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Determination and correlation of (liquid + liquid) equilibria of ternary and quaternary systems with octane, decane, benzene and [BMpyr][DCA] at T = 298.15 K and atmospheric pressure

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A R T I C L E I N F O	**A B S T R A C T**

The suitability of the ionic liquid 1-butyl-1-methylpyrrolidinium dicyanamide, [BMpyr][DCA], as extraction solvent of benzene from its mixtures with octane and decane has been analyzed. (Liquid + liquid) equilibrium (LLE) data for the quaternary system {octane (1) + decane (2) + benzene (3) + [BMpyr][DCA] (4)} and for the ternary systems {octane (1) + benzene (2) + [BMpyr][DCA] (3)} and {decane (1) + benzene (2) + [BMpyr][DCA] (3)} were determined at T = 298.15 K and atmospheric pressure. Solute distribution ratios and selectivities were calculated from the experimental LLE data in order to evaluate the capability of [BMpyr][DCA] as extraction solvent. Finally, experimental results for the ternary and quaternary systems were correlated using the Non-Random Two-Liquid (NRTL) thermodynamic model.

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1. Introduction

In recent years, environmental regulations have become more restrictive, requiring the use of more ecofriendly industrial processes and products. The new requirements on petroleum products, such as gasoline, diesel fuel or engine oils, demand a reduction of the level of sulfur and aromatic compounds to minimize their environmental impact [1–3].

The separation of aromatic hydrocarbons from aliphatic hydrocarbons is a challenging job in the refineries [4]. These compounds have close boiling points which leads to the formation of azeotropic mixtures. (Liquid + liquid) extraction is the process used for this kind of separation, but the traditional organic solvents used are generally toxic, flammable and volatile, and their recovery is costly and complicated. A promising alternative to replace these traditional organic solvents are the ionic liquids (ILs) since they present attractive and unique properties such as their negligible volatility and their thermal and chemical stability, among other. Besides, it is important to note the possibility of tuning their properties by the combination of different anion-cation to use

them for a specific application. Moreover, the ILs generally present low solubility in the aliphatic hydrocarbons and high solubility in the aromatic hydrocarbons, which means high selectivity in the separation of aromatic hydrocarbons from their mixtures with aliphatic hydrocarbons.

In the last years, ILs have been widely studied for their use in the aromatic/aliphatic hydrocarbons separation using the (liquid + liquid) equilibrium (LLE) as separation process. Most of the works reported in literature consider only one single aromatic hydrocarbon and/or one single hydrocarbon to study the LLE for binary and ternary mixtures of aromatic and aliphatic hydrocarbons [5,6]. The knowledge of the effect of the presence of more than one aromatic hydrocarbon and/or more than one aliphatic hydrocarbon on the extraction is needed since petrochemical streams present a large number of different compounds and therefore, the study of mixtures with more than three compounds are important and necessary to know the behavior of real mixtures.

Considering the above comments, in this work the ionic liquid 1-butyl-1-methylpyrrolidinium dicyanamide, [BMpyr][DCA], was investigated as solvent for the extraction of benzene from its mixtures with octane and decane. This ionic liquid was chosen since it presents low viscosity and low melting point [7–9] which make easier its handling and use. Furthermore, octane and decane were chosen as aliphatic hydrocarbon since the shorter chain length hydrocarbons have been widely studied [5,6].

For this, the LLE data for the ternary systems {octane (1) + benzene (2) + [BMpyr][DCA] (3)} and {decane (1) + benzene (2) + [BMpyr][DCA] (3)} together with the LLE of the quaternary system {octane (1) + decane (2) + benzene (3) + [BMpyr][DCA] (4)} were determined at T = 298.15 K and atmospheric pressure to analyze the effect of the presence of both aliphatic hydrocarbons on the extraction of benzene. Solute distribution ratio and selectivity were calculated from the experimental LLE data. Finally, experimental results for the ternary and quaternary systems were correlated using the Non-Random Two-Liquid (NRTL) thermodynamic model [10].

2. Experimental section

2.1. Chemicals

The ionic liquid [BMpyr][DCA] was procured from IoLitec GmbH. In order to reduce the initial water content and traces of other volatile compounds to negligible values, the ionic liquid was subjected to vacuum (p = 0.2 Pa) at moderate temperature (T = 343.15 K) for several days. The water content was measured by Karl Fisher tritration, using a Mettler Toledo C20 Coulometric KF Titrator using Coulomat CG and Coulomat AG, supplied by Sigma–Aldrich, as cathodic and anodic titrants, respectively. Benzene were supplied by Aldrich and octane and decane were purchased from Merck. All hydrocarbons were degassed ultrasonically and dried over molecular sieves of $3 \cdot 10^{-10}$ m supplied by Sigma–Aldrich. All compounds used in this work were kept and manipulated under an inert gas atmosphere to prevent the water absorption. A summary of the mass fraction purity given by the suppliers, experimental and literature density data [11–13] of all pure compounds at T = 298.15 K and atmospheric pressure are shown in table 1 together with the specifications related to the purification method of the ionic liquid. Experimental densities of the pure compounds were measured using an Anton Paar DSA-5000 M digital vibrating-tube densimeter with an uncertainty in the measurement of the density of $\pm 3 \cdot 10^{-3}$ g $\cdot$ cm^{-3} for the ionic liquid and $\pm 1 \cdot 10^{-3}$ g $\cdot$ cm^{-3} for the rest of the samples considering the purity of the compounds used in this work. These uncertainties were estimated following the comments made in the work reported by Chirico et al. [14].

