Ternary liquid–liquid equilibrium data for n-Hexane-Benzene-DES (choline chloride/ethylene glycol, choline chloride/glycerol, choline chloride/urea) at 303 K and 101.3 kPa

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Abstract

In this study, deep eutectic solvents (DESs) were prepared using choline chloride as hydrogen bond acceptor (HBA) and ethylene glycol (EG) or glycerol (GLY) or urea (U) as hydrogen bond donor (HBD) and were evaluated as solvents in the extraction of benzene from n-hexane. Six of such solvents were prepared using different molar ratios of HBA: HBD and code named DES1, DES2, DES3, DES4, DES5 and DES6. Liquid–liquid equilibria (LLE) data for the ternary systems of n-hexane-benzene-DESs were measured at 303 K and 101.3 kPa. Solubility data and mutual solubilities between n-hexane and DES were measured using the traditional cloud point method. The tie lines were obtained using titration and refractive index measurements on both phases (n-hexane phase and DES-phases). The ternary systems exhibit type-1 phase behavior. The Othmer-Tobias and Hand equations were applied to examine the reliability of the LLE data. The tie-line data were correlated using the nonrandom two-liquid (NRTL) and universal quasichemical (UNIQUAC) thermodynamic models, and their corresponding binary interaction parameters were determined. The results show that the maximum separation factors were 31.24, 462.00, 15.24, 37.83, 174.60 and 126.00 for DES1, DES2, DES3, DES4, DES5 and DES6, respectively. The glycerol based DES (DES2 and DES5) show the highest separation factors and thus considered the most suitable for separating benzene from hexane. The regression coefficient for both Othmer-Tobias and Hand equations are higher than 0.99 for all DESs, indicating the reliability and consistency of the data. Both NRTL and UNIQUAC models adequately capture the experimental data.

Keywords Liquid–liquid extraction · Choline chloride · Ethylene glycol · Glycerol · Urea · Separation factor

Introduction

Liquid–liquid extraction is the preferred commercial method for separating aromatics from mixtures containing low aromatic concentration (20–65 wt %). The key factor in the cost effectiveness of such separation is the choice of extraction solvent. The current industrial practice is that molecular solvents or volatile organic solvents such as sulfolane, furfuryl

alcohol, Dimethylformamide (DMF), ethylene glycols, N-methylpyrrolidone (NMP), and N-formylmorpholine (NFM) are used [4, 17, 18, 21]. Green synthesis or cleaner production stipulates a paradigm shift to green solvents and research efforts have considered ionic liquids (ILs) and deep eutectic solvents (DESs) in this regard. Furthermore, a volatile organic solvent like sulfolane is not cost effective for separating aromatic–aliphatic mixture with less than 20 wt % aromatic. Ionic liquid and DES offer advantage due to their non-volatile nature.

ILs have the ability to dissolve many different organic, inorganic and organometallic materials, they have low vapor pressures (non-volatile) and are immiscible with many organic solvents [13]. These properties and more make ILs very good solvents for liquid–liquid extraction. Numerous studies investigated ILs for extraction of aromatic–aliphatic mixture and the results were highly promising [4–7, 18, 21,

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22]. For example, Durski et al. [5] reported an impressive average selectivity of 43.9 and average solute distribution ratio of 1.82 for the extraction of thiophene from octane using ionic liquid (1-butyl-3-methylimidazolium trifluoromethanesulfonate) as the extracting solvent. The drawback of ILs is that they are expensive and not all of them can truly be classified as green solvent.

DESs are analogues of ILs but they are easier to synthesize, cheaper and generally green. Several studies have examined the performance of DESs in extracting aromatic–aliphatic mixtures. The determinant metrics for a suitable solvent in this regard are distribution ratio and separation factor. The latter influence the number of equilibrium stages, while the former underpin the solvent to feed ratio required to achieve desired purity of aromatic in the extract phase. Hadj-Kali et al. [9] chronicled the findings of such studies involving several DESs (using different salts, HBAs, and numerous HBDs and in varying molar ratios) to separate various aromatic–aliphatic pairs at different temperatures. For the particular case of benzene–hexane mixture, some further studies are worthy of our review.

