Aliphatic−Aromatic Separation Using Deep Eutectic Solvents as Extracting Agents

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S *Supporting Information*

ABSTRACT: The separation of aliphatic and aromatic compounds is a great challenge for chemical engineers. There is no efficient separation process for mixtures with compositions lower than 20 wt % in aromatics. In this work, the feasibility of two different deep eutectic solvents (DESs) as novel extracting agents for the separation of the mixture {hexane + benzene} were tested. In order to select the proper solvent for this separation, a solubility test of a set of DESs was done at room temperature and atmospheric pressure. The selected deep eutectic solvents for this work were (i) tetrahexylammonium bromide:ethylene glycol with molar ratio = 1:2 (DES 1) and (ii) tetrahexylammonium bromide:glycerol with molar ratio = 1:2 (DES 2). The selected DESs were characterized by measurement of density and viscosity at atmospheric pressure and temperatures $T = 293.2-343.2$ K. Next, the liquid−liquid equilibria (LLE) of the ternary systems {hexane + benzene + DES 1} and {hexane + benzene + DES 2} were determined at $T/K = 298.2$ and $T/K = 308.2$ and atmospheric pressure. Besides, the solute distribution coefficient and selectivity values were calculated and compared to LLE data available in the literature for the studied ternary system with other solvents. Finally, the experimental data were successfully correlated using the nonrandom two-liquid (NRTL) model. The obtained results show that DESs are promising extracting agents for the industrial separation of low aromatic concentration naphtha streams.

1. INTRODUCTION

The separation of aromatic from aliphatic compounds is not only of great importance, but also enormously challenging in the petrochemical industry. Aromatics recovery from naphtha cracking streams is critical because of two main reasons: (1) new requirements on the petroleum products which demand a reduction of the level of sulfur and aromatic compounds to minimize their environmental impact and (2) the economic value of the aromatic components as raw material. The separation of this mixture is difficult because of the presence of azeotropes and close boiling point components.[1,2]

Industrially, this separation is carried out using the sulfolane process. This process uses liquid−liquid extraction, with sulfolane as extracting agent, followed by extractive distillation for the solvent recovery.[3] However, due to the high energy investment needed for the sulfolane recovery, this is not an efficient separation process for mixtures with aromatics content lower than 20 wt %. Therefore, the separation of aromatics from aliphatic compounds is performed at the end of the naphtha cracking, where the aromatic content is higher. Nonetheless, if the solvent recovery problem was overcome, the separation could be performed at the beginning of the naphtha cracking; hence, the energy requirements throughout the whole cracking process would be reduced because of the decrease of the flows to be heated in the columns.[4]

In recent years, several solvents have been studied as alternatives to sulfolane. It has been stated that ionic liquids (ILs) could be used as extracting agents for this separation.[5,6] Some ILs show solute distribution coefficients and selectivity

values similar to those of sulfolane. Moreover, the negligible vapor pressure of ILs resolves the solvent recovery problem described above.[4] For example, ILs could be easily recovered after the extraction by flash distillation. Nevertheless, the high price of the ILs due to their complicated synthesis is the main disadvantage for large scale applications.

Around one decade ago, a new generation of solvents, called deep eutectic solvents (DESs), was reported for the first time.[7] DESs are mixtures of one or more hydrogen bond acceptors (HBAs) and one or more hydrogen bond donors (HBDs) that, when mixed together in the proper molar ratio, show a big decrease in the melting point compared to the initial compounds.[8−10] DESs share many properties with ILs, e.g., low vapor pressure, wide liquid range, water compatibility, and nonflammability.[11] All these properties are interesting regarding the solvent recovery problem previously mentioned. Moreover, compared to ILs, DESs can be more easily and cheaply prepared by mixing the individual components and applying some heat. Consequently, if any DES shows distribution coefficient and selectivity values similar to those of sulfolane, it would overcome both the solvent recovery problem of the conventional sulfolane process and the high synthesis price of the ILs.

The aim of this work is to evaluate the suitability of two different DESs as extracting agents for the aliphatic/aromatic hydrocarbons separation via liquid−liquid extraction. The mixture benzene/hexane was selected, since its separation has been widely studied using ILs,[12−25] but only a very few studies involving DESs are available (so far).[26,27] First, in order to select an adequate DES for this separation, the solubility of benzene in several DESs was determined at $T/K = 298.2$ and atmospheric pressure. Thereafter, for those DESs showing the highest benzene solubility, the hexane solubility was also measured. Based on the solubility difference, the selected DESs were (i) tetrahexylammonium bromide:ethylene glycol with molar ratio = 1:2 (DES 1) and (ii) tetrahexylammonium bromide:glycerol with molar ratio = 1:2 (DES 2). Second, the selected solvents have been characterized by measuring the density and the viscosity at $T/K = 293.2−343.2$ and atmospheric pressure. Third, the liquid−liquid equilibrium (LLE) data of the ternary systems {hexane + benzene + DES 1} and {hexane + benzene + DES 2} were determined at $T/K = 298.2$ and $T/K = 308.2$ and atmospheric pressure. This was done in order to study the influence of the temperature, as well as the role of the hydrogen bond donor (HBD) of the deep eutectic solvent on the extraction of benzene from hexane. To evaluate the separation suitability of the studied DESs, the solute distribution coefficient and the selectivity were also calculated from the experimental LLE data and compared to the literature. Finally, the experimental LLE data were correlated using the nonrandom two-liquid (NRTL) thermodynamic model. Throughout this paper, the DESs were treated as a single compound.

