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Ternary Liquid−Liquid Equilibria Ethanol + 2-Butanone + 1-Butyl-3-methylimidazolium Hexafluorophosphate, 2-Propanol + 2-Butanone + 1-Butyl-3-methylimidazolium Hexafluorophosphate, and 2-Butanone + 2-Propanol + 1,3-Dimethylimidazolium Methyl Sulfate at 298.15 K

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This research is focused on a study of the ionic liquid as a solvent in liquid−liquid extraction of azeotropic mixtures. Liquid−liquid equilibria (LLE) were determined for the ternary systems ethanol + 2-butanone + 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), 2-propanol + 2-butanone + [BMIM][PF_6], and 2-butanone + 2-propanol + 1,3-dimethylimidazolium methyl sulfate ([MMIM][$MeSO_4$]) at 298.15 K and atmospheric pressure. Selectivity and distribution ratio values, derived from the tie lines data, were calculated. Experimental LLE data were correlated by means of the nonrandom two-liquid, Othmer−Tobias, and Hand equations. The plait point compositions have been calculated by the Hand method.

Introduction

Traditionally, 2-butanone has been used as a solvent in paints and resin adhesives. A mixture of different alcohols with this ketone that form azeotropes is a very common product. Therefore, the purification of the ketone and recovery of the alcohol for recycling is usually impracticable by distillation. Given the wide diversity of alcohol + ketone mixtures, the study of the binary mixtures ethanol or 2-propanol with 2-butanone was considered.

At present, the separation of the azeotropic mixtures is made by azeotropic distillation[1−2] using as entrainers amyl acetate, methyl formate, 2,2-dimethyl butane, or 2,3-dimethyl butane for ethanol + 2-butanone and 3-methylpentane, amyl ether and acetonitrile for 2-propanol + 2-butanone. Liquid−liquid extraction[3−4] is one of the alternative separation processes preferred instead of distillation.

In this paper, the evaluation of two ionic liquids (ILs) as potential solvents in liquid−liquid extraction for the recovery of alcohols from 2-butanone through the analysis of liquid−liquid equilibria (LLE) data was carried out. These ILs have been selected because they have relatively low viscosity, are less expensive than other ILs, and have a thermodynamically favorable behavior for the separation of these mixtures that form azeotropes.

Ternary LLE of ethanol + 2-butanone + 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), 2-propanol + 2-butanone + [BMIM][PF_6], and 2-butanone + 2-propanol + 1,3-dimethylimidazolium methyl sulfate ([MMIM][$MeSO_4$]) at 298.15 K and atmospheric pressure were determined.

Ternary data were correlated by applying the nonrandom two-liquid (NRTL),[5] Othmer−Tobias[6,] and Hand[7] equations. The plait point compositions were calculated by the Hand method.[7] The selectivity values for the studied ternary systems were determined to investigate the possibility of using these ILs as solvents in liquid extraction processes. A comparison with other solvents has been made and the results are discussed.

Experimental Section

Chemicals. The chemicals were supplied by Merck for ethanol, 2-butanone, and 2-propanol (99.8 %, 99.5 %, and 99.7 % mass fraction, respectively). Chromatographic tests of the solvents showed purities that fulfilled purchaser specifications. 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 supplied by Green Solutions Chemicals S. L. with a certified purity higher than 98 % mass fraction. To reduce the water content to negligible values (mass fraction lower than 0.03 %, determined using a 756 Karl Fisher coulometer), vacuum ($2{\cdot}10^{-1}$ Pa) was applied to the ILs (to the [MMIM][$MeSO_4$] moderate temperature, 343.15 K, were also applied) for several days, always immediately prior to their use, and submitted to NMR and Positive fast atom bombardment mass spectrometry (FABMS) (FISONS VG AUTOSPEC mass spectrometer) to determine its purity. The density and the refractive index of the chemicals together with recent literature[8−14] values are presented in Table 1.

