

Application of Pyrrolidinium-Based Ionic Liquid as Solvent for the Liquid Extraction of Benzene from Its Mixtures with Aliphatic Hydrocarbons

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S Supporting Information

ABSTRACT: The ionic liquids 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate, [BMpyr][TfO], 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMpyr][NTf₂], and 1-butyl-1-methylpyrrolidinium dicyanamide, [BMpyr][DCA], have been studied as solvents for the extraction of benzene from its mixtures with several aliphatic hydrocarbons. The liquid–liquid equilibrium (LLE) of the ternary systems {octane (1) + benzene (2) + [BMpyr][TfO] (3)}, {decane (1) + benzene (2) + [BMpyr][TfO] (3)}, {dodecane (1) + benzene (2) + [BMpyr][TfO] (3)}, {dodecane (1) + benzene (2) + [BMpyr][NTf₂] (3)}, and {dodecane (1) + benzene (2) + [BMpyr][DCA] (3)} at *T* = 298.15 K and atmospheric pressure was carried out. The solute distribution ratio and selectivity values derived from the tie-lines were used to evaluate if the studied ionic liquids can be used as extraction solvents, and the obtained values were compared with those found in the literature for the traditional organic solvents. Finally, experimental LLE data for the ternary mixtures were correlated by means of the non-random two-liquid (NRTL) thermodynamic model.

1. INTRODUCTION

The extraction of aromatic compounds from petrochemical products is one of the most important processes in the petroleum refinery.¹ Processes for separating aromatic hydrocarbons in low concentrations (<20%) from aliphatic hydrocarbons present in the feed stream to naphta crackers have not been developed yet.² Besides this, there is a growing demand for petroleum products with lower contents in sulfur, aromatics, and olefins so they meet the requirements of the new environmental regulations.³ For these reasons, the design of environmentally friendly separation processes is of utmost importance in the chemical industry.

The most common processes for the extraction of aromatic compounds from petrochemical products use solvents such as sulfolane, *N*-formyl morpholine (NFM), *N*-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO), glycols, and carbonates.^{4–7} Although the processes based on these solvents are well-known, these solvents are frequently flammable, volatile, and toxic, and their recovery is costly and complicated. Ionic liquids (ILs) have emerged as a promising alternative to replace traditional organic solvents in liquid–liquid extraction of aromatic hydrocarbons⁸ due to their unique properties such as negligible volatilities, high thermal and chemical stabilities, noncorrosiveness, nonflammability, capability to be tailored to a specific application by the combination of different anion–cation, and immiscibility with aliphatic hydrocarbons.^{9,10} In addition, the research shows that the IL-based extraction process requires fewer process steps and less energy consumption than the traditional solvents due to their easy recuperation.^{2,8}

The number of works concerning liquid–liquid extraction of aromatic hydrocarbons from aliphatic hydrocarbons using ILs as solvents has increased considerably in recent years;^{8,11–15}

this increase is motivated by the search for a suitable IL presenting values of selectivity and solute distribution ratio of aromatic hydrocarbons higher than those for the conventional solvents. Therefore, the knowledge of LLE data for the ternary systems {aliphatic hydrocarbons (1) + aromatic hydrocarbons (2) + ILs (3)} is essential to evaluate the feasibility of the ILs as extractive solvents. Following this objective, in this work, the suitability of three pyrrolidinium based ILs to separate benzene from its mixtures with several aliphatic hydrocarbons (octane, decane, and dodecane) has been analyzed.

The studied ILs were 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate, [BMpyr][TfO], 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMpyr][NTf₂], and 1-butyl-1-methylpyrrolidinium dicyanamide, [BMpyr][DCA]; the pyrrolidinium-based ionic liquids are attracting interest because they present low viscosity, low melting points, high conductivity, a promising behavior in the separation of aromatic hydrocarbons from aliphatic hydrocarbon mixtures, and a toxicity lower than other cation-based ILs.^{16–20} Regarding the selected anions ([TfO][−], [NTf₂][−], and [DCA][−]), they have been widely used in the literature in extraction processes, showing satisfactory outcomes.^{18,20–24} Furthermore, the aliphatic hydrocarbons present in naphta range from C₄ to C₁₂,²⁵ since the shorter chain length hydrocarbons have been extensively studied, in the present work, octane, decane, and dodecane were chosen as aliphatic hydrocarbons.

