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Design Optimization of Deep Eutectic Solvent Composition and Separation Performance of Cyclohexane and Benzene Mixtures with Extractive Distillation

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Abstract: Deep eutectic solvents (DESs) have properties that make them suitable candidates to be used as entrainers for extractive distillation. In the previous work, it was proven that DES(1:2) (tetrabutylammonium bromide: levulinic acid, 1:2, molar ratio) can break the cyclohexane-benzene azeotrope. In the present work, the HBA and HBD ratio and molar concentration of DES were optimized to obtain a better constitute and condition of DES to be utilized in cyclohexane and benzene extractive distillation. The physical properties and structure of the prepared DESs were characterized. Vapor-liquid equilibrium data of the ternary system (benzene + cyclohexane + DESs) were also measured at atmospheric pressure. All experimental equilibrium data were correlated with Wilson, nonrandom two-liquid (NRTL), and universal quasichemical (UNIQUAC) activity coefficient models, from which the coefficient of determination (R2) of the three pseudo-ternary systems fitting was calculated. From the obtained results, the best HBA and HBD ratio in the DESs is elucidated as 1:2, the best molar concentration of DES is 0.1, and the NRTL model predicts the experimental data more accurately than the Wilson and UNIQUAC models. From the derived mechanism, the formation of stronger hydrogen bond and π - π bond interactions between DES and benzene is obtained when HBA and HBD ratio in DES is 1:2. In other conditions, the azeotrope cannot be broken, or the efficiency is low. The present work provides an environmentally friendly method to separate aromatic/aliphatic mixtures and act as a guide for further study of DESs in extractive distillation.

Keywords: deep eutectic solvents; extractive distillation; separation; (vapor + liquid) equilibrium; cyclohexane; benzene

1. Introduction

A new family of solvents originally called "deep eutectic solvents" (DESs), which are formed by a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), is proposed by Abbott, firstly, as an appropriate substitute to ILs [1], also called "low transition temperature mixtures" (LTTMs) [2–4]. They possess properties that gain great advantages in the field of mixtures separation, such as liquid-liquid extraction [5–26], extractive distillation [2,27–29], and gas absorption [30].

In the previous work, it was proven that the DES(1:2) (tetrabutylammonium bromide: levulinic acid, 1:2, molar ratio) can break the cyclohexane-benzene azeotrope. In the present paper, the influence of HBA and HBD ratio and molar concentration of DES on the



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). extractive effectiveness is studied to obtain the optimum input parameters for cyclohexane and benzene extractive distillation using DES.

In this paper, the HBA and HBD ratio (tetrabutylammonium bromide: levulinic acid) is fixed as 1:1, 1:2, 1:3, and 1:4, and the molar concentration of DES is selected as 0.05, 0.1 0.15, and 0.2. The DESs required for the tests are prepared, and their properties and structures are elucidated. VLE data of the ternary (benzene–cyclohexane–DESs) mixtures have been measured to investigate if the azeotrope can be broken to assess the DESs extraction ability. FT-IR and NMR are used in the study for determining the extractive mechanism.

2. Materials and Methods

2.1. Materials

The purity and source of all the chemicals used in the present work are listed in Table 1.

Name	Source	M (g/mol)	Purity
Benzene	Chemical Factory	78.11	>99%
	Engineering and Technology		
Cyclohexane	Research Center of Guangdong Fine	84.16	>99.5%
	Chemistry		
Tetrabutylammonium	Tianjin Fuchen Chemical Reagents	322.38	>99%
bromide (TBAB)	Factory	022100	
Levulinic acid (LA)	Xilong Chemical Co., Ltd.	116.12	>99%

Table 1. Chemicals Used in This Work and their Abbreviation.

2.2. Preparation of DESs

DESs are prepared by following the procedure reported in the literature [3]. Mixtures are weighed using a Mettler AX205 balance having a precision of ± 0.02 mg. Both HBD and HBA are added to a flask and are heated under constant stirring. The uncertainty in the molar mixing ratio is $\pm 2\%$, evaluated based on the uncertainty in the balance reading and the purity of the chemicals used. The synthesized DESs are dried in a vacuum oven at 100 °C for 24 h. According to the above synthesis method, four kinds of deep eutectic solvents were synthesized using TBAB as a hydrogen bond acceptor and LA as a hydrogen bond donor, as shown in Table 2.

Table 2. DESs used in the present work.

