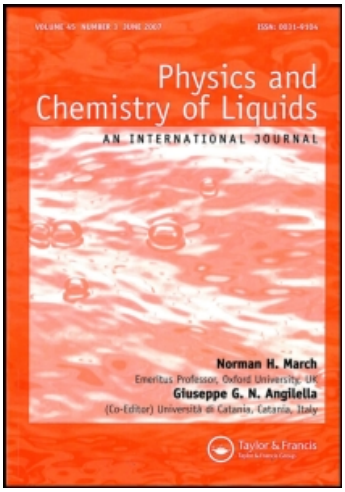

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Binary mixtures containing OMIM PF_6: density, speed of sound, refractive index and LLE with hexane, heptane and 2-propanol at several temperatures

A. B. Pereiro[a]; A. Rodríguez[a]
[a] Chemical Engineering Department, Vigo University, Vigo, Spain

To cite this Article Pereiro, A. B. and Rodríguez, A.(2008) 'Binary mixtures containing OMIM PF_6: density, speed of sound, refractive index and LLE with hexane, heptane and 2-propanol at several temperatures', Physics and Chemistry of Liquids, 46: 2, 162 — 174
To link to this Article: DOI: 10.1080/00319100701459327
URL: http://dx.doi.org/10.1080/00319100701459327

Physics and Chemistry of Liquids
Vol. 46, No. 2, April 2008, 162–174

Taylor & Francis
Taylor & Francis Group

Binary mixtures containing OMIM PF_6: density, speed of sound, refractive index and LLE with hexane, heptane and 2-propanol at several temperatures

A. B. PEREIRO and A. RODRÍGUEZ*

Chemical Engineering Department, Vigo University, P.O. Box 36210, Vigo, Spain

(*Received 27 January 2007; in final form 18 May 2007*)

Experimental densities, speeds of sound and refractive indices of the binary mixtures OMIM PF_6 (1-methyl-3-octylimidazolium hexafluorophosphate) with hexane, heptane, and 2-propanol were determined at $T = 293.15$, 298.15, and 303.15 K. Excess molar volumes, changes of refractive index on mixing and deviations in isentropic compressibility for the above systems were performed. The liquid–liquid equilibrium data of these binary mixtures were carried out experimentally and the NRTL and UNIQUAC correlative equations were applied.

Keywords: Density; Speed of sound; Refractive index; Liquid–liquid equilibria (LLE); Ionic liquids; Correlative equations

1. Introduction

Accurate representation of chemical and phase equilibria in mixed-solvents containing ionic liquids (ILs) is fundamental for researching and for the designing of a great deal of chemical processes [1] including liquid–liquid extraction [2]. This article is a continuation of the thermodynamic study of the influence of the alkyl imidazolium cation of the ILs, in the physical properties, on mixing [3–5] involving other organic compounds due to the increasing interest of the ILs as solvents. In this work, the densities, refractive indices and speeds of sound of the binary mixtures of OMIM PF_6 (1-methyl-3-octylimidazolium hexafluorophosphate) with hexane, heptane, and 2-propanol at $T = 293.15$, 298.15, and 303.15 K and atmospheric pressure were measured over the entire composition range. The ILs based on the PF_6 anion have been historically the most well-known and the most tested in several applications. But these ILs have one problem as they are not halogen free and then, they undergo hydrolysis producing HF in contact with water [6] and at high temperatures [7]. Taking into account this fact, our measurements were carried out until $T = 343.15$ K in the LLE with the aim to prevent this effect.

*Corresponding author. Tel.: +34 986 812312. Fax: +34 986 81 23 82. Email: aroguez@uvigo.es

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online © 2008 Taylor & Francis
DOI: 10.1080/00319100701459327

Excess and derived properties have been calculated from the experimental data and 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 gathered.

Liquid–liquid equilibria (LLE) data of the binary mixtures of OMIM PF_6 with hexane, heptane, and 2-propanol in the range from $T = 278.15$ to 328.15 K, from $T = 278.15$ to 343.15 K, and from $T = 278.15$ to 313.15 K were determined, respectively. The tie lines for the binary mixtures were correlated by applying the NRTL [9] and UNIQUAC [10] equations.

2. Experimental

2.1. *Materials*

The chemicals were supplied by Fluka for hexane (mass fraction ≥99%), by Sigma-Aldrich for heptane (mass fraction ≥99%), by Merck for 2-propanol (mass fraction ≥99%), and the IL by Green Solutions Chemicals S. L. with a certified purity mass fraction better than 98%. Before using, the organic solvents were degassed ultrasonically, dried over freshly activated molecular sieves (types 4 Å, supplied by Aldrich) for several weeks, and kept under an inert argon atmosphere as soon as the bottles were opened.

To reduce the OMIM PF_6 water content to negligible values (mass fraction lower than 0.03%, determined using a 756 Karl Fisher coulometer), vacuum ($P = 2 \cdot 10^{-1}$ Pa) was applied, always immediately prior to their use and submitted to NMR and Positive FABMS (FISONS VG AUTOSPEC mass spectrometer) to ensure its purity. The IL was kept in bottles under an inert gas.

Figure 1 shows the OMIM PF_6 structure. The physical properties of the pure IL and the organic solvents at $T = 298.15$ K were listed in table 1, together with recent literature values [11–15].

