	1.3476	−0.075	1.40869	0.0015	1441	358	−51
0.0011	0.7869	−0.012	1.37726	0.0002	1157	950	−2	0.9542	1.3615	−0.020	1.40976	0.0006	1449	350	−22
0.7136	1.2985	−0.350	1.40727	0.0062	1409	388	−131	1	1.3716	0	1.41069	0	1455	344	0
T = 298.15 K															
0	0.7810	0	1.37496	0	1139	986	0	0.8175	1.3240	−0.206	1.40689	0.0038	1417	376	−91
0.0008	0.7823	−0.008	1.37509	0.0001	1139	985	−1	0.8945	1.3434	−0.092	1.40738	0.0016	1429	365	−54
0.0011	0.7829	−0.014	1.37521	0.0002	1140	984	−2	0.9542	1.3572	−0.027	1.40844	0.0007	1437	357	−24
0.7136	1.2943	−0.370	1.40584	0.0063	1397	396	−138	1	1.3673	0	1.40937	0	1443	351	0
T = 303.15 K															
0	0.7766	0	1.37278	0	1121	1025	0	0.8175	1.3198	−0.236	1.40562	0.0040	1405	384	−96
0.0008	0.7780	−0.009	1.37301	0.0002	1121	1022	−2	0.8945	1.3393	−0.120	1.40595	0.0016	1417	372	−57
0.0011	0.7785	−0.017	1.37312	0.0003	1122	1021	−3	0.9542	1.3530	−0.039	1.40721	0.0008	1425	364	−25
0.7136	1.2900	−0.401	1.40450	0.0065	1385	404	−145	1	1.3630	0	1.40808	0	1431	358	0

Table 2 (Continued)

x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol	n_D	Δn_D	u / m·s^{-1}	κ_S / T·Pa^{-1}	$\Delta\kappa_S$ / T·Pa^{-1}	x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol	n_D	Δn_D	u / m·s^{-1}	κ_S / T·Pa^{-1}	$\Delta\kappa_S$ / T·Pa^{-1}
HMIM PF_6 (1) + 2-Propanol (2)															
T = 293.15 K															
0	0.7850	0	1.37707	0	1156	953	0	0.8110	1.2618	0.119	1.41602	0.0048	1408	400	−83
0.0011	0.7870	−0.031	1.37727	0.0002	1157	949	−3	0.9260	1.2839	0.231	1.41766	0.0015	1427	383	−33
0.0019	0.7884	−0.041	1.37764	0.0005	1158	946	−6	0.9933	1.2962	0.109	1.41900	0.0001	1437	373	−3
0.6123	1.2135	−0.230	1.41255	0.0097	1370	439	−158	1	1.2979	0	1.41923	0	1438	372	0
0.6958	1.2360	−0.118	1.41425	0.0078	1388	420	−129								
HMIM PF_6 (1) + 2-Propanol (2)															
T = 298.15 K															
0	0.7810	0	1.37496	0	1139	986	0	0.6958	1.2320	−0.156	1.41282	0.0080	1375	429	−136
0.0011	0.7828	−0.010	1.37513	0.0001	1140	983	−2	0.8110	1.2577	0.087	1.41451	0.0047	1396	408	−87
0.0019	0.7842	−0.022	1.37534	0.0003	1141	979	−6	0.9260	1.2799	0.193	1.41628	0.0016	1413	391	−35
0.0024	0.7854	−0.043	1.37542	0.0004	1141	978	−7	0.9933	1.2922	0.073	1.41766	0.0001	1423	382	−3
0.4893	1.1687	−0.402	1.40818	0.0122	1325	487	−203	1	1.2937	0	1.41787	0	1424	381	0
0.6123	1.2094	−0.262	1.41101	0.0098	1358	448	−167								
T = 303.15 K															
0	0.7766	0	1.37278	0	1121	1025	0	0.6958	1.2279	−0.192	1.41139	0.0082	1363	438	−145
0.0011	0.7785	−0.023	1.37296	0.0001	1122	1020	−4	0.8110	1.2538	0.047	1.41312	0.0049	1383	417	−93
0.0019	0.7800	−0.036	1.37319	0.0003	1124	1015	−8	0.9260	1.2759	0.176	1.41490	0.0017	1401	399	−37
0.0024	0.7811	−0.061	1.37337	0.0005	1124	1014	−9	0.9933	1.2883	0.036	1.41624	0.0001	1410	390	−3
0.4893	1.1646	−0.454	1.40669	0.0126	1313	498	−216	1	1.2896	0	1.41643	0	1411	389	0
0.6123	1.2053	−0.300	1.40962	0.0101	1346	458	−178								
OMIM PF_6 (1) + Ethylacetate (2)															
T = 293.15 K															
0	0.9005	0	1.37241	0	1162	822	0	0.6046	1.1827	−1.249	1.41759	0.0137	1358	458	−108
0.0547	0.9543	−0.729	1.38271	0.0075	1189	741	−58	0.7033	1.2001	−0.907	1.41968	0.0107	1375	441	−83
0.0964	0.9878	−1.063	1.38868	0.0112	1209	692	−89	0.8019	1.2153	−0.625	1.42153	0.0074	1391	425	−57
0.1996	1.0523	−1.540	1.39940	0.0166	1255	604	−134	0.9033	1.2287	−0.336	1.42308	0.0037	1408	411	−28
0.2941	1.0955	−1.673	1.40596	0.0183	1288	550	−147	0.9952	1.2390	0.001	1.42431	0.0002	1423	398	−2
0.3939	1.1306	−1.641	1.41079	0.0179	1315	511	−144	1	1.2396	0	1.42440	0	1424	398	0
0.4944	1.1583	−1.482	1.41443	0.0163	1337	483	−130								
T = 298.15 K															
0	0.8944	0	1.36977	0	1141	859	0	0.6046	1.1785	−1.313	1.41599	0.0140	1344	470	−117
0.0547	0.9486	−0.762	1.38058	0.0079	1168	773	−61	0.7033	1.1962	−0.983	1.41820	0.0110	1361	451	−91
0.0964	0.9823	−1.114	1.38636	0.0115	1189	720	−95	0.8019	1.2113	−0.649	1.42008	0.0076	1377	435	−62
0.1996	1.0472	−1.614	1.39757	0.0172	1236	625	−144	0.9033	1.2248	−0.351	1.42168	0.0038	1393	421	−31
0.2941	1.0908	−1.754	1.40405	0.0186	1271	567	−159	0.9952	1.2352	−0.008	1.42294	0.0002	1408	409	−2
0.3939	1.1261	−1.719	1.40900	0.0183	1299	526	−155	1	1.2357	0	1.42302	0	1408	408	0
0.4944	1.1539	−1.554	1.41271	0.0166	1323	495	−141								
T = 303.15 K															
0	0.8882	0	1.36712	0	1111	912	0	0.6046	1.1744	−1.381	1.41437	0.0143	1330	481	−133
0.0547	0.9429	−0.805	1.37906	0.0090	1147	807	−78	0.7033	1.1922	−1.044	1.41663	0.0112	1348	462	−103
0.0964	0.9768	−1.174	1.38508	0.0127	1169	750	−115	0.8019	1.2074	−0.694	1.41862	0.0078	1364	445	−71
0.1996	1.0422	−1.698	1.39557	0.0176	1218	647	−167	0.9033	1.2209	−0.363	1.42027	0.0039	1379	431	−36
0.2941	1.0860	−1.843	1.40226	0.0191	1253	586	−181	0.9952	1.2313	−0.009	1.42155	0.0002	1393	419	−2
0.3939	1.1216	−1.807	1.40728	0.0187	1284	541	−177	1	1.2319	0	1.42165	0	1393	418	0
0.4944	1.1496	−1.634	1.41112	0.0170	1309	507	−161								
MMIM CH_3SO_4 (1) + 2-Butanone (2)															
T = 293.15 K															
0	0.8056	0	1.37879	0	1212	845	0	0.7983	1.2738	−1.033	1.47479	0.0121	1750	256	−94
0.0006	0.8065	−0.037	1.37993	0.0011	1214	841	−4	0.9284	1.3106	−0.225	1.48045	0.0040	1803	235	−35
0.0012	0.8073	−0.072	1.38040	0.0015	1215	839	−5	0.9743	1.3235	−0.053	1.48218	0.0010	1819	228	−13
0.0029	0.8095	−0.140	1.38130	0.0022	1217	834	−9	1	1.3309	0	1.48392	0	1826	225	0
0.7074	1.2440	−1.498	1.47023	0.0171	1703	277	−129								
T = 298.15 K															
0	0.7997	0	1.37618	0	1192	880	0	0.7983	1.2701	−1.099	1.47366	0.0124	1737	261	−100
0.0006	0.8007	−0.052	1.37720	0.0010	1194	876	−3	0.9284	1.3071	−0.255	1.47914	0.0041	1791	239	−37
0.0012	0.8015	−0.075	1.37762	0.0013	1195	874	−5	0.9743	1.3199	−0.060	1.48086	0.0009	1806	232	−14
0.0029	0.8039	−0.170	1.37841	0.0019	1196	869	−8	1	1.3272	0	1.48270	0	1813	229	0
0.7074	1.2403	−1.587	1.46925	0.0177	1689	283	−137								
T = 303.15 K															
0	0.7949	0	1.37355	0	1163	931	0	0.7983	1.2664	−1.138	1.47229	0.0127	1724	266	−108
0.0006	0.7960	−0.069	1.37467	0.0011	1164	927	−3	0.9284	1.3035	−0.273	1.47781	0.0042	1778	243	−40
0.0012	0.7967	−0.082	1.37513	0.0015	1165	925	−5	0.9743	1.3163	−0.072	1.47945	0.0009	1794	236	−15
0.0029	0.7991	−0.172	1.37600	0.0021	1168	917	−11	1	1.3237	0	1.48129	0	1801	233	0
0.7074	1.2365	−1.639	1.46782	0.0181	1676	288	−149								

