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Phase Equilibria of the Azeotropic Mixture Hexane + Ethyl Acetate with Ionic Liquids at 298.15 K

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This work reports the results of a study on the use of the two ionic liquids as an extraction solvent in the separation of the azeotropic mixture of hexane with ethyl acetate. Experimental densities, speeds of sound, and refractive indices of the binary mixtures of ethyl acetate + hexane or + 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIM PF_6) were determined from (293.15 to 303.15) K, since they are necessary to determine liquid−liquid equilibria. Excess molar volumes, changes of refractive index on mixing, and deviations in isentropic compressibility for the above systems were calculated. Liquid−liquid equilibria (LLE) were determined for the ternary systems hexane + ethyl acetate + HMIM PF_6 or 1-octyl-3-methylimidazolium hexafluorophosphate (OMIM PF_6) at 298.15 K and atmospheric pressure. The values of selectivity and distribution ratio were derived from the tie-line data. Experimental liquid−liquid equilibria data were correlated with the NRTL and UNIQUAC equations. These equations were verified to accurately correlate the experimental data.

Introduction

During the last years, research concerning ionic liquids (ILs) has grown rapidly, as can be seen in the scientific literature. There is an increasing number of articles reporting new industrial applications[1,2] for the ILs showing the interest of these new chemicals and encouraging further research. Moreover, ILs are being extensively evaluated as environmentally friendly or "green" alternatives to conventional organic solvents in a variety of industrial processes.[3–6] In this paper, we have considered the use of two ILs formed by 1-alkyl-3-methylimidazolium (C_n-MIM) as cations and hexafluorophosphate (PF_6^-) as anions. These ILs are considered historically the most important and commonly investigated, despite that this anion can undergo hydrolysis producing HF in contact with water[7] and at high temperatures.[8] Consequently, the application of the hexafluorophosphate ILs is restricted to those at water-free conditions and moderate temperatures as is considered in this paper.

Liquid−liquid extraction is not only a cheap but also an often effective method to simplify the problem of separating azeotropic mixtures which is usually impracticable by distillation. In the selected processes, the knowledge of the equilibrium behavior is essential for the applied separation techniques. In this work, two ILs have been chosen for the separation of the azeotropic mixture hexane + ethyl acetate. This azeotrope is present in the process for purifying grafted polyolefins,[9] and its separation is made by azeotropic batch distillation with heterogeneous entrainers[10] such as methanol, acetonitrile, water, and nitromethane. The evaluation of these two ILs as extraction solvents for the recovery of ethyl acetate from its mixture with hexane was carried out through the analysis of LLE data.

This paper is a continuation of the thermodynamic study of ILs with the imidazolium cation of the physical properties of mixing[11–13] and the determination of the liquid−liquid equilibria (LLE)[14–17] for use in the separation of azeotropic mixtures. Densities, refractive indices, and speeds of sound of the binary mixtures of ethyl acetate with hexane or HMIM PF_6 from (293.15 to 303.15) K and atmospheric pressure were measured, since they are necessary to determine liquid−liquid equilibria. Excess and derived properties have been calculated from the experimental data. A function of the mole fraction and temperature polynomial equation[18] was used to fit these quantities. LLE data of hexane + ethyl acetate + HMIM PF_6 or + OMIM PF_6 were determined at 298.15 K and atmospheric pressure. The LLE data were correlated by the NRTL[19] and UNIQUAC[20] equations, thus facilitating their implementation and use in computerized applications for the design of a separation process.

Experimental Section

Chemicals. Hexane and ethyl acetate (99.0 % and 99.8 % mass fraction, respectively) were supplied by Fluka. The organic solvents were degassed ultrasonically, dried over molecular sieves (type 4 Å, supplied by Aldrich) for several weeks, and kept in an inert argon atmosphere as soon as the bottles were opened. The ILs were synthesized in our laboratory[21] and characterized by its NMR spectra and positive FABMS (FISONS VG AUTOSPEC mass spectrometer). To reduce the water content to negligible values (mass fraction lower than 0.02 %, determined using a 756 Karl Fisher coulometer), a vacuum ($2 \cdot 10^{-1}$ Pa) was applied to the ILs during several days, always immediately prior to its use. A comparison of the measured densities and the refractive indices of the chemicals together with recent literature values was presented in previous works.[18,21]

Experimental 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 it 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 mole fraction of the mixtures was $\pm 10^{-4}$.

The density and speed of sound of the pure liquids and mixtures were measured with an Anton Paar DSA 48 digital

