International Journal of Advance Research in Science and Engineering
Volume No. 12, Issue No. 01, January 2023
www.ijarse.com
IJARSE
ISSN 2319 - 8354

Separation of Aromatic-Aliphatic using extracting agent by Gas Chromatography

[1]Swati, [2]ChelluboyanaVaishnava Raghunath, [3]Amar Kumar

[1]Department of chemical engineering, BIT Sindri, Jharkhand University of Technology, India.

ABSTRACT

Chemical engineers faces a significant hurdle when attempting to separate aliphatic from aromatic molecules.For mixtures containing less than 20 wt% aromatics, there is no effective separation method.In this study, two distinct deep eutectic solvents (DESs) were investigated for their viability as brand-new extracting agents for the separation of the mixture "hexane + benzene."A set of DESs were tested for solubility at ambient temperature and atmospheric pressure in order to choose the best solvent for this separation.The deep eutectic solvents used in this study were I tetrahexylammonium bromide: ethylene glycol at a molar ratio of 1:2 (DES 1) and (ii) tetrahexylammonium bromide: glycerol at a molar ratio of 1:2 (DES 2). At atmospheric pressure and temperatures T = 293.2–343.2 K, measurements of density and viscosity were used to describe the chosen DESs.Next, it was determined what the liquid-liquid equilibria (LLE) were for the ternary systems(hexane + benzene + DES 1) and (hexane + benzene + DES 2) at T/K = 298.2 and T/K = 308.2, respectively.Additionally, for the investigated ternary system with different solvents, the solute distribution coefficient and selectivity values were determined and compared to LLE data found in the literature.Finally, the nonrandom two-liquid (NRTL) model was used to correctly correlate the experimental data.The results obtained indicate that DESs are promising extracting agents for the industrial separation of naphtha streams with low aromatic concentrations.

Keywords-*Benzene, Hexane, DES 1, DES 2, Aromatic, Aliphatic.*

1. INTRODUCTION

In the petrochemical sector, distinguishing aromatic from aliphatic chemicals is not only crucial but also incredibly difficult.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.This mixture contains azeotropes and components with close boiling points, making separation problematic. 1,2 Sulfolane is used in industry to carry out this separation.Sulfolane is used as the extracting agent in this method, which involves liquid-to-liquid extraction. Extractive distillation is then used to recover the solvent.For combinations with an aromatic content lower than 20%, this is not an effective separation technique due to the significant energy investment required for the sulfolane recovery.Due to the higher aromatic concentration at this point in the naphtha cracking process, the separation of aromatics from aliphatic compounds is carried out.However, if the solvent recovery issue could be solved, the separation could be carried out before naphtha cracking. As a result, the energy needs for the entire cracking process would be decreased because there would be fewer flows that needed to be heated in the columns.Several solvents have been researched recently as sulfolane substitutes.Ionic liquids (ILs) have been suggested as extracting agents for this separation. Some ILs have selectivity and solute dispersion coefficients that are comparable to those of sulfolane.Furthermore, the solvent recovery issue mentioned above is solved by ILs' minimal vapour pressure. For instance, flash distillation could make it simple to recover ILs following the extraction. However, the greatest drawback for large-scale applications is the high cost of the ILs as a result of their difficult synthesis.A novel class of solvents known as deep eutectic solvents (DESs) was originally identified about ten years ago.When combined in the right molar ratio, one or more hydrogen bond acceptors (HBAs) and one or more hydrogen bond donors (HBDs) form DESs, which have a markedly lower melting point than the original compounds.Many characteristics between DESs and ILs are similar, including low vapour pressure, a broad range of liquid compatibility, and nonflammability. In light of the previously noted solvent recovery issue, all of these characteristics are intriguing.Additionally, when compared to ILs, DESs are simpler and less expensive to make simply combining the various parts and heating them. The solvent recovery issue with the traditional sulfolane technique and the high synthesis cost of the ILs would therefore be solved if any DES exhibited distribution coefficient and selectivity values comparable to those of sulfolane.The purpose of this work is to assess the efficacy of two various DESs as extracting agents for the liquid–liquid extraction-based separation of aliphatic and aromatic hydrocarbons. The mixture of benzene and hexane was chosen since ILs have been extensively used in studies on its separation, whereas DES investigations have been quite rare (so far). First, the solubility of benzene in several DESs was measured at T/K = 298.2 and atmospheric pressure in order to choose an appropriate DES for this separation.After that, the hexane solubility of those DESs with the highest benzene solubility was also determined. The chosen DESs were I tetrahexylammonium bromide:glycerol with a molar ratio of 1:2 and (ii) tetrahexylammonium bromide:ethylene glycol with a molar ratio of 1:2 based on the solubility difference (DES 2). Second, the density and viscosity at T/K = 293.2-343.2 and air pressure were measured to describe the chosen solvents.Third, at T/K = 298.2 and T/K = 308,2 and atmospheric pressure, the liquid-liquid equilibrium (LLE) data of the ternary systems "hexane + benzene + DES 1" and "hexane + benzene + DES 2" were determined. This was done to investigate the effects of temperature as well as the role of the deep eutectic solvent's hydrogen bond donor (HBD) on the extraction of benzene from hexane.The solute distribution coefficient and the selectivity were also computed from the experimental LLE data and compared to the literature to assess the suitability of the tested DESs for separation. Finally, the nonrandom two-liquid (NRTL) thermodynamic model was used to corroborate the experimental LLE data. The DESs were handled as a single compound for the duration of this article.