Table 2 (Continued)

x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol	n_D	Δn_D	u / m·s^{-1}	κ_S / T·Pa^{-1}	$\Delta\kappa_S$ / T·Pa^{-1}	x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol	n_D	Δn_D	u / m·s^{-1}	κ_S / T·Pa^{-1}	$\Delta\kappa_S$ / T·Pa^{-1}
MMIM CH_3SO_4 (1) + Ethylacetate (2)															
T = 293.15 K															
0	0.9005	0	1.37241	0	1162	822	0	0.9294	1.3133	−0.224	1.48008	0.0040	1801	235	−33
0.8549	1.2966	−0.804	1.47633	0.0086	1765	247	−65	0.9491	1.3177	−0.093	1.48086	0.0026	1808	232	−24
0.8746	1.3011	−0.640	1.47752	0.0076	1775	244	−56	1	1.3309	0	1.48392	0	1826	225	0
0.9072	1.3083	−0.381	1.47884	0.0053	1792	238	−43								
T = 298.15 K															
0	0.8944	0	1.36977	0	1141	859	0	0.9294	1.3098	−0.261	1.47876	0.0040	1789	239	−35
0.8549	1.2930	−0.850	1.47553	0.0092	1752	252	−69	0.9491	1.3142	−0.129	1.47955	0.0026	1795	236	−25
0.8746	1.2975	−0.697	1.47640	0.0079	1765	247	−61	1	1.3272	0	1.48270	0	1813	229	0
0.9072	1.3047	−0.415	1.47750	0.0053	1778	243	−45								
T = 303.15 K															
0	0.8882	0	1.36712	0	1111	912	0	0.9294	1.3062	−0.290	1.47752	0.0043	1777	243	−38
0.8549	1.2893	−0.896	1.47440	0.0097	1739	256	−75	0.9491	1.3107	−0.154	1.47822	0.0027	1782	240	−27
0.8746	1.2938	−0.730	1.47522	0.0082	1746	254	−64	1	1.3237	0	1.48129	0	1801	233	0
0.9072	1.3010	−0.440	1.47618	0.0055	1764	247	−49								
MMIM CH_3SO_4 (1) + 2-Propanol (2)															
T = 293.15 K															
0	0.7850	0	1.37707	0	1156	953	0	0.5987	1.2040	−0.819	1.46137	0.0203	1611	320	−197
0.0490	0.8397	−0.258	1.38865	0.0063	1177	859	−58	0.6937	1.2399	−0.641	1.46768	0.0165	1684	284	−164
0.0981	0.8888	−0.433	1.39897	0.0114	1205	775	−106	0.7992	1.2742	−0.340	1.47404	0.0116	1743	258	−113
0.1987	0.9757	−0.670	1.41695	0.0186	1269	636	−172	0.9042	1.3048	−0.093	1.47881	0.0051	1791	239	−56
0.2961	1.0458	−0.810	1.43085	0.0221	1338	534	−204	0.9502	1.3175	−0.031	1.48087	0.0023	1807	232	−29
0.4055	1.1120	−0.892	1.44372	0.0233	1431	439	−219	1	1.3309	0	1.48392	0	1826	225	0
0.5043	1.1624	−0.886	1.45335	0.0224	1525	370	−216								
T = 298.15 K															
0	0.7810	0	1.37496	0	1139	986	0	0.5987	1.2003	−0.852	1.46001	0.0205	1605	324	−209
0.0490	0.8359	−0.287	1.38617	0.0059	1167	878	−72	0.6937	1.2363	−0.675	1.46641	0.0167	1670	290	−171
0.0981	0.8848	−0.449	1.39708	0.0116	1198	788	−124	0.7992	1.2707	−0.375	1.47250	0.0114	1729	263	−118
0.1987	0.9718	−0.701	1.41521	0.0188	1271	637	−199	0.9042	1.3014	−0.129	1.47743	0.0050	1777	243	−58
0.2961	1.0420	−0.850	1.42948	0.0226	1352	525	−237	0.9502	1.3140	−0.052	1.47960	0.0023	1797	236	−31
0.4055	1.1085	−0.958	1.44245	0.0238	1444	433	−247	1	1.3272	0	1.48270	0	1813	229	0
0.5043	1.1590	−0.956	1.45208	0.0228	1534	367	−238								
T = 303.15 K															
0	0.7766	0	1.37278	0	1121	1025	0	0.5987	1.1967	−0.909	1.45836	0.0206	1602	326	−225
0.0490	0.8316	−0.306	1.38391	0.0058	1166	884	−102	0.6937	1.2327	−0.720	1.46482	0.0168	1662	294	−182
0.0981	0.8808	−0.501	1.39509	0.0117	1207	779	−168	0.7992	1.2674	−0.437	1.47103	0.0115	1720	267	−125
0.1987	0.9679	−0.764	1.41455	0.0202	1292	619	−249	0.9042	1.2979	−0.155	1.47603	0.0051	1768	246	−62
0.2961	1.0383	−0.928	1.42882	0.0239	1370	513	−277	0.9502	1.3104	−0.058	1.47820	0.0023	1785	239	−33
0.4055	1.1047	−1.017	1.44156	0.0248	1459	425	−278	1	1.3237	0	1.48129	0	1801	233	0
0.5043	1.1550	−0.984	1.45073	0.0232	1534	368	−258								