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Table 1. 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 / $g\cdot cm^{-3}$	V_m^E / $cm^3\cdot mol^{-1}$	n_D	Δn_D	u / $m\cdot s^{-1}$	κ_s / $T\cdot Pa^{-1}$	$\Delta\kappa_s$ / $T\cdot Pa^{-1}$
Hexane (1) + Ethyl Acetate (2)							
$T = 293.15$ K							
0	0.9005	0	1.37241	0	1162	822	0
0.0469	0.8843	0.15	1.37193	−0.0006	1152	852	10
0.0969	0.8680	0.27	1.37157	−0.0011	1141	884	20
0.1898	0.8389	0.51	1.37105	−0.0018	1125	942	38
0.2962	0.8086	0.68	1.37060	−0.0026	1111	1002	52
0.3907	0.7835	0.83	1.37053	−0.0029	1101	1053	63
0.5028	0.7560	0.91	1.37066	−0.0030	1093	1107	68
0.5980	0.7345	0.91	1.37101	−0.0029	1090	1147	68
0.6995	0.7131	0.85	1.37180	−0.0024	1088	1184	61
0.8030	0.6933	0.65	1.37266	−0.0018	1089	1216	48
0.9005	0.6758	0.39	1.37381	−0.0009	1093	1238	29
0.9514	0.6673	0.19	1.37440	−0.0004	1096	1247	15
1	0.6595	0	1.37495	0	1100	1252	0
$T = 298.15$ K							
0	0.8944	0	1.36977	0	1141	859	0
0.0469	0.8782	0.16	1.36926	−0.0006	1129	893	13
0.0969	0.8620	0.28	1.36890	−0.0011	1119	926	23
0.1898	0.8331	0.53	1.36832	−0.0019	1103	987	42
0.2962	0.8030	0.71	1.36785	−0.0026	1089	1051	57
0.3907	0.7780	0.85	1.36776	−0.0029	1079	1105	68
0.5028	0.7507	0.94	1.36789	−0.0031	1071	1162	74
0.5980	0.7293	0.94	1.36823	−0.0030	1067	1204	73
0.6995	0.7081	0.88	1.36896	−0.0025	1066	1243	66
0.8030	0.6884	0.67	1.36980	−0.0019	1067	1276	52
0.9005	0.6711	0.40	1.37096	−0.0010	1071	1300	31
0.9514	0.6627	0.20	1.37157	−0.0005	1074	1309	17
1	0.6549	0	1.37217	0	1078	1314	0
$T = 303.15$ K							
0	0.8882	0	1.36712	0	1111	912	0
0.0469	0.8722	0.16	1.36660	−0.0006	1099	949	15
0.0969	0.8559	0.30	1.36622	−0.0011	1089	984	27
0.1898	0.8273	0.54	1.36559	−0.0020	1074	1048	47
0.2962	0.7973	0.73	1.36513	−0.0027	1061	1115	64
0.3907	0.7724	0.88	1.36500	−0.0030	1053	1169	74
0.5028	0.7453	0.97	1.36511	−0.0031	1046	1227	80
0.5980	0.7241	0.97	1.36547	−0.0030	1042	1271	79
0.6995	0.7031	0.90	1.36611	−0.0026	1041	1312	72
0.8030	0.6835	0.69	1.36689	−0.0020	1043	1344	55
0.9005	0.6664	0.42	1.36803	−0.0011	1047	1368	34
0.9514	0.6581	0.21	1.36866	−0.0006	1051	1376	18
1	0.6504	0	1.36936	0	1055	1380	0
HMIM PF_6 (1) + Ethyl Acetate (2)							
$T = 293.15$ K							
0	0.9005	0	1.37241	0	1162	822	0
0.0506	0.9526	−0.66	1.38064	0.0059	1185	748	−52
0.1040	0.9987	−1.13	1.38740	0.0101	1210	684	−91
0.1978	1.0638	−1.57	1.39645	0.0148	1252	600	−133
0.2924	1.1146	−1.74	1.40200	0.0159	1288	541	−150
0.4549	1.1797	−1.66	1.40845	0.0147	1335	476	−142
0.4974	1.1933	−1.58	1.40969	0.0140	1346	463	−136
0.5904	1.2195	−1.35	1.41237	0.0123	1366	440	−117
0.7015	1.2458	−1.03	1.41438	0.0091	1387	417	−89
0.7926	1.2638	−0.69	1.41592	0.0064	1403	402	−64
0.8941	1.2816	−0.35	1.41731	0.0030	1420	387	−33
0.9459	1.2898	−0.17	1.41797	0.0013	1429	380	−17
1	1.2979	0	1.41923	0	1438	372	0
$T = 298.15$ K							
0	0.8944	0	1.36977	0	1141	859	0
0.0506	0.9468	−0.70	1.37838	0.0062	1163	780	−54
0.1040	0.9932	−1.18	1.38537	0.0106	1189	712	−97
0.1978	1.0586	−1.66	1.39415	0.0149	1233	621	−143
0.2924	1.1098	−1.83	1.40007	0.0162	1271	558	−161
0.4549	1.1752	−1.77	1.40690	0.0153	1320	488	−153
0.4974	1.1889	−1.68	1.40821	0.0145	1331	475	−146
0.5904	1.2152	−1.44	1.41083	0.0127	1352	450	−126
0.7015	1.2415	−1.10	1.41296	0.0094	1374	427	−97
0.7926	1.2598	−0.77	1.41446	0.0066	1390	411	−70
0.8941	1.2776	−0.42	1.41594	0.0032	1407	395	−36
0.9459	1.2858	−0.22	1.41662	0.0014	1415	388	−19
1	1.2937	0	1.41787	0	1424	381	0