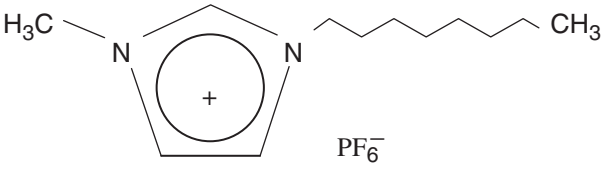

Figure 1. Schematic structure of OMIM PF_6.

Table 1. Density, ρ, and refractive index, n_D, of pure liquids at $T = 298.15$ K.

	ρ (g cm^{-3})		n_D	
Solvent	This work	Lit.	This work	Lit.
OMIM PF_6	1.2357	1.23684 [11]	1.42302	1.423 [12]
Hexane	0.6549	0.65484 [13]	1.37217	1.37226 [14]
Heptane	0.6795	0.67946 [14]	1.38517	1.38511 [14]
2-Propanol	0.7810	0.7810 [15]	1.37496	1.3752 [15]

2.2. *Apparatus and procedure*

The mixtures were prepared by transferring via syringe known mass of the pure liquids into stoppered bottles to prevent evaporation, using a Mettler AX-205 Delta Range balance with a precision of $\pm 10^{-5}$ g. The estimated uncertainty on the composition measurement was $\pm 10^{-4}$ mole fraction. Vials are closed with screw caps to ensure a secure seal and were flushed with dry argon to prevent humidity. The sample is taken from the vial with a syringe through a silicone septum and is immediately put into the apparatus.

2.2.1. Densities and speeds of sound. The densities and speeds of sound of the IL were measured with an Anton Paar DSA – 48 digital vibrating tube densimeter. The uncertainty in experimental measurements has been found to be less than $\pm 2 \times 10^{-4}$ g cm^{-3} for the density and ± 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 the instructions. The calibration was checked with pure liquids of known density and speed of sound.

2.2.2. Refractive indices. 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 of known refractive index.

2.2.3. Liquid–liquid equilibria. LLE was studied for the binary mixtures OMIM PF_6 with hexane, heptane, and 2-propanol in the range from $T = 278.15$ to 328.15 K, from $T = 278.15$ to 343.15 K, and from $T = 278.15$ to 313.15 K, respectively. The experimental tie-lines were determined in a jacketed glass vessel containing a magnetic stirrer connected to a temperature controlled circulating bath (controlled to 0.01 K). The vessel was closed to moisture and could be flushed with dry argon. Temperature in the cell was measured with a F200 ASL digital thermometer with an uncertainty of 0.01 K. The measurements were started with the addition of 100 mL of an immiscible binary mixture of known composition, the temperature was adjusted and the mixture was stirred vigorously for 1 h and left to settle for 3 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 binary mixtures.

Tie-line phase compositions were determined by the measurement of the density and the application of the corresponding fitting polynomials. Experimental densities at $T = 328.15$, 343.15, and 313.15 K, made with an Anton Paar DSA-48 digital vibrating tube densimeter, were used to determine the phase composition in the temperature range for binary mixtures OMIM PF_6 with hexane, heptane, and 2-propanol, respectively.

3. 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, ($\kappa_S = \rho^{-1}\,u^{-2}$) and deviations in isentropic compressibility of the binary mixtures OMIM PF_6 with hexane, heptane, and 2-propanol from $T = 293.15$ to 303.15 K are given in table 2. The immiscibility intervals at $T = 293.15$ K for the binary mixture are: $x_1 = 0.0002$–0.8721 for OMIM PF_6 (1) + hexane (2), $x_1 = 0.0001$–0.9027 for OMIM PF_6 (1) + heptane (2), and $x_1 = 0.0049$–0.3393 for OMIM PF_6 (1) + 2-propanol (2).

Excess molar volumes, changes of refractive index on mixing and deviations in isentropic compressibility were calculated from the experimental values, as follows:

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

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

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

In these equations, ρ and n_D are the density and refractive index of the mixture, ρ_i° and n_{Di}° are the density and 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:

$$\Delta Q = x \cdot (1 - x) \sum_{i=1}^{5} \sum_{j=1}^{3} A_{ij} \cdot 10^{1-j} \cdot (2x - 1)^{i-1} \cdot (T - 293.15)^{j-1} \tag{4}$$

where ΔQ is the excess or derived property, x is the mole fraction and A_{ij} is the fitting parameter. Applying the SOLVER function in Microsoft EXCEL, the degree of polynomial expression was optimized. The correlation parameters are listed in table 3, together with the standard deviations. These deviations were calculated by applying the following expression:

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

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

Excess molar volumes for the binary mixtures OMIM PF_6 with hexane, heptane, and 2-propanol *versus* the mole fraction over the whole composition range and the fitted curve, obtained from the polynomial equation at $T = 293.15$, 298.15, and 303.15 K, are shown in figure 2. In this figure, the excess molar volumes are negative for the miscible composition range for all the binary mixtures.