3 Å and 4 Å, supplied by Aldrich) for several weeks, and kept in an inert argon atmosphere as soon as the bottles were opened.

To reduce the ILs water content to negligible values (mass fraction lower than 0.03 %, determined using a 756 Karl Fisher coulometer), vacuum (2×10^{-1} Pa) and moderate temperature (343.15 K) were applied for RMIM PF_6 and MMIM CH_3SO_4 for several days, respectively, always immediately prior to their use. They were submitted to NMR and positive FABMS (FISONS VG AUTOSPEC mass spectrometer) to ensure purity.

The RMIM PF_6 and MMIM CH_3SO_4 structures are shown in Figure 1. The physical properties of the pure ILs and organic solvents at 298.15 K are listed in Table 1, together with recent literature[11−22] values.

Procedure. The samples were prepared by filling glass vials with the IL and the organic solvents. Vials are closed with screw caps to ensure a secure seal. The sample is taken from the vial with a syringe through a silicone septum and is immediately put into the apparatus. The mass of the chemicals was determined using a Mettler AX-205 Delta Range balance with a precision of $\pm 10^{-5}$ g. The estimated uncertainty of the composition of the mixtures was $\pm 10^{-4}$ mole fraction.

The density and speed of sound of the pure liquids and mixtures were measured with an Anton Paar DSA 48 digital vibrating-tube densimeter. The uncertainty in the measurement of the samples has been found to be lower than $\pm 10^{-4}$ g·cm^{-3} for the density and $\pm$ 1 m·s^{-1} for the speed of sound. The apparatus was calibrated by measuring the density of Millipore quality water and ambient air according to instructions. The calibration was checked with pure liquids with known density and speed of sound.

The refractive indices were determined by the automatic refractometer ABBEMAT-WR Dr. Kernchen with an uncertainty in the experimental measurements of $\pm 4 \times 10^{-5}$. The apparatus was calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene (supplied by the company) before each series of measurements according to instructions. The calibration was checked with pure liquids with known refractive index.

The tie lines were determined in a jacketed glass vessel containing a magnetic stirrer connected to a temperature-controlled circulating bath (controlled to $\pm$ 0.01 K). The vessel was closed to moisture and could be flushed with dry argon. The temperature in the cell was measured with a F200 ASL digital thermometer with an uncertainty of $\pm$ 0.01 K. The measurements were started with the addition of 100 mL of the immiscible binary mixture of known composition. The temper-

Table 3. Fitting Parameters A_{ij} Calculated from Equation 4 and Standard Deviations (σ)