2. EXPERIMENTAL PROCEDURE

2.1. Materials.

Table 1 lists the substances used to determine the LLE data, along with their purity and source. The substances employed for the solubility test, as well

Table 1.Chemicals Used in This Work

Chemical	Purity	Source
Acetone	≥99	VWR
benzene	≥99.9	VWR

ethylene glycol	≥99	Merck
Hexane	≥99	Sigma-Aldrich
Pentane	≥99	Reidel-de Haen
glycerol	≥99	Merck
tetrahexylammonium bromide	≥99	Across Organics

are displayed in the supporting information, Table 1, along with purity and source. None of the compounds were further purified before usage.

2.2.DES Preparation.

A Mettler AX205 balance was used to prepare the DESs, with a measurement uncertainty of 0.2 104 g. In a flask, the HBA and HBD were combined and heated while being stirred until a clear liquid was produced. A thermostatic bath with temperature controller (IKA ETS-D5) was used to regulate the temperature, and the measurement error was 0.1 K. T/K = 333.2 was used to create DES 1 and DES 2. Table 2 displays the molecular structures of DES 1 and DES 2.

2.3.DES Characterization.

Density and viscosity were measured using an Anton Paar SVM 3000/G2 Stabinger densimeter and viscosimeter respectively with a high-precision thermostat with a stability of 0.005K at T/K= 293.2-343.2 and atmospheric pressure.

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

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

The density (with viscosity correction) and viscosity measurements have uncertainties of ±0.0005 gcm3 and ±0.35%, respectively.

2.4. Solubility Test.

The cloud point approach was used to calculate the solubilities of benzene and hexane in the investigated DESs at T/K= 298.2 and atmospheric pressure.Hexane or benzene was added dropwise to a vial containing around 4 g of DES until a minor turbidity in the samples was noticed.The samples' components were then ascertained through weighing. A thermostatic bath with temperature controller (IKA ETS-D5) was used to regulate the temperature with a ±0.1 K accuracy.

2.5.LLE Determination.

Atmosphere-pressure conditions and T/K values of 298.2 and 308 were used to calculate the experimental LLE data. Weighed mixes of the investigated components within the immiscible area were created for the experimental determination of the tie lines.The mixes were put into 15 mL rubber-sealed vials to prevent losses from evaporation or moisture absorption.The two phases were then vigorously agitated for at least three hours to allow for close contact.They were then allowed to settle in a thermostatic bath overnight to ensure that the balance was attained.Following phase separation, both phases were sampled with a needled syringe, and gas chromatography was used to determine their contents (GC). Since DESs have a very low vapour pressure, GC cannot be used to analyse them. As a result, only hexane and benzene were examined in each phase, and a mass balance calculation was used to determine the concentration of DES in each phase. The gas chromatograph used was a GC Optima 3007 with FID (MDL< 1.8 Pg C/ s),capillary column, nitrogen as carrier gas with a flow rate of 2.5 ml mn^{-1} and sample is injected using syringe having capacity of 10µl.equipped with a flame ionization detector.The following were the analysis's parameters: DB-FFAP (30m × 0.538mm, 1µ)capillarycolumn, 313.2 K column oven temperature for 2 minutes; 373.2 K temperature ramp (rate = 40 K/min) for 2.75 minutes; nitrogen as the carrier gas; 2 mL/min flow rate; 548.2 K injector temperature; and 473.2 K detector temperature. The split ratio used for the injection was 250, and the injection volume was 1µL.The DES was collected in an empty injector liner, which was washed with water and acetone before being used, to prevent column contamination.After measuring each sample at least three times, it was discovered that the relative standard deviation was less than 1%.

