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Purification of ethyl *tert*-butyl ether from its mixtures with ethanol by using an ionic liquid

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Abstract

In the last years, ionic liquids have emerged as a new class of compounds with negligible vapour pressure and excellent solvation properties, thus avoiding atmospheric contamination and flammable substances handling. Therefore, we can label ionic liquids as *green solvents*, constituting a very reliable alternative to traditional solvents. In this work, our aim was to investigate the possibility of using a well-known ionic liquid, 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][OTf]), as solvent in extraction processes for the ethanol removal from its mixtures with ETBE. Hence, the experimental determination of the liquid–liquid equilibrium (LLE) for the ternary system ETBE + ethanol + [bmim][OTf] at 298.15 K was carried out. The correlation of LLE experimental data is commonly desirable as it allows the interpolation of tie-lines in the immiscible region of the system. The NRTL equation, a classical correlation model, was verified to accurately correlate the experimental data, even though it was not originally developed for systems containing electrolytes.

Keywords: LLE; ETBE; Ionic liquid

1. Introduction

Since the prohibition in many countries of lead derivates as additives for gasolines during the last decades, due to health and environmental reasons, oxygenated compounds like, e.g. ethers are used to enhance the octane index. In a first moment, methyl *tert*-butyl ether (MTBE) was prolifically used to replace tetraethyl lead [1]. But its replacement by ETBE is nowadays being promoted due to the detection of several cases of environmental contamination caused by MTBE. Thus, ETBE is called to become the most widely used octane booster on gasoline blending.

ETBE is mainly produced at an industrial scale by reaction of isobutene with an excess of ethanol. Thus, non-reacted ethanol comes alone with the ETBE. Downstream stages are then required to obtain the ETBE with an acceptable level of purity. This purification is typically carried out by distillation or liquid extraction. Liquid extraction processes present a series of advantages, but selection is conditioned to the existence of a suitable and accessible solvent. The most largely used solvent in industrial environments to perform liquid extraction of alcohols from ethers is water, partially due to its relatively low cost.

In the recent years, the scientific community has been paying an increasing attention to a family of compounds with very unique properties: ionic liquids. They are usually defined as ionic substances containing an organic cation and having a melting point below 100 °C [2]. They present a negligible vapour pressure, an excellent capability for solvating organic and inorganic compounds, a wide liquid range in the vicinity of room temperature and the possibility of tuning their anion or cation in order to modify their properties to achieve particular objectives, most of them (particularly the recently developed ones) being air and moisture stable [3,4]. Hence, these substances present a set of characteristics of great interest in many different backgrounds which invite us to use them as new and environmentally benign solvents.

Up to date, several authors have explored the use of ionic liquids in liquid extraction. Most works in this way report either a liquid–liquid equilibrium (LLE) for binary systems, solubility curves for ternary systems, or distribution ratios of different solutes in mixtures of two immiscible solvents, one of them being the ionic liquid. However, rather few works in the open literature include LLE data for ternary systems [5–9], despite

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their capital role as a chemical engineering tool in the design of extraction equipments. Concretely, LLE diagrams developed are mainly related to the separation of aromatic and aliphatic hydrocarbons, or alcohols and linear hydrocarbons. Recently, our group has published data concerning the extraction of ethanol from a tertiary ether—the *tert*-amyl ethyl ether [10,11]. In this paper, we continue with our research obtaining similar data for the removal of ethanol from ETBE, one of the major current octane boosters on gasoline blending.

1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][OTf]) was selected as the solvent because of its suitable density and viscosity, the possibility of synthesizing it by a halide-free method and its hydrophilic nature [12], in contrast with the hydrophobicity presented by ETBE. Therefore, the LLE for the ternary system ETBE + ethanol + [bmim] [OTf] at 298.15 K has been studied in this work.

2. Experimental

The main chemicals used in this work are listed in Table 1. ETBE with a purity of 99.4%, checked by gas chromatography, was obtained from the Department of Chemical Engineering of the University of Barcelona, Spain. Ethanol with a nominal purity of 99.9% was purchased from Merck, as well as the ionic liquid [bmim][OTf], whose nominal purity was claimed to be greater than 99%. In order to assess their validity, densities and refractive indices of these products were measured with an Anton Paar DMA 60-602 densimeter and an ATAGO RX-5000 refractometer, precise to $\pm 1 \times 10^{-5}$ g cm^{-3} and $\pm 4 \times 10^{-5}$, respectively. The characterization of the compounds used in this work was complemented with the measurement of the water content, determined by means of a Karl–Fischer titration method, carried out in a Metrohm 737 KF coulometer. All these data, which confirm the suitability of our chemicals to get accurate and reliable researching results, are summarized along with published values [13–15] in Table 1.