Experimental Procedure. 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. The uncertainty of the phase composition was estimated to be ± 0.005 in mole fraction. The samples were prepared by filling glass vials with the IL and the organic compound. Vials were closed with screw caps to ensure a secure seal and were flushed with dry argon to prevent water adsorption. The sample was taken from the vial with a syringe through a silicone septum and was immediately put into the densimeter and refractometer. 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 $\pm 10^{-4}$ in mole fraction.

The density of the pure liquids and the binary mixtures was measured with an Anton Paar DSA-48 digital vibrating tube densimeter. The uncertainty in the measurement of the samples was $\pm 2{\cdot}10^{-4}$ $g{\cdot}cm^{-3}$. The apparatus was calibrated by

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

component	ρ/g·cm^{-3} exptl	ρ/g·cm^{-3} lit	n_D exptl	n_D lit
ethanol	0.7851	0.78517[a]	1.35929	1.35924[a]
2-butanone	0.7997	0.79974[b]	1.37618	1.37685[c]
2-propanol	0.7810	0.7810[d]	1.37496	1.3752[d]
[BMIM][PF$_6$]	1.3673	1.36745[e]	1.40937	1.40925[f]
[MMIM][MeSO$_4$]	1.3272	1.328[g]	1.48270	na[h]

[a] Ref 8. [b] Ref 9. [c] Ref 10. [d] Ref 11. [e] Ref 12. [f] Ref 13. [g] Ref 14. [h] na (not available).

measuring the density of Millipore quality water and ambient air according to instructions.

The refractive indices were determined by the automatic refractometer ABBEMAT-WR Dr. Kernchen with an uncertainty in the experimental measurements of ± 4·10^{-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.

To determine the composition of the coexisting phase, the density and refractive index of the ternary mixtures were determined at 298.15 K.

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. Special care was taken to prevent the moisture. The vessel was sealed and flushed with dry argon. 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 50 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 in 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 (2-butanone or 2-propanol) maintaining the stirring till the "cloud point".

Results and Discussion

The compositions of the experimental tie-line ends for the ternary mixtures of ethanol + 2-butanone + [BMIM][PF$_6$], 2-propanol + 2-butanone + [BMIM][PF$_6$], and 2-butanone + 2-propanol + [MMIM][MeSO$_4$] at 298.15 K and atmospheric pressure are given in Table 2. The triangular diagrams with the experimental tie-lines for the systems are shown in Figure 1. These diagrams 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. A comparison of the ternary LLE data shows that the immiscibility area increases in changing ethanol by 2-propanol in the system 2-butanone + [BMIM]-[PF$_6$], and decreases slightly when the IL is changed from the [BMIM][PF$_6$] to [MMIM][MeSO$_4$] for 2-propanol + 2-butanone. In this mixture, [BMIM][PF$_6$] is miscible in the ketone and immiscible in the alcohol. An opposite behavior is observed in the [MMIM][MeSO$_4$], which is miscible in the alcohol and immiscible in the ketone. In contrast, the slopes for the tie-lines of this ternary mixture involving [MMIM][MeSO$_4$] are negative.

Table 2. 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
ethanol (1) + 2-butanone (2) + [BMIM][PF$_6$] (3)					
0.973	0.019	0.533	0.025	1.33	2.42
0.965	0.024	0.543	0.041	1.68	2.99
0.957	0.031	0.568	0.054	1.78	3.00
0.946	0.037	0.585	0.067	1.79	2.90
0.910	0.062	0.647	0.087	1.40	1.96
0.869	0.076	0.718	0.104	1.36	1.64
2-propanol (1) + 2-butanone (2) + [BMIM][PF$_6$] (3)					
0.967	0.033	0.344	0.041	1.27	3.58
0.949	0.049	0.347	0.070	1.43	3.93
0.938	0.059	0.351	0.104	1.76	4.71
0.928	0.069	0.355	0.131	1.90	4.97
0.910	0.086	0.362	0.165	1.92	4.83
0.889	0.105	0.365	0.179	1.70	4.14
0.871	0.122	0.376	0.218	1.80	4.16
0.851	0.140	0.407	0.243	1.73	3.61
0.821	0.159	0.435	0.273	1.71	3.23
0.776	0.185	0.489	0.280	1.51	2.40
0.718	0.221	0.561	0.281	1.27	1.63
2-butanone (1) + 2-propanol (2) + [MMIM][MeSO$_4$] (3)					
0.936	0.058	0.290	0.025	0.42	1.36
0.878	0.112	0.294	0.058	0.51	1.53
0.835	0.153	0.314	0.084	0.55	1.46
0.810	0.172	0.337	0.110	0.64	1.53
0.778	0.189	0.365	0.145	0.77	1.63
0.730	0.207	0.424	0.174	0.84	1.45
0.687	0.220	0.494	0.204	0.93	1.29