Name	HBA	HBD	Molar Ratio	\overline{M} (g/mol)
DES(1:1)			1:1	219.25
DES(1:2)		та	1:2	184.87
DES(1:3)	IBAB	LA	1:3	167.685
DES(1:4)			1:4	157.44

2.3. Characterization of DES

The melting point and glass transition temperature of the prepared DESs are investigated using differential scanning calorimetry (DSC). DSC analysis is carried out for all the prepared samples using a METTLER TOLEDO Differential Scanning Calorimeter type DSC1. The DSC measurements are performed under a nitrogen (N₂) atmosphere to prevent oxidation of the samples. The N₂ flow rate is fixed as 45 mL/min, where the continuous heating is carried out at a rate of 10 °C·min⁻¹ until the specimens are melted completely. Further, the density and viscosity of the synthesized DESs are measured at different temperatures using an Anton Paar, instrument type DMA 5000-AMVn. The structure of chemical constituents and mutual interactions between different constituents are investigated by Fourier-transformed infrared (FT-IR) type T27-Hyperion-Vector22 and nuclear magnetic resonance (NMR) type AVANCE III.

2.4. Vapor-Liquid Equilibrium Device

The Vapor–liquid balance device is shown in Figure 1, and the experimental process is as follows. A 30 mL aliquot of the liquid mixture is loaded in the equilibrium kettle. Then, the cooling water is turned on, and gradually, the mixture is heated at the beginning stage. The heating power is adjusted in such a way that the return rate of condensed water of 2–3 drops per second is achieved. To stabilize the reflux action, the device is refluxed for 0.5 h, and then, the temperature is noted every 5 min. After 0.5 h of the stabilization period, the temperature becomes stable, and the liquid and vapor phases are believed to have achieved equilibrium. Then, 0.6 μ L of the sample from the liquid phase and vapor phase is collected and tested using chromatography. Each test measurement is repeated three times to decline the test error. As the outlet of the condenser shown in the sketch map is connected with the outside ambient atmosphere, the pressure in the VLE experiment is kept at atmospheric pressure.



Figure 1. Constant pressure double circulation vapor–liquid equilibrium kettle. 1—heater rod; 2—thermometer sleeve tube; 3—liquid phase sample connection; 4—liquid phase sample connection; 5—thermal resistance; 6—condenser; 7—vapor phase sample connection; 8—mercury thermometer.

The samples are analyzed using chromatography with an FID detector employing the programmed temperature technique. The initial column temperature is kept at 50 °C for 1 min. Then, it is heated to 220 °C at a heating rate of 10 °C·min⁻¹ and held for 10 min. The gasification chamber temperature is maintained at 220 °C, where the temperature of the detector is 250 °C, to which high purity N₂ as a carrier gas is introduced with a flow rate of 30 mL·min⁻¹. Further, hydrogen and air are introduced with flow rates of 30 mL·min⁻¹ and 300 mL·min⁻¹, respectively. Gas chromatographic parameters are shown in Table 3.

 Table 3. GC conditions employed for analysis of the condensed vapor phase.

Condition	Parameter
Column type	KB-FFAP (30 m; 0.32 mm; 0.25 μm)
Detector type	FID
Detector temperature	523 K
Injector temperature	503 K
Injection volume	0.4 uL
Carrier gas	N ₂
Flow rate (constant)	$30 \text{ cm}^3 \cdot \text{min}^{-1}$
Split ratio	200

3. Results and Discussion

3.1. DESs Characterization

The melting point and glass transition temperature values evaluated for the four DESs are summarized in Table 4. The density and the viscosity of the four DESs are measured

at atmospheric pressure in the temperature range from T/K = 293.15 to 353.15, with a step increase of 10 K. The experimental values for the density and the viscosity at different temperatures are tabulated in Table 5. To study the interactions that exist in HBA and HBD, the FT-IR analysis is carried out for DESs, HBD, and HBA.

The Glass Transition **Melting Point of Melting Point of** Sample Temperature (°C) HBA (°C) HBD (°C) DES(1:1) ~30-~25 DES(1:2) ~70-~65 102-106 37.2 **DES(1:3)** ~60-~50 ~80-~70 **DES(1:4)**

Table 4. Glass transition temperature and melting point of the DESs.

Table 5. Experimental density and viscosity values at different temperatures and atmospheric pressures (*p* = 101.325 kPa).

Temperature (K)		Density	r (g/cm ³)		Viscosity (mPa·s)			
	1:1	1:2	1:3	1:4	1:1	1:2	1:3	1:4
293.15	-	1.0979	1.1050	1.1118	-	964.58	483.46	291.14
303.15	-	1.0909	1.0982	1.1045	-	426.89	223.73	142.22
313.15	-	1.0843	1.0912	1.0974	-	206.48	116.34	77.47
323.15	1.0639	1.0799	1.0840	1.0906	372.82	114.54	67.99	46.53
333.15	1.0589	1.0707	1.0770	1.0828	201.73	68.30	42.80	30.11
343.15	1.0523	1.0643	1.0703	1.0757	116.36	43.41	28.77	20.94
353.15	1.0466	1.0572	1.0631	1.0680	72.438	29.79	20.57	15.21

All the prepared DESs display a glass transition temperature, i.e., when the temperature reaches lower than their freezing point, they become supercooled liquids instead of undergoing crystallization process, and finally, they transform into a glassy state. The melting point of the pure HBD component, which forms DES, has a lower melting point, and therefore, all the glass transition temperatures of DES are compared with the melting point of HBD. The glass transition temperatures of all DES are lower than the melting point of HBD, substantiating that the hydrogen bonding is formed in the prepared DESs, which is very essential. The glass transition temperature of DES(1:4) is the least of all the DESs, indicating that the hydrogen bonds that exist in DES(1:4) are the strongest.