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, $\Delta\kappa_s$, at several temperatures.

x_1	ρ (g cm^{-3})	V_m^E (cm^3 mol^{-1})	n_D	Δn_D	u (m s^{-1})	κ_s (TPa^{-1})	$\Delta\kappa_s$ (TPa^{-1})
OMIM PF_6 (1) + hexane (2)							
$T = 293.15$ K							
0	0.6595	0	1.37495	0	1100	1252	0
0.8732	1.2053	−0.694	1.42206	0.0039	1380	436	−70
0.9107	1.2161	−0.523	1.42276	0.0028	1394	423	−51
0.9288	1.2210	−0.400	1.42314	0.0023	1401	418	−41
0.9532	1.2274	−0.244	1.42356	0.0015	1408	411	−27
1	1.2396	0	1.42440	0	1424	398	0
$T = 298.15$ K							
0	0.6549	0	1.37217	0	1078	1314	0
0.8732	1.2015	−0.728	1.42057	0.0040	1364	447	−76
0.9107	1.2122	−0.548	1.42133	0.0029	1378	434	−55
0.9288	1.2171	−0.423	1.42174	0.0023	1385	429	−44
0.9532	1.2236	−0.259	1.42216	0.0015	1393	421	−29
1	1.2357	0	1.42302	0	1408	408	0
$T = 303.15$ K							
0	0.6504	0	1.36936	0	1055	1380	0
0.8732	1.1976	−0.761	1.41939	0.0044	1349	459	−82
0.9107	1.2084	−0.571	1.41996	0.0030	1364	445	−59
0.9288	1.2133	−0.442	1.42042	0.0025	1370	439	−48
0.9532	1.2197	−0.267	1.42078	0.0016	1378	432	−32
1	1.2319	0	1.42165	0	1393	418	0
OMIM PF_6 (1) + heptane (2)							
$T = 293.15$ K							
0	0.6837	0	1.38776	0	1153	1101	0
0.9197	1.2161	−0.278	1.42315	0.0017	1396	422	−33
0.9484	1.2242	−0.072	1.42362	0.0011	1406	413	−21
0.9926	1.2374	−0.004	1.42426	0.0001	1421	400	−3
1	1.2396	0	1.42440	0	1424	398	0
$T = 298.15$ K							
0	0.6795	0	1.38517	0	1131	1150	0
0.9197	1.2122	−0.299	1.42173	0.0018	1381	433	−35
0.9484	1.2204	−0.088	1.42221	0.0011	1391	424	−23
0.9926	1.2335	−0.005	1.42290	0.0002	1406	410	−4
1	1.2357	0	1.42302	0	1408	408	0
$T = 303.15$ K							
0	0.6752	0	1.38258	0	1110	1202	0
0.9197	1.2084	−0.316	1.42033	0.0018	1366	443	−38
0.9484	1.2165	−0.092	1.42079	0.0012	1376	434	−25
0.9926	1.2297	−0.006	1.42152	0.0002	1391	420	−4
1	1.2319	0	1.42165	0	1393	418	0
OMIM PF_6 (1) + 2−propanol (2)							
$T = 293.15$ K							
0	0.7850	0	1.37707	0	1156	953	0
0.0004	0.7857	−0.004	1.37729	0.0002	1156	952	−1
0.0009	0.7866	−0.010	1.37736	0.0002	1157	950	−2
0.0014	0.7875	−0.018	1.37743	0.0003	1157	948	−4
0.0024	0.7891	−0.020	1.37752	0.0003	1158	945	−7
0.0030	0.7901	−0.024	1.37772	0.0005	1158	944	−7
0.3513	1.0885	−0.465	1.41129	0.0176	1293	550	−208
0.4011	1.1093	−0.467	1.41393	0.0179	1310	526	−205
0.5057	1.1451	−0.440	1.41743	0.0164	1340	486	−186
0.5991	1.1705	−0.396	1.41896	0.0135	1364	459	−161
0.6960	1.1920	−0.322	1.42004	0.0100	1379	441	−125

(*Continued*)

Table 2. Continued.

x_1	ρ (g cm^{-3})	V_m^E (cm^3 mol^{-1})	n_D	Δn_D	u (m s^{-1})	κ_s (TPa^{-1})	$\Delta\kappa_s$ (TPa^{-1})
0.7988	1.2109	−0.230	1.42137	0.0065	1395	424	−85
0.9035	1.2271	−0.140	1.42302	0.0032	1412	409	−43
0.9931	1.2388	−0.024	1.42426	0.0002	1422	399	−3
1	1.2396	0	1.42440	0	1424	398	0
$T = 298.15$ K							
0	0.7810	0	1.37496	0	1139	986	0
0.0004	0.7817	−0.010	1.37519	0.0002	1140	985	−1
0.0009	0.7826	−0.017	1.37520	0.0002	1140	983	−3
0.0014	0.7835	−0.024	1.37546	0.0004	1140	981	−4
0.0024	0.7851	−0.026	1.37562	0.0005	1141	978	−7
0.0030	0.7861	−0.029	1.37559	0.0005	1141	976	−8
0.0053	0.7900	−0.047	1.37596	0.0007	1142	970	−13
0.3036	1.0617	−0.467	1.40657	0.0170	1261	592	−219
0.3513	1.0845	−0.476	1.40992	0.0181	1279	563	−220
0.4011	1.1053	−0.487	1.41265	0.0184	1296	539	−216
0.5057	1.1412	−0.467	1.41622	0.0170	1327	498	−196
0.5991	1.1665	−0.415	1.41775	0.0140	1351	469	−171
0.6960	1.1881	−0.337	1.41888	0.0105	1366	451	−133
0.7988	1.2071	−0.251	1.42042	0.0071	1382	434	−91
0.9035	1.2233	−0.159	1.42216	0.0038	1397	419	−46
0.9931	1.2350	−0.033	1.42309	0.0004	1407	409	−3
1	1.2357	0	1.42302	0	1408	408	0
$T = 303.15$ K							
0	0.7766	0	1.37278	0	1121	1025	0
0.0004	0.7773	−0.011	1.37302	0.0002	1121	1023	−1
0.0009	0.7782	−0.019	1.37301	0.0002	1122	1021	−3
0.0014	0.7791	−0.026	1.37322	0.0004	1122	1019	−4
0.0024	0.7807	−0.028	1.37336	0.0005	1123	1016	−7
0.0030	0.7818	−0.042	1.37353	0.0006	1123	1014	−9
0.0053	0.7857	−0.062	1.37386	0.0008	1125	1006	−16
0.0098	0.7932	−0.107	1.37475	0.0015	1128	991	−28
0.2531	1.0297	−0.474	1.40116	0.0160	1235	637	−234
0.3036	1.0575	−0.485	1.40528	0.0177	1252	604	−237
0.3513	1.0803	−0.495	1.40861	0.0187	1267	576	−235
0.4011	1.1011	−0.500	1.41146	0.0191	1283	552	−230
0.5057	1.1371	−0.482	1.41501	0.0175	1315	509	−209
0.5991	1.1626	−0.438	1.41680	0.0147	1339	480	−182
0.6960	1.1842	−0.362	1.41792	0.0111	1353	461	−141
0.7988	1.2032	−0.266	1.41950	0.0077	1368	444	−96
0.9035	1.2195	−0.175	1.42128	0.0044	1384	428	−49
0.9931	1.2312	−0.036	1.42192	0.0006	1393	419	−4
1	1.2319	0	1.42165	0	1393	418	0