3. RESULTS AND DISCUSSION

3.1. Solubility Test.

The following criteria must be met by an ideal DES to effectively separate aromatic from aliphatic hydrocarbons: (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) simple recovery of the extracting agent.In addition, additional factors should be taken into account for simpler handling and utilisation (e.g., DESs liquid at room temperature, low viscosity).A solubility test was carried out to verify the first two requirements. 60 distinct DESs were created for this test (a list of the prepared DESs can be found in the Supporting Information, Table 2).The list displayed in Table 2 was condensed to 34 different DESs since only those DESs that stayed liquid at room temperature and demonstrated acceptable viscosity were taken into consideration for additional research.Using the cloud point method as stated in section 2.4, the solubility of benzene in the 34 different DESs that were chosen was experimentally calculated at T/K = 298.2 and atmospheric pressure.The solubility of hexane in those DESs with the highest benzene solubility was then measured in the same manner. The most encouraging results are displayed in Table 3.The experimental solubility of benzene in all the examined DESs may also be found in Table 3 (in the supporting information).

Table 3. **Solubility of Hexane and Benzene in the Most Promising DESs**

DES	X_{benzene}	X_{hexane}
Tetraethylammonium chloride: ethylene glycol (1:2)	0.003	0.193
Tetrahexylammonium bromide: ethylene glycol (1:2)	0.205	Fully soluble
Tetrahexylammonium bromide: glycerol (1:2)	0.157	0.844
Methyltriphenylphosphonium bromide: ethylene glycol (1:4)	0.005	0.135

Atmospheric pressure and T/K = 298.3 were used to measure the solubility (expressed as a mole fraction).

It is clear from Table 3 that all DESs are more soluble in benzene than hexane.The existence of -electrons around benzene (resulting from the molecule's aromatic character), which results in a larger electrostatic field around the aromatic molecule, can be used to explain this behaviour.Higher solubilities are implied by interactions between the -electron cloud and the solvents.Hexane-DES interactions are weaker than benzene-DES interactions because there is no -electron cloud surrounding the hexane molecule. All of the DESs listed in Table 3 meet the first two requirements for choosing the best extracting agent previously mentioned.However, because the high solubility in aromatic compounds is the most crucial condition, the following DESs were chosen for further study: I tetrahexylammonium bromide:ethylene glycol 1:2 (DES 1); and (ii) tetrahexylammonium bromide:glycerol 1:2. (DES 2).The LLE data of the ternary systems must be experimentally measured in order to calculate the solute distribution coefficient and the selectivity, even though the difference in solubilities is a sign that the separation will work.The viability of the separation will be determined by these two common criteria (see section 3.3)

3.2. Characterization. Some physicochemical parameters, such as density and viscosity, should be examined in order to utilise a solvent as an extracting agent for liquid–liquid extraction.Table 4 displays the experimentally determined densities and viscosities of the two chosen solvents at atmospheric pressure and at T/K = 293.15343.15 respectively.

Table4.Experimental Density and Viscosity of the Examined DESs at the Various Atmospheric Pressure and Temperature

DES1 DES2

T(K)	ρ(g/cm^3)	η(mPa. s)	T(K)	ρ(g/cm^3)	η(mPa. s)
293.15	1.005	229.4	293.15	1.0455	1198
298.15	1.0042	172.3	298.15	1.0430	810
303.15	1.0013	132.0	303.15	1.0390	560
308.15	0.9985	102.5	308.15	1.0355	403
313.15	0.9949	81.0	313.15	1.0329	295
318.15	0.9915	64.5	318.15	1.0290	216.4
323.15	0.9881	51.9	323.15	1.0261	162.4
328.15	0.9850	42.3	328.15	1.0229	123.1
333.15	0.9822	35.2	333.15	1.0200	97.4
338.15	0.9785	29.5	338.15	1.0160	77.9
343.15	0.9750	24.50	343.15	1.0130	63.5

A linear equation that describes the relationship between density and temperature exists:

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

where a and b are movable parameters that are described in the supporting information, and is the density in g/cm^3, T is the temperature in K. (Table 4).The experimental density data's standard relative deviation, from its fitting values was computed as

$$\sigma = \{\sum_i^{n_{dat}}((\frac{z - z_{cal}}{z_{cal}})^2/n_{dat})\}^{1/2} \qquad (2)$$

Wheren_{dat} is the quantity of experimental data points and z andz_{cal} are the values of the physical qualities that have been measured experimentally and calculatedly, respectively. The values are also displayed in Table S4 of the supporting data. With the help of the correlation shown in eq 1, the relationship between temperature and density. Both the Vogel-Fulcher-Tammann (VFT) and the Arhenius-like equations were used to fit the viscosity values, η. The Arrhenius-like law is the equation that is most frequently employed to relate viscosity variation to temperature:

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

where A (mPa.s), the viscosity at infinite temperature; B (kJ.mol^{-1}); and R (8.314 Jmol^{-1}. K^{-1}), the gas constant, are the fitting parameters. The relationship between viscosity and temperature was also fit using the Vogel-Fulcher-Tammann (VFT) equation using the following expression:

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

The supporting information, presents the fitting parameters for both viscosity correlations together with the standard relative deviations, (derived using eq 2). This table makes it feasible to see that the VFT equation provides the best fit for viscosity because its relative standard deviation is lower. But it should also be remembered that the Arrhenius equation only has two fitting parameters, but the VFT equation has three. As a result, a better match using the VFT equation should be anticipated. displays the experimental viscosity against temperature along with the VFT equation's fitting.Studying the effects of temperature and the HBD on the physical characteristics of the two examined DESs is possible. When would be expected, as the temperature rises, the density reduces linearly while the viscosity quickly decreases. Additionally, the glycerol-based DES exhibits higher densities and viscosities throughout the whole temperature range under study. Given that both DESs are made at the same molar ratio with the same HBA and that glycerol has higher densities and viscosities than ethylene glycol, this result was expected. The DES 1 (ethylene glycol-based DES) would be the best option for acting as the extracting agent in this separation, despite the fact that the LLE data are required for the evaluation of the selected solvents in the extraction. Furthermore, when compared to ethylene glycol and glycerol, respectively, DES 1 and DES 2 would be preferable. The explanation is that low viscosity solvents can alleviate both mass transfer restrictions and operating expenses related to problems like liquid pumping. Experimental LLE Data, section 3.3. {Hexane (1) + benzene (2) + DES 1 (3)} and {Hexane (1) + benzene (2) + DES 2 (3)} experimental LLE data were measured at T/K = 298.2 and T/K = 308.2, respectively, and atmospheric pressure. The solubility values of the investigated DESs at T/K = 298.2 and 302.5. The experimental results for the ternary systems including DES 1 and DES 2, respectively.The experimental data as a triangular diagram. The solute distribution coefficient (β) and the selectivity (S) are two measures that can be used to assess the separation's effectiveness. These expressions can be used to calculate these parameters:

$$\beta = \frac{x_{2,E}}{x_{2,R}} \qquad (5)$$

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

where "E" and "R" stand for the extract (DES-rich phase) and raffinate (aliphatic-rich phase), respectively, and "x1" and "x2" stand for the mole fractions of aliphatic and aromatic compounds, respectively.For systems containing DES 1 and DES 2, the solute distribution coefficient and selectivity values are displayed in.illustrate the solute distribution coefficients and selectivities 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, respectively, as a function of the aromatic concentration in the aliphatic-rich phase.Table 5 shows that an increase in temperature causes the solubility of hexane and benzene in the investigated DESs to slightly increase.Additionally, it should be noted that both hydrocarbons are more soluble in the DES (DES1) that is based on ethylene glycol than in the DES that is based on glycerol (DES 2).Last but not least, the total miscibility of benzene in the DES 1 is interesting since it deviates from benzene's typical behaviour in earlier extraction investigations that used both ILs and DESs.