The density of DES(1:1–1:4) is measured under different temperatures (293.15–353.15 K) under atmospheric pressure. As DES(1:1) is not in the liquid state at room temperature, it is measured from 323.15 K (Figure 2). From the figure, it is inferred that within the temperature range of 293.15 to 353.15 K, the densities of the samples are found to cover the range between 1.04 and 1.12 g/cm³, which is close to the density of water, and also, the density tends to decrease with an increase in temperature. The obtained results follow the general liquid density characteristic. Further, with the increase in HBD content, the density increases.



Figure 2. The change in experimental density with respect to temperature for the prepared DESs.

The viscosity of DES(1:1–1:4) was measured under different temperatures between 293.15 and 353.15 K at atmospheric pressure. Since DES(1:1) is not in the liquid state at room temperature, its viscosity is measured from 323.15 K (Figure 3). From Figure 3, it is inferred that between 293.15 and 353.15 K, the viscosity values of DES are found in the range from 1000 to 10 mPa·s, which follows the same trend as observed in the ionic liquid. Till the temperature is 333.15 K, the viscosity decreases enormously with each step increase in temperature rise. After reaching 333.15 K, the change in viscosity is slow, showing a gradual decrease. Furthermore, it is to be noted that with the increase in HBD content, the density decreases.



Figure 3. The change in experimental viscosity values of prepared DESs with temperature.

In Figure 4, the FT-IR spectra of LA, TBAB, and DESs display the hydroxy peak v(OH) at 3200 cm⁻¹. Compared to LA, the peak intensity becomes stronger and wider in DES(1:1–1:4) and is shifted to 3000 cm⁻¹. These interpretations show that the hydrogen bonds are formed between LA and TBAB since there are active hydrogens in LA that can act as HBD and high electron density in the Br atom of TBAB that can act as HBA. At different HBD and HBA ratios, the hydroxy peak intensity strength and width are different, which substantiates that the strength of the hydrogen bond is different for DES(1:1–1:4) and is developed by different ratios.



Figure 4. FT-IR spectra of LA, TBAB, and DESs formed by LA and TBAB with a 1:1–1:4 mol ratio.

3.2. Selection of HBA and HBD Ratio

3.2.1. VLE Experiment

A series of DESs developed using LA and TBAB at different mole ratios, including 1:1, 1:2, 1:3, and 1:4, are used to separate the azeotrope (cyclohexane + benzene) at 101.325 kPa where the mole concentration of DESs is fixed as 0.1.

For a better understanding of the pseudo-ternary VLE behavior, both relative volatility (a_{ij}) and selectivity (S) are assessed using the following expressions:

$$\alpha_{ij} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}}$$
$$S = \frac{\alpha_{ij}^{\text{with entrainer}}}{\alpha_{ij}^{\text{without entrainer}}}$$

where *y* is the molar fraction of the vapor phase, *x* the molar fraction of the liquid phase, and the subscripts *i* and *j* refer to the more volatile component (cyclohexane) and the less volatile component (benzene), respectively. The estimated relative volatility and selectivity values are provided in Table 6.

Table 6 summarizes the Vapor–liquid equilibrium data of the pseudo-ternary systems cyclohexane (1) + benzene (2) + DES (3) at a pressure of 101.325 kPa, where X_3 is the DES molar fraction in the liquid phase, X_1 is the cyclohexane molar fraction in the liquid phase, X'_1 is the DES-free cyclohexane molar fraction in the liquid phase, Y_1 is the cyclohexane molar fraction in the vapor phase, T is the temperature, α_{ij} is the relative volatility, and S is the selectivity.