2. EXPERIMENTAL PROCEDURE

2.1. Materials. The chemicals used for the determination of the LLE data, including their purity and source, are shown in Table 1. The chemicals used for the solubility test, also
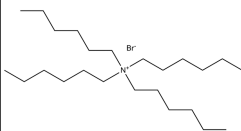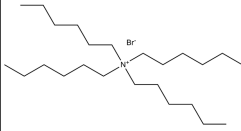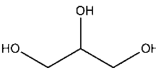
Table 1. Chemicals Used in This Work

chemical	purity (wt %)	source
hexane	≥99	Sigma-Aldrich
benzene	≥99.9	VWR
tetrahexylammonium bromide	≥99	Acros Organics
ethylene glycol	≥99	Merck
glycerol	≥99	Merck
acetone	≥99	VWR
pentane	≥99	Reidel-de Haën

including purity and source, are shown in the Supporting Information, Table S1. All chemicals were used without further purification.

2.2. DES Preparation. The DESs were prepared using a Mettler AX205 balance with an uncertainty in the measurement of $\pm 0.2 \times 10^{-4}$ g. Both the HBA and the HBD were mixed in a flask and heated under stirring until a clear liquid was formed. The temperature was controlled using a thermostatic bath with temperature controller (IKA ETS-D5) with an uncertainty in the measurement of ± 0.1 K. DES 1 and DES 2 were prepared at $T/K = 333.2$. The molecular structures of DES 1 and DES 2 are presented in Table 2.

2.3. DES Characterization. Density and viscosity were measured at $T/K = 293.2−343.2$ and atmospheric pressure using an Anton Paar SVM 3000/G2 Stabinger densimeter−viscosimeter with a high-precision thermostat with a stability of

Table 2. DESs Selected for This Work; HBA, HBD, and Molar Ratios between Them

Abbreviation	HBA	Molar ratio	HBD
DES 1	Tetrahexylammonium bromide	1:2	Ethylene glycol
DES 2	Tetrahexylammonium bromide	1:2	Glycerol

0.005 K. The uncertainties of the density (with viscosity correction) and viscosity measurements are ± 0.0005 g·cm^{-3} and $\pm 0.35\%$, respectively.

2.4. Solubility Test. The solubilities of benzene and hexane in the studied DESs were determined at $T/K = 298.2$ and atmospheric pressure using the cloud point method.[28] Approximately 4 g of DES was placed in a vial and hexane or benzene was added dropwise until a slight turbidity in the samples was observed. Then, the compositions of the samples were determined by weighing. The temperature was controlled using a thermostatic bath with temperature controller (IKA ETS-D5) with a precision of ± 0.1 K.

2.5. LLE Determination. The experimental LLE data were determined at $T/K = 298.2$ and 308.2 and atmospheric pressure. For the experimental determination of the tie lines, mixtures of the studied components within the immiscible region were prepared by weighing. The mixtures were placed into vials of 15 mL sealed with rubber covers to avoid losses by evaporation or moisture absorption. Then, they were vigorously stirred for at least 3 h in order to allow an intimate contact between the two phases. Thereafter, they were left to settle overnight in a thermostatic bath to guarantee that the equilibrium was completely reached. After the phase separation, both phases were sampled using a needled syringe and their compositions were determined using gas chromatography (GC).

DESs have very low vapor pressure; thus, they cannot be analyzed by GC. Therefore, only hexane and benzene were analyzed in both phases and the DES concentration was obtained in both phases from a mass balance calculation. The gas chromatograph used was a Varian 430 GC equipped with a flame ionization detector. The parameters of analysis were as follows: (i) column, Varian CP-SIL 5CB (25 m × 0.25 mm × 1.25 μm); (ii) column oven temperature, 313.2 K for 2 min; (iii) temperature ramp, 373.2 K (rate = 40 K/min) for 2.75 min; (iv) carrier gas, helium; (v) flow rate, 2 mL/min; (vi) injector temperature, 548.2 K; and (vii) detector temperature, 473.2 K. Injection was done with a split ratio of 250 and the injection volume was 1 μL. To avoid column contamination, the DES was collected in an empty injector liner which was cleaned with water and acetone and dried before its use. All samples were measured at least three times, and the relative standard deviation was found to be smaller than 1%.

3. RESULTS AND DISCUSSION

3.1. Solubility Test. An optimal DES for the separation of aromatic from aliphatic hydrocarbons must fulfill the following requirements: (i) high solubility of aromatic hydrocarbons in the DES, (ii) no or low solubility of aliphatic hydrocarbons in the DES, (iii) high selectivity and high solute distribution coefficient, and (iv) easy recovery of the extracting agent.[1] Besides, other criteria should also be considered for an easier handling and usage (e.g., DESs liquid at room temperature, low viscosity).

In order to validate the first two criteria, a solubility test was performed. In this test, 60 different DESs were prepared (a list of the prepared DESs can be found in the Supporting Information, Table S2). Only those DESs which remained liquid at room temperature and showed acceptable viscosity were considered for further study; therefore, the list shown in Table S2 was reduced to 34 different DESs.

The solubility of benzene in the selected 34 different DESs was experimentally determined at T/K = 298.2 and atmospheric pressure using the cloud point method as described in section 2.4. Thereafter, the solubility of hexane in those DESs showing the highest solubility in benzene was also measured under the same conditions. In Table 3, the most promising results are shown. In Table S3 (in the Supporting Information), the experimental solubility of benzene in all the studied DESs can also be found.