Table 1. Continued

x_1	$\frac{\rho}{\mathrm{g \cdot cm^{-3}}}$	$\frac{V_m^E}{\mathrm{cm^3 \cdot mol^{-1}}}$	n_D	Δn_D	$\frac{u}{\mathrm{m \cdot s^{-1}}}$	$\frac{\kappa_s}{\mathrm{T \cdot Pa^{-1}}}$	$\frac{\Delta\kappa_s}{\mathrm{T \cdot Pa^{-1}}}$
T = 303.15 K							
0	0.8882	0	1.36712	0	1111	912	0
0.0506	0.9410	−0.74	1.37606	0.0064	1142	815	−71
0.1040	0.9876	−1.25	1.38312	0.0109	1169	741	−117
0.1978	1.0534	−1.75	1.39194	0.0151	1215	643	−165
0.2924	1.1049	−1.93	1.39821	0.0167	1254	576	−184
0.4549	1.1705	−1.84	1.40523	0.0157	1305	502	−173
0.4974	1.1842	−1.74	1.40664	0.0150	1317	487	−165
0.5904	1.2107	−1.50	1.40893	0.0127	1338	461	−142
0.7015	1.2372	−1.15	1.41150	0.0098	1361	437	−109
0.7926	1.2556	−0.83	1.41307	0.0069	1378	420	−78
0.8941	1.2738	−0.49	1.41454	0.0033	1395	404	−41
0.9459	1.2820	−0.30	1.41526	0.0015	1403	396	−21
1	1.2896	0	1.41643	0	1411	389	0

Table 2. Fitting Parameters A_{ij} and Standard Deviations (σ) Calculated from Equations 4 and 5, Respectively

			Hexane (1) + Ethyl Acetate (2)			
$V_m^E/\mathrm{cm^3 \cdot mol^{-1}}$	$A_{11} = 3.63$	$A_{21} = 0.90$	$A_{31} = 0.24$	$A_{41} = -0.39$	$A_{51} = -0.14$	$\sigma = 0.01$
	$A_{12} = 0.22$	$A_{22} = 0.10$	$A_{32} = 0.44$	$A_{42} = -0.27$	$A_{52} = -0.56$	
	$A_{13} = 0.02$	$A_{23} = -0.07$	$A_{33} = -0.57$	$A_{43} = 0.29$	$A_{53} = 0.91$	
Δn_D	$A_{11} = -0.0121$	$A_{21} = 0.0003$	$A_{31} = 0.0019$	$A_{41} = 0.0018$	$A_{51} = -0.0009$	$\sigma = 0.00003$
	$A_{12} = -0.0005$	$A_{22} = -0.0001$	$A_{32} = -0.0028$	$A_{42} = -0.0003$	$A_{52} = 0.0031$	
	$A_{13} = 8.8\mathrm{E}\text{-}05$	$A_{23} = 9.4\mathrm{E}\text{-}05$	$A_{33} = 0.0008$	$A_{43} = -0.0018$	$A_{53} = -0.0029$	
$\Delta\kappa_s/\mathrm{T \cdot Pa^{-1}}$	$A_{11} = 273$	$A_{21} = 42$	$A_{31} = -3.0$	$A_{41} = 21$	$A_{51} = 15$	$\sigma = 0.3$
	$A_{12} = 44$	$A_{22} = 16$	$A_{32} = -30$	$A_{42} = -46$	$A_{52} = 94$	
	$A_{13} = 2.4$	$A_{23} = -11$	$A_{33} = 42$	$A_{43} = 12$	$A_{53} = -62$	
			HMIM PF_6 (1) + Ethyl Acetate (2)			
$V_m^E/\mathrm{cm^3 \cdot mol^{-1}}$	$A_{11} = -6.30$	$A_{21} = 3.93$	$A_{31} = -1.48$	$A_{41} = 2.26$	$A_{51} = -1.60$	$\sigma = 0.01$
	$A_{12} = -0.95$	$A_{22} = 0.22$	$A_{32} = 0.50$	$A_{42} = -0.63$	$A_{52} = -1.57$	
	$A_{13} = 0.28$	$A_{23} = 0.40$	$A_{33} = -0.75$	$A_{43} = -0.61$	$A_{53} = -0.12$	
Δn_D	$A_{11} = 0.0560$	$A_{21} = -0.0368$	$A_{31} = 0.0280$	$A_{41} = -0.0206$	$A_{51} = -0.0079$	$\sigma = 0.00008$
	$A_{12} = 0.0047$	$A_{22} = 0.0032$	$A_{32} = -0.0194$	$A_{42} = -0.0131$	$A_{52} = 0.0331$	
	$A_{13} = -0.0012$	$A_{23} = -0.0033$	$A_{33} = 0.0123$	$A_{43} = 0.0103$	$A_{53} = -0.0172$	
$\Delta\kappa_s/\mathrm{T \cdot Pa^{-1}}$	$A_{11} = -540$	$A_{21} = 345$	$A_{31} = -192$	$A_{41} = 85$	$A_{51} = -14$	$\sigma = 0.5$
	$A_{12} = -52$	$A_{22} = 46$	$A_{32} = -62$	$A_{42} = -169$	$A_{52} = 230$	
	$A_{13} = -66$	$A_{23} = 19$	$A_{33} = 34$	$A_{43} = 268$	$A_{53} = -356$	

vibrating tube densimeter. The uncertainty in the measurement of the samples has been found to be lower than ± 10^{-4} $\mathrm{g \cdot cm^{-3}}$ for the density and ± 1 $\mathrm{m \cdot s^{-1}}$ 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 ± $4 \cdot 10^{-5}$. 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.