	Cyclohe	xane (1) + Ben	zene (2) + DE	S(1:1)(3), at 10	1.325 kPa	
X_3	X_1	X'_1	<i>Y</i> ₁	T/K	α _{ij}	S
0.1	0.0000	0.0000	0.0000	353.25	-	_
0.1	0.0652	0.0724	0.0964	352.80	1.3670	1.0081
0.1	0.0952	0.1058	0.1448	352.27	1.4310	1.0950
0.1	0 1470	0 1633	0 2134	351.63	1.3895	1 1049
0.1	0 2525	0 2805	0.3206	351.05	1 2106	1 0446
0.1	0.3909	0.4343	0.4307	350.73	0.9852	0.8878
0.1	0.5058	0.5620	0 5348	350.69	0.8961	0.8075
0.1	0.5867	0.6519	0.6098	350.77	0.8346	0.9602
0.1	0.6807	0.7563	0.7265	351 33	0.8561	1 0402
0.1	0.7461	0.8290	0.8023	351.77	0.8371	1.0102
0.1	0.7778	0.8642	0.8452	352.20	0.8580	1 1699
0.1	0.9000	1 0000	1 0000	353.85	0.0500	1.10))
0.1	Cyclob	$\frac{1.0000}{000}$	$n_{2} = \frac{1.0000}{1.0000}$	ES(1.2) at 101	225 LP2	
v	v	$\frac{v'}{v'}$	$\frac{112 \text{ effe}(2) + D}{v}$	ES(1:2), at 101.	525 KF d	6
<u>A3</u>	A1	A 1	11 0.00000	1/K	a ij	5
0.1	0.0000	0.0000	0.0000	353.25	-	-
0.1	0.1668	0.1853	0.3191	351.20	2.0601	1.7051
0.1	0.2406	0.2673	0.4939	350.64	2.6752	2.4107
0.1	0.3015	0.3351	0.6053	351.28	3.0438	3.6984
0.1	0.3529	0.3921	0.7107	351.74	3.8089	4.8976
0.1	0.4507	0.5008	0.8091	352.34	4.2229	5.7580
0.1	0.5597	0.6219	0.8868	352.67	4.7632	6.4947
0.1	0.7232	0.8035	0.9420	353.17	3.9681	5.4106
0.1	0.9000	1.0000	1.0000	353.85	-	-
	Cycloh	exane (1) + Be	nzene (2) + D	ES(1:3), at 101.	325 kPa	
X3	X_1	X'_1	<i>Y</i> ₁	T/K	α _{ij}	S
0.1	0.0000	0.0000	0.0000	353 25	_	_
0.1	0.0395	0.0439	0.0543	352 47	1 2522	0 9581
0.1	0.0902	0 1002	0 1123	351.80	1 1360	0.9033
0.1	0.1430	0.1589	0.1725	351.28	1.1000	0.9133
0.1	0.2686	0.2984	0.3190	350.67	1 1015	0.9926
0.1	0.2000	0.2704	0.5013	350.36	1.1013	1 0794
0.1	0.5557	0.4775	0.6031	350.50	0.9414	1.0774 1.0275
0.1	0.6402	0.0174	0.0001	351.35	0.0414	1.0275
0.1	0.0402	0.7114	0.7001	252.27	0.9475	1.2101
0.1	0.7217	0.8019	0.7875	252.27	0.9137	1.2400
0.1	0.7029	0.0477	0.0230	352.71	0.6505	0.8405
0.1	0.8741	0.9712	0.9541	353.60	0.0104	0.8405
0.1	0.9000	1.0000	1.0000	555.65 EE(1.4) -+ 101	- 205 1.D.	-
37	Cyclon	exane (1) + be	nzene(2) + D	ES(1:4), at 101.	325 KPa	0
X3	<i>X</i> ₁	Χ΄1	¥1	1/K	α_{ij}	5
0.1	0.0000	0.0000	0.0000	353.25	-	-
0.1	0.0921	0.1024	0.1852	352.50	1.9930	1.5250
0.1	0.1325	0.1472	0.2577	352.10	2.0114	1.5391
0.1	0.2071	0.2302	0.4174	351.20	2.3966	1.9836
0.1	0.2550	0.2834	0.5197	350.77	2.7368	2.3615
0.1	0.3356	0.3729	0.5713	350.97	2.2410	2.7230
0.1	0.5201	0.5779	0.6318	351.08	1.2535	1.5231
0.1	0.5913	0.6570	0.6728	351.33	1.0737	1.3046
0.1	0.6516	0.7240	0.7086	351.60	0.9267	1.1916
0.1	0.7583	0.8425	0.8016	352.17	0.7554	1.0300
0.1	0.8252	0.9169	0.8779	352.85	0.6516	0.8885
0.1	0.9000	1.0000	1.0000	353.85	-	-

Table 6. Vapor–liquid equilibrium data of the pseudo-ternary systems (cyclohexane (1) + benzene (2) + DES (3)).

