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Cation effect of ammonium imide based ionic liquids in alcohols extraction from alcohol-alkane azeotropic mixtures

Nuria M. Aranda, Begoña González *

Advanced Separation Processes Group, Department of Chemical Engineering, University of Vigo, Campus Lagoas-Marcosende, 36310 Vigo, Spain

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ABSTRACT

During recent last years, outstanding properties of ionic liquids such as low melting point, large liquid range and negligible volatility have turned them into possible volatile organic solvents replacers to break alcohol-alkane azeotropic mixtures. On this basis, two ionic liquids, butyltrimethylammoniumbis(trifluoromethylsulfonyl)imide, [BTMA][NTf$_2$], and tributylmethylammoniumbis(trifluoromethylsulfonyl)imide, [TBMA][NTf$_2$], were studied through ternary liquid+liquid equilibrium (LLE) of {alkane(1) + alcohol (2) + IL(3)} at T = 298.15 K and atmospheric pressure in order to consider the effect of ionic liquid cation alkyl chain length on the extraction process.

The ILs capability as azeotrope breakers was determined by the calculation of parameters such as solute distribution ratio, β, and selectivity, S and this capability was compared with other bis (trifluoromethylsulfonyl)imide based ionic liquids from literature. The consistency of tie-line data was ascertained by applying the Othmer–Tobias and Hand equations. Finally, the experimental LLE were correlated by the Non Random Two Liquid (NRTL) thermodynamic model.

1. Introduction

The development of ionic liquids (ILs) has received particular attention during the last two decades [1] due to properties such as low vapour pressure, excellent chemical and thermal stability, non-flammability, large liquid range [2] and the possibility of tuning the desirable ionic liquid structure according to the specific target process.

Due to these reasons, ILs have been proposed as extraction solvents for a large number of mixtures [3–6]. In this work, two hydrophobic room-temperature ILs based on the combination of bis (trifluoromethylsulfonyl)imide anion and quaternary tetraalkylammoniumcations, so-called ammoniums imide salts [7], were studied for alcohol-alkane mixtures since the extraction capability of these ammonium based ionic liquids is not really known and has been little studied.

The difficulty in extracting alcohol from alkane lies in the fact that similarities between both boiling point values are found and, consequently, an azeotropic system is formed [8]. From a technological point of view, this azeotrope is obtained in the production of oxygen additives, which are added to gasoline to diminish lead levels [8–12]. Until now, the usual method used to achieve the separation between these compounds has been the extractive distillation [13]. The use of ILs as possible substitutes of volatile organic compounds required in this extractive process could be regarded as a worthwhile and more environmentally friendly alternative [14].

For this reason, numerous studies have been realized with the objective of improving understanding about ILs extraction capacity and, specifically, their application in the extraction of alcohols from alkanes [9–12,14–23].

This work focuses on the study of the influence of the ionic liquid cation alkyl chain length and the alkane linear length over the extraction process of alcohols from aliphatic hydrocarbons For this purpose, ternary liquid+liquid equilibriums (LLE) of {hexane or heptane (1) + ethanol or methanol (2) + [BTMA][NTf$_2$] (butyltrimethylammoniumbis(trifluoromethylsulfonyl)imide (3)} and{hexane or heptane (1) + ethanolor methanol (2) + [TBMA][NTf$_2$](tributylmethylammoniumbis(trifluoromethylsulfonyl)imide (3)}were studied at T = 298.15 K and atmospheric pressure. Furthermore, the extraction capability of ILs was estimated by the calculation of parameters such as solute distribution ratio and selectivity. The consistency of tie-line data was ascertained by applying the Othmer–Tobias [24] and Hand [25] equations.

Finally, the experimental LLE values were correlated with the Non Random Two Liquid (NRTL) model [26].

2. Experimental

2.1. Chemicals

Heptane and hexane were obtained from Sigma-Aldrich; ethanol and methanol were acquired from Merck and VWR,

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* Corresponding author. Tel.: +34 986812292.
E-mail address: bgp@uvigo.es (B. González).

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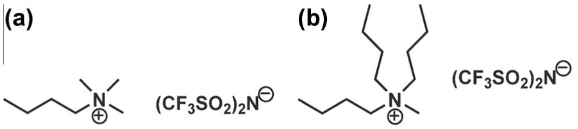

FIGURE 1. Structures of the ionic liquids studied in this work: (a) [BTMA][NTf_2], (b) [TBMA][NTf_2].

respectively. The ILs, *viz.* [BTMA][NTf_2], [TBMA][NTf_2], studied were purchased from IoLiTec and their chemical structure can be seen in figure 1. Mass fraction purity, concentration of halides, W_{halide}, water content by mass, W_w, density and refractive index values for each compound are presented in table 1, where comparisons between experimental and literature data for density and refractive index of pure compounds at $T = 298$ K are also included [7,14,27–30].