The solubility information in Table can be compared to that in Supporting Informationwhich lists the solubilities of benzene and hexane in pure glycerol and ethylene glycol.It is clear that the DES has substantially higher solubilities for both hydrocarbons than pure glycerol or ethylene glycol. The rise in solubility, particularly for benzene, is striking.For instance, while benzene is completely soluble in the ethylene glycol-based DES, it is only partially soluble in pure ethylene glycol (Xbenzene = 0.023). (DES 1).The solubility of benzene in pure glycerol is Xbenzene = 0.007, but in the glycerol-based DES, it is Xbenzene = 0.844. (DES 2).When a DES is formed, the connections between the molecules of glycerol or ethylene glycol are broken, resulting in intramolecular hydrogen bond interactions that increase the solubility of the DES.Figure 3 shows that the ternary systems containing ethylene glycol-based DESs fall into the type 1 category, where two pairs of compounds exhibit complete miscibility (hexane + benzene and benzene + DES 1) and one pair exhibits partial miscibility (hexane + DES 1), in accordance with the classification proposed by Srensen et al.29.Additionally, the ternary systems containing glycerol-based DESs fall into the type 2 category because only one pair of compounds{hexane + benzene}is miscible across the whole range of compositions, while two pairs {hexane + DES 2} and {benzene + DES 2} show partial miscibility.The impact of temperature on separation can be examined.The effect of temperature may be seen to be rather minimal in both systems.However, for T/K = 298.2 compared to T/K = 308, both the solute distribution coefficients and the selectivity values are marginally greater.In other words, cold temperatures encourage the separation. Therefore, it is recommended to extract at T/K = 298.2 in order to reduce the energy requirement.As seen in Figure 4, the solute distribution coefficient values of DES 1 and DES 2 drop as the concentration of aromatic in the aliphatic-rich phase rises, reaching an aromatic mole fraction in the aliphatic-rich phase of around Xbenzene = 0.5 in all the systems under study.The solute distribution coefficient rises with the concentration of aromatic compounds in the aliphatic-rich phase, starting from the concentration specified, when it finds its minimal value.The extraction of aromatic components is therefore more advantageous at low aromatic concentrations or at high aromatic concentrations, but less advantageous in the area from 0.35 to Xbenzene to 0.6 in the aliphatic-rich phase.Sulfolane exhibits a similar pattern of solute distribution coefficient behaviour.It is clear that when the concentration of aromatic component in the aliphatic-rich phase increases, the selectivity values of DES 1 and DES 2 drop.Additionally, it was discovered that the selectivity values in every system under study were higher than unity, suggesting that the separation utilising these DESs would be possible.Additionally, the behaviours of DES 1 and DES 2 as extracting agents for the separation of "hexane + benzene" can be compared.In terms of solute distribution coefficient, DES 1 displays greater values than DES 2, while in terms of selectivity, DES 2 displays higher values over the entire range of concentrations.The electrostatic potential of the HBD could be used to explain this behaviour. The HBD-HBA interactions of the glycerol-based DES (DES 2) are stronger than those of the ethylene glycol-based DES because glycerol exhibits a larger electrostatic potential than ethylene glycol (DES 1).The interactions with benzene and hexane are reduced as a result of the greater contacts in DES 2 producing a more delocalized charge.This explains why DES 1 has larger distribution coefficient values due to the increased solubility of benzene and hexane.After analysing the data, it is feasible to draw the conclusion that using DES 1 rather than DES 2 would be preferable for separating benzene from "hexane + benzene."Higher solute distribution coefficients are more profitable overall because they suggest lower solvent-to-feed ratios, which translate into less volumes of solvent that need to be recovered and thus reduced energy demands.On the other hand, high selectivity values (DES 2) primarily influence the size of the equipment, resulting in an initial expenditure with a less significant economic impact on the effectiveness of the separation.Additionally, DES 1 displays lower density and significantly lower viscosity values than DES 2, which is also advantageous for the process' economy.