For the tie-lines' experimental determination, ternary mixtures (or binary, for the pair ETBE/[bmim][OTf]) with compositions lying on the immiscible region of the system were introduced inside glass vials, covered by open-top lids sealed with combined silicone/Teflon septa. These vials were placed into a thermostatic bath with a coupled magnetic multi-stirring plate, which was used to stir the samples and to keep them at a constant temperature (checked by means of a Heraeus Quat 100 thermometer with an accuracy of $\pm 1 \times 10^{-2}$ K). All the mixtures were vigorously stirred for at least 1 h and then allowed to settle for no less than 4 h to ensure equilibrium state. Preliminary tests showed this time was enough to obtain equilibrium. Finally, a sample of each layer was withdrawn using glass syringes with coupled stainless steel needles.

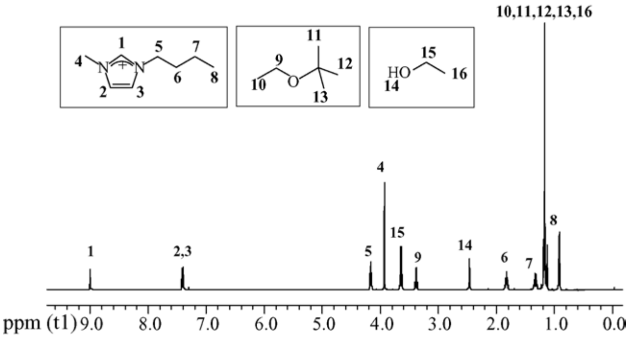

Fig. 1. Typical NMR spectrum of a ternary mixture, structure of the molecules and peak assignment.

Nuclear magnetic resonance (NMR) spectroscopy was selected to determine the composition of the samples. Thus, a drop of each sample was dissolved in ca. 0.5 mL of $CDCl_3$ (Aldrich, 99.8 at.% D, stabilized with 0.5 wt.% silver foil) and placed inside NMR-tubes which were properly sealed. The spectrometer used to perform the analysis was a 11.74 T (500 MHz resonance for ^{1}H) and shielded magnet Bruker DRX-500.

First, this technique was tested to be quantitative. Samples of known composition were prepared by mass using a Mettler Toledo AT261 (precise to within $\pm 10^{-4}$ g). A drop of these samples was dissolved in ca. 0.5 mL of $CDCl_3$ and introduced into the NMR-tubes. Then the analysis were performed on the NMR spectrometer, with 32 scans and a relaxation time of 25 s. Fig. 1 shows a typical ^{1}H NMR spectrum of the ternary system, the structure of the molecules and the correspondence between hydrogen positions and peaks. Only peak 9 for ETBE and peak 15 for ethanol, both corresponding to two hydrogens, were suitable for integration (see Fig. 1). Peaks 4 (two hydrogens) and 5 (three hydrogens) were integrated and the pondered average value calculated for [bmim][OTf]. Peaks areas are proportional to hydrogen moles associated to the referred peak. Thus, dividing the peak area by the number of hydrogen atoms we obtain an area proportional to the moles of the referred component. Finally, the molar fraction is obtained by dividing this last area by the summation of the areas of the three components. In this way, calculated compositions are independent of sample size. Plots of calculated compositions against real compositions (calculated by weight) were done. The standard deviations of the fits, in molar fraction, were found to be 0.003 for ETBE and 0.002 for ethanol and the ionic liquid, the largest overall deviation being 0.005.

Table 1
Water content, density (ρ) and refractive index (n_D) of the pure components of the ternary system studied in this work, at 298.15 K and atmospheric pressure

Component	CAS number	Water content (%)	ρ/(g cm^{-3})		n_D	
			Experimental	Literature	Experimental	Literature
ETBE	637-92-3	0.14	0.73551	0.7350 [13]	1.37298	1.3730 [14]
Ethanol	64-17-5	0.04	0.78509	0.78493 [15]	1.35923	1.35941 [15]
[bmim][OTf]	174899-66-2	0.03	1.29868	Not found	1.43737	Not found

3. Results and discussion

The measured compositions of the experimental tie-lines' ends for the ternary system ETBE + ethanol + [bmim] [OTf] are reported in Table 2, together with the corresponding values of solute distribution ratio (β) and selectivity (S). These parameters are defined as:

$$\beta = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \quad (1)$$

$$S = \frac{x_1^{\mathrm{I}}}{x_1^{\mathrm{II}}} \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \quad (2)$$

where x is the molar composition, subscripts 1 and 2 refer to ETBE (inert) and ethanol (solute) and superscripts I and II indicate the organic-rich-phase and the solvent-rich-phase, respectively.