At the azeotropic point, the value of the relative volatility is found to be one, which means that both the components in the mixture have the same vapor pressure. As the boiling points of the two components are close to each other, the relative volatility of the two components can be increased by adding a low eutectic solvent. Table 7 and Figures 5–8 depict that when the four DESs are added separately, as entrainers in a molar fraction of 0.1, only the relative volatility (a_{ij}) of the system added with DES(1:2) is higher than one at all concentrations, while the relative volatility of the other three systems is not higher than one at all concentrations. This phenomenon is attributed to the fact that the DES(1:2) breaks the azeotrope, whereas DES(1:1), DES(1:3), and DES(1:4) cannot break it. It also depicts the same results. The pseudo-ternary system added with DES(1:1) and DES(1:3) show the same azeotropic point as the binary system validating that the DES (TBAB:LA) (1:2) and DES (ChCI:LA) (1:2) have no influence on the azeotrope. Although the azeotropic point in the pseudo-ternary system added with DES(1:4) is changed to the cyclohexane side, the azeotrope is not broken. With these data, it is clear that only DES(1:2) acts as an effective entrainer in the present work.

Table 7. Coefficient of determination (R^2) of the pseudo-ternary systems fitted using the three thermodynamic models.

Caralteria		R ²	
System	NRTL	WILSON	UNIOUAC
cyclohexane-benzene-DES(1:1)	0.999990073	0.999050672	0.999206835
cyclohexane-benzene-DES(1:2)	0.876057425	0.615250142	0.823243826
cyclohexane-benzene-DES(1:3)	0.999428449	0.99838839	0.999021115
cyclohexane-benzene-DES(1:4)	0.999999997	0.885377491	0.889570028



Figure 5. Experimental and calculated data X'Y diagram for cyclohexane (1) + benzene (2) + DES(1:1) (3) at constant pressure (101.325 kPa) and constant DES molar fraction ($X_3 = 0.1$).

3.2.2. VLE Data Correlation

The local composition activity coefficient models UNIQUAC, WILSON, and NRTL are used for regression analysis of the VLE data of three ternary systems. For each system, the coefficient of determination is estimated to perceive the goodness of fit of the models. The obtained results are provided in Table 7. In the systems containing DES(TBAB:LA) (1:2) and DES(ChCl:LA) (1:2) [31], the prediction is satisfactory as the coefficient of determination is >0.99 assessed from all the three models. In the system containing DES(TBAB:LA) (1:2), the prediction is not satisfactory since the coefficient of determination is <0.99 using the three models.











Figure 8. Experimental and calculated data X'Y diagram for cyclohexane (1) + benzene (2) + DES(1:4) (3) at constant pressure (101.325 kPa) and constant DES molar fraction ($X_3 = 0.1$).

For a better understanding of the fitness of the three thermodynamic models, the coefficient of determination (correlation index, R²) is calculated using the following expressions:

$$R^2 = \frac{Q_R'}{Q_\Sigma'} = 1 - \frac{Q}{Q_\Sigma'} = 1 - \frac{\sum (y_i - u_i)^2}{\sum (y_i - \overline{y})^2}$$

where y_i and u_i are the experimental data and the estimated value of the vapor phase molar fraction, respectively, and \overline{y} is the average value of the experimental data of the vapor phase molar fraction.

According to Table 8, the NRTL model displays the best fitness. For each system, the correlation index R^2 value follows the relation NRTL > UNIQUAC > Wilson, validating that the NRTL model is more suitable for predicting mixtures containing low eutectic solvents. Theoretical analysis demonstrates that the deep eutectic solvent is immiscible with benzene and cyclohexane, and thereby, a miscibility gap is created between the mixed solution resulting in the inefficient correlation by the Wilson model. At the same time, the correlation made by each model for the system containing extractant DES(1:2) is low, but the extraction effect of DES(1:2) is the best. This fact is consistent with the conclusion that the better the extraction effect is, the lower the applicability of the prediction model.

Table 8. Estimated values for the binary parameters using the NRTL model for correlating the pseudo-binary VLE data at a constant DES molar fraction of 0.1 within a pressure of 101.325 kPa.

Extractant	Comp. i	Comp. j	a _{ij}	a _{ji}	b_{ij}	b_{ji}	c _{ij}
DES(1:1) DES(1:2) DES(1:3) DES(1:4)	Cyclohexane	Benzene	-4.2995 -17.895 23.870 56.508	-12.027 26.168 -11.683 -17.710	1605.6 10,000 7796.4 52504	4218.2 10,000 4218.2 6357.4	-2.7 0.1717 2.1377 0.0306

3.3. Selection of DES Concentration

In the process of the selection of HBD and HBA ratios, the results validate that DES(1:2) is the most effective choice from the prepared DESs. Therefore, the concentration of DES(1:2) should be selected next. In the present work, the molar concentrations of DES(1:2) is chosen as 0.05, 0.10, 0.15, and 0.20.

3.3.1. VLE Experiment

Four kinds of DES(1:2)-cyclohexane-benzene mixture are used to conduct the VLE experiments at 101.325 kPa, where the mole concentrations of DES(1:2) are 0.05, 0.10, 0.15, and 0.20, respectively.