BMIM PF_6 (1) + 2-Butanone (2)						
V_m^E/cm^3·mol^{-1}	$A_{11} = -6.923$	$A_{21} = 5.196$	$A_{31} = -2.064$	$A_{41} = 1.467$	$A_{51} = -0.560$	$\sigma = 0.006$
	$A_{12} = -1.3210$	$A_{22} = -1.554$	$A_{32} = 1.661$	$A_{42} = 5.879$	$A_{52} = -5.873$	
	$A_{13} = 0.505$	$A_{23} = 1.636$	$A_{33} = -1.895$	$A_{43} = -4.829$	$A_{53} = 5.470$	
Δn_D	$A_{11} = 0.0478$	$A_{21} = -0.0319$	$A_{31} = 0.0134$	$A_{41} = -0.0069$	$A_{51} = 0.0234$	$\sigma = 0.0001$
	$A_{12} = 0.0019$	$A_{22} = 0.0035$	$A_{32} = -0.0011$	$A_{42} = -0.0152$	$A_{52} = 0.0342$	
	$A_{13} = 0.0019$	$A_{23} = -0.0019$	$A_{33} = -0.0058$	$A_{43} = -0.0079$	$A_{53} = -0.0100$	
	$A_{61} = -0.0213$	$A_{62} = -0.0191$	$A_{63} = 0.0273$			
$\Delta\kappa_s$/T·Pa^{-1}	$A_{11} = -655$	$A_{21} = 397$	$A_{31} = -201$	$A_{41} = 288$	$A_{51} = -271$	$\sigma = 0.9$
	$A_{12} = -94$	$A_{22} = 87$	$A_{32} = -35$	$A_{42} = -25$	$A_{52} = -24$	
	$A_{13} = -12$	$A_{23} = -55$	$A_{33} = 2.9$	$A_{43} = 130$	$A_{53} = -32$	
BMIM PF_6 (1) + Ethylacetate (2)						
V_m^E/cm^3·mol^{-1}	$A_{11} = -7.334$	$A_{21} = 4.360$	$A_{31} = -0.004$	$A_{41} = 1.652$	$A_{51} = -3.124$	$\sigma = 0.009$
	$A_{12} = -1.439$	$A_{22} = -0.930$	$A_{32} = 3.675$	$A_{42} = 2.151$	$A_{52} = -4.830$	
	$A_{13} = 0.408$	$A_{23} = 0.792$	$A_{33} = -2.602$	$A_{43} = -1.011$	$A_{53} = 3.454$	
Δn_D	$A_{11} = 0.0505$	$A_{21} = -0.0289$	$A_{31} = 0.0138$	$A_{41} = -0.0102$	$A_{51} = 0.0088$	$\sigma = 0.0001$
	$A_{12} = 0.0031$	$A_{22} = 0.0016$	$A_{32} = -0.0070$	$A_{42} = -0.0084$	$A_{52} = 0.0145$	
	$A_{13} = -0.0001$	$A_{23} = -0.0010$	$A_{33} = 0.0020$	$A_{43} = -0.0014$	$A_{53} = 0.0036$	
$\Delta\kappa_s$/T·Pa^{-1}	$A_{11} = -567$	$A_{21} = 289$	$A_{31} = -31$	$A_{41} = 68$	$A_{51} = -131$	$\sigma = 0.5$
	$A_{12} = -75$	$A_{22} = 201$	$A_{32} = -392$	$A_{42} = -348$	$A_{52} = 635$	
	$A_{13} = -46$	$A_{23} = -139$	$A_{33} = 294$	$A_{43} = 445$	$A_{53} = -627$	
BMIM PF_6 (1) + 2-Propanol (2)						
V_m^E/cm^3·mol^{-1}	$A_{11} = -2.875$	$A_{21} = 3.984$	$A_{31} = -5.103$	$A_{41} = 5.861$	$A_{51} = -1.995$	$\sigma = 0.001$
	$A_{12} = 0.210$	$A_{22} = -0.600$	$A_{32} = -1.322$	$A_{42} = 2.195$	$A_{52} = -0.677$	
	$A_{13} = -0.914$	$A_{23} = 2.958$	$A_{33} = -1.409$	$A_{43} = -3.913$	$A_{53} = 3.077$	
Δn_D	$A_{11} = -0.0107$	$A_{21} = 0.1732$	$A_{31} = -0.1170$	$A_{41} = -0.2362$	$A_{51} = 0.2056$	$\sigma = 0.0001$
	$A_{12} = -0.0241$	$A_{22} = 0.1036$	$A_{32} = -0.0813$	$A_{42} = -0.1191$	$A_{52} = 0.1345$	
	$A_{13} = -0.0236$	$A_{23} = 0.0989$	$A_{33} = -0.0824$	$A_{43} = -0.0627$	$A_{53} = 0.0699$	
$\Delta\kappa_s$/T·Pa^{-1}	$A_{11} = -797$	$A_{21} = 552$	$A_{31} = -779$	$A_{41} = 1043$	$A_{51} = -525$	$\sigma = 0.1$
	$A_{12} = -87$	$A_{22} = 70$	$A_{32} = 135$	$A_{42} = -492$	$A_{52} = 354$	
	$A_{13} = -23$	$A_{23} = 17$	$A_{33} = 4.9$	$A_{43} = 81$	$A_{53} = -111$	
HMIM PF_6 (1) + 2-Propanol (2)						
V_m^E/cm^3·mol^{-1}	$A_{11} = -1.661$	$A_{21} = 4.335$	$A_{31} = -8.305$	$A_{41} = 11.270$	$A_{51} = 1.212$	$\sigma = 0.015$
	$A_{12} = 0.506$	$A_{22} = -6.754$	$A_{32} = 17.423$	$A_{42} = -13.878$	$A_{52} = -0.667$	
	$A_{13} = -0.595$	$A_{23} = 5.213$	$A_{33} = -14.724$	$A_{43} = 13.974$	$A_{53} = -2.415$	
Δn_D	$A_{11} = 0.0474$	$A_{21} = -0.0390$	$A_{31} = 0.0570$	$A_{41} = -0.0715$	$A_{51} = 0.0210$	$\sigma = 0.0001$
	$A_{12} = 0.0008$	$A_{22} = 0.0115$	$A_{32} = -0.0770$	$A_{42} = 0.1333$	$A_{52} = 0.0725$	
	$A_{13} = 0.0012$	$A_{23} = -0.0086$	$A_{33} = 0.0588$	$A_{43} = -0.1105$	$A_{53} = 0.0659$	
$\Delta\kappa_s$/T·Pa^{-1}	$A_{11} = -765$	$A_{21} = 528$	$A_{31} = -532$	$A_{41} = 667$	$A_{51} = -360$	$\sigma = 0.3$
	$A_{12} = -54$	$A_{22} = -54$	$A_{32} = 101$	$A_{42} = -218$	$A_{52} = 229$	
	$A_{13} = -32$	$A_{23} = 105$	$A_{33} = -296$	$A_{43} = 665$	$A_{53} = -526$	
OMIM PF_6 (1) + Ethylacetate (2)						
V_m^E/cm^3·mol^{-1}	$A_{11} = -5.939$	$A_{21} = 4.078$	$A_{31} = -1.117$	$A_{41} = 1.865$	$A_{51} = -3.323$	$\sigma = 0.011$
	$A_{12} = -0.576$	$A_{22} = 0.039$	$A_{32} = -0.448$	$A_{42} = 0.816$	$A_{52} = 0.580$	
	$A_{13} = -0.035$	$A_{23} = 0.128$	$A_{33} = -0.120$	$A_{43} = -0.123$	$A_{53} = -0.115$	
Δn_D	$A_{11} = 0.0649$	$A_{21} = -0.0407$	$A_{31} = 0.0246$	$A_{41} = -0.0202$	$A_{51} = 0.0121$	$\sigma = 0.0001$
	$A_{12} = 0.0019$	$A_{22} = -0.0022$	$A_{32} = 0.0151$	$A_{42} = 0.0039$	$A_{52} = -0.0250$	
	$A_{13} = 0.0012$	$A_{23} = 0.0027$	$A_{33} = -0.0213$	$A_{43} = -0.0183$	$A_{53} = 0.0519$	
$\Delta\kappa_s$/T·Pa^{-1}	$A_{11} = -515$	$A_{21} = 348$	$A_{31} = -228$	$A_{41} = 147$	$A_{51} = -16$	$\sigma = 0.6$
	$A_{12} = -57$	$A_{22} = 125$	$A_{32} = 77$	$A_{42} = -389$	$A_{52} = -90$	
	$A_{13} = -65$	$A_{23} = -56$	$A_{33} = -77$	$A_{43} = 485$	$A_{53} = -93$	
MMIM CH_3SO_4 (1) + 2-Butanone (2)						
V_m^E/cm^3·mol^{-1}	$A_{11} = -6.874$	$A_{21} = -0.757$	$A_{31} = -9.510$	$A_{41} = 26.404$	$A_{51} = -10.287$	$\sigma = 0.008$
	$A_{12} = -0.332$	$A_{22} = -1.293$	$A_{32} = -4.172$	$A_{42} = 10.389$	$A_{52} = -5.431$	
	$A_{13} = 0.153$	$A_{23} = -0.428$	$A_{33} = 3.428$	$A_{43} = -3.267$	$A_{53} = -0.098$	
Δn_D	$A_{11} = 0.2139$	$A_{21} = -0.5687$	$A_{31} = 0.6132$	$A_{41} = 0.1449$	$A_{51} = -0.3843$	$\sigma = 0.0003$
	$A_{12} = 0.0106$	$A_{22} = 0.0139$	$A_{32} = -0.1089$	$A_{42} = 0.1895$	$A_{52} = -0.1184$	
	$A_{13} = 0.0124$	$A_{23} = -0.0882$	$A_{33} = 0.1623$	$A_{43} = -0.1048$	$A_{53} = 0.0271$	
$\Delta\kappa_s$/T·Pa^{-1}	$A_{11} = -740$	$A_{21} = 421$	$A_{31} = -682$	$A_{41} = 1024$	$A_{51} = -547$	$\sigma = 0.6$
	$A_{12} = 2.4$	$A_{22} = -159$	$A_{32} = 257$	$A_{42} = -565$	$A_{52} = 503$	
	$A_{13} = -149$	$A_{23} = 372$	$A_{33} = -510$	$A_{43} = 632$	$A_{53} = -444$	
MMIM CH_3SO_4 (1) + Ethylacetate (2)						
V_m^E/cm^3·mol^{-1}	$A_{11} = -3.359$	$A_{21} = -7.632$	$A_{31} = -9.202$	$A_{41} = 11.463$	$A_{51} = 11.251$	$\sigma = 0.005$
	$A_{12} = -2.110$	$A_{22} = 0.587$	$A_{32} = 2.911$	$A_{42} = 3.383$	$A_{52} = -7.386$	
	$A_{13} = -2.527$	$A_{23} = 3.016$	$A_{33} = 2.827$	$A_{43} = -1.420$	$A_{53} = -1.638$	
Δn_D	$A_{11} = 0.0513$	$A_{21} = 0.0189$	$A_{31} = 0.0771$	$A_{41} = -0.0589$	$A_{51} = -0.0502$	$\sigma = 0.0001$
	$A_{12} = 0.0624$	$A_{22} = -0.0379$	$A_{32} = -0.0445$	$A_{42} = -0.0443$	$A_{52} = 0.0499$	
	$A_{13} = 0.0253$	$A_{23} = -0.0460$	$A_{33} = -0.0380$	$A_{43} = 0.0398$	$A_{53} = 0.0437$	
$\Delta\kappa_s$/T·Pa^{-1}	$A_{11} = -690$	$A_{21} = 506$	$A_{31} = -875$	$A_{41} = 1005$	$A_{51} = -430$	$\sigma = 0.3$
	$A_{12} = -49$	$A_{22} = 27$	$A_{32} = 94$	$A_{42} = -494$	$A_{52} = 407$	
	$A_{13} = -11$	$A_{23} = -17$	$A_{33} = -21$	$A_{43} = 83$	$A_{53} = -75$	