As expected, the interactions between the IL and hexane, heptane, and 2-propanol components are stronger than in the pure components. In this effect, the size of the second component plays an important role in the association trend on mixing. 2-Propanol exhibits the worst packing effect with the OMIM PF_6 due to the sterically hindrance of the molecule by the OH group; however, hexane shows the best packing effect due to the more flexible bond of the alkane components.

On the other hand, changes of refractive index on mixing for the binary mixtures plotted against mole fraction together with the fitted curve, obtained from the polynomial equation at the studied temperatures are shown in figure 3. These quantities are positive over the whole miscible composition range. For the deviations in isentropic

Table 3. Fitting parameters, A_{ij}, calculated from equation (4) and standard deviations, σ.

OMIM PF_6 (1) + hexane (2)						
V_m^E ($cm^3\ mol^{-1}$)	$A_{11} = 11.375$	$A_{21} = -20.846$	$A_{31} = -19.972$	$A_{41} = 5.117$	$A_{51} = 21.278$	$\sigma = 0.002$
	$A_{12} = 1.306$	$A_{22} = -2.627$	$A_{32} = -1.397$	$A_{42} = 0.763$	$A_{52} = -1.652$	
	$A_{13} = 1.640$	$A_{23} = -1.778$	$A_{33} = -2.357$	$A_{43} = 0.108$	$A_{53} = 3.094$	
Δn_D	$A_{11} = 0.1996$	$A_{21} = -0.4661$	$A_{31} = 0.2767$	$A_{41} = 0.2242$	$A_{51} = -0.2030$	$\sigma = 0.00003$
	$A_{12} = 0.0832$	$A_{22} = -0.1733$	$A_{32} = 0.0284$	$A_{42} = 0.1329$	$A_{52} = -0.0674$	
	$A_{13} = 0.1101$	$A_{23} = -0.1611$	$A_{33} = -0.0427$	$A_{43} = 0.0821$	$A_{53} = 0.0160$	
$\Delta\kappa_s$ (TPa^{-1})	$A_{11} = -758$	$A_{21} = 350$	$A_{31} = -726$	$A_{41} = 589$	$A_{51} = -91$	$\sigma = 0.06$
	$A_{12} = -144$	$A_{22} = 73$	$A_{32} = -26$	$A_{42} = 43$	$A_{52} = -49$	
	$A_{13} = 24$	$A_{23} = -104$	$A_{33} = 28$	$A_{43} = 155$	$A_{53} = -114$	
OMIM PF_6 (1) + heptane (2)						
V_m^E ($cm^3\ mol^{-1}$)	$A_{11} = -73.617$	$A_{21} = 57.125$	$A_{31} = 53.555$	$A_{41} = 29.639$	$A_{51} = -67.775$	$\sigma = 0.001$
	$A_{12} = -3.134$	$A_{22} = 2.371$	$A_{32} = 1.330$	$A_{42} = 1.381$	$A_{52} = -2.270$	
	$A_{13} = 0.979$	$A_{23} = -0.755$	$A_{33} = -3.641$	$A_{43} = 0.820$	$A_{53} = 3.752$	
Δn_D	$A_{11} = 0.4470$	$A_{21} = -1.0496$	$A_{31} = 0.4796$	$A_{41} = 0.4931$	$A_{51} = -0.3459$	$\sigma = 0.00001$
	$A_{12} = 0.1901$	$A_{22} = -0.3575$	$A_{32} = 0.0081$	$A_{42} = 0.2593$	$A_{52} = -0.0955$	
	$A_{13} = -0.2411$	$A_{23} = 0.1286$	$A_{33} = 0.3245$	$A_{43} = 0.2335$	$A_{53} = -0.4707$	
$\Delta\kappa_s$ (TPa^{-1})	$A_{11} = -998$	$A_{21} = 748$	$A_{31} = -236$	$A_{41} = 608$	$A_{51} = -603$	$\sigma = 0.01$
	$A_{12} = -269$	$A_{22} = 222$	$A_{32} = 141$	$A_{42} = 91$	$A_{52} = -281$	
	$A_{13} = -30$	$A_{23} = -37$	$A_{33} = 46$	$A_{43} = 160$	$A_{53} = -140$	
OMIM PF_6 (1) + 2-propanol (2)						
V_m^E ($cm^3\ mol^{-1}$)	$A_{11} = -1.879$	$A_{21} = 0.696$	$A_{31} = 0.256$	$A_{41} = 0.603$	$A_{51} = -2.421$	$\sigma = 0.005$
	$A_{12} = -0.174$	$A_{22} = -0.052$	$A_{32} = 0.376$	$A_{42} = -0.516$	$A_{52} = -0.393$	
	$A_{13} = 0.056$	$A_{23} = -0.296$	$A_{33} = -0.936$	$A_{43} = 3.143$	$A_{53} = -1.719$	
Δn_D	$A_{11} = 0.0683$	$A_{21} = -0.0487$	$A_{31} = -0.0199$	$A_{41} = 0.0610$	$A_{51} = -0.0105$	$\sigma = 0.00005$
	$A_{12} = 0.0047$	$A_{22} = 0.0015$	$A_{32} = -0.0003$	$A_{42} = -0.0134$	$A_{52} = 0.0363$	
	$A_{13} = 0.0009$	$A_{23} = 0.0053$	$A_{33} = 0.0030$	$A_{43} = -0.0352$	$A_{53} = 0.0248$	
$\Delta\kappa_s$ (TPa^{-1})	$A_{11} = -794$	$A_{21} = 477$	$A_{31} = -219$	$A_{41} = 255$	$A_{51} = -248$	$\sigma = 0.46$
	$A_{12} = -93$	$A_{22} = 45$	$A_{32} = -56$	$A_{42} = 203$	$A_{52} = -188$	
	$A_{13} = -15$	$A_{23} = -11$	$A_{33} = -49$	$A_{43} = 501$	$A_{53} = -498$	