Taking into account all the mentioned aspects, the liquid–liquid equilibrium (LLE) data for the ternary systems {octane

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Table 1. Table of the Pure Components Used in This Work at $T = 298.15$ K and Atmospheric Pressure

component	supplier	molar mass ($\text{g}\cdot\text{mol}^{-1}$)	purity (mass fraction)	ρ ($\text{g}\cdot\text{cm}^{-3}$)		water content (ppm)
				exp.	lit.	
[BMpyr][TfO]	Iolitec	291.33	>0.99	1.25213	1.25271 ²⁷	72
[BMpyr][NTf ₂]	Iolitec	422.41	>0.99	1.39468	1.39459 ²⁸	158
[BMpyr][DCA]	Iolitec	208.30	>0.98	1.01447	1.013 ²⁹	114
benzene	Aldrich	78.11	≥ 0.99	0.87371	0.87360 ³⁰	
octane	Merck	114.23	≥ 0.99	0.69886	0.69862 ³⁰	
decane	Merck	142.29	≥ 0.99	0.72615	0.72616 ³¹	
dodecane	Merck	170.34	≥ 0.99	0.74528	0.74514 ³¹	

(1) + benzene (2) + [BMpyr][TfO] (3)}, {decane (1) + benzene (2) + [BMpyr][TfO] (3)}, {dodecane (1) + benzene (2) + [BMpyr][TfO] (3)}, {dodecane (1) + benzene (2) + [BMpyr][NTf₂] (3)}, and {dodecane (1) + benzene (2) + [BMpyr][DCA] (3)} at $T = 298.15$ K and at atmospheric pressure have been experimentally determined. Moreover, a comparison with available literature data for the ternary systems studied with traditional organic solvents will be presented and discussed.

Finally, the experimental LLE data was satisfactorily correlated by the non-random two liquid (NRTL) model for the ternary systems.²⁶

2. EXPERIMENTAL SECTION

2.1. Chemicals. Benzene, octane, decane, and dodecane were procured from commercial suppliers with purities greater than 0.99 in mass fraction in all cases. They were degassed ultrasonically and dried over molecular sieves of 3×10^{-10} m supplied by Sigma-Aldrich. Then, they were kept in bottles under an inert atmosphere without any further treatment.

All the studied ionic liquids were acquired at IoLiTec GmbH with a high purity. Prior to their use, ILs were subjected to a vacuum ($p = 0.2$ Pa) at moderate temperature ($T = 343.15$ K) for at least 48 h in order to reduce the moisture and any volatile compounds to negligible values. Afterward, their water contents were measured by the Karl Fischer method, using a Mettler Toledo C20 Coulometric KF Titrator using Coulomat CG and Coulomat AG, supplied by Sigma-Aldrich, as cathodic and anodic titrants, respectively. Then, they were kept under an inert atmosphere. The summary of the suppliers, purity, molar mass, and experimental density of all the studied compounds at $T = 298.15$ K together with literature data^{27–31} as well as the water content of the studied ILs are given in Table 1.

2.2. Apparatus. A Mettler AX-205 Delta Range balance with an uncertainty in the measurement of $\pm 3 \times 10^{-4}$ g was used during the sample preparation, and the densities were determined using an Anton Paar DSA-5000 M digital vibrating-tube densimeter with an uncertainty in the measurement of $\pm 3 \times 10^{-5}$ $\text{g}\cdot\text{cm}^{-3}$. The thermostatic bath used to ensure the two-phase equilibrium was a PoliScience digital temperature controller, with a precision of ± 0.01 K. The temperature was controlled with a digital thermometer ASL model F200 with an uncertainty of ± 0.01 K.

The gas chromatograph used was an HP 5890 Series II with a HP 5971 mass selective detector. The parameters of analysis were as follows: column: HP-5MS capillary column ((5% phenyl)-methylpolysiloxane), 60 m length, 0.250 mm internal diameter, 0.25 μm film thickness; column oven temperature: 343.15 K for 8 min; temperature ramp: 373.15 K (rate = 55 K/min) for 7 min and 473.15 K (rate = 55 K/min) for 6 min; carrier gas: helium; flow rate: 1 mL/min; injector temperature:

553.15 K; detector temperature: 553.15 K. Injection was done by splitless, and the injection volume was 1 μL . To avoid the column contamination, the ionic liquid was collected in the injector liner (filled with quartz glass) and in the precolumn.