Table 3 (Continued)

			MMIM CH_3SO_4 (1) + 2-Propanol (2)			
V_m^E/cm^3·mol^{-1}	$A_{11} = -3.596$	$A_{21} = 0.754$	$A_{31} = 1.390$	$A_{41} = 2.525$	$A_{51} = -0.777$	$\sigma = 0.007$
	$A_{12} = -0.573$	$A_{22} = 0.313$	$A_{32} = 2.709$	$A_{42} = -1.037$	$A_{52} = -4.234$	
	$A_{13} = 0.162$	$A_{23} = -0.100$	$A_{33} = -3.179$	$A_{43} = 0.771$	$A_{53} = 4.189$	
Δn_D	$A_{11} = 0.0900$	$A_{21} = -0.0313$	$A_{31} = 0.0157$	$A_{41} = -0.0194$	$A_{51} = -0.0140$	$\sigma = 0.0001$
	$A_{12} = 0.0024$	$A_{22} = -0.0005$	$A_{32} = -0.0047$	$A_{42} = 0.0043$	$A_{52} = -0.0124$	
	$A_{13} = 0.0090$	$A_{23} = -0.0132$	$A_{33} = 0.0199$	$A_{43} = 0.0155$	$A_{53} = -0.0172$	
$\Delta\kappa_s$/T·Pa^{-1}	$A_{11} = -864$	$A_{21} = 238$	$A_{31} = -49$	$A_{41} = 164$	$A_{51} = -62$	$\sigma = 0.8$
	$A_{12} = -172$	$A_{22} = 332$	$A_{32} = 123$	$A_{42} = -419$	$A_{52} = -21$	
	$A_{13} = -0.5$	$A_{23} = -30$	$A_{33} = -345$	$A_{43} = 568$	$A_{53} = -168$	

ature was adjusted, and the mixture was stirred vigorously during 1 h and left to settle for 4 h. Samples were taken by a syringe from the upper and lower layers. A series of LLE measurements were made by changing the temperature in the binary mixtures.

Tie line phase compositions were determined by the measurement of density at 343.15 K from an Anton Paar DSA 48 digital vibrating-tube densimeter and the application of the corresponding fitting polynomials. The uncertainty of the phase composition is estimated to be ± 0.0005.

Results and Discussion

The density, refractive index, speed of sound, excess molar volume, changes of refractive index on mixing, isentropic compressibility (determined by means of Laplace equation ($\kappa_S = \rho^{-1}\cdot u^{-2}$), and deviations in isentropic compressibility of the binary mixtures BMIM PF_6 (1) or MMIM CH_3SO_4 (1) + 2-butanone (2) or ethylacetate (2) or 2-propanol (2), HMIM PF_6 (1) + 2-propanol (2), and OMIM PF_6 (1) + ethylacetate (2) from (293.15 to 303.15) K are given in Table 2. Immiscibility intervals of the binary mixtures from $x_1 = (0.0012$ to $0.6820)$ for BMIM PF_6 (1) + 2-propanol (2), from $x_1 = (0.0024$ to $0.5208)$ for HMIM PF_6 (1) + 2-propanol (2), from $x_1 = (0.0041$ to $0.7036)$ for MMIM CH_3SO_4 (1) + 2-butanone (2). and from $x_1 = (0$ to $0.8397)$ for MMIM CH_3SO_4 (1) + ethylacetate (2) in the range (293.15 to 303.15) K were found.

Excess molar volumes V_m^E, changes of refractive index on mixing Δn_D, and deviations in isentropic compressibility $\Delta\kappa_S$ were calculated from the experimental values, as follows:

$$V_m^E = \sum_{i=1}^{N} x_i M_i(\rho^{-1} - \rho_i^{\circ -1}) \quad (1)$$

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{Di}^{\circ} \quad (2)$$

$$\Delta\kappa_S = \kappa_S - \sum_{i=1}^{N} x_i \kappa_{S,i} \quad (3)$$

In these equations, ρ and n_D are the density and the refractive index of the mixture; ρ_i° and n_{Di}° are the density and the refractive index of the pure components; κ_S is the isentropic compressibility of the mixture; and $\kappa_{S,i}$ is the isentropic compressibility of the pure component.

The excess and derived quantities of the binary mixtures were fitted to a function of the mole fraction and temperature polynomial equation developed as follows:

$$\Delta Q = x_1\cdot(1 - x_1)\sum_{i=1}^{n}\sum_{j=1}^{3} A_{ij}\cdot 10^{1-j}\cdot(2x_1 - 1)^{i-1}\cdot (T/\mathrm{K} - 293.15)^{j-1} \quad (4)$$

where ΔQ is the excess or derived property, x_1 is the first component mole fraction, and A_{ij} is the fitting parameter. Applying the Marquardt's algorithm,[23] the degree of polynomial expression was optimized. The correlation parameters are listed in Table 3 together with the standard deviations (σ). These deviations were calculated by applying the following expression:

$$\sigma = \left(\frac{\sum_{i}^{n_{DAT}} (z_{exp} - z_{pred})^2}{n_{DAT}}\right)^{1/2} \quad (5)$$

where property values and the number of experimental data are represented by z and n_{DAT}, respectively.