With the objective of reducing the water and volatile compounds contents, ILs were subjected to a vacuum process ($P = 0.2$ Pa) at moderate temperature ($T = 343$ K) always prior to their use. Then, the bottles containing ILs were preserved under an inert atmosphere to avoid an increase in moisture content.

2.2. Apparatus

Densities of pure components and their mixtures were measured using an Anton Paar DSA-5000M digital vibrating-tube densimeter with an uncertainty in the experimental measurements of $\pm 3 \cdot 10^{-5}$ g · cm^{-3}. Refractive indices were determined by an automatic refractometer Abbemat-HP Dr. Kernchen with an uncertainty in the experimental measurements of $\pm 4 \cdot 10^{-5}$. Water content by mass was obtained by a columetric KF titration (Mettler Toledo C20). Moreover, all samples were prepared by weight just before their use, using a Mettler AX-205 Delta Range balance with an uncertainty of $\pm 3 \cdot 10^{-4}$ g.

2.3. Experimental LLE procedure

Experiments were carried out by preparation of immiscible ternary mixtures of known composition in order to determine the experimental liquid+liquid equilibrium tie-lines.

The mixtures were prepared by mass, placed in glass cells with silicon stoppers and subject to stirring for 6 h with controlled temperature at $T = 298.15$ K. Previous studies have shown the mentioned time of stirring is enough to achieve the experimental liquid+liquid equilibrium. Then, the two phases were left to settle down in a thermostatic bath for overnight (PoliScience digital temperature controller, with a digital thermsometer ASL model F200 with an uncertainty of ±0.01 K).

After phase separation, a sample of the upper phase (alkane-rich phase) and the lower one (IL-rich phase) was taken by a syringe to determine density and refractive index for each equilibrium point.

Not only were such density values necessary to calculate the composition of both phases but also the binodal curves, which were obtained using "the cloud point" method [31,32].

Basically, this method consists of preparing binary mixtures (IL + alcohol) with known composition and by adding drops of the third component (the alkane, in this case) until turbidity was reached. Then, samples were weighed and the density versus mole fraction curves with their respective fitting polynomial expressions were obtained by means of the density data determination.

Thus, this equation was used to obtain ionic liquid and alcohol mole fraction of the lower phase for each equilibrium point through density data. The alkane mole fraction was found by subtraction.

Moreover, in order that the upper phase mole fraction calculation was feasible, the absence of IL in this phase was verified by ^{1}H-NMR. Once this confirmation was realized, it was also necessary to prepare binary mixtures (alkane + alcohol) with known composition [33,34] and, following the procedure described above, obtain their density values, the corresponding density versus mole fraction curve and its polynomial expression.

Finally, technique validity was assessed by the preparation of three confirmation points and a maximum uncertainty was established as ±0.007 in mole fraction.

3. Results and discussion

3.1. Liquid+liquid equilibrium data

The experimental tie-lines for the ternary systems {alkane (1) + alcohol (2) + IL (3)} were obtained at $T = 298.15$ K and atmospheric pressure. The corresponding compositions and triangular diagrams for each system are also included in table 2 and figure 2, respectively.

As can be seen in the triangular diagrams, a positive slope was obtained for all representations. According to Corderí *et al.* [16], they show the preference of the solute (alcohol) to move into the solvent-rich phase (ionic liquid) instead of the diluent-rich phase (alkane).

Moreover, low ionic liquid mole fractions were necessary to extract alcohol from alkane and a small amount of this component was found in each lower phase of the equilibrium points.

TABLE 1
Purity, water content by mass, w_w, concentration of halides, w_{halide}, density, ρ, and refractive index, n_D, of pure components at $T = 298.15$ K.

Component (supplier)	Mass fraction purity	w_w (10^{-6})	w_{halide} (10^{-6})	ρ/(g · cm^{-3})		n_D	
				Exp.	Lit.	Exp.	Lit.
[BTMA][NTf_2] (**IoLiTec**)	0.999	50	<100	1.3930	1.3940[a] 1.3930[b]	1.40806	n.a.
[TBMA][NTf_2] (**IoLiTec**)	0.997	80	<100	1.2613	1.2569[c]	1.42614	n.a.
Heptane (Sigma-Aldrich)	>0.99	n.a.	n.a.	0.6796	0.6795[d]	1.38529	1.38511[d]
Hexane (Sigma-Aldrich)	>0.99	n.a.	n.a.	0.6552	0.6548[e]	1.37241	1.37226[d]
Methanol (VWR	>0.99	n.a.	n.a.	0.7869	0.7864[e]	1.32636	1.32652[e]
Ethanol (Merck)	>0.99	n.a.	n.a.	0.7859	0.7851[f]	1.35936	1.35929[f]

Standard uncertainties u are $u(\rho) = 0.00003$ g · cm^{-3}, $u(n_D) = 0.00004$ and $u(T) = 0.01$ K.
[a] From Ref. [27].
[b] From Ref. [28].
[c] From Ref. [7].
[d] From Ref. [29].
[e] From Ref. [30].
[f] From Ref. [14].