The results of vapor–liquid equilibrium of the pseudo-ternary systems cyclohexanebenzene-DES(1:2) are summarized in Table 9, where X_3 is the DES molar fraction in the liquid phase, X_1 is the cyclohexane molar fraction in the liquid phase, X'_1 is the DES(1:2)free cyclohexane molar fraction in the liquid phase, Y_1 is the cyclohexane molar fraction in the vapor phase, T is the temperature, a_{ii} is the relative volatility, and S is the selectivity.

At the azeotropic point, the value of the relative volatility obtained will be one, which represents that both components in the mixture have the same vapor pressure. If the azeotrope is not broken, the relative volatility will be lower than one for all concentrations. However, if the azeotrope is broken, the relative volatility becomes higher than one at all concentrations. Table 9 and Figure 9 display that when the DESs are added as entrainers in a molar fraction of 0.05 to 0.2, the relative volatility (α_{ij}) of the system with 0.1, 0.15, and 0.2 molar concentrations of DES(1:2) is higher than one at all concentrations, whereas the relative volatility of system with 0.05 molar concentration of DES is lower than one. Figure 10 also depicts the same result, where in the pseudo-ternary system with 0.1, 0.15, and 0.2 molar concentrations of DES(1:2), Y_1 is greater than X_1 in all concentrations and, therefore, validates that the azeotrope is broken.

	C	yclohexane (1) + Benzene (2	2) + DES(1:2) (3	3)	
X_3	X_1	X'_1	<i>Y</i> ₁	T/K	α_{ij}	S
0.05	0.0000	0.0000	0.0000	353.25	-	-
0.05	0.0676	0.0712	0.1325	352.32	0.5019	0.3840
0.05	0.1335	0.1405	0.1976	351.96	0.6638	0.5079
0.05	0.1993	0.2098	0.2615	351.65	0.7498	0.5962
0.05	0.3190	0.3358	0.3649	351.13	0.8799	0.7283
0.05	0.4286	0.4512	0.4526	351.10	0.9944	1.2083
0.05	0.5045	0.5311	0.5102	351.15	1.0874	1.3213
0.05	0.6382	0.6718	0.6352	351.30	1.1756	1.4284
0.05	0.7273	0.7656	0.7192	351.77	1.2752	1.6397
0.05	0.7849	0.8262	0.7841	352.20	1.3089	1.7847
0.05	0.8450	0.8895	0.8513	352.73	1.4061	1.9172
0.05	0.9500	1.0000	1.0000	353.85	-	-
X_3	X_1	X'_1	Y_1	T/K	α_{ij}	S
0.1	0.0000	0.0000	0.0000	353.25	-	-
0.1	0.1668	0.1853	0.3191	351.20	2.0601	1.7051
0.1	0.2406	0.2673	0.4939	350.64	2.6752	2.4107
0.1	0.3015	0.3351	0.6053	351.28	3.0438	3.6984
0.1	0.3529	0.3921	0.7107	351.74	3.8089	4.8976
0.1	0.4507	0.5008	0.8091	352.34	4.2229	5.7580
0.1	0.5597	0.6219	0.8868	352.67	4.7632	6.4947
0.1	0.7232	0.8035	0.9420	353.17	3.9681	5.4106
0.1	0.9000	1.0000	1.0000	353.85	-	-
X_3	X_1	X'_1	Y_1	T/K	α_{ij}	S
0.15	0.0000	0.0000	0.0000	353.25	-	-
0.15	0.0780	0.0918	0.1920	351.20	2.3509	1.9458
0.15	0.1346	0.1583	0.3311	350.64	2.6319	2.3717
0.15	0.2360	0.2777	0.5393	351.28	3.0448	3.6996
0.15	0.2824	0.3322	0.6154	351.74	3.2166	4.1360
0.15	0.3827	0.4502	0.7380	352.34	3.4400	4.6905
0.15	0.4338	0.5103	0.7870	352.67	3.5457	4.8346
0.15	0.5195	0.6112	0.8413	352.96	3.3722	4.5980
0.15	0.6038	0.7104	0.9011	353.13	3.7143	5.0645
0.15	0.7020	0.8259	0.9589	353.40	4.9182	6.7060
0.15	0.8500	1.0000	1.0000	353.85	-	-
X_3	X_1	X'_1	Y_1	T/K	α_{ij}	S
0.2	0.0000	0.0000	0.0000	353.25	-	-
0.2	0.0862	0.1077	0.1845	352.35	1.8747	1.4345
0.2	0.1477	0.1846	0.3432	351.35	2.3081	2.1979
0.2	0.1776	0.2220	0.4209	351.04	2.5471	2.3257
0.2	0.2117	0.2647	0.4924	351.00	2.6953	4.1499
0.2	0.2844	0.3555	0.6403	351.67	3.2274	4.6699
0.2	0.3298	0.4123	0.7141	351.96	3.5603	4.8545
0.2	0.4302	0.5377	0.8061	352.33	3.5747	4.8741
0.2	0.4735	0.5919	0.8410	352.67	3.6459	4.9712
0.2	0.5254	0.6567	0.8672	353.00	3.4121	4.6524
0.2	0.6498	0.8123	0.9425	353.56	3.7876	4.4239
0.2	0.8000	1.0000	1.0000	353.85	-	-