Shekaari et al. [29] investigated the use of DESs, synthesized from choline chloride (HBA) and several HBDs, ethanolamines (mono-, di- and tri-) and ethylene glycol (mono-, di- and tri-), in the extraction of benzene from n-hexane. Their results show high selectivity for benzene, with ethanolamine based DES outperforming the ethylene glycol based DES. In another study, Shekaari et al. [30] examined the performance of DES based on choline chloride (HBA) and a number of HBDs, N-formylmorpholine or sulfolane or diglycolamine. The results revealed the superiority of diglycolamine based DES.

Salehi et al. [27] used molecular dynamics simulation to compute the Hilderbrand and Hansen solubility parameters for DESs. Relatively large values were obtained for chlorine chloride based DES (Choline chloride/urea, choline chloride/glycerol, choline chloride/ethylene glycol) compared to molecular solvents and ILs. These choline chloride based DESs were classified by the authors as polar solvents. Polarity is a key feature of the organic solvents currently used for extracting aromatics from aliphatics. Yet, the foregoing literature review show that these choline chloride based DESs have not been previously explored for separating benzene from n-hexane, thus constituting a research gap.

In this study, the suitability of choline chloride based DESs (Choline chloride/urea, choline chloride/glycerol, choline chloride/ethylene glycol) for separating benzene from n-hexane was investigated. Six of such solvents were prepared using different molar ratios of HBA: HBD (1:2 or 1:3) and code named DES1, DES2, DES3, DES4, DES5 and DES6. These DESs were chosen based on their highly polar nature as revealed by Salehi et al. [27] and the eutectic feature of the specified molar ratios. Liquid–liquid equilibria

(LLE) data for the ternary systems of n-hexane–benzene–DESs were measured at 303 K and 101.3 kPa. The performance or extraction efficiency of each DES was evaluated using distribution ratio and separation factor.

Experimental

Materials

Benzene, n-hexane, Choline chloride, Ethylene glycol, Urea and Glycerol were purchased from Sigma-Aldrich (Germany) with a mass fraction purity higher than 0.98. All chemicals were used as received without further purification and they were stored in a desiccator in their original tightly closed bottles. Refractive index of Benzene, n-Hexane, Ethylene glycol, Glycerol, Urea, Choline Chloride, DESs were measured via refractometer.

Preparation of DES

Choline chloride (ChCl) was used as HBA, while ethylene glycol (EG), urea (U) and glycerol (Gly) were used as HBD and the preparation was according to literature [17, 28, 30]. Two molar ratios (1:2 and 1:3) were prepared for each combination of HBA and HBD, giving six DESs as listed in Table 1. Preparations of the DESs were carried out in a 250 ml neck flask equipped with magnetic stirrer. In each case, 100 g of the ChCl was weighed out and mixed with appropriate mass of HBD. For example, in the preparation of DES1, 100 g of ChCl and 89 g of EG (1:2 mol ratio), while for DES2, 100 g of ChCl and 133.37 g of EG (1:3 mol ratio) were weighed by a high-precision digital balance with an accuracy of ± 0.001 grams and were mixed in the neck or reaction flask. This reaction flask was then placed in a water bath and stirred for 60 min using a magnet stirrer at $T = 373$ K until a transparent eutectic solvent was formed. The physical properties of the DESs such as density, viscosity and water content were measured according to standard protocol [2, 30].

Table 1 List of the prepared DESs for this study

DES composition (mole ratio)	Abbreviation
DES (ChCl:EG)(1:2)	DES 1
DES (ChCl:EG)(1:3)	DES 2
DES (ChCl:Gly)(1:2)	DES 3
DES (ChCl:Gly)(1:3)	DES 4
DES (ChCl:U) (1:2)	DES 5
DES (ChCl:U)(1:3)	DES 6

Binodal curve or solubility data measurement

A bench scale process was used for the extraction. A measured volume of DES was introduced into a 250 mL beaker together with a measured volume of benzene at different concentration, the resulting mixture was then titrated with the solute (n-hexane), and the end point is the point at which turbidity develops [14, 30]. The volume of n-hexane used was recorded and the refractive index values were measured. The binodal curve of the ternary system was determined by preparing several mixtures of n-hexane + Benzene + DES, the refractive index of those ternary mixtures was determined. The measurements of refractive indexes were performed at 303 K and atmospheric pressure, using an automated Anton Paar Refractometer Abbemat 500 with an absolute uncertainty of the refractive indexes of ± 0.00005 .