3.4.Literature Comparison A literature comparison was done to assess the performances of DES 1 and DES 2.We contrasted our solvents' solute distribution coefficient and selectivity values with those of previously investigated solvents (sulfolane/ILs) in the literature.The selectivity values and the solute dispersion coefficients are compared.Sulfolane and the ILs have very different molar masses, hence the comparison was done using mass fractions rather than moles in order to provide more accurate estimates of how well the solvents applied.When DES 1 and DES 2 are contrasted with sulfolane, it is evident that the performance of the latter is comparable to that of the former for low aromatic concentrations in the aliphatic rich phase.However, starting from a concentration of around Wbenzene = 0.15 in the aliphatic-rich phase, the solute distribution coefficient values of sulfolane are higher than those of DES 1 and DES 2.Only ILs based on bis(trifluoromethylsulfonyl)imides, such as 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C10MimNTF2) and 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imid (C12MimNTF2), which contain relatively long alkyl chain length.DES 1, DES 2, C10MimNTF2, and C12MimNTF2 exhibit lower selectivity values than sulfolane.In terms of industrial application, we will, however, choose larger distribution coefficient values above higher selectivity values.This is due to the fact that high distribution coefficient values indicate a reduced requirement for solvent during the extraction process, which means a reduction in operational costs related to energy (solvent recovery) and chemicals (solvent makeup stream).High selectivity values, on the other hand, imply lesser equipment requirements; nonetheless, equipment scaling is often advantageous and only requires an initial capital cost expenditure.Furthermore, they appear to be an intriguing commercial option when taking into account the distribution coefficient values of the DESs at low aromatic concentrations.Due to their insignificant vapour pressures, the investigated DESs and the aforementioned ILs provide a simpler and less expensive solvent recovery compared to volatile solvents (such as sulfolane).The fundamental drawback of the sulfolane process—the substantial energy requirements for the solvent recovery—is overcome by the straightforward solvent recovery.Therefore, using DES 1 and DES 2 as extracting agents for the "hexane + benzene" separation seems more promising and economically viable than using ILs.

3.4. Correlation. The NRTL thermodynamic model,30 which treats the DESs as a single component, was used to correlate the experimental LLE data.By minimising the subsequent objective function, the model was put into practise.where n is the number of ingredients in the mixture, m denotes the number of tie lines, and $(1/\beta)^{exp}$ and $(1/\beta)^{cal}$denote the inverse experimental and calculated values of the solute distribution ratio, respectively.The following formula has been used to get the composition's root-mean-square deviation, x:

$$OF = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{\left(\frac{1}{\beta_{ij}}\right)^{cal} - \left(\frac{1}{\beta_{ij}}\right)^{exp}}{\left(\frac{1}{\beta_{ij}}\right)^{exp}} \right)^{2} \qquad (7)$$

where m is the number of tie lines, n is the total number of mixture's components, and (1/β) exp and (1/β) cal. are, respectively, the inverse experimental and calculated values of the solute distribution ratio.The following formula has been used to get the composition's root-mean-square deviation, σx:

σ x=100.

$$\left(\frac{\sum_i^m \sum_j^{n-1}\left(x_{ij}{}^{I,exp}-x_{ij}{}^{I,cal}\right)^2-\left(x_{ij}{}^{II,exp}-x_{ij}{}^{II,cal}\right)^2}{2mn}\right)^{\frac{1}{2}} \qquad (8)$$

The mole fractions of the components for each tie line are compared between experimental and computed values in this deviation.The fitting parameters and the composition's root-mean-square deviation.The nonrandomness parameter was varied between 0.05 and 0.30 during the fitting.The values for a_{ij} shown in Table 8 produced the best results.A suitable model for fitting LLE data containing ILs is NRTL.

1. CONCLUSIONS

The use of a novel class of solvents, known as DESs, as extracting agents for the separation of the benzene + hexane combination has been investigated in this work.To select DESs that meet the solubility requirements for this separation, a solubility test was conducted first.The DESs with the highest benzene solubility have been chosen for more study.The solvents in question were I tetrahexylammonium bromide: ethylene glycol with a molar ratio of 1:2 (DES 1) and (ii) tetrahexylammonium bromide: glycerol with a molar ratio of 1:2. (DES 2).Second, the chosen solvents have been characterised; experimental measurements of density and viscosity as a function of temperature have been made.Second, the solvents were characterised by taking experimental measurements of density and viscosity as a function of temperature.It was discovered that as temperature rises, both density and viscosity decrease.It was also discovered that the glycerol-based DES has higher density and viscosity values across the entire temperature range studied.Following that, the LLE data of the systems hexane (1) + benzene (2) + DES (3) were measured at T/K = 298.2 and T/K = 308.2, as well as atmospheric pressure.The solute distribution coefficient and selectivity values were calculated and compared to previously investigated solvents.The temperature effect on separation has also been investigated, with low temperatures promoting separation and lowering energy requirements.Given the solute distribution coefficient and selectivity values, DES 1 would be preferred for this separation over DES 2.The lower density and viscosity values of DES 1 compared to DES 2 also indicate that DES 1 will be the best option among the DESs studied.Finally, by treating the DESs as a single component, the NRTL model was successfully applied to the experimental data.The solute distribution coefficients of the investigated DESs were found to be lower than that of sulfolane.Only DES 2 has a higher solute distribution coefficient than sulfolane and the previously studied ILs at low aromatic concentrations in the aliphatic-rich phase.It was also discovered that the selectivity values for sulfolane are higher than those for any of the other DESs studied.However, if the negligible volatility of the DESs is taken into account, the main disadvantage of the sulfolane process, the amount of energy required for solvent recovery, may be overcome.It was also discovered that the performance of the DESs under consideration is comparable to that of the ILs. Because DESs are two times cheaper, they can overcome ILs' main disadvantage, which is their high price.As a result, preliminary results indicate that this new generation of solvents can be used as effective extracting agents for the separation of the hexane + benzene mixture.