Values of solute distribution ratio β and selectivity *S* are shown in Table 2. These parameters are defined as follows:

$$S = \left(\frac{x_1^{I}}{x_1^{II}}\right)\left(\frac{x_2^{II}}{x_2^{I}}\right) \tag{1}$$

$$\beta = \frac{x_2^{II}}{x_2^{I}} \tag{2}$$

where x is the mole fraction, subscripts 1 and 2 refer to first (inert) and second component (solute), respectively, and superscripts I and II indicate the organic (raffinate) and IL (extract) phases, respectively.

The values of the selectivity for the studied ternary systems as a function of the solute composition in the organic phase are plotted in Figure 2. A comparison with conventional organic extractive solvents[15−16] and other IL[17] was made and also plotted.

An important parameter in 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 from the azeotropic system is indeed possible. A comparison between the selectivity values for the ternary system shows that the [MMIM][MeSO$_4$] obtains higher values than [BMIM][PF$_6$] for the ethanol + 2-butanone and the opposite behavior is observed for 2-propanol + 2-butanone. In Figure 2a, the values at low concentration of ethanol for the separation of the ethanol + 2-butanone are similar in the [MMIM][MeSO$_4$] and glycerol and higher than they are in water and [BMIM][PF$_6$]. On the other hand, for 2-propanol + 2-butanone, the selectivity values