Determination of tie lines and equilibrium data

First, in the pre-experiment, the cloud point method was utilized to approximately obtain the two-phase region. Seven appropriate points were selected within the two-phase region, and known masses of benzene, n-hexane and DESs were added to a vial accordingly. After placing the vial in a water bath at a constant temperature the mixture was then allowed to settle at a constant temperature for 4 h to ensure that the system reached the phase equilibrium. Throughout the procedure, a thermostatted water bath was used to keep the temperature constant, with an uncertainty of 0.05 K. Finally, samples from both phases were taken with a syringe and their refractive indexes were determined [14, 30]. The composition of both phases in equilibrium was determined using the fitting refractive indexes with the composition along the binodal curve. The Standard uncertainties (u) for our experimental data are $u(T) = 0.1$ K, $u(P) = 1$ kPa, $u(x) = 0.0014$. Samples from both phases were taken with a syringe and their measurements were determined in triplicate. Deviation between the triplicates of the measurements was always lower than 0.00005.

Results and discussion

Physical properties of prepared DESs

Appropriate selection of solvent for liquid–liquid extraction is dependent on the physical properties such as viscosity and density. Water content of DES is critical as the structure of DES is significantly affected by it and thus the physical properties [2, 10]. The viscosity, density and water content of the six DESs used in this study are presented in Table 2. The water content for all the DESs are less than 1 wt % and as such their viscosities and densities have not been

Table 2 Viscosity, density and water content of prepared DESs

DES HBA/HBD, Molar ratio	Viscosity [cP]	Density [gcm ⁻³]	Water content wt %
ChCl:EG, 1:2	35.5	1.12	0.03
ChCl:EG, 1:3	18.3	1.12	0.02
ChCl:Gly, 1:2	330.4	1.18	0.03
ChCl:Gly, 1:3	444.5	1.18	0.02
ChCl:U, 1:2	650.5	1.25	0.04
ChCl:U, 1:3	170.4	1.25	0.03

Table 3 Equilibrium composition, Distribution coefficient (β) and selectivity (S) for Hexane + Benzene + DES1 system

Aliphatic phase		DES rich phase		β	S
x_1	x_2	x_1	x_2		
0.8710	0.1290	0.0131	0.0610	0.4729	31.24
0.7901	0.2099	0.0671	0.1001	0.4769	5.61
0.7310	0.2690	0.1031	0.1410	0.5242	3.72
0.7189	0.2811	0.1331	0.1635	0.5816	3.14
0.6551	0.3449	0.1619	0.1869	0.5419	2.19
0.5579	0.4421	0.1862	0.2154	0.4872	1.46
0.4338	0.5662	0.1983	0.2987	0.5276	1.15

significantly affected. Al-Murshedi et al. [2] reported that the viscosity of DESs do not change when the water content is between 1 and 2.5 wt %. Thus, the interaction between the HBA and HBD, both intra-molecular and inter-molecular, remain intact within the specified range of water content.

Experimental LLE data

A basic method for the understanding of liquid–liquid extraction process is the study of liquid–liquid equilibrium. Accurate liquid–liquid equilibrium (LLE) data in particular are employed in the design and optimal operation of the solvent extraction processes. The experimental results for the liquid–liquid equilibrium (tie line) data of n-heptane + benzene + DESs at 303 K & 101.3 kPa were measured and shown in Tables 3, 4, 5, 6, 7, 8. To evaluate the capability of DESs to extract benzene from n-hexane, this work used the distribution coefficient (β) and selectivity (S) to determine the solvent capacity and efficiency of DESs as an extraction agent.