Table 3. Solubility of Hexane and Benzene in the Most Promising DESs[a]

DES	x_{hexane}	$x_{benzene}$
methyltriphenylphosphonium bromide:ethylene glycol (1:4)	0.005	0.135
tetraethylammonium chloride:ethylene glycol (1:2)	0.003	0.193
tetrahexylammonium bromide:glycerol (1:2)	0.157	0.844
tetrahexylammonium bromide:ethylene glycol (1:2)	0.205	fully soluble

[a]The solubility (expressed in mole fraction) was measured at T/K = 298.2 and atmospheric pressure.

From Table 3 it can be noticed that all the DESs show higher solubility in benzene than in hexane. This behavior can be explained considering the presence of π-electrons around the benzene (due to the aromatic nature of the molecule), which causes a stronger electrostatic field around the aromatic molecule. The π-electron cloud induces the interactions with the solvents and implies higher solubilities. This π-electron cloud is not present around the hexane molecule; therefore, the hexane−DES interactions are weaker compared to the benzene−DES interactions.[5,13]

All the DESs shown in Table 3 fulfill the first two criteria for the selection of an optimal extracting agent presented above. However, considering that the most important criterion is the high solubility in aromatic compounds, the selected DESs for further study were (i) tetrahexylammonium bromide:ethylene glycol 1:2 (DES 1) and (ii) tetrahexylammonium bromide:glycerol 1:2 (DES 2).

Although the difference in solubilities is an indicator of the workability of the separation, the LLE data of the ternary systems must be experimentally determined in order to calculate the solute distribution coefficient and the selectivity. These two common parameters will indicate the feasibility of the separation (see section 3.3).

3.2. Characterization. In order to apply a solvent as extracting agent for liquid−liquid extraction, some physico-chemical properties should be analyzed, i.e., density and viscosity. The experimental values of the density and the viscosity determined at atmospheric pressure and at T/K = 293.15−343.15 of the two selected solvents are shown in Table 4.

Table 4. Experimental Density and Viscosity Values of the Studied DESs at Different Temperatures and Atmospheric Pressure

DES 1			DES 2		
T (K)	ρ (g·cm^{-3})	η (mPa·s)	T (K)	ρ (g·cm^{-3})	η (mPa·s)
293.15	1.0078	229.5	293.15	1.0458	1197
298.15	1.0045	172.2	298.15	1.0426	813
303.15	1.0013	131.9	303.15	1.0393	567
308.15	0.9983	102.4	308.15	1.0360	402
313.15	0.9951	80.7	313.15	1.0327	291
318.15	0.9919	64.4	318.15	1.0295	215.1
323.15	0.9886	52.1	323.15	1.0263	162.5
328.15	0.9854	42.6	328.15	1.0231	125.1
333.15	0.9822	35.1	333.15	1.0200	97.9
338.15	0.9789	29.3	338.15	1.0168	77.7
343.15	0.9757	24.71	343.15	1.0137	62.6

The dependence of the density with the temperature can be expressed through a linear equation:

$$\rho\left(\frac{g}{cm^3}\right) = a + bT \text{ (K)} \tag{1}$$

where ρ is the density in g·cm^{-3}, T is the temperature in K, and a and b are adjustable parameters, given in the Supporting Information (Table S4). The standard relative deviation, σ, of the experimental density data from its fitting values was calculated as

$$\sigma = \left\{ \sum_i^{n_{dat}} \left(((z - z_{cal})/z_{cal})^2 / n_{dat} \right) \right\}^{1/2} \tag{2}$$

where z and z_{cal} are the values of experimental and calculated physical properties, respectively, and n_{dat} is the number of experimental data points. The σ values are also shown in the Supporting Information, Table S4. In Figure 1, the influence of the temperature on the density is graphically shown, including the calculated values using the correlation presented in eq 1.

The viscosity values, η, were fitted using both the Arrhenius-like and the Vogel−Fulcher−Tammann (VFT) equations. The most commonly used equation to correlate the variation of viscosity with temperature is the Arrhenius-like law:

$$\eta = A \exp\left(\frac{-B}{RT}\right) \tag{3}$$

where the fitting parameters are A (mPa·s), the viscosity at infinite temperature; B (kJ·mol^{-1}), the activation energy; and R (8.31 J·mol^{-1}·K^{-1}), the gas constant. The Vogel−Fulcher−Tammann (VFT) equation was also used to fit the dependence of viscosity with temperature using the following expression:

$$\eta = A \exp\left(\frac{B}{T - T_0}\right) \tag{4}$$

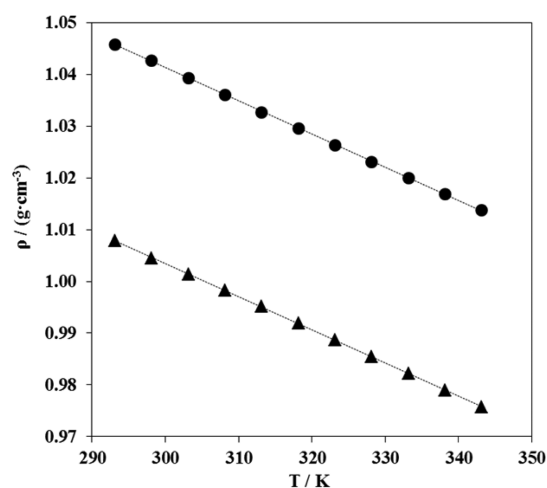where A (mPa·s), B (K), and T_0 (K) are the fitting parameters.