Table 9. Vapor–liquid equilibrium data of the pseudo-ternary systems cyclohexane (1) + benzene (2)+ DES(1:2) (3) at a pressure of 101.335 kPa.



Figure 9. Experimental X'Y diagram for the pseudo-ternary systems (cyclohexane (1) + benzene (2) + DES(1:2)(3)) at atmospheric pressure and constant DES molar fraction ($X_3 = 0.1$), and the experimental XY diagram for binary system (cyclohexane (1) + benzene (2)).



Figure 10. Experimental relative volatility (a_{ij}) of the pseudo-ternary system cyclohexane (1) + benzene (2) + DES(1:2) (3) and binary system cyclohexane (1) + benzene (2).

3.3.2. VLE DATA Correlation

In most cases of DES(1:2) molar concentration, the NRTL model shows the best fitness. The coefficient of determination value (\mathbb{R}^2) follows the trend NRTL > UNIQUAC > Wilson in Table 10. The model regression results for different molar concentrations of DES(1:2) are shown in Figures 11–14. The results depicted from the Figure 15 are also in accordance with the data of the relative volatility (α_{ij}) in Table 11. In the system added with 0.1, 0.15, and 0.2 molar concentrations of DES(1:2), the azeotrope is broken. For each system, the two binary interaction parameters of cyclohexane/benzene through the NRTL model are obtained, which are shown in Table 11.

Table 10. Coefficient of determination (R^2) of the pseudo-ternary systems fitting using the three thermodynamic models.

DES System		R ²	
DES(1:2) mole concentration	UNIQUAC	WILSON	NRTL
0.05	0.999274739	0.999161341	0.999263945
0.10	0.823243826	0.615250142	0.877053812
0.15	0.691208105	0.691251575	0.725252503
0.20	0.708145398	0.692945634	0.818531606



Figure 11. Experimental and calculated data X'Y diagram for cyclohexane (1) + benzene (2) + DES (3) at constant pressure (101.325 kPa) and constant DES molar fraction ($X_3 = 0.1$).



Figure 12. Experimental and calculated data X'Y diagram for cyclohexane (1) + benzene (2) + DES (3) at constant pressure (101.325 kPa) and constant DES molar fraction ($X_3 = 0.15$).



Figure 13. Experimental and calculated data X'Y diagram for cyclohexane (1) + benzene (2) + DES (3) at constant pressure (101.325 kPa) and constant DES molar fraction ($X_3 = 0.2$).



Figure 14. FT–IR spectra of DES(1:1), benzene and DES(1:1) + benzene(DES 0.1 (molar concentration)).



Figure 15. Experimental and calculated data X'Y diagram for cyclohexane (1) + benzene (2) + DES (3) at constant pressure (101.325 kPa) and DES molar fraction ($X_3 = 0.05$).

Table 11. Estimated values for the binary parameters using the NRTL model for correlating the pseudo-binary VLE data.

DES(1:2) Mole Concentration	Comp. i	Comp. j	a _{ij}	a _{ji}	b _{ij}	b _{ji}	c _{ij}
0.05			5.7781	21.790	-2897.1	-6397.7	-2.7
0.10	Cuclobovana	D	-17.895	26.168	10,000	-10,000	0.1717
0.15	Cyclonexalle	Benzene	-16.288	27.070	10,000	-10,000	2.1377
0.2			-20.707	-20.290	10,000	1000	0.0306

3.4. Extractive Distillation Mechanism

Extraction mechanisms are very important to understand the extractive distillation process and will provide significant insights for the development of molecule design and the smart design of DES entrainers. FT-IR and NMR are employed to elucidate the extraction mechanism. In the present research, benzene acts as the heavy component and is kept at the bottom along with DESs, where the interaction of benzene and DESs is studied.

3.4.1. Selection of HBD and HBD Ratio

FT-IR analysis is used to elucidate the mechanism for the process of selection of HBD and HBD ratios and to validate the results of the selection. The infrared spectrograms of the test samples are provided in Figures 16–18.



Figure 16. FT–IR spectra of DES(1:2), benzene and DES(1:2) + benzene(DES 0.1 (molar concentration)).