2.3. Liquid–Liquid Equilibrium (LLE) Determination.

The experimental LLE data were determined by preparation of ternary mixtures of the studied systems. Mixtures were placed into the glass equilibrium cells, which were sealed with silicon covers. The equilibrium temperature was maintained at $T = 298.15$ K using a thermostatic bath. Samples were vigorously stirred for 6 h to reach a complete contact between the two phases, and then, they were allowed to settle overnight to guarantee that the equilibrium was completely reached. After the phase separation, samples of both phases were collected using a syringe and analyzed to determine their composition with an adequate method.

The method followed for the determination of LLE data of the ternary systems {octane or decane (1) + benzene (2) + [BMpyr][TfO] (3)} was through the determination of the solubility curves by the “cloud point” method.³³ The tie-lines were calculated using the density measurements for the determination of the phase compositions; for the systems containing dodecane as aliphatic hydrocarbon, the determination of the tie-line compositions was carried out by gas chromatography mass spectrometry (GC-MS). These ternary systems containing dodecane had to be performed by a different method due to the very low solubility of this aliphatic hydrocarbon in the studied ILs, which made it impossible to determine the phase compositions by the method involving density measurements.

For the determination of LLE data of the ternary systems {octane or decane (1) + benzene (2) + [BMpyr][TfO] (3)}, mixtures of two components of known composition were titrated with the third component until the phase transition in the samples was observed. The density of each sample was measured, and a polynomial expression for density versus mole fraction was obtained. These polynomial expressions are summarized in Table S1 in the Supporting Information. To estimate the error of the technique used, three validation points were performed. The maximum error using this technique between experimental and calculated compositions was estimated to be ± 0.007 in mole fraction. Once the equilibrium was reached and a sample of both phases was collected, the densities were determined and the compositions were calculated: for the IL-rich phase, the composition was determined using the above-mentioned polynomial expression, and in the case of the aliphatic hydrocarbon-rich phase, its composition was calculated using the density curves of the binary systems {octane (1) + benzene (2)}³² and {decane (1) + benzene (2)} at $T = 298.15$ K, shown in Table S2 in the