2.2. (Liquid + liquid) equilibrium (LLE) determination

The study of the (liquid + liquid) equilibria for the investigated ternary and quaternary systems was performed at T = 298.15 K and atmospheric pressure. The LLE data for the ternary system {octane (1) + benzene (2) + [BMpyr][DCA] (3)} were obtained by means of the previous determination of the solubility curve by the "cloud point" method [15] and the determination of the

tie-lines using density measurements for the calculation of the phase compositions. This procedure has been described in detail in previous works [16,17]. The composition of the aliphatic hydrocarbon-rich phase (upper phase) was calculated using literature data of density vs. composition for the binary system {octane (1) + benzene (2)}[18]; whereas in the case of the IL-rich phase (lower phase), its composition was calculated using a polynomial expression of density vs. composition obtaining from the solubility curves, their corresponding data are presented in tables S1 and S2, respectively (given as Supplementary material). Otherwise, the LLE data for the ternary system {decane (1) + benzene (2) + [BMpyr] [DCA] (3)} and the quaternary system {octane (1) + decane (2) + benzene (3) + [BMpyr][DCA] (4)} were obtained by the determination of the tie-lines compositions using gas chromatography-mass spectrometry (GC–MS). The determination of the compositions of the ternary system involving decane as aliphatic hydrocarbon had to be performed by the chromatographic method due to the very low solubility of decane in the ionic liquid [BMpyr][DCA], which made it impossible to determine the phase compositions by the method involving density measurements and solubility curves. The initial compositions of the ternary and quaternary mixtures of known composition were prepared in the immiscible region. The preparation of the ternary mixtures was carried out by weighing the three compounds, while the quaternary mixtures were prepared by addition of octane, decane and benzene to a fixed amount of ionic liquid. The composition of the ionic liquid was selected taking a sectional plane (M1) perpendicular to the tie-lines in which the mole fraction of the ionic liquid is constant (x_4 = 0.242), as it can be seen in the tetrahedron diagram shown in figure 1. The selected sectional plane is perpendicular to the tie-lines and the composition of the ionic liquid was selected taking into account the minimum amount of ionic liquid required to achieve a feasible sample collection. The composition of the other three compounds involved in the initial quaternary mixtures was calculated in this sectional plane, paying close attention to completely cover the selected plane. In order to improve the covering of the selected surface, different fixed compositions of benzene (from 0.1 to 0.7 in mole fraction of benzene) were chosen. In this way, tie-lines within the whole heterogeneous region of the quaternary system were obtained.

The initial ternary and quaternary mixtures of known composition were placed into glass equilibrium cells, which were sealed with rubber covers. The temperature of the equilibrium was controlled using a thermostatic bath, PoliScience digital temperature controller, with a precision of T = ±0.01 K. Samples were vigorously stirred for at least 5 h to ensure a complete contact between both phases. Following, the cells were left to settle overnight in order to guarantee that the equilibrium was completely reached. After equilibrium was reached, samples of each phase were taken using a syringe and analyzed to determine their composition with the corresponding method, as it has been previously commented.

TABLE 1
Specifications of the pure compounds used in this work.[a]

Component	Supplier	Purity/(mass fraction)	Initial w_w/ppm	Purification method	Final w_w/ppm	ρ/(g $\cdot$ cm^{-3})	
						Exp.	Lit.
[BMpyr][DCA]	IoLiTec	>0.98	293	Vacuum treatment T = 343.15 K p = 0.2 Pa Several days	114	1.01447	1.013[b]
Benzene	Aldrich	⩾0.99	–		–	0.87371	0.87360[c]
Octane	Merck	⩾0.99	–		–	0.69886	0.69862[c]
Decane	Merck	⩾0.99	–		–	0.72615	0.72616[d]

[a] Standard uncertainties u are $u(\rho)$ = ±0.003 g $\cdot$ cm^{-3} (for the IL) and ±0.001 g $\cdot$ cm^{-3} (for the hydrocarbons), $u(T)$ = ±0.01 K, $u(p)$ = ±10 kPa and $u(water\ content)$ = ±5%.
[b] From reference [11].
[c] From reference [12].
[d] From reference [13].