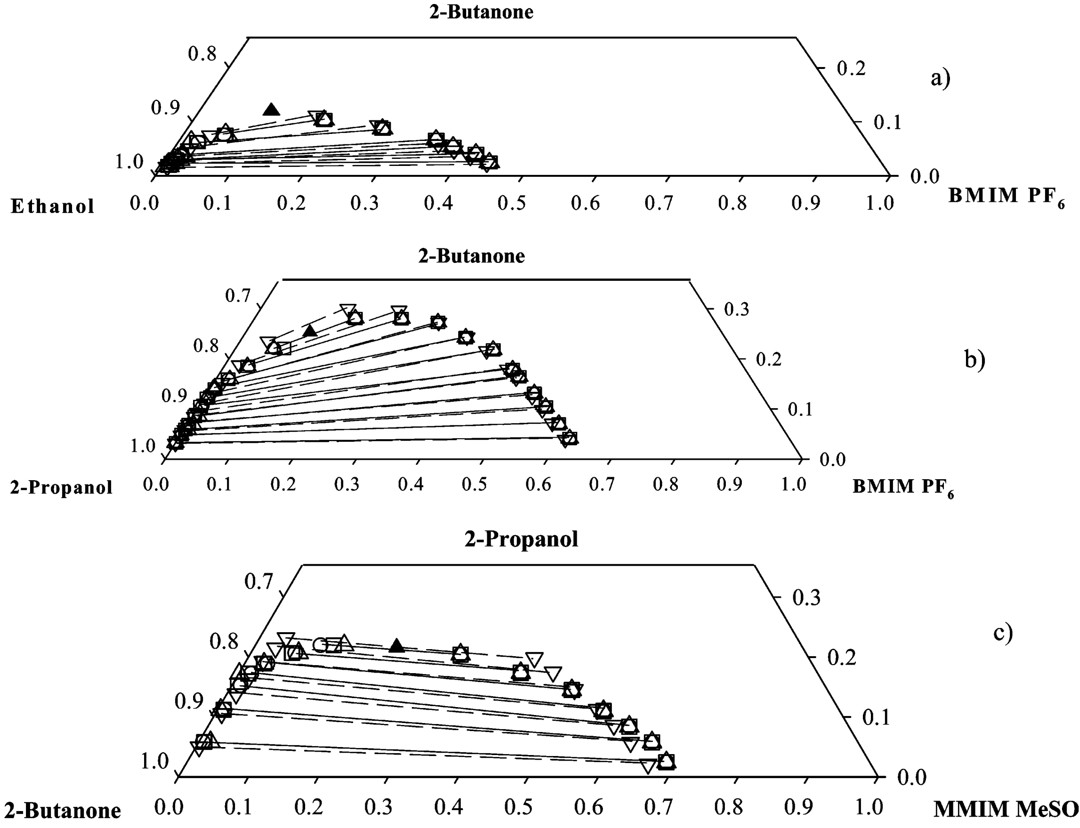

Figure 1. Experimental tie-lines of the ternary systems: (a) ethanol (1) + 2-butanone (2) + [BMIM][PF$_6$] (3); (b) 2-propanol (1) + 2-butanone (2) + [BMIM][PF$_6$] (3); (c) 2-butanone (1) + 2-propanol (2) + [MMIM][MeSO$_4$] (3) at 298.15 K: ○ and solid line, this work; ▽ and dashed line, NRTL correlation; □, △ Othmer−Tobias and Hand correlations, respectively; ▲, plait point with Hand method.

of the [BMIM][PF$_6$] are higher than for the other solvents and IL.

Liquid−Liquid Equilibria Correlation. The experimental data were correlated by means of the NRTL equation despite being a model initially developed for nonelectrolyte solutions. However, literature works confirm that the equation can correlate satisfactorily LLE data involving electrolytes as ILs.[17−21]

The activity coefficients were calculated by the equation

$$\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l}\left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj} x_l}\right) \qquad (3)$$

where

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \qquad (4)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \qquad (5)$$

where x is the mole fraction, $g_{ji} - g_{ii}$ are the fitting parameters, and the nonrandomness parameter $\alpha_{ji} = \alpha_{ij} = \alpha$ was fixed at 0.3 and was not optimized. The DISTILL 3.0 spreadsheet[22] was employed to minimize the difference between the experimental and calculated mole fraction defined as

$$\text{O.F.} = \sum_{i=1}^{n} [(x_{1i}^{\text{I}} - x_{1i}^{\text{I}}(\text{calc}))^2 + (x_{2i}^{\text{I}} - x_{2i}^{\text{I}}(\text{calc}))^2 + (x_{1i}^{\text{II}} - x_{1i}^{\text{II}}(\text{calc}))^2 + (x_{2i}^{\text{II}} - x_{2i}^{\text{II}}(\text{calc}))^2] \qquad (6)$$

Table 3. Fitting Parameters and Root-Mean-Square Deviation of the LLE Data by Means of the NRTL Equation

system	ij	$g_{ij} - g_{jj}$ J·mol^{-1}	$g_{ji} - g_{ii}$ J·mol^{-1}	σ
ethanol (1) + 2-butanone (2) + [BMIM][PF$_6$] (3)	12	−3950.16	7278.75	0.008
	13	−631.495	13039.9	
	23	1239917	−1603.35	
2-propanol (1) + 2-butanone (2) + [BMIM][PF$_6$] (3)	12	−377.577	4235.91	0.008
	13	2334.56	18108.9	
	23	626496	1868.51	
2-butanone (1) + 2-propanol (2) + [MMIM][MeSO$_4$] (3)	12	−3470.75	−122487	0.022
	13	1480.07	13486.6	
	23	−124532	3307.58	

where x_{1i}^{I}, x_{2i}^{I}, x_{1i}^{II}, x_{2i}^{II} are the experimental mole fraction; $x_{1i}^{\text{I}}(\text{calc})$, $x_{2i}^{\text{I}}(\text{calc})$, $x_{1i}^{\text{II}}(\text{calc})$, and $x_{2i}^{\text{II}}(\text{calc})$ are the calculated mole fraction; and superscripts I and II indicate the organic (raffinate) and IL (extract) phases, respectively.