A triangular diagram containing the experimental data is presented in Fig. 2, thus providing a clear visualization of the shape and dimensions of the immiscibility region, as well as the slopes of the tie-lines.

Table 2

Composition of the experimental tie-line ends, solute distribution ratio (β) and selectivity (S) for the system ETBE + ethanol + [bmim] [OTf] at 298.15 K, being x_1, x_2 and x_3 the mole fractions of ETBE, ethanol and the ionic liquid, respectively

Organic phase			Ionic liquid phase			β	S
x_1	x_2	x_3	x_1	x_2	x_3		
1.000	0.000	0.000	0.160	0.000	0.840	–	–
0.958	0.042	0.000	0.161	0.144	0.695	3.40	20.28
0.934	0.066	0.000	0.148	0.234	0.618	3.54	22.35
0.898	0.102	0.000	0.167	0.315	0.518	3.10	16.69
0.842	0.158	0.000	0.179	0.377	0.444	2.38	11.18
0.752	0.248	0.000	0.221	0.460	0.319	1.85	6.31
0.676	0.322	0.002	0.261	0.505	0.234	1.57	4.06
0.565	0.412	0.023	0.342	0.519	0.139	1.26	2.09

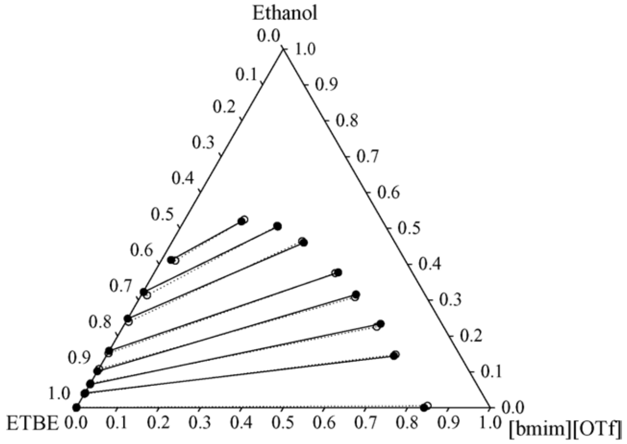

Fig. 2. Experimental tie-lines (●, solid line) for the LLE of the ternary system ETBE + ethanol + [bmim][OTf] at 298.15 K. The corresponding tie-lines correlated by means of the NRTL equation, with $\alpha = 0.2$ and fixing a previously optimised value of the solute distribution ratio at infinite dilution, are also plotted (○, dashed line).

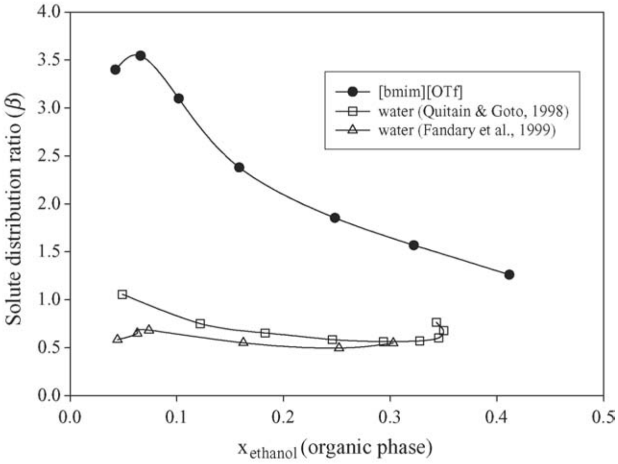

Fig. 3. Solute distribution ratio for the systems ETBE + ethanol + [bmim][OTf] (●) and ETBE + ethanol + water [16,17] (□, △) as a function of the molar fraction of solute in the organic-rich-phase, at 298.15 K. (Note: Splines are merely indicative and have been exclusively plotted for facilitating the graph visualization).

Behaviour of the solute distribution ratio throughout the heterogeneous region of the system, as a function of the solute concentration in the organic phase, can be observed in Fig. 3. With the aim of comparing the behaviour of [bmim][OTf] to water, which is one of the most widely used solvents for this kind of extractions in industry, two data series corresponding to the LLE of the ternary system ETBE + ethanol + water, taken from literature [16,17], have also been plotted. As it can be concluded from the figure, the replacement of water by [bmim][OTf] comes to a considerable increase in the solute distribution ratios.