Distribution coefficient or ratio

Distribution coefficient (β) is used to assess the separation efficiency of the systems, the distribution ratio of any

Table 4 Equilibrium composition, Distribution ratio (β) and selectivity (S) for n-Hexane + Benzene + DES3 system

Aliphatic phase		DES rich phase		β	S
x_1	x_2	x_1	x_2		
0.8489	0.1511	0.0011	0.1088	0.72	462.00
0.7608	0.2392	0.0045	0.2116	0.88	146.23
0.6600	0.3400	0.1213	0.3086	0.91	4.94
0.5372	0.4628	0.1413	0.3996	0.86	3.28
0.3266	0.6734	0.1966	0.4883	0.73	1.20
0.3033	0.6967	0.2289	0.4991	0.72	1.12
0.2912	0.7088	0.2517	0.5103	0.72	1.10

Table 5 Equilibrium composition, Distribution coefficient (β) and selectivity (S) for n-Hexane + Benzene + DES5 system

Aliphatic phase		DES rich phase		β	S
x_1	x_2	x_1	x_2		
0.8156	0.1844	0.0091	0.0317	0.17	15.24
0.6864	0.3136	0.0131	0.1013	0.32	14.86
0.6150	0.3850	0.0139	0.1241	0.32	14.13
0.5396	0.4604	0.0178	0.1395	0.30	9.18
0.4545	0.5455	0.0263	0.1886	0.35	5.99
0.3571	0.6429	0.0331	0.1976	0.31	3.31
0.2598	0.7402	0.0414	0.2007	0.27	1.70

Table 6 Equilibrium composition, Distribution ratio (β) and selectivity (S) for n-Hexane + Benzene + DES2 system

Aliphatic phase		DES rich phase		β	S
x_1	x_2	x_1	x_2		
0.8905	0.1095	0.0112	0.0510	0.50	37.83
0.8013	0.1987	0.0833	0.1121	0.55	5.54
0.7243	0.2757	0.1322	0.1410	0.52	2.80
0.6447	0.3553	0.1638	0.1655	0.47	2.00
0.5586	0.4414	0.1877	0.1969	0.43	1.33
0.5273	0.4727	0.1997	0.2194	0.44	1.23
0.5007	0.4993	0.2059	0.3109	0.63	1.91

component describes its distribution behaviour between the extract and raffinate phase at equilibrium. In this particular separation, the distribution ratio of solute is more important because aromatic compounds (benzene) represent the targeted component to be extracted. To analyze the performance of the selected DESs as aromatic extraction solvents from aliphatic phase (n-Hexane), distribution ratios (β) have been calculated from the liquid–liquid equilibrium data according to Eq. 1:

Table 7 Equilibrium composition, Distribution ratio (β) and selectivity (S) for n-Hexane + Benzene + DES4 system

Aliphatic phase		DES rich phase		β	S
x_1	x_2	x_1	x_2		
0.8023	0.1977	0.0023	0.1088	0.55	174.60
0.7344	0.2656	0.0045	0.2116	0.79	129.50
0.6615	0.3385	0.1213	0.3086	0.91	4.97
0.5789	0.4211	0.1413	0.3996	0.95	3.89
0.4256	0.5744	0.1966	0.4883	0.85	1.84
0.3859	0.6141	0.2289	0.4991	0.81	1.37
0.2811	0.7189	0.2517	0.5103	0.71	1.09

Table 8 Equilibrium composition, distribution ratio (β) and selectivity (S) for n-Hexane + Benzene + DES6 system

Aliphatic phase		DES rich phase		β	S
x_1	x_2	x_1	x_2		
0.7899	0.2101	0.0094	0.0319	0.15	126.00
0.6623	0.3377	0.0133	0.1020	0.30	115.00
0.5990	0.4010	0.0149	0.1245	0.31	12.43
0.5396	0.4604	0.0178	0.1405	0.31	9.24
0.4545	0.5455	0.0263	0.1889	0.35	6.01
0.3571	0.6429	0.0331	0.1976	0.31	3.31
0.2345	0.7655	0.0420	0.2107	0.89	1.53

$$\beta = \frac{x_{23}}{x_{21}}, \quad (1)$$

where x_{23} is the mole fraction of benzene in the extract (DES) phase and x_{21} is the mole fraction of benzene in the raffinate (n-hexane) phase.