Figure 1. Experimental density values as a function of temperature for DES 1 (▲) and DES 2 (●). Dashed lines represent the linear fitting.

The fitting parameters for both viscosity correlations, together with the standard relative deviations, σ (calculated with eq 2), are presented in the Supporting Information, Table S5. From this table it is possible to observe that the best fit for the viscosity is given by the VFT equation, because the relative standard deviation with this fitting is smaller. However, it should also be considered that the VFT equation has three fitting parameters, while the Arrhenius equation only has two; therefore, a better fitting with the VFT equation should be expected. Figure 2 shows the experimental viscosity against temperature together with the fitting using the VFT equation.
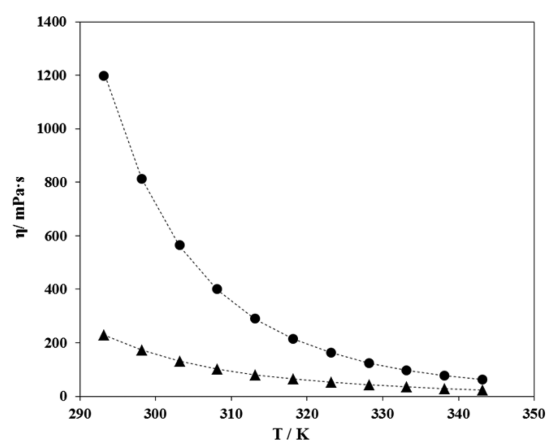

Figure 2. Experimental viscosity values as a function of temperature for DES 1 (▲) and DES 2 (●). Dashed lines represent the fitting using the VFT equation.

From Figures 1 and 2 it is possible to study the influence of temperature as well as the role of the HBD on the physical properties of the two studied DESs. As expected, the density decreases linearly with the temperature, while the viscosity decreases sharply when the temperature is increased. It can also be observed that the glycerol based DES shows higher densities and viscosities over the whole range of studied temperatures. This behavior was expected, because glycerol has higher densities and viscosities compared to ethylene glycol, and both DESs are prepared at the same molar ratio with the same HBA.

Although the LLE data are needed for the evaluation of the selected solvents in the extraction, in terms of physicochemical properties the DES 1 (ethylene glycol based DES) would be the best choice for acting as extracting agent in this separation. Moreover, both DES 1 and DES 2 would be preferred compared to ethylene glycol and glycerol, respectively. The reason is that both mass transfer limitations and operational costs associated with issues such as liquid pumping can be improved by low viscosity solvents.

3.3. Experimental LLE Data. The experimental LLE data of the systems {hexane (1) + benzene (2) + DES 1 (3)} and {hexane (1) + benzene (2) + DES 2 (3)} were measured at $T/K = 298.2$ and $T/K = 308.2$ and atmospheric pressure. The solubility values of the studied DESs at $T/K = 298.2$ and 302.5 are presented in Table 5. The obtained experimental data for

Table 5. Solubilities of Hexane and Benzene in the Studied DESs, Expressed in Mole Fraction of the Corresponding Hydrocarbon

DES	T (K)	x_{hexane}	$x_{benzene}$
DES 1	298.2	0.205	fully soluble
	308.2	0.230	fully soluble
DES 2	298.2	0.157	0.844
	308.2	0.169	0.858

the ternary systems containing DES 1 and DES 2 are presented in Table 6 and Table 7, respectively. The experimental data are plotted by means of a triangular diagram in Figure 3.

The efficiency of the separation can be evaluated using two parameters: the solute distribution coefficient (β) and the selectivity (S). These parameters can be calculated using the following expressions:

Table 6. Experimental LLE Data, in Mole Fraction, for the Ternary Systems {Hexane (1) + Benzene (2) + DES 1 (3)} at Atmospheric Pressure, Including Solute Distribution Coefficient (β) and Selectivity (S) Values[a]

aliphatic-rich phase		DES-rich phase			
x_1	x_2	x_1	x_2	β	S
		$T/K = 298.2$			
0.929	0.071	0.202	0.076	1.07	4.94
0.872	0.128	0.210	0.129	1.01	4.19
0.812	0.188	0.209	0.178	0.95	3.67
0.710	0.290	0.215	0.264	0.91	3.01
0.603	0.397	0.229	0.344	0.87	2.28
0.473	0.527	0.235	0.439	0.83	1.67
0.383	0.617	0.244	0.539	0.87	1.38
0.309	0.691	0.242	0.634	0.92	1.17
		$T/K = 308.2$			
0.949	0.051	0.225	0.051	1.00	4.24
0.886	0.114	0.225	0.108	0.94	3.71
0.822	0.178	0.225	0.165	0.93	3.38
0.710	0.290	0.229	0.254	0.88	2.71
0.597	0.403	0.231	0.339	0.84	2.17
0.463	0.537	0.239	0.448	0.84	1.62
0.361	0.639	0.245	0.564	0.88	1.30
0.297	0.703	0.240	0.653	0.93	1.15

[a]Standard uncertainties u are $u(T) = 0.1$ K and $u(x) = 0.015$.