Analogously, Fig. 4 shows the selectivity of [bmim] [OTf] plotted against the molar fraction of solute in the ether-rich-phase, as well as data taken from literature [16,17] for the system involving water as solvent. In this case, lower values of selectivity are reached with the [bmim][OTf]. Despite their lower values, our selectivity data follow a consistent trend, decreasing

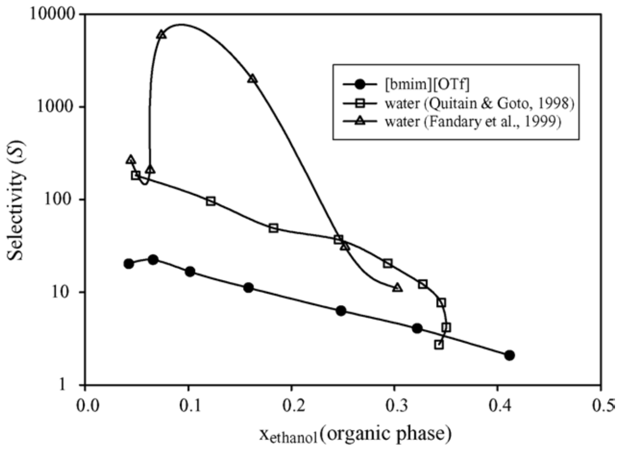

Fig. 4. Selectivity for the systems ETBE + ethanol + [bmim][OTf] (●) and ETBE + ethanol + water [16,17] (□, △) as a function of the molar fraction of solute in the organic-rich-phase, at 298.15 K. (Note: Splines are merely indicative and have been exclusively plotted for facilitating the graph visualization).

almost linearly with the increment of the ethanol concentration in the organic phase.

4. Data correlation

The experimental data were correlated by means of the NRTL equation [18], despite being a model initially developed for non-electrolyte solutions. Later modifications on the original equation, in order to extend its applicability to systems with electrolytes, were published in literature. However, previous works confirm that the original version can satisfactorily correlate LLE data of systems involving electrolytes such as ionic liquids [6–8,10,11]. For this reason, in this work the classical NRTL equation, without any specific modification for electrolytes consideration, was used for data correlation. The non-randomness parameter α was previously set to 0.1, 0.2 and 0.3 and the correlation was performed for each value.

A computer program designed by Sørensen [19] was used to calculate the binary interaction parameters of the NRTL equation. This program tries to minimize two objective functions. A first one, F_a, is a function of the activities and is used at the beginning as it does not require any preliminary guess for the binary parameters:

$$F_a = \sum_k \sum_i \sum_j \left(\frac{a^{\mathrm{I}}_{ijk} - a^{\mathrm{II}}_{ijk}}{a^{\mathrm{I}}_{ijk} + a^{\mathrm{II}}_{ijk}} \right)^2 + Q \sum_n P_n^2 \tag{3}$$

where a is the activity, Q the constant and P is the interaction parameter; subscripts i and j indicate, respectively, the components (1, 2, 3) and the phases (I, II), whereas k refers to the tie-lines (1,2, ..., M; being M the total number of experimental tie-lines) and n to the parameters to be determined (1,2, ..., 6).

The results obtained from the convergence of the first objective function are introduced as the initial parameters estimation for a second objective function, F_b, which eventually fits the experimental concentrations:

$$F_b = \sum_k \min \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum_n P_n^2 + \left[\ln \left(\beta_\infty \frac{\hat{\gamma}^{\mathrm{I}}_{s,\infty}}{\hat{\gamma}^{\mathrm{II}}_{s,\infty}} \right) \right]^2 \tag{4}$$

where Q, P, superscripts I and II, subscripts i, j, k and n have the same meaning than in the expression of the first objective function, x is the mole fraction, β the solute distribution ratio, γ the activity coefficient and “min” refers to the minimum obtained by the Nelder–Mead method; subscripts s and ∞ refer to the solute (ethanol) and to infinite dilution, respectively; and finally the symbol “^” on top indicates a calculated value.

The second term on the right hand side on both objective functions is a penalty term designed to reduce the risk of multiple solutions caused by high parameters values. At the same time, the last term in F_b guaranties that the final binary interaction parameters set leads to an accurate fit of a previously user-defined value of the solute distribution ratio at infinite dilution, β_∞.

The goodness of the correlation fitting was evaluated by means of the residual function F and the mean error of the solute distribution ratio, $\Delta\beta$, defined as:

$$F = 100 \left[\sum_k \min \sum_i \sum_j \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M} \right]^{0.5} \tag{5}$$

$$\Delta\beta = 100 \left[\frac{1}{M} \sum_k \left(\frac{\beta_k - \hat{\beta}_k}{\beta_k} \right)^2 \right]^{0.5} \tag{6}$$

Two different ways were used to correlate the experimental data, in a similar manner to the procedure followed by Sørensen. Firstly, the correlation was performed without fixing a previous value for β_∞. Later, an optimal value of this parameter, found by trial and error considering the minimization of $\Delta\beta$ as the optimality criterion, was specified before carrying out the correlation.