The distribution coefficients for the studied ternary systems are presented in Tables 3, 4, 5, 6, 7, 8. Figure 1 shows plot of distribution coefficient against mole fraction of benzene in the extract (DES) phase for the six DESs systems. The distribution coefficients are generally less than unity for all studied systems. This implies that large solvent to feed ratio would be necessary to effect separation using these DESs. There is an increase in distribution coefficient with benzene up to a point and thereafter a decrease with further increase of benzene composition. Similar trend have been reported in some extraction studies [8, 34]. The glycerol based DES show the highest values of distribution coefficient and is, therefore, superior on this count. The ethylene glycol based DES is next in value to the glycerol based DES, while the urea based DES show the least values. These results can also be explained by the different HBD present in the DES. In DES 1, DES 2, DES 3 and DES 4, the HBD are Ethylene glycol (DES 1 & DES 2) and Glycerol (DES 3 & DES 4), which have 2 and 3 hydroxyl groups (–OH),

Fig. 1 Distribution ratio as a function of benzene composition in the DES-phase

respectively. This structural feature enhances dipole strength and allows for the creation of a higher number and stronger dipoles, thus forming a larger number and stronger –OH-bonds with other substances capable of H-bonding interactions, meaning that DES1, DES 2, DES 3 & DES 4 has higher solute-carrying capacity than the other DES used, which is explained by the higher distribution coefficients obtained [23].

Selectivity (S)

Selectivity (*S*) indicates the capacity of solvent for solvation of solute without extracting other components from the primary solutions. In all extraction processes, the important feature is the selective nature of the solvent, because the separation of compounds is based on preferential solubilities. The separation efficiency is also evaluated through selectivity; these measurements are obtained from measured molar compositions of each component in the extract (DES rich) and raffinate (n-hexane-rich) phase.

To make a quantitative comparison of the performance of the DES-based solvent, Selectivities (*S*) have been calculated from the LLE data using Eq. 2:

$$S = \frac{x_{23} \cdot x_{11}}{x_{21} \cdot x_{13}}, \quad (2)$$

where x_{13} is the mole fraction of n-hexane in the extract (DES) phase and x_{11} is the mole fraction of n-hexane in the raffinate (hexane) phase. The selectivity for all studied

systems are reported in Tables 3, 4, 5, 6, 7, 8 and plotted in Fig. 2. The Figure reveal decreasing values of selectivity as the composition of benzene in the extract phase increases. Similar trend was reported in other extraction studies [14, 15, 31, 34]. The values of selectivity for all studied systems were generally higher than 1. This indicates the suitability of these DESs to extract benzene from n-hexane. At a molar ratio of HBA:HBD of 1:2, DES3 (glycerol based) showed the highest value of selectivity ($S=462.00$) followed by DES1 (ethylene glycol based) with a value of 31.24 and the least is DES5 (urea based) with a value of 15.24. with increase in the molar ratio of HBA:HBD to 1:3, though the glycerol based DES retain its superior value of selectivity relative to the other two, it is instructive to note that its maximum selectivity actually plummeted remarkably from 462.00 to 174.60. For the urea based DES, there was a significant increase in its selectivity as it ramped up sharply from 15.24 to 126.00. It was, however, observed that the ethylene glycol based did not show appreciable change in its selectivity with changing molar ratio. This result demonstrates that the glycerol based DES have a high solvation power for benzene compared to ethylene and urea based DES. Furthermore, the best among the studied solvents is DES5 (ChCl/Gly; 1:2).

Comparative analysis

Table S8 in the supporting material presents a comparative analysis of solvent performance in extracting benzene from n-hexane using distribution coefficient and selectivity as

Fig. 2 Selectivity as a function of benzene composition in the DES-phase

metrics. Three categories of solvent are compared namely organic solvent [19, 20], ionic liquids [3] and deep eutectic solvents [12, 16, 26]. Considering the fact that organic solvent is the state-of-the art in industrial practice, it is appropriate to make one of them (sulfolane) the reference for comparison. In terms of distribution coefficient, it can be seen that the value for most of the solvents are less than unity. This implies that a large solvent to feed ratio would be required to effect separation for most of the listed solvents. Distribution coefficient is, therefore, not a very good discriminatory parameter in this instance. There is, however, a sharp contrast in the selectivity values for the listed solvents. The maximum selectivity for sulfolane is 20.14, whereas all of the DES studied in the work exhibited higher values. It is instructive to note that of all the listed solvents across the three categories, the highest value of selectivity was exhibited by $\text{ChCl}:\text{Gly}$ (1:2). This is a major revelation of this study.