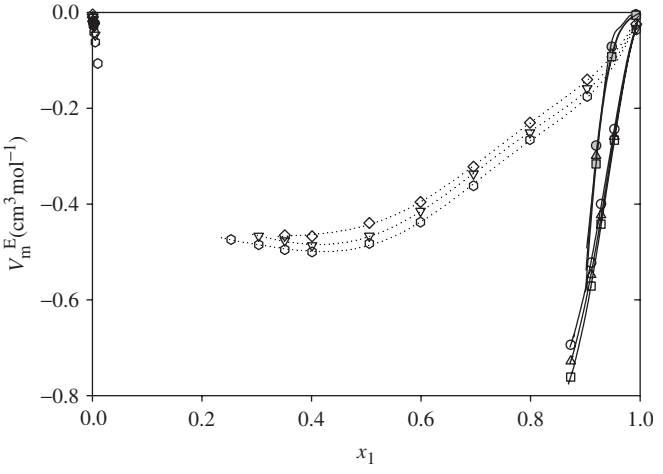

Figure 2. Effect of temperature (T) on excess molar volumes (V_m^E) of the binary mixtures against mole fraction x_1 for: OMIM PF_6 (1) + Hexane (2) at $T = 293.15$ K (◯), at $T = 298.15$ K (△), at $T = 303.15$ K (□) and fitted line (solid line); OMIM PF_6 (1) + heptane (2) at $T = 293.15$ K (●), at $T = 298.15$ K (▲), at $T = 303.15$ K (■) and fitted line (solid line); OMIM PF_6 (1) + 2-Propanol (2) at $T = 293.15$ K (◇), at $T = 298.15$ K (▽), at $T = 303.15$ K (⬡) and fitted line (dotted line).

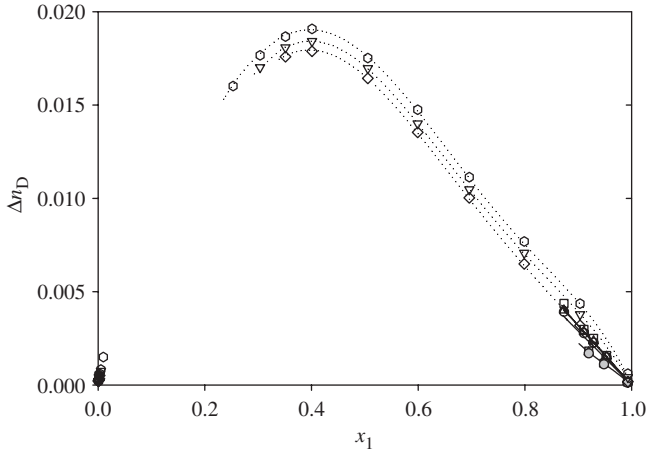

Figure 3. Effect of temperature (T) on changes of refractive indices on mixing (Δn_D) of the binary mixtures against mole fraction x_1 for: OMIM PF_6 (1) + Hexane (2) at $T = 293.15$ K (◯), at $T = 298.15$ K (△), at $T = 303.15$ K (□) and fitted line (solid line); OMIM PF_6 (1) + Heptane (2) at $T = 293.15$ K (●), at $T = 298.15$ K (▲), at $T = 303.15$ K (■) and fitted line (solid line); OMIM PF_6 (1) + 2-Propanol (2) at $T = 293.15$ K (◇), at $T = 298.15$ K (▽), at $T = 303.15$ K (⬡) and fitted line (dotted line).

compressibility, negative values are observed over the entire miscible composition range in figure 4.