A calibration curve for the density and the refractive index of the coexisting phase was made with known mole fraction samples of the ternary mixture to determine the mole fraction at 298.15 K. The uncertainty of the phase composition was estimated to be ± 0.005 in mole fraction. For the experimental determination of the LLE tie-lines, a jacketed glass vessel containing a magnetic stirrer connected to a temperature-controlled circulating bath (controlled to ± 0.01 K) was used. For the jacketed cell, the temperature was controlled with a F200 ASL digital thermometer with an uncertainty of ± 0.01 K. The measurements of the ternary LLE started with the addition of 30 mL of immiscibility ternary components of known mole fraction to the vessel. The temperature was kept constant, and the mixture was stirred vigorously during 1 h and left to settle for 4 h to ensure a complete separation of the phases. Samples were taken by a syringe from the upper and lower phases to carry out the mole fraction analysis.

Two techniques based on the experimental determination of the tie-lines and the determination of the binodal curve for the immiscible area of the ternary system were used to determine the compositions of the ternary LLE. The binodal curve was determined by adding known quantities of the three components corresponding to the immiscible area into the equilibrium cell. Then, we slowly added known quantities of solute (ethyl acetate) maintaining the stirring until the "cloud point".

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 the Laplace equation ($\kappa_s = \rho^{-1} \cdot u^{-2}$), and deviations in isentropic compressibility of the binary mixtures hexane (1) + ethyl acetate (2) and HMIM PF_6 (1) + ethyl acetate (2) from (293.15 to 303.15) K are given in Table 1. The physical properties of OMIM PF_6 (1) + ethyl acetate (2) were published previously.[13] The binary mixture hexane (1) + ethyl acetate (2) presents azeotropic behavior at 101.3 kPa, and the azeotropic composition[22] is $x_1 = 0.63$.

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

$$V_{\mathrm{m}}^{\mathrm{E}} = \sum_{\mathrm{i}=1}^{N} x_i M_i\left(\rho^{-1} - \rho_{\mathrm{i}}^{\circ^{-1}}\right) \qquad (1)$$

$$\Delta n_{\mathrm{D}} = n_{\mathrm{D}} - \sum_{i=1}^{N} x_i n_{\mathrm{D}i}^{\circ} \qquad (2)$$

$$\Delta \kappa_{\mathrm{s}} = \kappa_{\mathrm{s}} - \sum_{i=1}^{N} x_i \kappa_{\mathrm{s},i} \qquad (3)$$

In these equations, ρ and n_{D} are the density and the refractive index of the mixture; ρ_i° and $n_{\mathrm{D}i}^{\circ}$ are the density and the refractive index of the pure components; κ_{s} is the isentropic compressibility of the mixture; $\kappa_{\mathrm{s},i}$ is the isentropic compressibility of the pure component; and the subscript i refers to 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

$$\Delta Q = x_1 \cdot (1 - x_1) \sum_{i=1}^{5} \sum_{j=1}^{3} A_{ij} \cdot 10^{1-j} \cdot (2x_1 - 1)^{i-1} \cdot (T/\mathrm{K} - 293.15)^{j-1} \qquad (4)$$

where ΔQ is the excess or derived property; x_1 is the first component mole fraction; A_{ij} is the fitting parameter; and subscripts i and j refer to the pure component and parameter number, respectively. Applying the SOLVER function in Microsoft EXCEL, the degree of polynomial expression was optimized. The correlation parameters are listed in Table 2, together with the standard deviations (σ). These deviations were calculated by applying the following expression

$$\sigma = \left(\frac{\sum^{\mathrm{DAT}} (z_{\mathrm{exptl}} - z_{\mathrm{pred}})^2}{n_{\mathrm{DAT}}} \right)^{1/2} \qquad (5)$$

where property values and the number of experimental data are represented by z and n_{DAT}, respectively, and subscripts exptl and pred refer to the experimental and predicted values, respectively.