Table 7. Experimental LLE data, in Mole Fraction, for the Ternary Systems {Hexane (1) + Benzene (2) + DES 2 (3)} at Atmospheric Pressure, Including Solute Distribution Coefficient (β) and Selectivity (S) Values[a]

aliphatic-rich phase		DES-rich phase			
x_1	x_2	x_1	x_2	β	S
		$T/K = 298.2$			
0.927	0.073	0.152	0.103	1.41	8.58
0.798	0.202	0.140	0.204	1.01	5.77
0.700	0.300	0.146	0.276	0.92	4.43
0.596	0.404	0.138	0.321	0.79	3.42
0.482	0.518	0.133	0.384	0.74	2.69
0.368	0.632	0.138	0.493	0.78	2.09
0.277	0.723	0.127	0.566	0.78	1.70
0.202	0.798	0.110	0.628	0.79	1.45
0.138	0.862	0.087	0.684	0.79	1.26
		$T/K = 308.2$			
0.939	0.061	0.147	0.077	1.27	8.11
0.841	0.159	0.144	0.146	0.92	5.37
0.805	0.195	0.141	0.175	0.90	5.15
0.704	0.296	0.141	0.237	0.80	3.99
0.590	0.410	0.140	0.317	0.77	3.26
0.478	0.522	0.137	0.402	0.77	2.69
0.358	0.642	0.133	0.486	0.76	2.03
0.268	0.732	0.128	0.583	0.80	1.67
0.194	0.806	0.108	0.656	0.81	1.46
0.133	0.867	0.085	0.723	0.83	1.30

[a]Standard uncertainties u are $u(T) = 0.1$ K and $u(x) = 0.015$.

$$\beta = \frac{x_{2,E}}{x_{2,R}} \tag{5}$$

$$S = \frac{\left(\dfrac{x_2}{x_1}\right)_E}{\left(\dfrac{x_2}{x_1}\right)_R} \tag{6}$$

where x_1 and x_2 refer to the mole fractions of aliphatic and aromatic compounds, respectively; the subscripts "E" and "R" refers to the extract (DES-rich phase) and the raffinate (aliphatic-rich phase), respectively. The solute distribution coefficient and the selectivity values are shown in Table 6 for the systems containing DES 1 and in Table 7 for the systems containing DES 2.

The solute distribution coefficients and the selectivities as a function of the aromatic concentration in the aliphatic-rich phase for the systems {hexane (1) + benzene (2) + DES 1 (3)} at $T/K = 298.2$ and $T/K = 308.2$ and {hexane (1) + benzene (2) + DES 2 (3)} at $T/K = 298.2$ and $T/K = 308.2$ are shown in Figure 4 and Figure 5, respectively.

From Table 5, it can be observed that a temperature increment leads to a slight increase of the solubility of hexane and benzene in the studied DESs. It can also be noticed that both hydrocarbons are more soluble in the ethylene glycol based DES (DES1) than in the glycerol based DES (DES 2). Finally, the total miscibility of benzene in the DES 1 is remarkable, since this is not the usual behavior of benzene in previous extraction studies using both ILs and DESs.
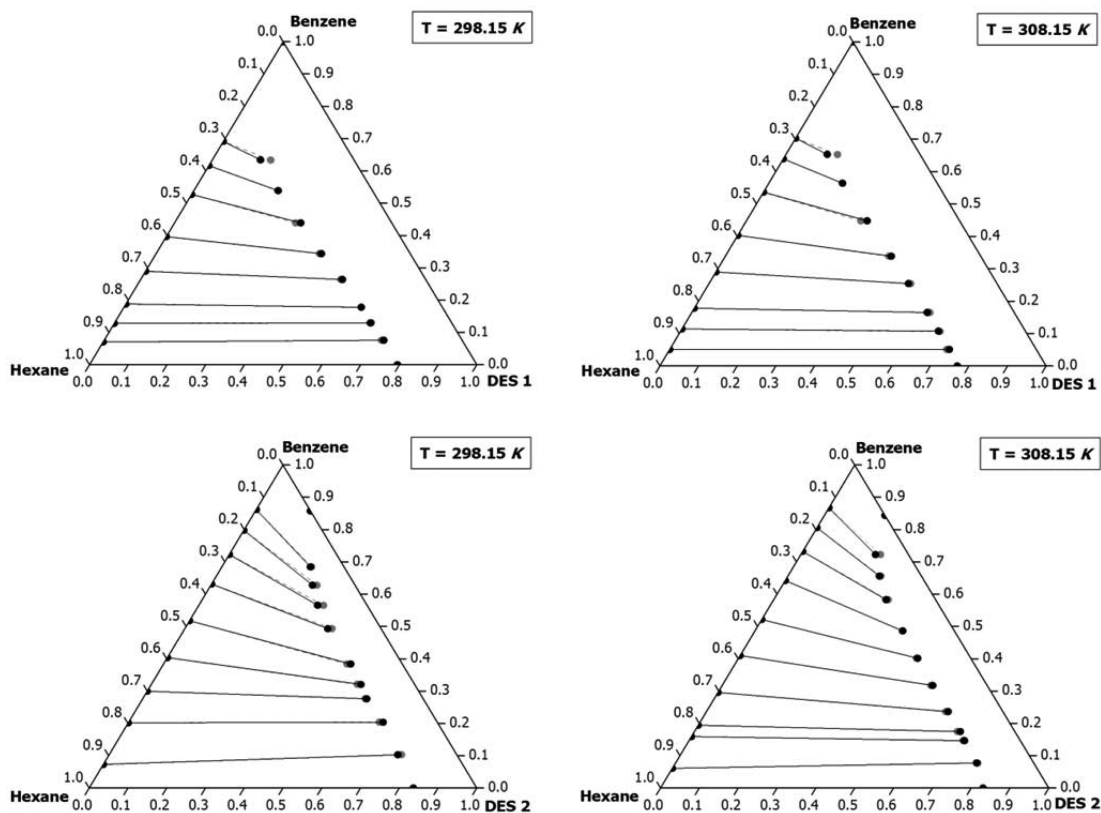