The effect of the length of the hydrocarbon alkyl chain in the alkanes can be observed clearly by examining the figures 2–4. The excess molar volumes and deviations in isentropic compressibility present negative values and increase as the length of the alkyl

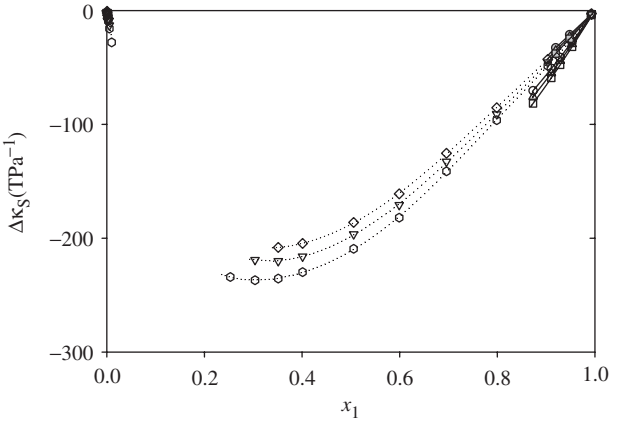

Figure 4. Effect of temperature (T) on deviations in isentropic compressibility ($\Delta\kappa_S$) of the binary mixtures against mole fraction x_1 for: OMIM PF_6 (1) + Hexane (2) at $T = 293.15$ K (◯), at $T = 298.15$ K (△), at $T = 303.15$ K (□) and fitted line (solid line); OMIM PF_6 (1) + Heptane (2) at $T = 293.15$ K (●), at $T = 298.15$ K (▲), at $T = 303.15$ K (■) and fitted line (solid line); OMIM PF_6 (1) + 2-Propanol (2) at $T = 293.15$ K (◇), at $T = 298.15$ K (▽), at $T = 303.15$ K (⬡) and fitted line (dotted line).

chain in the second component is increased. However, in the changes of refractive index on mixing, an opposite behavior is shown, the values of the derived magnitude are positive and decrease as the length of the alkyl chain in the second component is increased.

LLE for the binary mixtures of OMIM PF_6 with hexane, heptane, and 2-propanol in the range from $T = 278.15$ to 328.15 K, from $T = 278.15$ to 343.15 K, and from $T = 278.15$ to 313.15 K, respectively, were determined experimentally and gathered in table 4. Experimental phase diagrams of the investigated LLE are shown in figure 5.

A study of the mixtures of OMIM PF_6 with different alkanes show that the immiscible region is constant although the temperature is increased. Besides, this region increases when the hydrocarbon alkyl chain is increased. Both effects are shown in the literature [16–19] for other mixtures of ILs with alkanes.

Figure 6 shows the liquid phase behavior for different ILs involving hexafluorophosphate cation (EMIM PF_6 [20], BMIM PF_6 [5], HMIM PF_6 [5], and OMIM PF_6 (present work)) with 2-propanol. The UCST is significantly higher for the ILs with the shorter alkyl chain. Similar trend is observed in the literature [21] for other ILs with other alcohols.

3.1. *Correlation of LLE*

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 optimized. The volume R_k and surface area Q_k parameters of the UNIQUAC equation were obtained from the literature [22].

Table 4. LLE for the binary mixtures of OMIM PF_6 with solvents.

T (K)	x_1 Poor phase	x_1 Rich phase
OMIM PF_6 (1) + hexane (2)		
278.15	0.0001	0.8852
283.15	0.0001	0.8827
288.15	0.0001	0.8754
293.15	0.0002	0.8721
298.15	0.0002	0.8690
303.15	0.0002	0.8669
308.15	0.0002	0.8659
313.15	0.0002	0.8650
318.15	0.0002	0.8646
323.15	0.0002	0.8636
328.15	0.0002	0.8615
OMIM PF_6 (1) + heptane (2)		
278.15	0.0001	0.9124
283.15	0.0001	0.9034
288.15	0.0001	0.9035
293.15	0.0001	0.9027
298.15	0.0001	0.9014
303.15	0.0001	0.9003
308.15	0.0002	0.8997
313.15	0.0002	0.8981
318.15	0.0002	0.8975
323.15	0.0002	0.8951
328.15	0.0002	0.8937
333.15	0.0002	0.8928
338.15	0.0002	0.8919
343.15	0.0002	0.8915
OMIM PF_6 (1) + 2-propanol (2)		
278.15	0.0023	0.4606
283.15	0.0028	0.4229
288.15	0.0035	0.3827
293.15	0.0049	0.3393
298.15	0.0073	0.2929
303.15	0.0113	0.2357
308.15	0.0162	0.1674
313.15	0.0289	0.0985

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

$$\frac{\Delta G^{\mathrm{E}}}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \tag{6}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}), \quad \alpha_{12} = \alpha_{21} \tag{7}$$

$$\tau_{ij} = \tau_{12} = \frac{\Delta g_{ij}}{RT} \tag{8}$$

$$\frac{\Delta G^{\mathrm{E}}}{RT} = \sum_{i=1}^{2} x_i \ln \frac{\psi_i}{x_i} + 5 \sum_{i=1}^{2} x_i q_i \ln \frac{\theta_i}{\psi_i} - \sum_{i=1}^{2} x_i q_i \ln \left(\sum_{j=1}^{2} \theta_j \tau_{ji} \right) \tag{9}$$

$$\psi_i = \frac{x_i \gamma_i}{\sum_{i=1}^{2} x_i \gamma_i} \quad \text{and} \quad \theta_i = \frac{x_i q_i}{\sum_{i=1}^{2} x_i q_i} \tag{10}$$