Table 3 summarizes the values of the residuals F and $\Delta\beta$ obtained from the data correlation. As it can be observed, the best results correspond to a value of $\alpha = 0.2$ although results for $\alpha = 0.1$ are considerably close. It has been widely reported in literature that a notable decrease in $\Delta\beta$, at the same time that a slight increase in F, is found when β_∞ is previously fixed [20]. However, just a tiny variation in the residuals is found in this case, a fact which is in good agreement with correlation results of some similar system recently reported including ionic liquids as solvents [11]. The standard NRTL equation is therefore suitable to correlate the experimental data achieving a high accuracy even for low values of solute concentration, which will probably correspond to the most interesting region from a practical point of view.

The binary interaction parameters for the correlation with $\alpha = 0.2$, both fixing and without fixing a previous value of β_∞, are reported in Table 4. No significant differences are remarkable between both parameters sets, except for the binary interaction parameter ether–alcohol. The higher value of this parameter when fixing β_∞ leads to an interesting decrease of $\Delta\beta$ while F increases very slightly.

A comparison between the experimental data and the ones obtained from their correlation by the NRTL equation, with $\alpha = 0.2$ and fixing a previously optimised value of β_∞, can be seen in Fig. 2. It is clear from direct observation of this figure, that the NRTL equation successfully corre-

Table 3

Values of the residual function F and the mean error of the solute distribution ratio, $\Delta\beta$ as defined in Eqs. (5) and (6), for the NRTL correlation model, both fixing and without fixing a previous value of the solute distribution ratio at infinite dilution, β_∞

α	β_∞	F ($\times 10^2$)	$\Delta\beta$ ($\times 10^2$)
0.1	–	0.5894	8.5
	5.26	0.5882	8.5
0.2	–	0.5838	8.4
	4.93	0.5879	8.1
0.3	–	0.7482	10.5
	4.65	0.7718	9.5

Table 4
Binary interaction parameters (Δg_{ij},Δg_{ji}) for the correlation with the NRTL equation ($\alpha = 0.2$) at 298.15 K, both fixing and without fixing a priori the value of the solute distribution ratio at infinite solution, β_∞

β_∞	Components	Parameters ($\alpha = 0.2$)	
	i–*j*	Δg_{ij} (J mol^{-1})	Δg_{ji} (J mol^{-1})
(−)	1–2	−119.42	1708.8
	1–3	20806	1541.0
	2–3	3069.9	−4822.5
4.93	1–2	−403.92	1673.1
	1–3	20865	1559.0
	2–3	2993.0	−5246.5

Components legend: 1, ETBE; 2, ethanol; 3, [bmim][OTf].

lates data and tie-lines corresponding to the ternary system ETBE + ethanol + [bmim][OTf], thus opening a gate for future computational simulations involving these compounds.

5. Conclusions

In this work, the experimental determination of the liquid–liquid equilibrium for the ternary system ETBE + ethanol + [bmim] [OTf] at 298.15 K was carried out. The NRTL model accurately correlates the experimental data. The non-randomness parameter (α) was fixed to 0.1, 0.2 and 0.3, the best results being achieved with $\alpha = 0.2$, but very close to those with $\alpha = 0.1$. These results facilitate the LLE data management and, in addition, they might be useful for future computational treatment and simulation of thermodynamical data concerning systems involved in the purification of ethers by means of ionic liquids.

Behaviour of the ionic liquid and water on the purification of ethyl *tert*-butyl ether (ETBE) from its mixtures with ethanol, can be compared by means of solute distribution ratios and selectivities. Solute distribution ratios of [bmim][OTf] are much higher, leading to a more effective removal of the alcohol. Selectivities are in both cases higher than one, but values of this parameter reached with ionic liquid are clearly lower that those found with water. Nevertheless, the presence of an important quantity of ether in the solvent-rich-phase leaving the extraction unit is less problematic: as the ionic liquid has a negligible vapour pressure, it is easier to recover the ether and reintroduce it into the purification process. Moreover, there are no losses of ionic liquid to the atmosphere, thus not contributing to the air pollution and being fully recoverable. For these reasons, the [bmim][OTf] ionic liquid could be an alternative solvent for ETBE purification. A current limitation for the introduction of [bmim][OTf] as the solvent might be its relatively high price. Prices of ionic liquids are expected to critically decrease as soon as they are produced in a ton-scale.

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