The fitting parameters of the equation are listed in Table 3 together with the standard deviations. These deviations were calculated by applying the following expression

$$\sigma = \left(\frac{\sum_{i} (x_{ilm}^{\text{exp}} - x_{ilm}^{\text{calc}})^2}{6k} \right)^{1/2} \qquad (7)$$

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.

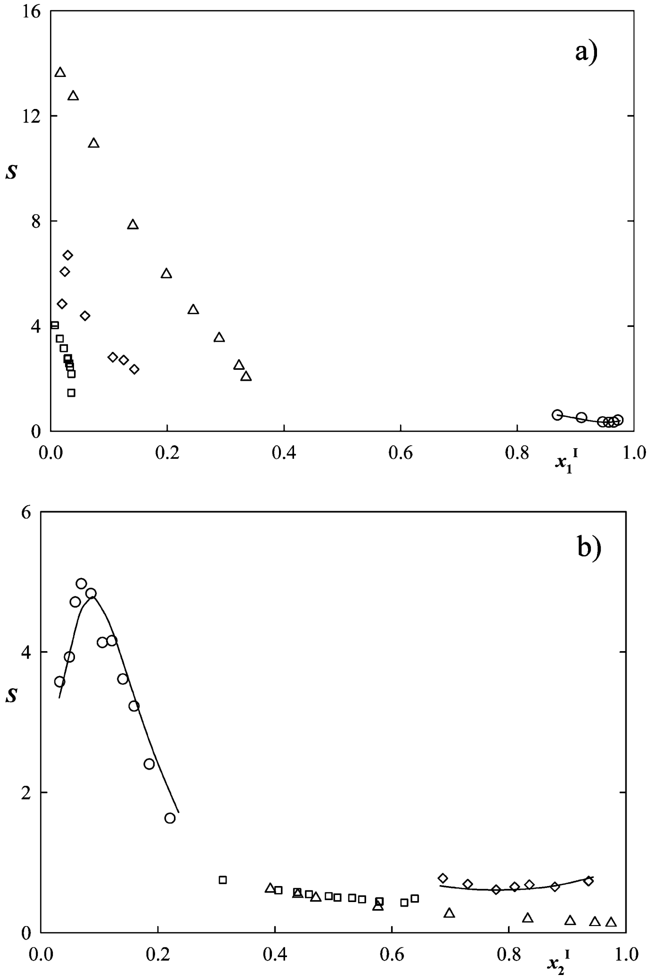

Figure 2. Selectivity S of the systems presenting azeotrope: (a) ethanol (1) + 2-butanone (2); (b) 2-propanol (1) + 2-butanone (2) with ○, [BMIM]-[PF$_6$], this work; △, glycerol (ref 15); □, water (ref 16); ◇, [MMIM][MeSO$_4$] (panel a, ref 17 and panel b, this work); solid line, NRTL correlation as a function of the solute mole fraction (ethanol or 2-butanone) in the organic phases at 298.15 K.