Binodal curve or ternary diagrams for the studied DESs

The triangular diagrams or binodal curves for the six studied DES solvents for extraction of benzene from n-hexane are plotted in Figs. 3, 4, 5, 6, 7, 8 using the solubility data in supporting material (Tables S1 to S6). The figures show the immiscibility region of the ternary diagram for the system n-Hexane + Benzene + DESs as well as the binodal curve and the tie lines (plotted from Tables 3, 4, 5, 6, 7, 8). It can be seen that the DESs and hexane are practically immiscible, with large biphasic region. For all studied DES, the biphasic area and extent of immiscibility are largest for the glycerol based DES and least for the urea based DES. Essentially,

only benzene gets distributed between the n-hexane phase and the DES phase. This is type 1 behavior according to Treybal's classification [33]. The highly polar nature of the studied DES may be responsible for its immiscibility with n-hexane. Finally, the negative slopes of tie lines show that benzene solubility in n-hexane is higher.

LLE data correlation

In this study, the NRTL and UNIQUAC activity coefficient models were applied to correlate the experimental tie-line data. Our experimental data were predicted using the NRTL model of [25] and the UNIQUAC (Universal-Quasi Chemical) model of [1].

NRTL model

The NRTL equation can be used for highly non-ideal systems as well as for partially miscible systems [25]. The activity coefficients (γ_i) in the NRTL model for each component (i) of studied ternary mixtures are calculated by the following equations (3–7) for multicomponent systems:

$$\ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} X_{ji}}{\sum_{l=1}^m G_{li} X_{li}} + \sum_{j=1}^m \frac{G_{ij} X_j}{\sum_{l=1}^m G_{lj} X_l} \left\{ \tau_{ij} - \frac{\sum_{r=1}^m \tau_{rj} G_{rj} X_r}{\sum_{l=1}^m G_{lj} X_l} \right\} \quad (3)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (4)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ij}}{RT} = \frac{\Delta g_{ji}}{RT} \quad (5)$$

Fig. 3 Binodal curve for n-hexane + Benzene + ChCl:EG (1:2 mol ratio) system

Fig. 4 Binodal curve for n-hexane + Benzene + ChCl:Gly(1:2 mol ratio) system

Fig. 5 Binodal curve of Hexane + Benzene + ChCl:U (1:2 mol ratio) system

$$\tau_{ij} = a_{ij} + b_{ij}/T \quad (6)$$

and

$$\alpha = \alpha_{ji} = \alpha_{ij}, \quad (7)$$

where i and j refer to the i th and j th components, τ_{ij} are the binary interaction parameters, α_{ij} are the non-randomness parameters, g is an energy parameter representing the interaction of the species, x is the mole fraction of components

and R is the universal gas constant. Although the parameter of α can be used as an adjustable parameter, in our study, the parameter α was set equal between 0.2 and 0.3 since this is the most commonly used value of the α_{ij} parameter in fitting of data of liquid–liquid extraction of hydrocarbons [31, 32].

Uniquac model

The activity coefficients (γ_i) for the UNIQUAC model for each component (i) of the studied ternary mixtures are given by Eqs. (8, 9):

$$\ln \gamma_i = \ln \frac{\theta_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} - q_i^t \frac{\sum_j \theta_j \tau_{ij}}{t_j} + l_i + q_i^t - \frac{\theta_i}{x_i} \sum_j x_j l_j - q_i \ln (\theta_j \tau_{ij}) + q_i - q_i \sum_{j=1}^m \frac{\theta_j \tau_{ij}}{\sum_{k=1}^m \theta_k \tau_{kj}} \quad (8)$$

Fig. 6 Binodal curve for Aromatic (Benzene) + Aliphatic (n-Hexane) + ChCl:EG (1:3 mol ratio) system

$$\tau_{ij} = \exp(a_{ij} + b_{ij}/T), \quad (9)$$

where the coordination number (z) was set as $z = 10$. The parameters q_i and r_i are the molecular surfaces and molecular van der Waals volumes for the pure component i , respectively.