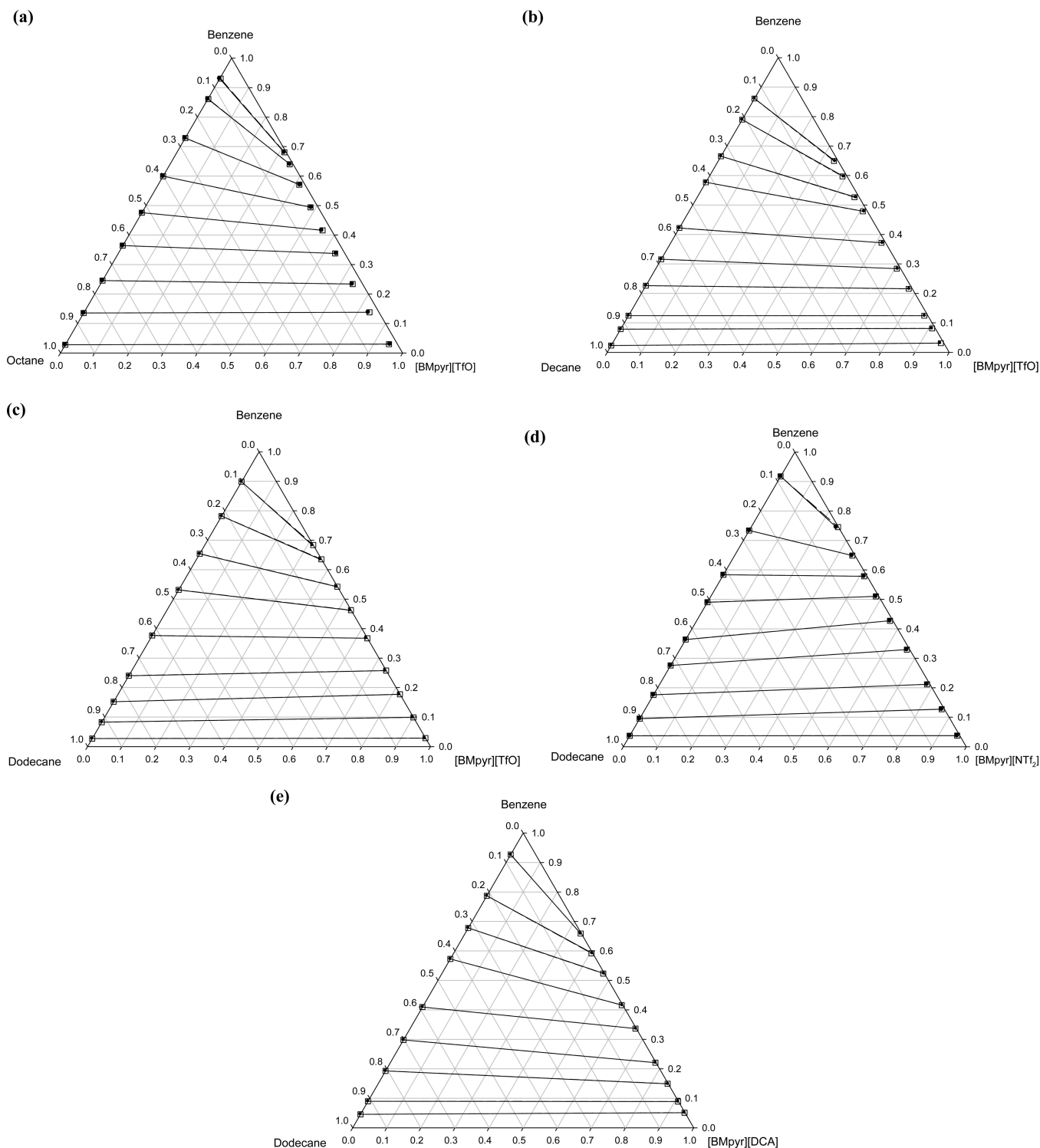


Figure 1. LLE of the ternary systems (a) {octane (1) + benzene (2) + [BMpyr][TfO] (3)}, (b) {decane (1) + benzene (2) + [BMpyr][TfO] (3)}, (c) {dodecane (1) + benzene (2) + [BMpyr][TfO] (3)}, (d) {dodecane (1) + benzene (2) + [BMpyr][NTf₂] (3)}, and (e) {dodecane (1) + benzene (2) + [BMpyr][DCA] (3)} at $T = 298.15$ K and atmospheric pressure. Solid lines and full points indicate experimental tie-lines, and dashed lines and empty squares indicate calculated data from the NRTL model.

Supporting Information, since the presence of IL in this phase was not detected (as it was checked by ¹H NMR).

As already commented, the analyses of the tie-line compositions of the systems containing dodecane were carried out using gas chromatography. Once the samples were taken from both phases, acetone was used to avoid the phase splitting and to maintain a homogeneous mixture, and nonane was used

as an internal standard. Since ionic liquids have negligible vapor pressure, they cannot be analyzed by GC, so only the aliphatic hydrocarbon and benzene were analyzed. For a ternary mixture, only two components need to be analyzed, thereupon the ionic liquid composition was calculated by difference. All the samples were injected in duplicate, and the average value was calculated. To obtain the error of the technique used for the determination