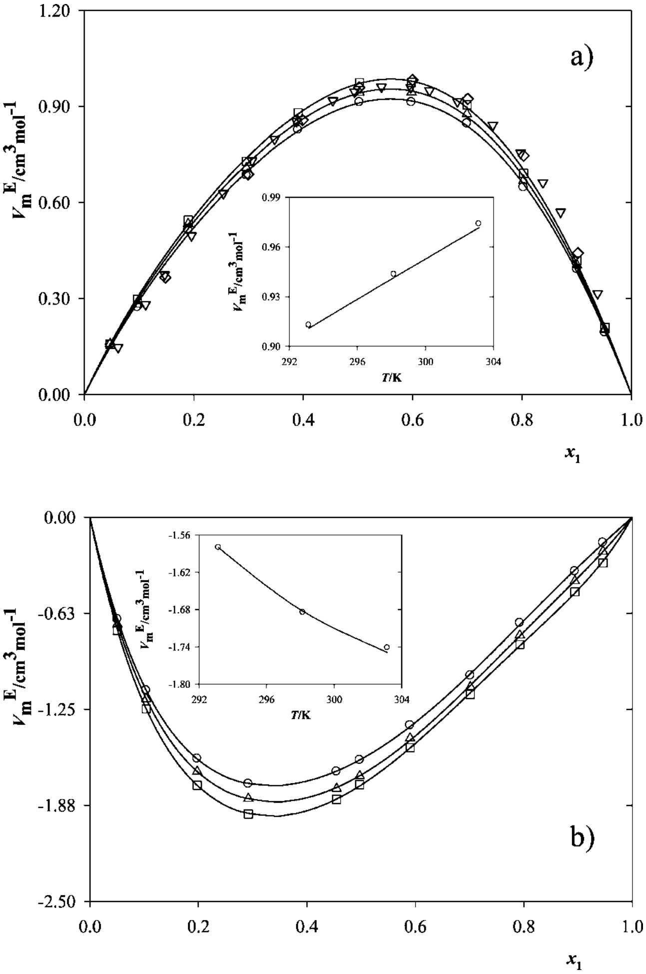

Figure 1. Excess molar volumes $V_{\mathrm{m}}^{\mathrm{E}}$ of the binary mixtures against mole fraction x_1 for: (a) hexane (1) + ethyl acetate (2): ○, T = 293.15 K; △, T = 298.15 K; ▽, ref 23; □, T = 303.15 K; ◇, ref 24. (b) HMIM PF$_6$ (1) + ethyl acetate (2): ○, T = 293.15 K; △, T = 298.15 K; □, T = 303.15 K. Inset figures: $V_{\mathrm{m}}^{\mathrm{E}}$ of the binary mixtures against the temperature at equimolar composition.

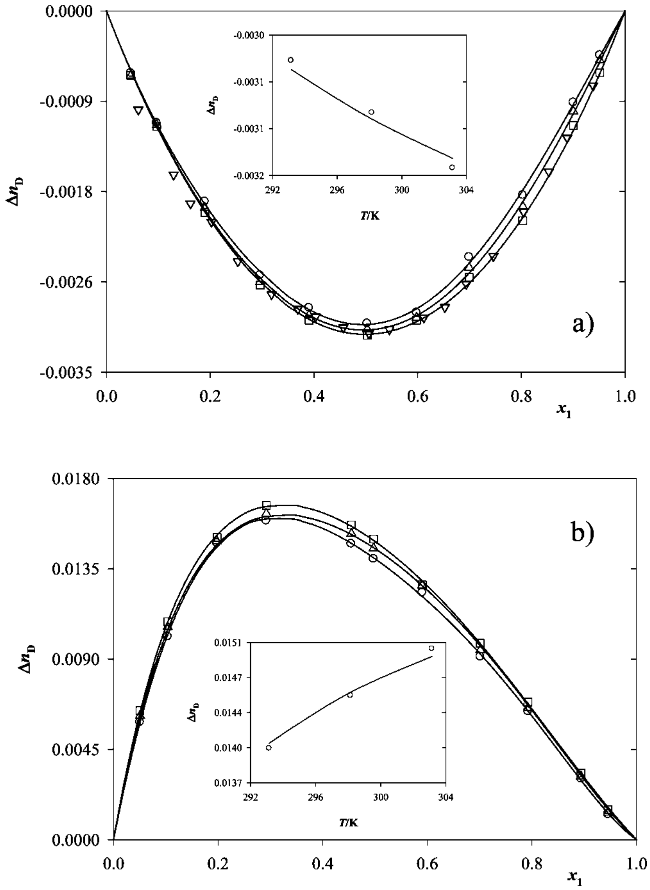

Figure 2. Changes of refractive indices on mixing Δn_{D} of the binary mixtures against mole fraction x_1 for (a) hexane (1) + ethyl acetate (2): ○, T = 293.15 K; △, T = 298.15 K; ▽, ref 23; □, T = 303.15 K. (b) HMIM PF$_6$ (1) + ethyl acetate (2): ○, T = 293.15 K; △, T = 298.15 K; □, T = 303.15 K. Inset figures: Δn_{D} of the binary mixtures against the temperature at equimolar composition.

Excess molar volumes for the binary mixtures hexane (1) + ethyl acetate (2) and HMIM PF$_6$ (1) + ethyl acetate (2) and the fitted curves from (293.15 to 303.15) K versus the mole fraction are shown in Figure 1. The comparison with literature[23,24] data is enclosed, and the results agree with the experimental data. Excess molar volumes are positive over the entire composition range for hexane (1) + ethyl acetate (2). However, opposite behavior is observed for the binary mixture HMIM PF$_6$ (1) + ethyl acetate (2).

On the other hand, changes of refractive index on mixing for the binary mixtures, plotted against mole fraction, together with the fitted curves at the studied temperatures are shown in Figure 2. These quantities are negative for hexane (1) + ethyl