Table 4. Experimental Liquid−Liquid Equilibria for the Binary Mixtures 1-Alkyl-3-methylimidazolium Hexafluorophosphate (1) + 2-Propanol (2)

	x_1			x_1	
T/K	IL-poor phase	IL-rich phase	T/K	IL-poor phase	IL-rich phase
	BMIMPF_6 (1) + 2-Propanol (2)				
278.15	0.0008	0.7516	313.15	0.0027	0.5592
283.15	0.0008	0.7309	318.15	0.0036	0.5335
288.15	0.0009	0.7070	323.15	0.0044	0.4905
293.15	0.0012	0.6820	328.15	0.0059	0.4661
298.15	0.0014	0.6517	333.15	0.0081	0.4339
303.15	0.0017	0.6238	338.15	0.0109	0.4057
308.15	0.0022	0.5910	343.15	0.0133	0.3678
	HMIMPF_6 (1) + 2-Propanol (2)				
278.15	0.0013	0.6218	308.15	0.0047	0.4054
283.15	0.0014	0.5904	313.15	0.0064	0.3709
288.15	0.0016	0.5574	318.15	0.0103	0.3141
293.15	0.0024	0.5208	323.15	0.0215	0.2821
298.15	0.0027	0.4856	328.15	0.0377	0.2106
303.15	0.0035	0.4458			

The excess molar volumes are negative over the entire composition range for all the binary mixtures except for the system HMIM PF_6 (1) + 2-propanol (2), where the excess molar volumes present a maximum at approximately $x_1 = 0.9$ and negative values for x_1 from (0.5 to 0.75), respectively. On the other hand, changes of refractive index on mixing for the binary mixtures are positive over the whole composition range. For the deviations in isentropic compressibility negative values are observed over the entire composition range. In general terms, the excess molar volumes and the deviations properties increase when the temperature is increased.

For example, excess molar volumes, changes of refractive index on mixing and deviations in isentropic compressibility for the binary mixtures BMIM PF_6 (1) + 2-butanone (2) versus the mole fraction over the whole composition range and the fitted curve, obtained from the polynomial equation from (293.15 to 303.15) K, are shown in Figure 2. A comparison with the literature data in terms of excess molar volumes is made in Figure 3.

LLE studied for the binary mixtures BMIM PF_6 (1) + 2-propanol (2) and HMIM PF_6 (1) + 2-propanol (2) are shown

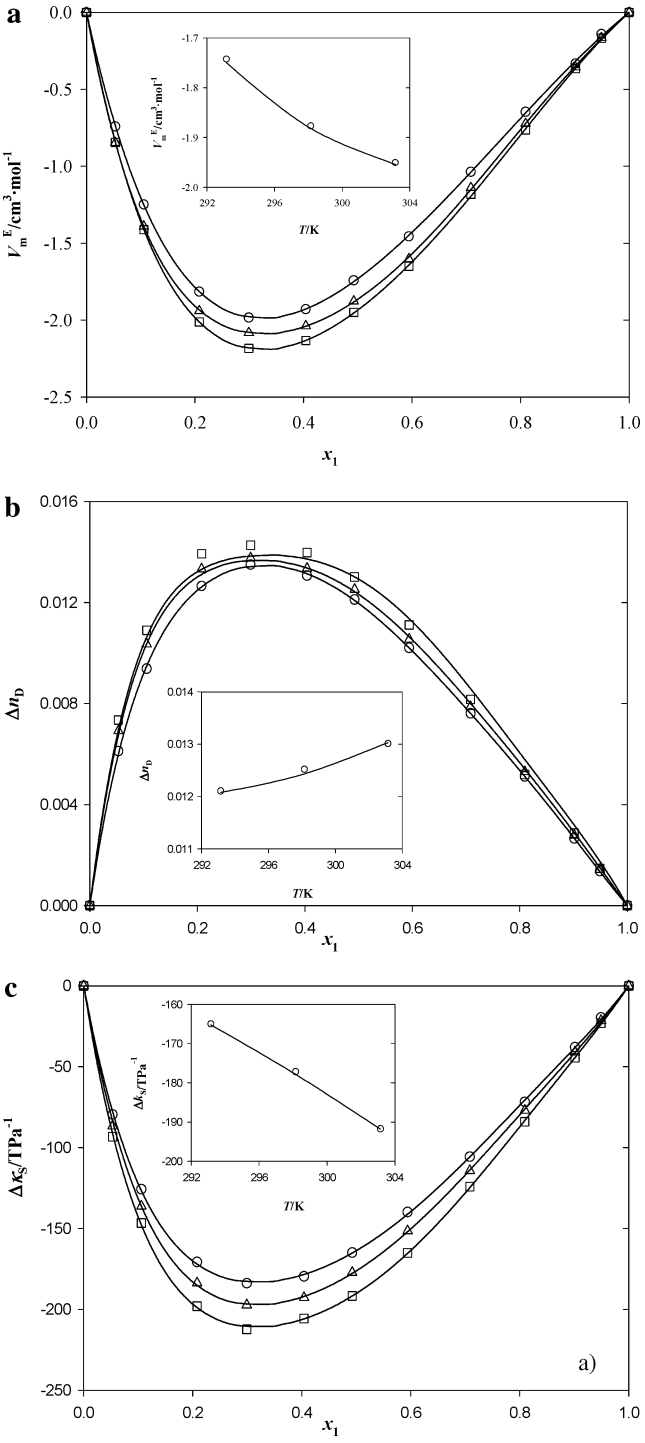

Figure 2. (a) Excess molar volumes V_m^E of the binary mixtures against mole fraction x_1 for BMIM PF_6 (1) + 2-butanone (2), at ○, T = 293.15 K; △, T = 298.15 K; □, T = 303.15 K. Inset shows excess molar volumes of the binary mixtures against the temperature at equimolar composition. (b) Changes of refractive indices on mixing Δn_D of the binary mixtures against mole fraction for BMIM PF_6 (1) + 2-butanone (2) at ○, T = 293.15 K; △, T = 298.15 K; □, T = 303.15 K. Inset shows changes of refractive indices of the binary mixtures against the temperature at equimolar composition. (c) Deviations in isentropic compressibility $\Delta\kappa_S$ of the binary mixtures against mole fraction for BMIM PF_6 (1) + 2-butanone (2) at ○, T = 293.15 K; △, T = 298.15 K; □, T = 303.15 K. Inset shows deviations in isentropic compressibility of the binary mixtures against the temperature at equimolar composition.

in Table 4 from (278.15 to 343.15) K and from (278.15 to 328.15) K, respectively. Experimental phase diagrams of LLE investigated are shown in Figure 4. The LLE of the binary