Figure 3. (●, solid line) Experimental tie lines for the ternary systems {hexane + benzene + DES 1} and {hexane + benzene + DES 2} at $T/K = 298.2$ and 308.2 and atmospheric pressure. (gray solid circles, dashed line) Calculated tie lines using the NRTL model. Please notice that the four ternary diagrams are presented in mole fractions.
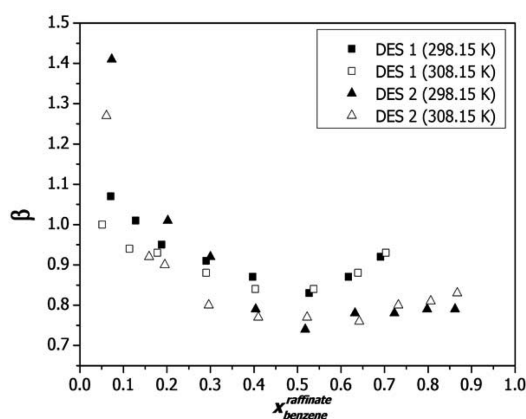
Figure 4. Experimental solute distribution coefficient values (β) as a function of the mole fraction of benzene in the aliphatic-rich phase for the systems {hexane + benzene + DES 1} at 298.2 (■) and 308.2 K (□) and atmospheric pressure and {hexane + benzene + DES 2} at 298.2 (▲) and 308.2K (△) and atmospheric pressure.
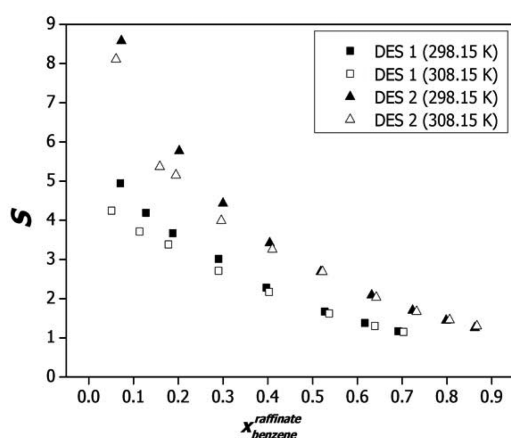

Figure 5. Experimental selectivity values (S) as a function of the mole fraction of benzene in the aliphatic-rich phase for the systems {hexane + benzene + DES 1} at 298.2 (■) and 308.2 K (□) and atmospheric pressure and{hexane + benzene + DES 2} at 298.2 (▲) and 308.2 K (△) and atmospheric pressure.

The solubility data of Table 5 can be compared to those of pure glycerol and ethylene glycol presented as Supporting Information (Table S6), in which the solubilities of benzene and hexane in pure glycerol and ethylene glycol are presented. It can be observed that the solubilities of both hydrocarbons are much higher in the DES than in pure glycerol or ethylene glycol. Specifically for benzene, the increase in solubility is impressive. For example, the solubility of benzene in pure ethylene glycol is only $x_{benzene} = 0.023$, while it is fully soluble in the ethylene glycol based DES (DES 1). The solubility of benzene in pure glycerol is $x_{benzene} = 0.007$, while it is $x_{benzene} = 0.844$ in the glycerol based DES (DES 2). The formation of a DES breaks the bonds between the glycerol or ethylene glycol molecules, producing intramolecular hydrogen bond interactions around the DES, which allows an increase of the solubility.

From Figure 3 it can be observed that, according to the classification proposed by Sørensen et al.,[29] the ternary systems containing ethylene glycol based DESs correspond to the type 1 category, in which two of the pairs of compounds exhibit complete miscibility ({hexane + benzene} and {benzene + DES

1}) and only one pair is partially miscible ({hexane + DES 1}). Moreover, the ternary systems involving glycerol based DESs correspond to the type 2 category, since two of the pairs of compounds exhibit partial miscibility ({hexane + DES 2} and {benzene and DES 2}) and only one pair is miscible in the whole range of compositions ({hexane + benzene}).

From Figure 4 and Figure 5, the effect of the temperature on the separation can be analyzed. It can be observed that the effect of the temperature is rather small in both systems. However, both the solute distribution coefficients and the selectivity values are slightly higher at $T/K = 298.2$ than at $T/K = 308.2$. That is, the separation is promoted by low temperatures. Therefore, extraction at $T/K = 298.2$ is advised in order to diminish the energy demand.

From Figure 4, it can be observed that the solute distribution coefficient values of DES 1 and DES 2 decrease when the concentration of aromatic in the aliphatic-rich phase increases, until an aromatic mole fraction in the aliphatic-rich phase of around $x_{benzene} = 0.5$ is reached in all the studied systems. Starting from the mentioned concentration, in which the solute distribution coefficient finds its minimum value, the solute distribution coefficient increases with the concentration of aromatic compound in the aliphatic-rich phase. Hence, the extraction of aromatic components is more favorable either at low aromatic concentration or at high aromatic concentrations, but less favorable in the region from $0.35 < x_{benzene} < 0.6$ in the aliphatic-rich phase. This kind of behavior of the solute distribution coefficient is also observed for sulfolane. From Figure 5, it can be noticed that the selectivity values of DES 1 and DES 2 decrease with an increase of the concentration of aromatic component in the aliphatic-rich phase. Moreover, in all the studied systems the selectivity values were found to be higher than unity, indicating that the separation using these DESs could be feasible.