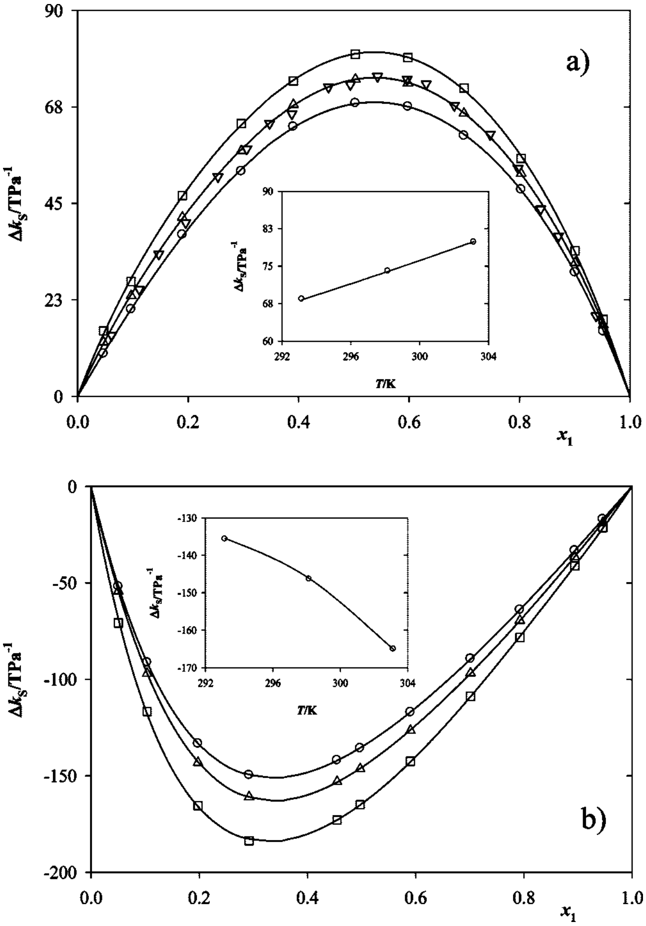

Figure 3. Deviations in isentropic compressibility $\Delta\kappa_S$ of the binary mixtures against mole fraction x_1 for (a) hexane (1) + ethyl acetate (2): ○, T = 293.15 K; △, T = 298.15 K; ▽, ref 23; □, T = 303.15 K. (b) HMIM PF_6 (1) + ethyl acetate (2): ○, T = 293.15 K; △, T = 298.15 K; □, T = 303.15 K. Inset figures: $\Delta\kappa_s$ of the binary mixtures against the temperature at equimolar composition.

acetate (2) and positive for HMIM PF_6 (1) + ethyl acetate (2) over the whole composition range. The deviations in isentropic compressibility show the same behavior as excess molar volumes over the entire composition range in Figure 3. The comparison with literature[23] data is enclosed.

A study of the temperature effect over the derived properties at equimolar composition of the binary mixtures is made, and the results are shown in Figures 1 to 3. When the temperature is increased for hexane (1) + ethyl acetate (2), the excess molar volumes and deviations in isentropic compressibilities increase, while the refractive index on mixing decreases. However, when we increase the temperature for HMIM PF_6 (1) + ethyl acetate (2), the behavior is opposite: the excess molar volumes and deviations in isentropic compressibilities decrease, whereas the changes in refractive index on mixing increase.

The composition of the experimental tie-line ends for the ternary mixtures of hexane (1) + ethyl acetate (2) + HMIM PF_6 (3) or OMIM PF_6 (3) at 298.15 K and atmospheric pressure are given in Table 3. The triangular diagrams with the experimental tie-lines for the systems are shown in Figure 4. These figures provide a visualization of the difference in the size of the immiscibility region, as well as the slopes of the tie-lines for the ternary systems. The positive slope shows that the solute (ethyl acetate) goes preferentially to the solvent-rich phase. For the case in which the IL is HMIM PF_6, the system shows solutropy;[25] that is, the sign of the tie-line slopes changes, becoming negative as the mole fraction of ethyl acetate becomes greater.

Table 3. Composition of the Experimental Tie-Lines, Solute Distribution Ratio β, and Selectivity S for the Ternary Systems at 298.15 K

organic-rich phase		ionic liquid-rich phase			
x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}	β	S
Hexane (1) + Ethyl Acetate (2) + HMIM PF_6 (3)					
0.940	0.060	0.019	0.218	3.66	186.19
0.877	0.123	0.033	0.302	2.45	66.01
0.816	0.184	0.039	0.384	2.08	43.06
0.743	0.258	0.051	0.415	1.61	23.62
0.648	0.352	0.064	0.482	1.37	13.96
0.582	0.417	0.076	0.520	1.25	9.57
0.501	0.498	0.091	0.578	1.16	6.37
0.427	0.571	0.108	0.631	1.11	4.40
0.371	0.626	0.111	0.658	1.05	3.52
0.326	0.670	0.125	0.675	1.01	2.63
0.286	0.710	0.134	0.696	0.98	2.10
0.244	0.747	0.141	0.720	0.96	1.68
0.193	0.782	0.159	0.745	0.95	1.16
Hexane (1) + Ethyl Acetate (2) + OMIM PF_6					
0.972	0.028	0.087	0.209	7.45	83.29
0.920	0.080	0.099	0.267	3.34	31.03
0.889	0.111	0.116	0.332	3.00	23.09
0.825	0.175	0.132	0.393	2.24	14.07
0.764	0.236	0.147	0.444	1.88	9.77
0.698	0.302	0.158	0.490	1.62	7.18
0.653	0.345	0.163	0.544	1.58	6.31
0.592	0.406	0.173	0.600	1.48	5.07
0.532	0.466	0.178	0.620	1.33	3.96
0.492	0.505	0.195	0.650	1.29	3.26
0.462	0.534	0.204	0.670	1.26	2.85
0.396	0.598	0.228	0.681	1.14	1.98
0.350	0.639	0.262	0.681	1.07	1.42

Values of solute distribution ratio β and selectivity S are shown in Table 3. These parameters are defined as follows

$$S=\left(\frac{x_1^{I}}{x_1^{II}}\right)\cdot\left(\frac{x_2^{II}}{x_2^{I}}\right) \tag{6}$$

$$\beta=\frac{x_2^{II}}{x_2^{I}} \tag{7}$$

where x is the mole fraction; subscripts 1 and 2 refer to hexane and ethyl acetate, respectively; and superscripts I and II refer to the organic and IL phases, respectively.