The regression of the experimental data was performed using Aspen Plus V9.0 software. The UNIQUAC structural parameters r and q are also obtained from the Aspen Plus data bank. The detailed explanation of how these parameters were estimated and their values for the components are provided in the supporting material. All the corresponding binary model parameters were acquired by minimizing the objective function (OF) as shown below:

$$OF = \sum_{k=1}^M \sum_{s=1}^2 \sum_{i=1}^3 (w_{isk}^{\text{exp}} - w_{isk}^{\text{cal}}) \quad (10)$$

where M is the number of tie lines and w is the mass fraction of component i . The subscripts i , s , and k refer to the components, the phases, and the tie-line, respectively, and

the superscripts exp and cal denote the experimental and calculated values, respectively.

For evaluating the correlation accuracy, the root-mean-square deviation (rmsd) was calculated to judge the difference between the calculated data and experimental data and was defined as follows (Eq. 11):

$$\text{rmsd} = 100 \left\{ \sum_{k=1}^M \sum_{s=1}^2 \sum_{i=1}^3 \frac{(w_{isk}^{\text{exp}} - w_{isk}^{\text{cal}})^2}{6M} \right\}^{1/2} \quad (11)$$

where M is the number of tie lines and w is the mass fraction of component i . The subscripts i , s , and k refer to the components, the phases, and the tie-line, respectively, and the superscripts exp and cal denote the experimental and calculated values, respectively.

The values of rmsd were calculated and are listed in Table 9. As can be seen from the table, the largest number is 0.0308, which indicates that both NRTL and UNIQUAC models can fit the experimental data well.

Fig. 7 Binodal curve for Hexane + Benzene + ChCl:Gly(1:3 mol ratio) System

In addition, the NRTL model shows a slightly better result than the UNIQUAC model for the ternary systems of Benzene + Hexane + DES.

Binary interaction parameters

The binary interaction parameters for the studied system given in Table 9 were achieved by correlating the LLE data with the UNIQUAC and NRTL equations, and regressed using Eq. 10.

Consistency of Tie-line data

Othmer-Tobias equation

The Othmer-Tobias equation [24] was used to ensure the consistency of measured LLE data.

Consistency testing of experimental data is an important method to evaluate data reliability. The expression is as follows (Eq. 12):

$$\ln \left\{ \frac{1 + w_{HC}^{HC}}{w_{HC}^{HC}} \right\} = A + B \ln \left\{ \frac{1 + w_{DES}^{DES}}{w_{DES}^{DES}} \right\}, \quad (12)$$

where w_{HC}^{HC} relates to the mass fraction of hexane in the n-hexane-rich phase and w_{DES}^{DES} relates to the mass fraction of deep eutectic solvents (DESs) in the DES rich phase, where A and B are the fitting parameters of Othmer-Tobias.

The correlation factors (R^2) were determined using a partial least-square regression. The obtained results from the correlation for the studied systems are reported in Table 10. The closeness of R^2 to unity show the good degree of consistency of the measured LLE data for the studied systems.

Hand equation

To check the reliability of the experimental tie-line data, Hand equation [11] is also applied, and the equation is expressed as follows (Eq. 13):

$$\ln \left\{ \frac{1 + w_{HC}^{HC}}{w_{HC}^{HC}} \right\} = A + B \ln \left\{ \frac{1 + w_{DES}^{DES}}{w_{DES}^{DES}} \right\} \quad (13)$$

where m and n are the fitting parameters of Hands equation, w_{23} = mass fraction of benzene in extract phase, w_{33} = mass fraction of DES in the extract phase, w_{11} = mass fraction of n-Hexane in raffinate phase, w_{21} = mass fraction of n-benzene in raffinate phase.

The measured LLE data were fitted by the Eq. 13 using the linear least-square method. The fitting parameters and correlation factors (R^2) are listed in Table 11. It can be seen from the table that all of the correlation factors (R^2) are greater than 0.98 and very close to unity, indicating the degree of regularity of the measured tie-line data.