Table 4. Constants of Othmer−Tobias and Hand Equations and Root-Mean-Square Deviation σ at 298.15 K

	a	b	σ
Othmer−Tobias			
ethanol (1) + 2-butanone (2) + [BMIM][PF$_6$] (3)	0.0887	0.7327	0.014
2-propanol (1) + 2-butanone (2) + [BMIM][PF$_6$] (3)	0.0979	0.7806	0.044
2-butanone (1) + 2-propanol (2) + [MMIM][MeSO$_4$] (3)	−0.0847	0.7098	0.065
Hand			
ethanol (1) + 2-butanone (2) + [BMIM][PF$_6$] (3)	0.3693	1.4205	0.031
2-propanol (1) + 2-butanone (2) + [BMIM][PF$_6$] (3)	0.2815	1.4542	0.022
2-butanone (1) + 2-propanol (2) + [MMIM][MeSO$_4$] (3)	0.1370	1.7224	0.051

A comparison between the experimental data and the values obtained from the correlation by the NRTL equation are shown in Figures 1 and 2. In these figures, the NRTL equation successfully correlated the data of the ternary mixtures.

The reliability of experimental measured tie-line data is ascertained by applying the Othmer−Tobias and Hand correlations for each studied system as the following equations show:

$$\log\left(\frac{1-w_3^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right) = a + b\log\left(\frac{1-w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) \tag{8}$$

$$\log\left(\frac{w_2^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right) = a + b\log\left(\frac{w_2^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) \tag{9}$$

where a and b are the fitting parameters, w is the mass fraction, subscripts 1, 2, and 3 refer to first component (inert), second component (solute) and the IL, respectively, and superscripts I and II indicate the organic (raffinate) and IL (extract) phases, respectively. These correlations relate the tie-lines concentration of the top phase with the bottom phase to obtain a linear function. In Table 4, the fitting parameters and the standard deviations for the ternary systems are shown. The deviations were calculated by applying the following expression:

$$\sigma = \left(\frac{\sum_i^{n_{\mathrm{DAT}}} (z_{\mathrm{exp}} - z_{\mathrm{pred}})^2}{n_{\mathrm{DAT}}}\right)^{1/2} \tag{10}$$

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

The correlation factor values were all very close to the unit, revealing the degree of consistency of the related data. Taking into account Table 4 data, the Hand correlation makes a better description of these systems than Othmer−Tobias as shown in σ values. Othmer−Tobias correlation does not include the distributed component (solute), which could have led to inferior results respect to those obtained through Hand correlation.

Plait point values of the ternary systems have been obtained from the Hand method and are shown in Figure 1. The plait point compositions are $x_1 = 0.781$ and $x_2 = 0.120$ for ethanol + 2-butanone + [BMIM][PF$_6$], $x_1 = 0.646$ and $x_2 = 0.253$ for 2-propanol + 2-butanone + [BMIM][PF$_6$], and $x_1 = 0.580$ and $x_2 = 0.216$ for 2-butanone + 2-propanol + [MMIM][MeSO$_4$].

In Figure 1, a comparison between the experimental data and the ones obtained from the Othmer−Tobias and Hand correlations are shown. Both correlative equations are similar for experimental data and are better than using the NTRL equation.

Conclusions

This research has focused on a comparative study of two different ILs as solvents in liquid−liquid extraction. Binodal curves and the tie lines were obtained for the mixtures of ethanol + 2-butanone + [BMIM][PF$_6$], 2-propanol + 2-butanone + [BMIM][PF$_6$], and 2-butanone + 2-propanol + [MMIM]-[MeSO$_4$] at 298.15 K and atmospheric pressure. Experimental LLE data were compared with the ones obtained by means of the NRTL, Othmer−Tobias and Hand equations. These models correlate the experimental data satisfactorily. The selectivity values for the azeotrope ethanol + 2-butanone were higher for the [MMIM][MeSO$_4$] than for the [BMIM][PF$_6$], indicating that it would be a better choice as solvent in this separation process. The opposite behavior is observed in the selection of the solvent in the separation of the azeotrope 2-propanol + 2-butanone, where the [BMIM][PF$_6$] is the best solvent. Nevertheless in the last years, the ILs based on the PF$_6^-$ anion have been weakened because they can degrade in the presence of water[23] and at high temperatures[24] leading to the formation of HF; consequently the application of the hexafluorophosphate ILs is restricted to those under water-free conditions and moderate temperatures as in this separation.

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