It is also possible to compare the behaviors of DES 1 and DES 2 as extracting agents for the separation of {hexane + benzene}. In general trends, DES 1 shows higher solute distribution coefficient values than DES 2, and in terms of selectivity DES 2 shows higher values over the whole range of concentrations. This behavior could be explained on the basis of the electrostatic potential of the HBD. Glycerol shows a higher electrostatic potential compared with ethylene glycol; therefore, the HBD−HBA interactions of the glycerol based DES (DES 2) are stronger compared to the ethylene glycol based DES (DES 1). The stronger interactions present in DES 2 produce a more delocalized charge which decreases the interaction with both benzene and hexane. That is the reason for the higher solubility of both benzene and hexane in DES 1, producing the higher distribution coefficient values.

After the analysis of the results, it is possible to conclude that the usage of DES 1 for the separation of benzene from {hexane + benzene} would be preferred over the usage of DES 2. The reason is that higher solute distribution coefficients are generally more profitable because they imply lower solvent-to-feed ratios and, therefore, smaller amounts of solvent to be recovered and thus lower energy requirements. Contrarily, the high selectivity values (DES 2) mainly affect the equipment size, which results in an initial investment with a smaller economic impact in the performance of the separation. Moreover, DES 1 shows lower density and much lower viscosity values than DES 2, which is also beneficial for the economy of the process.

3.4. Literature Comparison. In order to evaluate the performances of DES 1 and DES 2, a literature comparison was done. We compared the solute distribution coefficient and selectivity values of our solvents to those of previously studied solvents in the literature (sulfolane/ILs). The comparison of the solute distribution coefficients and the selectivity values are depicted in Figure 6 and Figure 7, respectively. Due to the high
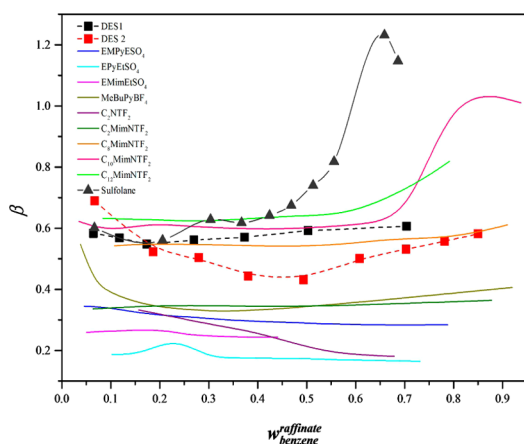

Figure 6. Solute distribution coefficient values as a function of the aromatic content in the aliphatic-rich phase for the system {hexane + benzene + extractant}.[13−16,18−21]
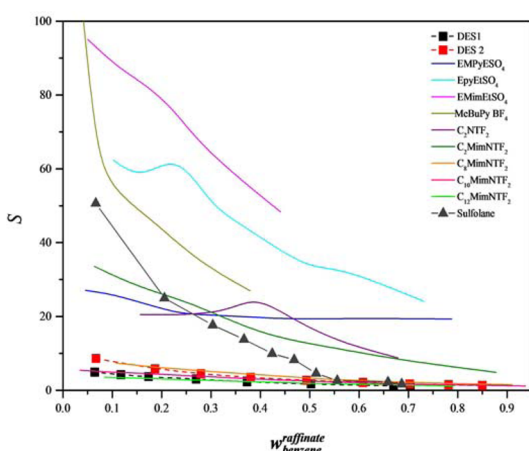

Figure 7. Selectivity values as a function of the aromatic content in the aliphatic-rich phase for the system {hexane + benzene + extractant}.[13−16,18−21]

difference in molar masses between sulfolane and the ILs, the comparison was made in mass fraction (instead of mole fraction) in order to obtain more realistic values concerning the applicability of the solvents.

When DES 1 and DES 2 are compared to sulfolane, it can be observed that, for low aromatic concentrations in the aliphatic-rich phase, the performance of sulfolane is similar to that of the studied DESs. However, starting from a concentration of around $w_{benzene} = 0.15$ in the aliphatic-rich phase, the solute distribution coefficient values of sulfolane are higher than those of DES 1 and DES 2. If sulfolane is compared with the ILs, the solute distribution coefficient values of sulfolane are higher than those of any IL; only bis(trifluoromethylsulfonyl)imide based ILs (e.g., 1-decyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ($C_{10}MimNTF_2$) and 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

($C_{12}MimNTF_2$)), which contain rather long alkyl chain lengths on the imidazolium cation, show higher solute distribution coefficient values than sulfolane at low aromatic concentrations in the aliphatic-rich phase. In terms of selectivity, DES 1, DES 2, $C_{10}MimNTF_2$ and $C_{12}MimNTF_2$ show lower values than sulfolane. However, in terms of industrial application, we will prefer higher values of the distribution coefficient better than higher values of selectivity. This is because high distribution coefficient values mean less solvent needed during the extraction process and therefore this implies a reduce in the operational cost, both in terms of energy (solvent recovery) and in terms of chemicals (solvent makeup stream). Contrarily, high selectivity values imply smaller equipment needed; however, the equipment scaling is generally favorable and is only an initial investment of capital cost. Moreover, considering the distribution coefficient values of the DESs at low aromatic concentrations, they seem to be an interesting industrial alternative.