ACKNOWLEDGMENT

The authors of this paper would like to thank the Dutch Organization for Scientific Research (NWO) for funding this project (Grant ECHO.11.TD.006).The authors would also like to thank the Ministerio de Economia y Competitividad (Spain) for the FPI grant (BES-2011-050308).

REFERENCES

(1) Meindersma, G. W.; Podt, A.; Klaren, M. B.; De Haan, A. B. Separation of aromatic and aliphatic hydrocarbons with ionic liquids. Chem. Eng. Commun. 2006, 193, 1384.

(2) Rawat, B. S.; Gulati, I. B. Liquid-liquid equilibrium studies for separation of aromatics. J. Appl. Chem. Biotechnol. 1976, 26, 425.

(3) Meindersma, G. W.; De Haan, A. B. Cyano-containing ionic liquids for the extraction of aromatic hydrocarbons from an aromatic/ aliphatic mixture. Sci. China: Chem. 2012, 55, 1488.

(4)Meindersma, G.; de Haan, A. Conceptual process design for aromatic/aliphatic separation with ionic liquids. Chem. Eng. Res. Des. 2008, 86, 745.

(5) Hossain, M. A.; Lee, J.; Kim, D. H.; et al. Ionic Liquids as benign Solvents for the Extraction of Aromatics. Bull. Korean Chem. Soc. 2012, 33, 3241.

(6)Dominguez, I.; Gonzalez, E. J.; Dominguez, A´´ . Liquid extraction of aromatic/cyclic aliphatic hydrocarbon mixtures using ionic liquids as solvent: Literature review and new experimental LLE data. Fuel Process. Technol. 2014, 125, 207.

(7) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. Novel solvent properties of choline chloride/urea mixtures. Chem. Commun. 2003, 70.

(8) Dai, Y.; van Spronsen, J.; Witkamp, G.-J.; Verpoorte, R.; Choi, Y. H. Natural deep eutectic solvents as new potential media for green technology. Anal. Chim. Acta 2013, 766, 61.

(9) Zhang, Q.; De Oliveira Vigier, K.; Royer, S.; Jeró ̂me, F. Deep eutectic solvents: syntheses, properties and applications. Chem. Soc. Rev. 2012, 41, 7108.

(10) Hayyan, A.; Mjalli, F. S.; AlNashef, I. M.; et al. Glucose-based deep eutectic solvents: Physical properties. J. Mol. Liq. 2012, 178, 137.

(11) Francisco, M.; van den Bruinhorst, A.; Kroon, M. C. Low Transition-Temperature Mixtures (LTTMs): A New Generation of Designer Solvents. Angew. Chem., Int. Ed. 2013, 52, 3074.

(12)Gonzalez, A.; Dominguez, I.; Go´´mez, E.; Canosa, J.; Dominguez, A. Separation of Benzene from Hexane Using 3-butyl-1- methylimidazolium Bis (trifluoromethylsulfonyl) imide as Entrainer: Liquid-Liquid Equilibrium Data, Process Simulation and Process Separation in a Packed Bed Column. Procedia Eng. 2012, 42, 1606.

(13) Arce, A.; Earle, M. J.; Rodriguez, H.; Seddon, K. R. Separation of benzene and hexane by solvent extraction with 1-alkyl-3-methylimidazolium bis (trifluoromethyl) sulfonyl amide ionic liquids: effect of the alkyl-substituent length. J. Phys. Chem. B 2007, 111, 4732.

(14) Meindersma, G. W.; Podt, A. J.; de Haan, A. B. Ternary liquid liquid equilibria for mixtures of toluene+ n-heptane+ an ionic liquid. Fluid Phase Equilib. 2006, 247, 158.