The values of the solute distribution ratio and selectivity for the studied ternary systems as a function of the solute composition in the organic phase are plotted in Figure 5. An important parameter assessing the efficiency of the IL in the selective extraction of the solute from the azeotropic system is the selectivity. All the selectivity values for all areas of the binodal curves are higher than the unit, from which it can be inferred that the extraction of the solute is indeed possible. A comparison between the selectivity values for the ternary system shows that the HMIM PF_6 obtains better values than OMIM PF_6 for the removal of hexane from its azeotropic mixture with ethyl acetate.

Liquid–Liquid Equilibria Correlation. The experimental data were correlated by means of the NRTL and UNIQUAC equations. For the NRTL model, the third randomness parameter α was optimized, and their values are reported in Table 4. The volume R_k and surface area Q_k parameters of the UNIQUAC equation were obtained from the literature.[26] In these equations,

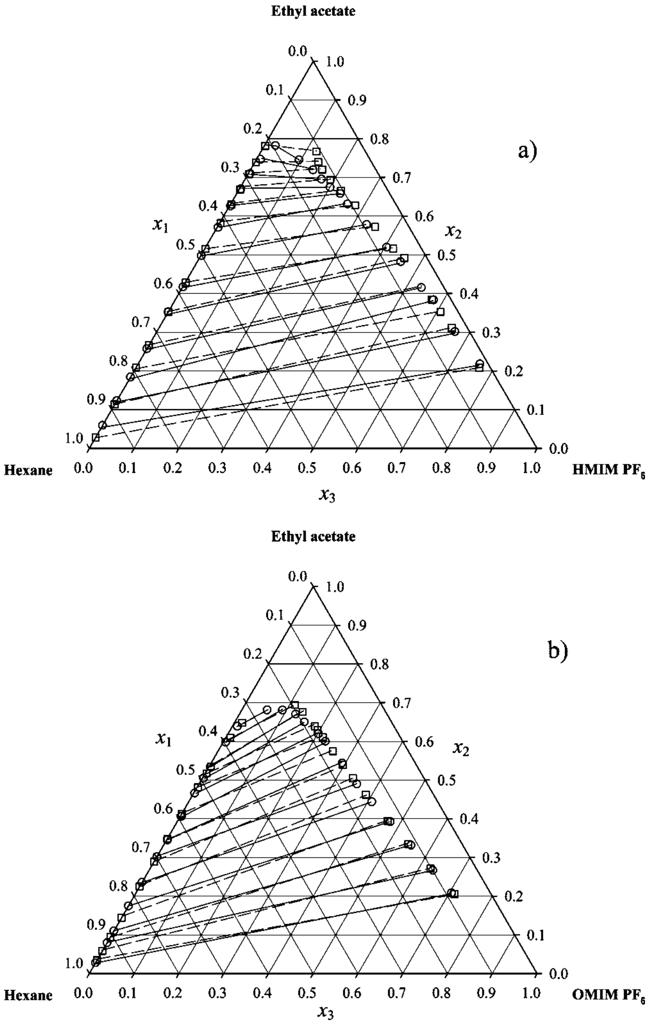

Figure 4. Experimental tie-lines of the ternary systems at 298.15 K (a) hexane (1) + ethyl acetate (2) + HMIM PF$_6$ (3): ○ and solid line, this work; □ and dashed line, UNIQUAC correlation. (b) Hexane (1) + ethyl acetate (2) + OMIM PF$_6$ (3): ○ and solid line, this work; □ and dashed line, NRTL correlation.

the adjustable parameter was defined as follows for NRTL and UNIQUAC, respectively

$$\tau_{ji} = \frac{\Delta g_{ij}}{R \cdot T} \tag{8}$$

$$\tau_{ji} = \exp\left(\frac{\Delta u_{ij}}{R \cdot T}\right) \tag{9}$$

The DISTILL 3.0 spreadsheet[27] was employed to minimize the difference between the experimental and calculated mole fraction defined as

$$\mathrm{OF} = \sum_{i=1}^{n} \left[\left(x_{1i}^{\mathrm{I}} - x_{1i}^{\mathrm{I}}(\mathrm{calcd})\right)^2 + \left(x_{2i}^{\mathrm{I}} - x_{2i}^{\mathrm{I}}(\mathrm{calcd})\right)^2 + \left(x_{1i}^{\mathrm{II}} - x_{1i}^{\mathrm{II}}(\mathrm{calcd})\right)^2 + \left(x_{2i}^{\mathrm{II}} - x_{2i}^{\mathrm{II}}(\mathrm{calcd})\right)^2\right] \tag{10}$$

where x_{1i}^{I}, x_{2i}^{I}, x_{1i}^{II}, and x_{2i}^{II} are the experimental mole fractions; $x_{1i}^{\mathrm{I}}(\mathrm{calcd})$, $x_{2i}^{\mathrm{I}}(\mathrm{calcd})$, $x_{1i}^{\mathrm{II}}(\mathrm{calcd})$, and $x_{2i}^{\mathrm{II}}(\mathrm{calcd})$ are the calculated mole fractions; and superscripts org-phase and IL-phase indicate the organic and IL phases, respectively.