Figure 17. FT-IR spectra of DES(1:3), benzene and DES(1:3) + benzene(DES 0.1 (molar concentration)).



Figure 18. FT–IR spectra of DES(1:4), benzene and DES(1:4) + benzene(DES 0.1 (molar concentration)).

From Figure 17, the FT-IR spectra of DES(1:1–1:4), benzene and DES(1:1–1:4) + benzene shows the peak corresponding to the hydroxy v(OH) group at 3200 cm⁻¹ and the peak ascribed to the carboxyl group v(C=O) at 1722 cm⁻¹. In the mixture containing DES(1:1–1:4) + benzene, the hydroxy and carboxy peaks become weaker. This fact is attributed to the formation of hydrogen bond and π – π bond interaction between DES(1:1–1:4) and benzene that have destroyed the hydrogen bond within the DES(1:1–1:4) system, and subsequently, the strength of each system is found to be different due to different molar ratios. The results validate that the C=O double bond in LA of DES interacts with benzene by forming a π – π

bond, and the O-H bond in LA of DES interacts with benzene by forming the hydrogen bond. However, the change in peak intensity of DES(1:2) is the largest, substantiating that the hydrogen bond and π - π bond interaction between DES(1:2) and benzene is the strongest, leading to the breaking of the azeotrope.

3.4.2. Selection of DES Concentration

Since the change in concentration of the constituents cannot be exactly revealed by FT-IR analysis, NMR is employed in the selection of the DES concentration study. Using ChemDraw software, the magnetic resonance hydrogen spectrum of tetrabutylammonium bromide, levulinic acid, and benzene is simulated, and chemical shift values are obtained, as shown in Figures 19–21. The experimental test of ¹H NMR spectra and magnified view of a particular range are shown in Figures 22 and 23. From Figures 21 and 22, it is inferred that the NMR spectrum simulated from the ChemDraw software highly corroborates with the test measured spectra, confirming that the test samples are highly pure and they are target material.

ChemNMR ¹H Estimation



Figure 19. Chemical shift values of intramolecular hydrogen atoms of TBAB, LA, and benzene estimated by ChemDraw.



Figure 20. ¹H NMR of TBAB, LA and benzene estimated by ChemDraw.







9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 fl (gas)









From the expanded spectra shown in Figures 22 and 23, it is inferred that compared to pure DES(1:2), different concentrations of DES(1:2) all have apparent spectral peak shifts and are shifted towards the low field. This is ascribed to the formation of hydrogen bonds between different concentrations of DES(1:2) and benzene. As a result, the electron cloud density around the hydrogen nucleus has declined due to the induced effect. As can be seen from Figure 23, the chemical shift of spectral peak offset value is different for

different concentrations of DES(1:2); the offset distance is positively correlated with the DES(1:2) concentration. This substantiates that the hydrogen bonding strength formed between different concentrations of DES(1:2) and benzene is different, and it is positively correlated with the concentration. From these interpretations of the NMR results, the vapor–liquid equilibrium results are verified, i.e., low concentrations of DES(1:2) cannot break the benzene-cyclohexane azeotrope, but high concentrations of DES can break the azeotrope.

4. Conclusions

The eutectic solvent is prepared, and its physical properties are characterized. Through the vapor–liquid phase equilibrium experiments, the X-Y phase diagram and relative volatility diagram are compared, and the optimal HBA and HBD molar ratio and optimal molar concentration are estimated as 1:2 and 0.1, respectively. Other DES systems changed the azeotropic point but did not break the azeotrope. The results show that the extraction effect of DES is dependent on the system to be separated, the type and ratio of DES, and the DES concentration.

Here, three thermodynamic models are used to fit vapor–liquid phase equilibrium data. By comparing the model-related indices (R²), the correlation degree of the NRTL model is found to be the highest, and the binary interaction parameters of each system are obtained. The results proved the NTRL model is more suitable for predicting the vapor–liquid equilibrium behavior of a system containing DESs. In the best extraction system, cyclohexane-DES(1:2) (molar concentration 0.1) system, R² is 0.8771, NRTL model binary interaction parameters: a_{ij} , -17.895; a_{ji} , 26.168; b_{ij} , 10000; b_{ji} , -10000; c_{ij} , 0.1717 (*i* = cyclohexane, *j* = benzene).

The screening and optimized results of DES are verified by FT-IR and NMR analyses. It is proven that there is a formation of a strong hydrogen bond and π - π bond between benzene and DES with an extraction effect, and this effect can break the azeotrope. There are weak or no obvious hydrogen bonds and π - π bonds between benzene and DES without an extraction effect, and some can only change the azeotropic point but cannot break the azeotrope. These interpretations substantiate the results of the vapor–liquid phase equilibrium experiments. Combined with thermodynamics research, the present work provides a theoretical basis for the design and optimization of DES.

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