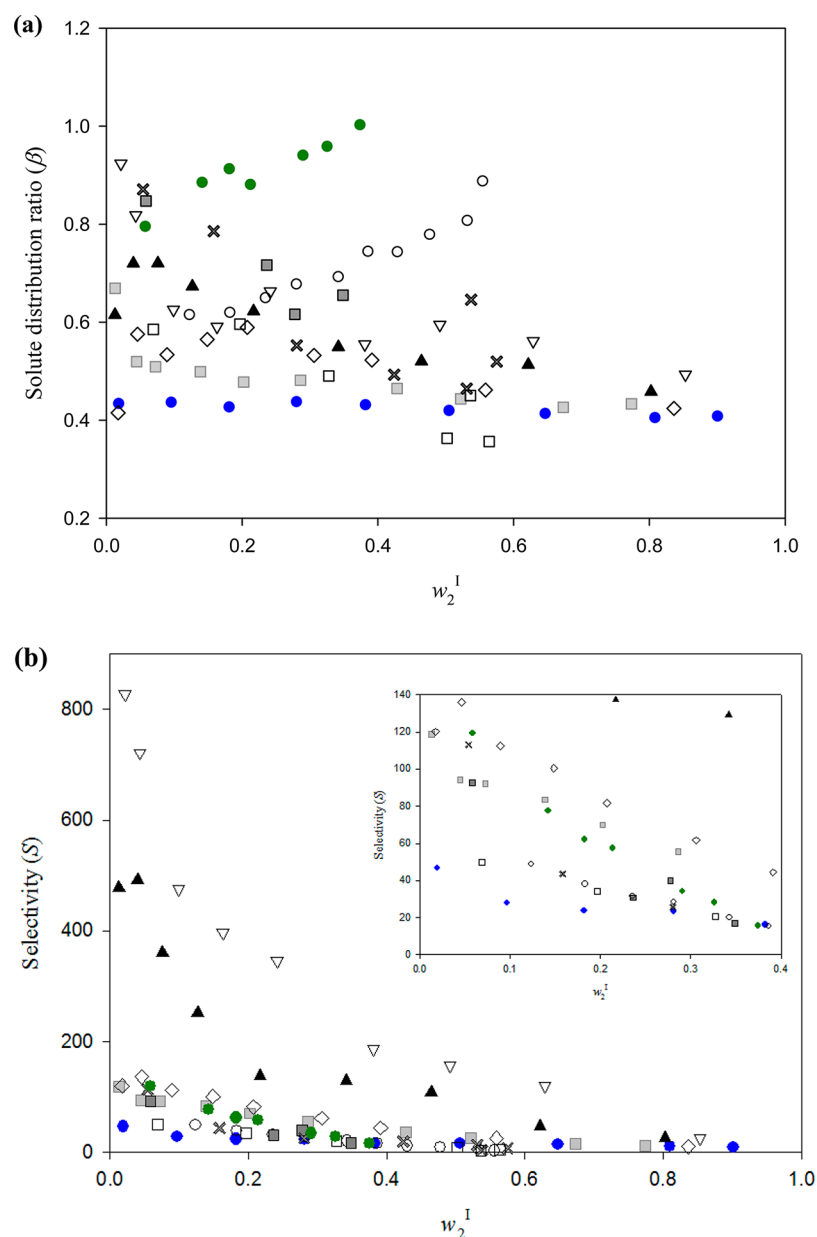


Figure 2. (a) Solute distribution ratio and (b) selectivity as a function of the mass fraction of aromatic compound in the aliphatic hydrocarbon-rich phase for the ternary systems {octane (1) + benzene (2) + [BMpyr][TfO] (3)} (blue ●), {decane (1) + benzene (2) + [BMpyr][TfO] (3)} (light gray ■), {dodecane (1) + benzene (2) + [BMpyr][TfO] (3)} (▲), {dodecane (1) + benzene (2) + [BMpyr][NTf₂] (3)} (◇), {dodecane (1) + benzene (2) + [BMpyr][DCA] (3)} (▽), {octane (1) + benzene (2) + sulfolane (3)} (○),⁴⁰ {octane (1) + benzene (2) + sulfolane (3)} (green ●),⁴¹ and {decane (1) + benzene (2) + *N*-formylmorpholine (3)} (dark gray ■)⁴² at $T = 298.15$ K and {decane (1) + benzene (2) + sulfolane (3)} (□)⁴³ and {dodecane (1) + benzene (2) + sulfolane (3)} [BMpyr][NTf₂] (×)⁴³ at $T = 303.15$ K.

of the compositions, ternary mixtures of known composition were prepared by mass. These mixtures were analyzed with the chromatographic method, and their values were compared with those obtained by mass. This comparison showed that the largest deviation of the phase composition was ± 0.004 in mole fraction.

3. RESULTS AND DISCUSSION

3.1. Experimental LLE Data. The compositions of the experimental tie-lines for the ternary system {octane or decane or dodecane (1) + benzene (2) + [BMpyr][TfO] (3)} and {dodecane (1) + benzene (2) + [BMpyr][NTf₂] or [BMpyr][DCA] (3)} at $T = 298.15$ K and atmospheric pressure are reported in Table S3 in the Supporting

Information, and the corresponding triangular diagrams with the experimental tie-lines for each system are presented in Figure 1. According to the classification proposed by Sørensen et al.,³⁴ all of these systems correspond to the type 2 category, in which two of the pairs of compounds exhibit partial miscibility and only one pair is miscible in the whole range of compositions. In this case, each aliphatic hydrocarbon and benzene are completely soluble in all proportions.