(15)Arce, A.; Earle, M. J.; Rodriguez, H.; Seddon, K. R.; Soto, A. Bis (trifluoromethyl) sulfonylamide ionic liquids as solvents for the extraction of aromatic hydrocarbons from their mixtures with alkanes: effect of the nature of the cation. Green Chem. 2009, 11, 365.

(16)Chen, J.; Duan, L.-P.; Mi, J.-G.; Fei, W.-Y.; Li, Z.-C. Liquid- liquid equilibria of multi-component systems including n-hexane, noctane, benzene, toluene, xylene and sulfolane at 298.15 K and atmospheric pressure. Fluid Phase Equilib. 2000, 173, 109.

(17) Mokhtarani, B.; Musavi, J.; Parvini, M.; et al. Ternary (liquid- liquid) equilibria of nitrate based ionic liquid+ alkane+ benzene at 298.15 K: Experiments and correlation. Fluid Phase Equilib. 2013, 341, 35.

(18) Garcia, J.; Fernandez, A.; Torrecilla, J. S.; Oliet, M.; Rodriguez,́ F. Liquid-liquid equilibria for {hexane+ benzene+ 1-ethyl-3-methylimidazolium ethylsulfate} at (298.2, 313.2 and 328.2) K. Fluid Phase Equilib. 2009, 282, 117.

(19) Domanska, U.; Pobudkowska, A.; Krolikowski, M. Separation of́ aromatic hydrocarbons from alkanes using ammonium ionic liquid C 2 NTf 2 at T= 298.15 K. Fluid Phase Equilib. 2007, 259, 173.

(20) Gómez, E.; Dominguez, I.; Calvar, N.; Dominguez, Á . Separation of benzene from alkanes by solvent extraction with 1- ethylpyridiniumethylsulfate ionic liquid. J. Chem. Thermodyn. 2010, 42, 1234.

(21) Gonzalez, E. J.; Calvar, N.; Gonza´ lez, B.; Dominguez, A´´.(Liquid+ liquid) equilibria for ternary mixtures of (alkane+ benzene+ [EMpy][ESO 4]) at several temperatures and atmospheric pressure. J. Chem. Thermodyn. 2009, 41, 1215.

(22) Arce, A.; Earle, M. J.; Rodriguez, H.; Seddon, K. R.; Soto, A. 1- Ethyl-3-methylimidazolium bis (trifluoromethyl) sulfonylamide as solvent for the separation of aromatic and aliphatic hydrocarbons by liquid extraction-extension to C 7-and C 8-fractions. Green Chem. 2008, 10, 1294.

(23) Manohar, C.; Rabari, D.; Kumar, A. A. P.; Banerjee, T.; Mohanty, K. Liquid-liquid equilibria studies on ammonium and phosphonium based ionic liquid-aromatic-aliphatic component at T= 298.15 K and p= 1bar: Correlations and a-priori predictions. Fluid Phase Equilib. 2013, 360, 392.

(24) Kareem, M. A.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M. Liquid-Liquid Equilibria for the Ternary System (Phosphonium Based Deep Eutectic Solvent-Benzene-Hexane) at Different Temperatures: a new Solvent Introduced. Fluid Phase Equilib. 2012, 314, 52.

(25) Al-Rashed, O. A.; Fahim, M. A.; Shaaban, M. Prediction and measurement of phase equilibria for the extraction of BTX from naphtha reformate using BMIMPF 6 ionic liquid. Fluid Phase Equilib. 2014, 363, 248.

(26) Kareem, M. A.; Mjalli, F. S.; Hashim, M. A.; et al. Phase equilibria of toluene/heptane with tetrabutylphosphonium bromide based deep eutectic solvents for the potential use in the separation of aromatics from naphtha. Fluid Phase Equilib. 2012, 333, 47.

(27) Gonzalez, A. S.; Francisco, M.; Jimeno, G.; de Dios, S. L. G.; Kroon, M. C. Liquid-liquid equilibrium data for the systems {LTTM+ benzene+ hexane} and {LTTM+ ethyl acetate+ hexane} at different temperatures and atmospheric pressure. Fluid Phase Equilib. 2013, 360, 54.

(28) Kaul, A. The Phase Diagram; Springer: Berlin, 2000.

(29) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, A. Liquid-liquid equilibrium data: Their retrieval, correlation and prediction Part I: Retrieval. Fluid Phase Equilib. 1979, 2, 297.

(30) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. AIChE J. 1968, 14, 135.