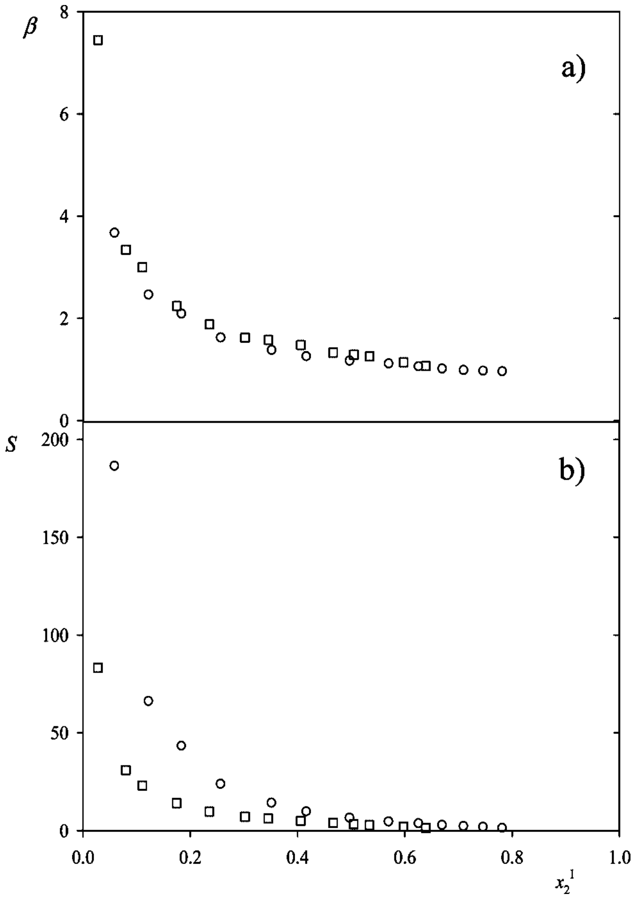

Figure 5. Solute distribution ratio β and selectivity S of the systems presenting azeotrope hexane (1) + ethyl acetate (2) with: ○, HMIM PF$_6$ and □, OMIM PF$_6$ versus ethyl acetate mole fraction in the organic phases at 298.15 K.

Table 4. Fitting Parameters and Root-Mean-Square Deviation of the LLE Data by Means of the NRTL Equation

system	ij	Δg_{ij} / J·mol^{-1}	Δg_{ji} / J·mol^{-1}	α	σ
hexane (1) +	12	2093.9	2802.1	0.33	0.062
ethyl acetate (2) +	13	12756	13331		
HMIM PF$_6$ (3)	23	2233.7	1072918		
hexane (1) +	12	−3443.2	5532.0	0.15	0.019
ethyl acetate (2) +	13	6871.4	48822		
OMIM PF$_6$ (3)	23	−10365	16712		

Table 5. Fitting Parameters and Root-Mean-Square Deviation of the LLE Data by Means of the UNIQUAC Equation

system	ij	Δu_{ij} / J·mol^{-1}	Δu_{ji} / J·mol^{-1}	σ
hexane (1) +	12	−2064.8	5032.5	0.018
ethyl acetate (2) +	13	233.52	6178.5	
HMIM PF$_6$ (3)	23	−2669.9	5578.5	
hexane (1) +	12	177416	−47106	0.028
ethyl acetate (2) +	13	330.65	4568.2	
OMIM PF$_6$ (3)	23	−46126	93.562	

The fitting parameters of the equation are listed in Tables 4 and 5 together with the standard deviations. These deviations were calculated by applying the following expression

$$\sigma = \left(\frac{\sum_i \left(x_{ilm}^{\mathrm{expt}} - x_{ilm}^{\mathrm{calcd}}\right)^2}{6k}\right)^{1/2} \tag{11}$$

where x is the mole fraction and the subscripts i, l, and m provide the component, the phase, and the tie-line, respectively. The k

value refers to the number of interaction components.

A comparison between the experimental data and the values obtained from the best correlation are shown in Figure 4. A view of the standard deviation indicates that the UNIQUAC model is more adequately able to correlate the immiscible region of these mixtures. The better correlation results were obtained for OMIM PF_6 than for HMIM PF_6, especially with high ethyl acetate compositions where the correlation models do not accurately correlate the experimental data. This behavior was also found for other solutropic mixtures in the literature.[28]

Conclusions

Experimental research has been focused on the study of the liquid−liquid extraction using two ILs as solvents. Density, refractive index, and speed of sound as a function of the temperature for the binary mixtures ethyl acetate with hexane or HMIM PF_6 were presented, as they are necessary to determine the liquid−liquid equilibria. The binary mixture HMIM PF_6 with ethyl acetate exhibits negative excess molar volume values due to the interactions between the IL and ethyl acetate being stronger than those between hexane and ethyl acetate ones.

The equilibrium behavior of the mixtures of hexane + ethyl acetate + HMIM PF_6 or OMIM PF_6 was carried out at 298.15 K and atmospheric pressure. Experimental liquid−liquid equilibria data were compared with the ones obtained by means of the NRTL and UNIQUAC equations. The results show that the best correlation equation is the UNIQUAC model. The use of HMIM PF_6 as solvent leads to higher values of selectivity than the OMIM PF_6, and it indicates that the alkyl chain (R) length of the imidazolium ring plays a negative role in the capability of the RMIM PF_6 to act as an azeotrope breaker in liquid−liquid extraction.

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