As can be observed in Figure 1a–c, an increase in the chain length of the aliphatic hydrocarbon leads to a slight increase in the size of the immiscibility region; i.e., the increase of the alkane chain length decreases the solubility in the corresponding ionic liquid. Actually, in a previous study on the solubility of the hydrocarbons in the ILs studied, the solubility values in

mole fraction of the aliphatic hydrocarbon in the ionic liquid [BMpyr][TfO] were calculated to be $x_{\text{octane}} = 0.016$, $x_{\text{decane}} = 0.012$, and $x_{\text{dodecane}} = 0.002$. This behavior agrees with results obtained in the literature.^{35–38} Furthermore, the influence of the anion of the IL on the solubility of dodecane was also analyzed, obtaining the following solubility values in mole fraction: 0.002, 0.004, and 0.004 for [BMpyr][TfO], [BMpyr][NTf₂], and [BMpyr][DCA], respectively.

Moreover, it is possible to observe that the solubility of benzene in the studied ILs is much higher than the solubility of the aliphatic hydrocarbons, with the values being obtained as a function of the mole fraction of benzene: 0.727, 0.810, and 0.709 for [BMpyr][TfO], [BMpyr][NTf₂], and [BMpyr][DCA], respectively. These results agree with those reported in the literature.^{18,28}

Since one of the requirements to be a suitable extraction solvent in the separation of aromatic and aliphatic hydrocarbons is for the aromatic hydrocarbons to present a high solubility in the solvent combined with a high selectivity and a low or null solubility of the aliphatic hydrocarbon in the solvent,^{8,39} the chosen ILs seem *a priori* promising extraction solvents.

With the aim to evaluate the feasibility of the ILs [BMpyr][TfO], [BMpyr][NTf₂], and [BMpyr][DCA] to perform the liquid–liquid extraction of benzene from its mixtures with the studied aliphatic hydrocarbons, the solute distribution ratio (β) and the selectivity (S) were calculated from the experimental LLE data as follows:

$$\beta = x_2^{\text{II}}/x_2^{\text{I}} \quad (1)$$

$$S = x_2^{\text{II}}x_1^{\text{I}}/x_2^{\text{I}}x_1^{\text{II}} \quad (2)$$

where x is the mole fraction, superscripts I and II indicate the upper (aliphatic hydrocarbon-rich phase) and lower (ionic liquid-rich phase) phases, respectively, and subscripts 1 and 2 refer to the corresponding aliphatic hydrocarbon and benzene, respectively. Due to the differences in molar masses of the studied ILs and the traditional solvents, solute distribution ratios calculated using mass fraction instead of mole fraction were used to compare the LLE data obtained in this work with those reported in the literature for traditional solvents, which will be discussed later. Values of β calculated using mole and mass fractions and S for each experimental tie-line are presented in Table S3 in the Supporting Information.

Parts a and b of Figure 2 show β and S for the studied ternary systems as a function of the benzene mass fraction in the aliphatic hydrocarbon-rich phase (w_2^{I}). Note that the selectivity values are independent from the mole or mass basis. The representation of β in mass fraction gives an idea of the quantity of solvent needed for the extraction process. In this figure, it is also possible to observe a comparison with literature LLE data using sulfolane and *N*-formyl morpholine as solvents.^{40–43} Liquid–liquid equilibrium data for the systems containing decane and dodecane with sulfolane as solvent have been reported at $T = 303.15$ K;⁴³ nevertheless, the comparison can be performed, since the effect of the temperature on the LLE is not determining, as it has been demonstrated by several authors.^{44–46}

In Figure 2a, it can be observed that the solute distribution ratio values tend to decrease with an increase in the concentration of benzene in the aliphatic hydrocarbon-rich phase, except for the system {octane (1) + benzene (2) +

[BMpyr][TfO] (3)} in which β is practically constant along the whole concentration range.