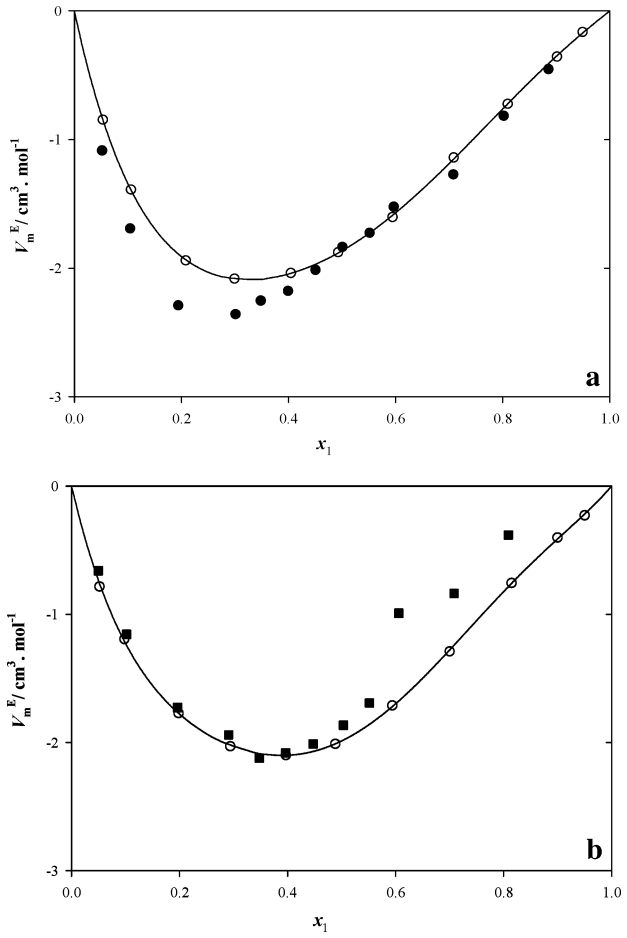

Figure 3. Comparison of V_m^E against mole fraction for the binary mixtures. (a) BMIM PF_6 (1) + 2-butanone (2): ○, T = 298.15 K; ●, ref 16. (b) BMIM PF_6 (1) + ethylacetate (2): □, T = 298.15 K; ■, ref 16.

Table 5. Parameters of the NRTL and UNIQUAC Equation for the Binary Mixtures

NRTL (α = 0.3)				
a_{12} / J·mol^{-1}	a_{21} / J·mol^{-1}	b_{12} / J·mol^{-1}·K^{-1}	b_{21} / J·mol^{-1}·K^{-1}	σ
BMIMPF$_6$ (1) + 2-Propanol (2)				
24999	20999	−79.11	−20.20	0.68
HMIMPF$_6$ (1) + 2-Propanol (2)				
24999	20999	−86.08	−25.23	0.79
UNIQUAC				
a_{12} / J·mol^{-1}	a_{21} / J·mol^{-1}	b_{12} / J·mol^{-1}·K^{-1}	b_{21} / J·mol^{-1}·K^{-1}	σ
BMIMPF$_6$ (1) + 2-Propanol (2)				
−2871	−1470	24.65	6.816	1.77
HMIMPF$_6$ (1) + 2-Propanol (2)				
−2871	−1470	25.24	7.231	1.26

mixtures MMIM CH_3SO_4 (1) + 2-butanone (2) or ethylacetate (2) were published previously.[24]

Liquid−Liquid Equilibria Correlation. In this work, the NRTL and UNIQUAC equations with temperature-dependent interaction parameters are used to correlate the experimental binary LLE data. For the NRTL model, the third randomness parameter α_{ij} was fixed at (0.3) and was not optimized. The volume R_k and surface area Q_k parameters of the UNIQUAC equation were obtained from the literature.[25]

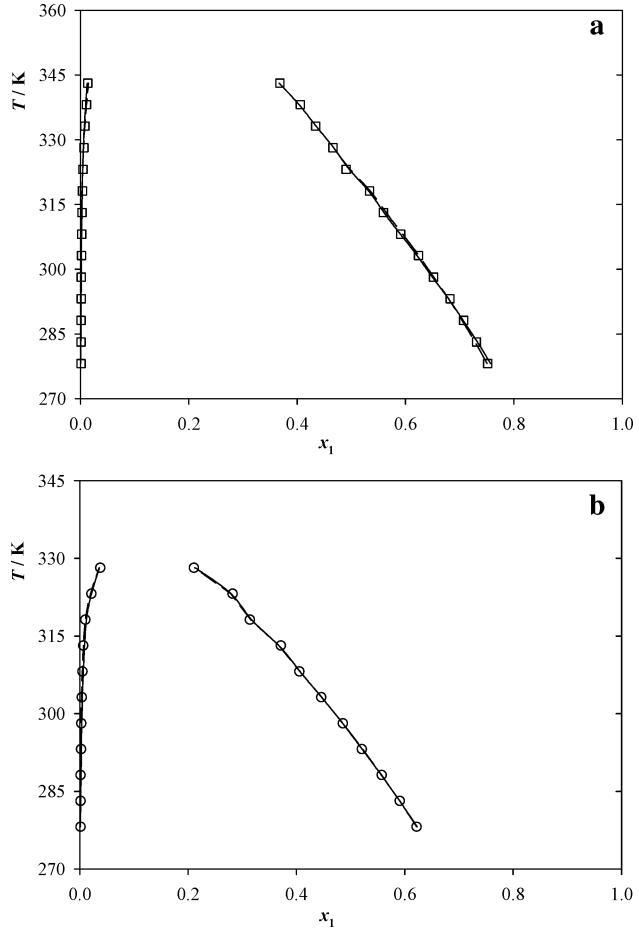

Figure 4. Equilibrium temperature for LLE against IL mole fraction of (a) BMIM PF_6 (1) + 2-propanol (2): □; (b) HMIM PF_6 (1) + 2-propanol (2): ○. experimental tie-lines and correlated NRTL (solid) and UNIQUAC (dashed) curves.

In these equations the adjustable parameter was defined as a linear temperature dependence, described as follows for NRTL and UNIQUAC, respectively:

$$\Delta g_{ij} = a_{ij} + b_{ij} \cdot T/\mathrm{K} \text{ and } \Delta u_{ij} = a_{ij} + b_{ij} \cdot T/\mathrm{K} \qquad (6)$$

The SOLVER function in Microsoft EXCEL was used to adjust the parameters so that the objective function was minimized, providing the set of temperature-dependent adjustable parameters for the binary systems. The objective function is defined as follows:

$$\text{objective function} = \sum_{i=1}^{2} (x_i^{\mathrm{l,exp}} - x_i^{\mathrm{l,calc}})^2 \qquad (7)$$

The calculated values of the equations are presented in Table 5. The standard deviation of the mole fraction and the temperature dependence of the correlative parameters are listed in Table 5. These deviations were calculated by applying the following expression for the binary mixtures:

$$\sigma = \left(\sum_{i=1}^{2} \left(\frac{x_i^{\mathrm{l,exp}} - x_i^{\mathrm{l,calc}}}{x_i^{\mathrm{l,exp}}} \right)^2 \right)^{0.5} \qquad (8)$$

where x is the mole fraction and the indexes i and l provide a designation for the component and the phase, respectively. The correlative results are shown in Figure 4. The correlative equations are good to correlate the experimental data, and similar results are obtained using both equations.