In terms of economic efficiency, the studied DESs and the mentioned ILs imply a simpler and cheaper solvent recovery compared to volatile solvents (e.g., sulfolane) due to the negligible vapor pressures of these solvents. The simple solvent recovery overcomes the main disadvantage of the sulfolane process: the huge energy requirements for the solvent recovery. Therefore, the application of DES 1 and DES 2 as extracting agents for the {hexane + benzene} separation seems economically feasible and more promising than ILs.

3.5. Correlation. The experimental LLE data were correlated using the NRTL thermodynamic model,[30] in which the DESs have been treated as a single component. The model was applied by minimizing the following objective function.

$$\mathrm{OF} = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{\left(\frac{1}{\beta_{ij}}\right)^{cal} - \left(\frac{1}{\beta_{ij}}\right)^{exp}}{\left(\frac{1}{\beta_{ij}}\right)^{exp}} \right)^2$$

(7)

where m is the number of tie lines, n is the number of components in the mixture, and $(1/\beta)^{exp}$ and $(1/\beta)^{cal}$ are experimental and calculated inverse values of the solute distribution ratio, respectively.

The root-mean-square deviation of the composition, σx, has been calculated as follows:

$$\sigma x = 100 \cdot \left(\frac{\sum_i^m \sum_j^{n-1} (x_{ij}^{I,exp} - x_{ij}^{I,cal})^2 + (x_{ij}^{II,exp} - x_{ij}^{II,cal})^2}{2mn} \right)^{1/2}$$

(8)

This deviation compares the experimental and calculated mole fractions of the components for each tie line.

In Table 8, the fitting parameters and the root-mean-square deviation of the composition are presented. During the fitting, the nonramdomness parameter was set to different values between 0.05 and 0.30. The best results were obtained with the values for α_{ij} presented in Table 8. In Figure 3 the experimental and calculated data are shown, and the goodness of the fitting can be observed. NRTL is a good model for the fitting of LLE data containing ILs.

Table 8. NRTL Parameters Obtained for the Systems {Hexane (1) + Benzene (2) + DES (3)}, along with the Root-Mean-Square Deviation of the Composition

ij	T (K)	Δg_{ij} (kJ mol^{-1})	Δg_{ji} (kJ mol^{-1})	α_{ij}	σx
{Hexane (1) + Benzene (2) + DES 1 (3)}					
1–2	298.2	−23.438	1.483		
1–3	298.2	73.694	5.696	0.15	0.444
2–3	298.2	173.87	−28.034		
1–2	308.2	−23.018	1.464		
1–3	308.2	78.043	5.941	0.15	0.488
2–3	308.2	166.75	−28.260		
{Hexane (1) + Benzene (2) + DES 2 (3)}					
1–2	298.2	−6.303	12.866		
1–3	298.2	105.942	5.023	0.10	0.395
2–3	298.2	149.047	0.837		
1–2	308.2	4.199	1.256		
1–3	308.2	106.913	4.876	0.10	0.235
2–3	308.2	153.132	2.114		

4. CONCLUSIONS

In this work, the applicability of a new generation of solvents, so-called DESs, as extracting agents for the separation of the {benzene + hexane} system has been studied. First, a solubility test has been made in order to find DESs fulfilling the solubility requirements for this separation. The DESs showing the highest solubility of benzene have been selected for further investigation. Those solvents were (i) tetrahexylammonium bromide:ethylene glycol with molar ratio = 1:2 (DES 1) and (ii) tetrahexylammonium bromide:glycerol with molar ratio = 1:2 (DES 2). Second, the selected solvents have been characterized; density and viscosity as a function of temperature have been experimentally determined. The density and the viscosity as a function of temperature have been successfully correlated using a linear regression and both the Arrhenius and VFT equations, respectively. It was found that both the density and the viscosity decrease when the temperature is increased. It was also found that the glycerol based DES shows higher density and viscosity values over the whole range of measured temperatures. Thereafter, the LLE data of the systems {hexane (1) + benzene (2) + DES (3)} have been measured at T/K = 298.2 and T/K = 308.2 and atmospheric pressure. The solute distribution coefficient and selectivity values have been calculated and compared to several solvents previously investigated. The temperature effect on the separation has also been studied, showing that low temperatures promote the separation and reduce the energy requirements. Considering the solute distribution coefficient and selectivity values, DES 1 would be preferred over DES 2 for this separation. The lower values of density and viscosity of DES 1 compared to DES 2 also suggest that DES 1 will be the best option from the studied DESs. Finally, the NRTL model has been satisfactorily applied to the experimental data by treating the DESs as a single component.

It was found that the solute distribution coefficients of the studied DESs are lower than that of sulfolane. Only for DES 2 at low aromatic concentrations in the aliphatic-rich phase the solute distribution coefficient is higher than that of sulfolane and also higher than the previously studied ILs. It has also been found that the selectivity values are higher for the sulfolane than for any of the studied DESs. However, if the negligible volatility of the DESs is considered, then the main disadvantage of the sulfolane process, which is the amount of energy needed

for the solvent recovery, could be overcome. It has also been found that the performance of the studied DESs is comparable to that of the ILs. Since the DESs are 2 times cheaper, they can overcome the main disadvantage of ILs, i.e., their high price. Therefore, preliminary results show that this new generation of solvents can be used as efficient extracting agents for the separation of the mixture {hexane + benzene}.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b02611.

Details about all the chemicals used in this work, solubility data of several DESs, density and viscosity fitting parameters for selected DESs, pure glycerol and ethylene glycol solubility data (PDF)

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Notes

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