The effect of the alkyl chain length of the aliphatic hydrocarbon on the extraction of benzene can be analyzed in the systems containing [BMpyr][TfO] as solvent. The β values increase in the order octane < decane < dodecane, showing that longer aliphatic hydrocarbon chains lead to higher β values. When the systems containing decane and octane as aliphatic hydrocarbon are compared, the β values follow the order decane > octane until $w_2^{\text{I}} \cong 0.66$, from where the β values are quite similar for both ternary systems. Moreover, the effect the anion of the ILs has on the LLE extraction can be studied in the system {dodecane (1) + benzene (2) + ILs (3)}. As it can be observed in Figure 2a, the β values obtained are similar for the three studied ILs, although it is possible to infer a slight trend in the form [BMpyr][DCA] > [BMpyr][TfO] > [BMpyr][NTf₂].

As shown in Figure 2b, the selectivity values are much greater than the unity in all the systems studied, which confirms that these ILs can be used for the separation of benzene from its mixtures with the studied aliphatic hydrocarbons. The obtained selectivity values show similar trends to those presented by the solute distribution ratio values. In the comparison of the behavior of the ternary systems containing [BMpyr][TfO], the S values decrease in the order dodecane > decane in the whole range of concentration of benzene. Regarding the study of the influence of the anion of the ionic liquid, the S values decrease in the order [BMpyr][DCA] > [BMpyr][TfO] > [BMpyr][NTf₂], in a similar way to the β values.

The comparisons of the β and S values obtained in this work with those reported in the literature for sulfolane and *N*-formyl morpholine^{40–43} are also plotted in Figure 2. In this figure, it can be seen that the β values reported for the ternary systems with sulfolane as solvent and octane as aliphatic hydrocarbon are higher than those obtained in this work. When the aliphatic hydrocarbon is changed to decane, the values of β for the system with [BMpyr][TfO] as solvent are similar to those reported for the system with sulfolane from $w_2^{\text{I}} = 0.50$. However, in the systems containing dodecane, it is observed that all the compared systems exhibit similar values of β in concentrations of benzene above $w_2^{\text{I}} \cong 0.30$. Finally, it can be concluded that the β values for the system in which *N*-formyl morpholine is the solvent are higher than those shown for the other two systems with decane as aliphatic hydrocarbon.

Regarding the comparison of the S values that can be observed in Figure 2b, the highest values of S are found for the systems involving dodecane and the studied ILs, following the order [BMpyr][DCA] > [BMpyr][TfO] > [BMpyr][NTf₂] > sulfolane. This result is in concordance with the low solubility of dodecane in the ionic liquids. It is also possible to conclude that the experimental S values for the systems {decane or dodecane (1) + benzene (2) + [BMpyr][TfO] (3)} are higher than those reported for the systems with sulfolane as solvent, while the system {octane (1) + benzene (2) + [BMpyr][TfO] (3)} only shows higher selectivities than the traditional organic solvent from $w_2^{\text{I}} \cong 0.385$.

3.2. Thermodynamic Correlation. The NRTL thermodynamic model²⁶ was employed to correlate the experimental LLE data for all the ternary systems. Even though this model was not initially developed to correlate systems involving electrolytes, it has provided adequate correlating capability for binary and ternary systems containing ILs.^{47–49}

The fitting parameters were determined minimizing the following objective function

$$\text{O.F.} = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{(1/\beta_{ij})^{\text{cal}} - (1/\beta_{ij})^{\text{exp}}}{(1/\beta_{ij})^{\text{exp}}} \right)^2 \quad (3)$$

where $\beta_{ij} = x_{ij}^{\text{II}}/x_{ij}^{\text{I}}$ is the solute distribution ratio of the component j for the tie-line i and where $j = 1$ or 2 for the ternary systems, x represents the mole fraction, the superscripts cal and exp denote the calculated and experimental values, respectively, and m and n are the number of the experimental tie-lines and the number of components, respectively.