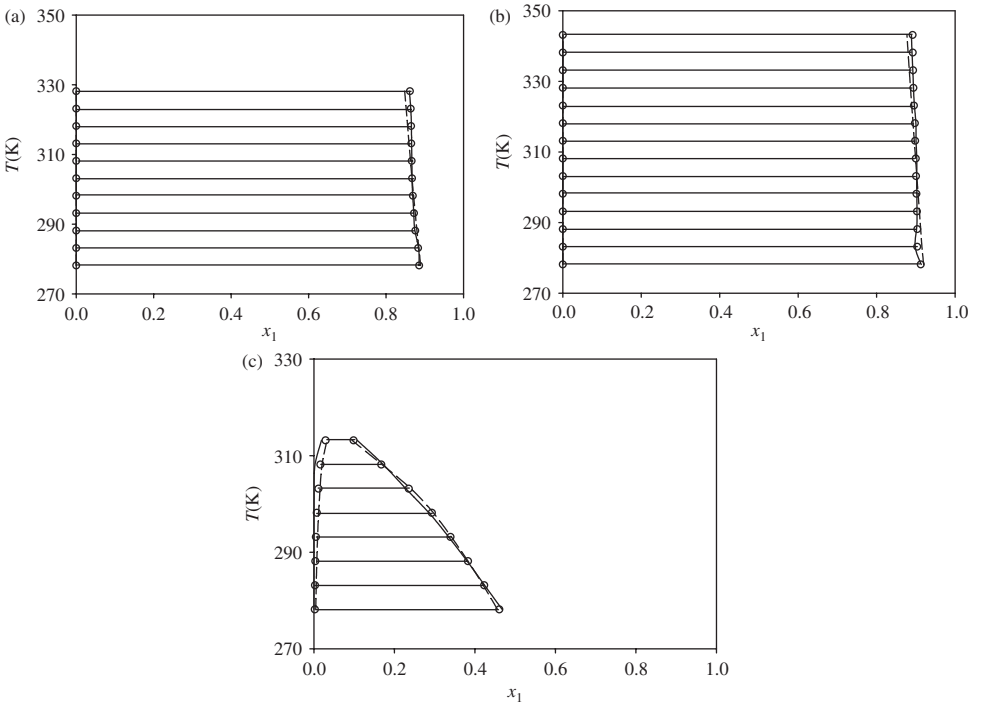

Figure 5. Equilibrium temperature for LLE against IL mole fraction for: (a) OMIM PF_6 (1) + Hexane (2); (b) OMIM PF_6 (1) + Heptane (2); (c) OMIM PF_6 (1) + 2-Propanol (2). Experimental data (◯) and correlated curves of NRTL (solid line) and UNIQUAC (dashed line) are from the equations of this work.

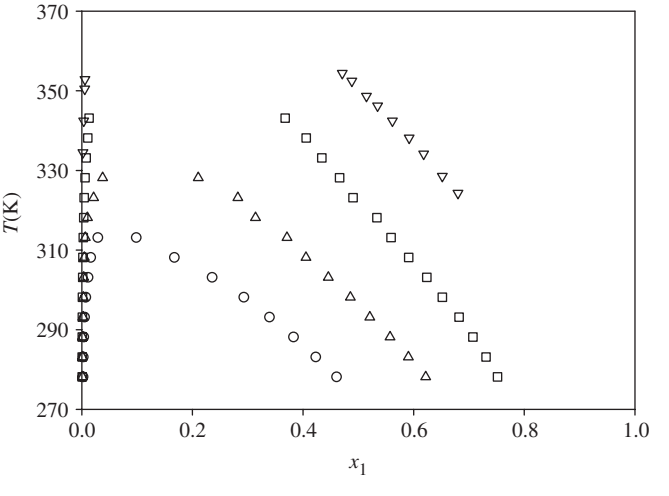

Figure 6. Equilibrium temperature for LLE against IL mole fraction for RMIM PF_6 (1) + 2-Propanol (2), where RMIM PF_6 is: EMIM PF_6 from 20 (▽), BMIM PF_6 from 5 (□), HMIM PF_6 from 5 (△), and OMIM PF_6 from this work (◯).

Table 5. Parameters of the NRTL and UNIQUAC equations for the binary mixtures.

a_{12} (J mol^{-1})	a_{21} (J mol^{-1})	b_{12} (J mol^{-1} K^{-1})	b_{21} (J mol^{-1} K^{-1})	α	σ
NRTL					
OMIM PF_6 (1) + hexane (2)					
24999	20999	−44.95	36.59	0.30	3.29
OMIM PF_6 (1) + heptane (2)					
24998	21000	−35.21	108.8	0.29	3.74
OMIM PF_6 (1) + 2-propanol (2)					
24999	21000	−43.80	189.9	0.15	2.60
UNIQUAC					
OMIM PF_6 (1) + hexane (2)					
−1619	137.1	15.10	2.652		0.62
OMIM PF_6 (1) + heptane (2)					
−1601	95.33	15.54	2.577		0.69
OMIM PF_6 (1) + 2-propanol (2)					
−2356	−687.8	21.93	6.032		2.19

$$\tau_{ij} = \exp\left(-\frac{\Delta u_{ij}}{RT}\right) \tag{11}$$

$$\Delta g_{ij} = a_{ij} + b_{ij} \cdot T \quad \text{and} \quad \Delta u_{ij} = a_{ij} + b_{ij} \cdot T \tag{12}$$