Conclusions

In this paper, density, refractive index, and speed of sound as a function of the temperature for the binary mixtures of four ILs (BMIM PF_6, HMIM PF_6, OMIM PF_6, and MMIM CH_3SO_4) with three organic solvents (2-butanone, ethylacetate, and 2-propanol) are presented.

LLE of the binary mixtures involving BMIM PF_6 and HMIM PF_6 with 2-propanol were determined experimentally at several temperatures. An increase in the alkyl chain length of the IL results a decrease in the UCST when the second component is 2-propanol. Besides, the addition of the methyl group to the IL increases the solubility between IL and 2-propanol. The binary systems were modeled using the NRTL and UNIQUAC equations with linear temperature-dependence, adjustable parameters, and good fit of the experimental data provided.

Literature Cited

(1) Swatloski, R. P.; Rogers, J. D.; Rogers, R. D. Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. *Green Chem.* **2003**, *5*, 361−363.

(2) Najdanovic-Visak, V.; Esperanca, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; Szydlowski, J. Phase behaviour of room temperatura ionic liquid solutions: an unusually large co-solvent effect in (water + ethanol). *Phys. Chem. Chem. Phys.* **2002**, *4*, 1701−1703.

(3) Wasserscheid, P.; van Hal, R.; Bössann, A. 1-*n*-Butyl-3-methylimidazolium ([bmim]) octylsulfate—an even "greener" ionic liquid. *Green Chem.* **2002**, *4*, 400−404.

(4) Pereiro, A. B.; Tojo, E.; Rodriguez, A.; Canosa, J.; Tojo, J. Properties of ionic liquid $HMIMPF_6$ with carbonates, ketones and alkyl acetates. *J. Chem. Thermodyn.* **2006**, *38*, 651−661.

(5) Pereiro, A. B.; Santamarta, F.; Tojo, E.; Rodriguez, A.; Tojo, J. Temperature dependence of physical properties of ionic liquid 1,3-dimethylimidazolium methyl sulfate. *J. Chem. Eng. Data* **2006**, *51*, 952−954.

(6) Pereiro, A. B.; Tojo, E.; Rodriguez, A.; Canosa, J.; Tojo, J. $HMImPF_6$ ionic liquid that separates the azeotropic mixture ethanol + heptane. *Green Chem.* **2006**, *8*, 307−310.

(7) Pereiro, A. B.; Rodriguez, A. Study on the phase behavior and thermodynamic properties of ionic liquids containing imidazolium cation with ethanol at several temperatures. *J. Chem. Thermodyn.* (in press).

(8) Tovar, C. A.; Carballo, E.; Cerdeirina, C. A.; Romani, L. Excess molar volumes and excess molar heat capacities of mixtures containing (mono and poly)ethers + ethyl acetate. *J. Chem. Eng. Data* **1997**, *42*, 1085−1089.

(9) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.

(10) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116−128.

(11) Comelli, F.; Francesconi, R. Densities and excess molar volumes of propylene carbonate + linear and cyclic ketones at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 808−810.

(12) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley: New York, 1986.

(13) Das, A.; Frenkel, M.; Gadalla, N. M.; Marsh, K.; Wilhoit, R. C. *TRC Thermodynamic Tables*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1994.

(14) Ritzoulis, G.; Fidantsi, A. Relative permittivities, refractive indices, and densities for the binary mixtures *N*,*N*′-dimethylacetamide with methanol, ethanol, 1-butanol, and 2-propanol at 298.15 K. *J. Chem. Eng. Data* **2000**, *45*, 207−209.

(15) Harris, K. R. H.; Woolf, L. A.; Kanakudo, M. Temperature and pressure dependence of the viscosity of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. *J. Chem. Eng. Data* **2005**, *50*, 1777−1782.

(16) Wang, J.; Zhu, A.; Zhao, Y.; Zhuo, K. Excess molar volumes and excess logarithm viscosities for binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with some organic compounds. *J. Solution Chem.* **2005**, *34*, 585−596.

(17) Letcher, T. M.; Reddy, P. Ternary (liquid + liquid) equilibria for mixtures of 1-hexyl-3-methylimidazolium (tetrafluoroborate or hexaflu-

orophosphate) + benzene + an alkane at $T = 298.2$ K and $p = 0.1$ MPa. *J. Chem. Thermodyn.* **2005**, *37*, 415−421.
(18) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and pressure dependence of the viscosity of the ionic liquids 1-methyl-3-octylimidazolium hexafluorophosphate and 1-mehyl-3-octylimidazolium tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1161−1167.
(19) Chiappe, C.; Pieraccini, D. Review commentary. Ionic liquids: solvent properties and organic reactivity. *J. Phys. Org. Chem.* **2005**, *18*, 275−297.
(20) Gu, Z.; Brennecke, J. F. Volume expansivities and isothermal compressibilities of imidazolium and pyridinium-based ionic liquids. *J. Chem. Eng. Data* **2002**, *47*, 339−345.
(21) Domanska, U.; Pobudkowska, A.; Wisniewska, A. Solubility and excess molar properties of 1,3-dimethylimidazolium methylsulfate, or 1-butyl-3-methylimidazolium methylsulfate, or 1-butyl-3-methylimidazolium octylsulfate ionic liquids with *n*-alkanes and alcohols: analysis in terms of the PFP and FBT models. *J. Solution Chem.* **2006**, *35*, 311−334.
(22) Kato, R.; Gmehling, J. Activity coefficients at infinite dilution of various solutes in the ionic liquids $[MMIM]^+[CH_3SO_4]^-$, $[MMIM]^+[CH_3OC_2H_4SO_4]^-$, $[MMIM]^+[(CH_3)_2PO_4]^-$, $[C_5H_5NC_2H_5]^+[(CF_3SO_2)_2N]^-$ and $[C_5H_5NH]^+[C_2H_5OC_2H_4OSO_3]^-$. *Fluid Phase Equilib.* **2004**, *226*, 37−44.
(23) Marquardt, D. W. An algorithm for least-squares estimation of nonlinear parameters. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431−435.
(24) Pereiro, A. B.; Canosa, J.; Rodríguez, A. Liquid−liquid equilibria of 1,3-dimethylimidazolium methyl sulfate with ketones, dialkyl carbonates and acetates. *Fluid Phase Equilib.* (in press).
(25) Banerjee, T.; Singhi, M. K.; Sahoo, R. K.; Khanna, A. Volume, surface and UNIQUAC interaction parameters for imidazolium based ionic liquids via polarizable continuum model. *Fluid Phase Equilib.* **2005**, *234*, 64−76.

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