The values of the binary interaction parameters, Δg_{ij} , the non-randomness parameters, α_{ij} , and the root-mean-square deviation of the composition, σx , obtained using the NRTL model to correlate the experimental LLE data are summarized in Table 2. The non-randomness parameter in the NRTL

Table 2. NRTL Parameters, Δg_{ij} and α_{ij} , and Root-Mean-Square Deviation of the Composition, σx , Obtained from Ternary LLE Data Correlation at $T = 298.15$ K and Atmospheric Pressure

$i-j$	Δg_{ij} (kJ·mol ⁻¹)	Δg_{ij} (kJ·mol ⁻¹)	α_{ij}	σx
	{Octane (1) + Benzene (2) + [BMpyr][TfO] (3)}			
1-2	3.995	-6.297	0.100	0.090
1-3	39.748	1.405		
2-3	30.029	-13.050		
	{Decane (1) + Benzene (2) + [BMpyr][TfO] (3)}			
1-2	-11.122	15.805	0.100	0.102
1-3	4.956	7.923		
2-3	108.735	-4.940		
	{Dodecane (1) + Benzene (2) + [BMpyr][TfO] (3)}			
1-2	-11.844	19.569	0.100	0.113
1-3	60.930	15.428		
2-3	101.360	-5.212		
	{Dodecane (1) + Benzene (2) + [BMpyr][NTf ₂] (3)}			
1-2	-1.522	7.535	0.100	0.079
1-3	53.942	6.105		
2-3	134.696	2.265		
	{Dodecane (1) + Benzene (2) + [BMpyr][DCA] (3)}			
1-2	-3.865	12.932	0.100	0.048
1-3	146.495	17.346		
2-3	123.712	-2.889		

equation, α_{ij} was set to different values between 0.05 and 0.30 during the calculations, and the best results achieved are those presented in Table 2. The deviation was calculated using the following expression:

$$\sigma x = \sqrt{100 \left(\frac{\sum_i^m \sum_j^{n-1} (x_{ij}^{\text{I,exp}} - x_{ij}^{\text{I,calc}})^2 + (x_{ij}^{\text{II,exp}} - x_{ij}^{\text{II,calc}})^2}{2mn} \right)} \quad (4)$$

Taking into account the values of the deviations shown in Table 2, the NRTL model seems to be adequate to correlate the LLE data. The good adjustment of this thermodynamic model can be visually confirmed in Figure 1, where experimental and calculated tie-lines data are plotted.

4. CONCLUSIONS

LLE data for the ternary systems {octane (1) + benzene (2) + [BMpyr][TfO] (3)}, {decane (1) + benzene (2) + [BMpyr][TfO] (3)}, {dodecane (1) + benzene (2) + [BMpyr][TfO] (3)}, {dodecane (1) + benzene (2) + [BMpyr][NTf₂] (3)},

and {dodecane (1) + benzene (2) + [BMpyr][DCA] (3)} were experimentally determined at $T = 298.15$ K and atmospheric pressure. Solute distribution ratios and selectivities were calculated and compared with those reported in the literature for traditional organic solvents. In the systems containing [BMpyr][TfO] as solvent, it is observed that the β values increase with the increase of the alkyl chain length of the aliphatic hydrocarbon. The study of the effect of the anion of ILs shows that the β values are practically constant as the concentration of benzene increases, with it being possible to observe a light trend in the order [BMpyr][DCA] > [BMpyr][TfO] > [BMpyr][NTf₂]. Even though it is not the usual behavior, the described trends for the β values are the same as those for the S values. Taking into account all results, the highest values of the solute distribution ratio and selectivity were obtained for the system {dodecane (1) + benzene (2) + [BMpyr][DCA] (3)}. Therefore, this ionic liquid would be the most adequate solvent of the studied ILs for the extraction of benzene from its mixtures with dodecane. Moreover, all the studied systems show selectivity values higher than unity; hence, these ILs could be used for extraction processes for the separation of aromatic and aliphatic hydrocarbons. The values of the solute distribution ratio of the studied ternary systems are not so high, which implies a big quantity of solvent to be used. However, the very low solubility of the IL in aliphatic hydrocarbons minimizes the loss of the IL and the contamination of the refined stream. Regarding the comparison of the obtained results and those found in the literature for sulfolane and *N*-formyl morpholine as solvents, the studied ILs present higher selectivity values than the traditional organic solvents.

Finally, the NRTL model was used to correlate satisfactorily the experimental LLE data for all the studied systems.

■ ASSOCIATED CONTENT

Supporting Information

Fitting parameters of the polynomial expressions for density versus mole fraction obtained for the {octane or decane (1) + benzene (2) + [BMpyr][TfO] (3)}, density curve of the binary system {decane (1) + benzene (2)}, and experimental LLE data on mole fraction together with β and S for the studied ternary systems at $T = 298.15$ K and atmospheric pressure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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