The SOLVER function in Microsoft EXCEL was used to adjust these 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:

$$\text{Objective function} = \sum_{i=1}^{2} \left(x_i^{l,\text{exp}} - x_i^{l,\text{calc}}\right)^2 \tag{13}$$

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:

$$\sigma = \left(\sum_{i=1}^{2} \left(\frac{x_i^{l,\text{exp}} - x_i^{l,\text{calc}}}{x_i^{l,\text{exp}}}\right)^2\right)^{0.5} \tag{14}$$

where x is the mole fraction and the subscripts i and l provide a designation for the component and the phase, respectively.

The correlative results are shown in figure 5. A satisfactory description of the results is shown to correlate the experimental data and suitable results are obtained using both equations.

4. Conclusions

In this article, density, refractive index, and speed of sound as a function of the temperature for the binary mixtures of OMIM PF_6 with hexane, heptane, and 2-propanol

were presented. To test the quality of the experimental values, the excess molar volumes, changes of refractive index on mixing, isentropic compressibilities, and deviations in isentropic compressibility for the above binary mixtures at the studied temperature interval have been calculated. In this case, the derived magnitudes of all the mixtures increase as the temperature is increased.

LLE of the binary mixtures involving OMIM PF_6 with hexane, heptane, and 2-propanol were determined experimentally at several temperatures. In general terms, the size of the immiscible region is constant when the temperature is increased for the binary mixtures of OMIM PF_6 with alkanes. On the other hand, the immiscible area disappears at relative moderate temperature for the binary mixture IL with 2-propanol.

The NRTL and UNIQUAC equations with temperature dependence have been used to correlate the LLE data. From the analysis of the standard deviation results, the UNIQUAC equation fits reliable the immiscible region of the binary mixtures.

Acknowledgment

We want to thank the Ministerio de Educación y Ciencia (Spain) for the financial support through Project CTQ 2004 – 00454.

References

[1] R.D. Rogers, K.S. Seddon. ACS Symposium Series 818, ACS, 1988. *Ionic Liquids Industrial Applications for Green Chemistry*, Washington, DC (2002).
[2] A.B. Pereiro, E. Tojo, A. Rodríguez, J. Canosa. *J. Tojo. Green Chem.*, **8**, 307 (2006).
[3] A.B. Pereiro, E. Tojo, A. Rodríguez, J. Canosa. *J. Tojo. J. Chem. Thermodyn.*, **38**, 651 (2006).
[4] A.B. Pereiro, A. Rodríguez. *J. Chem. Thermodyn.*, **39**, 978 (2007).
[5] A.B. Pereiro, A. Rodríguez. *J. Chem. Eng. Data*, **52**, 600 (2007).
[6] R.P. Swatloski, J.D. Rogers, R.D. Rogers. *Green Chem.*, **5**, 361 (2003).
[7] V. Najdanovic-Visak, J.M.S.S. Esperanca, L.P.N. Rebelo, M. Nunes da Ponte, H.J.R. Guedes, K.R. Seddon, J. Szydlowski. *Phys. Chem. Phys.*, **4**, 1701 (2002).
[8] A.B. Pereiro, A. Rodríguez, J. Canosa, J. Tojo. *J. Chem. Eng. Data*, **49**, 1392 (2004).
[9] H. Renon, J.M. Prausnitz. *AIChE J.*, **14**, 135 (1968).
[10] D.S. Abrams, J.M. Prausnitz. *AIChE J.*, **21**, 116 (1975).
[11] K.R. Harris, M. Kanakubo, L.A. Woolf. *J. Chem. Eng. Data*, **51**, 1161 (2006).
[12] C. Chiappe, D. Pieraccini. *J. Phys. Org. Chem.*, **18**, 275 (2005).
[13] J.A. Riddick, W.B. Bunger, T.K. Sakano. *Organic Solvents Techniques of Chemistry*, 4th Edn, Vol. II, Wiley, New York (1986).
[14] A. Das, M. Frenkel, N.M. Gadalla, K. Marsh, R.C. Wilhoit. *TRC Thermodynamic Tables; Thermodynamic Research Center*, Texas A&M University, College Station, TX (1994).
[15] G. Ritzoulis, A. Fidantsi. *J. Chem. Eng. Data*, **45**, 207 (2000).
[16] U. Domańska, A. Pobudkowska, F. Eckert. *Green Chem.*, **8**, 268 (2006).
[17] U. Domańska, A. Pobudkowska, A. Wiśniewska. *J. Solut. Chem.*, **35**, 311 (2006).
[18] U. Domańska, A. Marciniak. *J. Chem. Thermodyn.*, **37**, 577 (2005).
[19] U. Domańska, A. Marciniak. *J. Chem. Eng Data*, **48**, 451 (2003).
[20] U. Domańska, A. Marciniak. *J. Phys. Chem. B*, **108**, 2376 (2004).
[21] J.M. Crosthwaite, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke. *J. Phys. Chem. B*, **108**, 5113 (2004).
[22] T. Banerjee, M.K. Singhi, R.K. Sahoo, A. Khanna. *Fluid Phase Equilib.*, **234**, 64 (2005).