Fig. 8 Binodal curve for n-Hexane + Benzene + ChCl:U(1:3 mol ratio) system

Table 9 Binary interaction parameters of NRTL and uniquac models for the systems of Benzene (1)+Hexane (2)+DES (3) at 303 K

Components $i-j$	NRTL											
	a_{ij}	a_{ji}	$b_{ij}(k)$	$b_{ji}(k)$	α	rmsd	a_{ij}	a_{ji}	$b_{ij}(k)$	$b_{ji}(k)$		rmsd
Benzene + n-Hexane + ChCl:EG (1:2)												
1–2	– 1.554	0.4066	1435.63	– 384.723	0.3	0.0307	1.2281	– 1.1078	– 694.26	529.39		0.0308
1–3	– 1.1609	– 0.0918	1872.33	883.74			0.4605	0.1622	– 820.16	– 353.74		
2–3	– 11.7974	4.6582	9985.91	– 853.66			4.2717	– 0.5026	– 4202.46	– 159.37		
Benzene + n-Hexane + ChCl:Gly (1:2)												
1–2	– 1.554	0.4066	1435.63	384.723	0.3	0.0222	1.2281	– 1.1078	– 694.26	529.39		0.0227
1–3	3.2422	2.6595	0	0			– 0.1561	0.0252	– 888.96	– 1278.34		
2–3	5.9798	4.8169	0	0			0.40887	0.06453	0	0		

Table 10 *A* and *B* constants of the Othmer-Tobias equation for the studied systems at *T* = 303 K and atmospheric pressure

Systems Ben- zene + n-Hex- ane + DESs	Abbreviation	Othmer-Tobias correlation		
		<i>A</i>	<i>B</i>	<i>R</i> ²
ChCl:EG(1:2)	DES1	− 1.9098	− 4.8283	0.9962
ChCl:Gly(1:2)	DES2	− 1.7259	− 2.0923	0.9978
ChCl:Ur(1:2)	DES3	− 1.4867	− 3.1583	0.9982
ChCl:EG(1:3)	DES4	− 2.0963	− 2.7136	0.9968
ChCl:Gly(1:3)	DES5	− 1.4008	− 2.0802	0.9984
ChCl:Ur(1:3)	DES6	− 1.3246	− 3.1403	0.9985

Table 11 *m* and *n* constants of the Hand equation for the studied systems at *T* = 303 K and atmospheric pressure

Systems Ben- zene + n-Hex- ane + DESs	Abbreviation	Hand correlation		
		m	n	R^2
ChCl:EG(1:2)	DES1	− 2.7211	− 4.1997	0.9923
ChCl:Gly(1:2)	DES2	− 2.1021	− 6.6454	0.9889
ChCl:Ur(1:2)	DES3	− 3.4112	− 4.4918	0.9929
ChCl:EG(1:3)	DES4	− 2.9114	− 4.3759	0.9933
ChCl:Gly(1:3)	DES5	− 2.1005	− 5.8546	0.9991
ChCl:Ur(1:3)	DES6	− 3.4029	− 4.4312	0.9935

Conclusion

The performances of six deep eutectic solvents, synthesized based on choline chloride as hydrogen bond acceptor and ethylene glycol/glycerol/urea as hydrogen bond donors, as extracting solvents for n-hexane and benzene mixture were investigated in this study. Experimental LLE data for the n-hexane + benzene + DESs systems were obtained at 303 K and 1 atm. The results indicated that all studied DESs show good extraction capacity for benzene from n-hexane, as their separation factors or selectivities were much larger than one. The glycerol based DESs show superior performance with selectivity values far exceeding reported values for organic solvents and ionic liquids in the literature. Glycerol based DES, particularly ChCl:Gly (1:2), is, therefore, recommended as suitable replacement for sulfolane in the liquid–liquid extraction of aromatics from aliphatics. The reliability of the LLE data was confirmed by both Othmer-Tobias and Hand equations. The thermodynamic activity coefficient models of both NRTL and UNIQUAC adequately represent the experimental LLE data.

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