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Liquid-liquid Equilibria of Cyclohexene-cyclohexane with Betaine-glycerol DES: Experiments and Correlation

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Abstract – This study investigates the liquid-liquid equilibria (LLE) of a ternary system comprising cyclohexene, cyclohexane, and a betaine-glycerol deep eutectic solvent (DES) at 303.2 K, 313.2 K, and 323.2 K. The DES was synthesized using a 1:5 molar ratio of betaine to glycerol. LLE data were correlated using Non-Random Two-Liquid (NRTL) and Universal Quasi-Chemical (UNIQUAC) models. Distribution coefficients (D_1) for cyclohexene decreased with increasing temperature, ranging from 0.06 at 303.2 K to 0.02 at 323.2 K for a cyclohexene mole fraction of 0.8 in the raffinate phase. Selectivity (S) values exceeded 1 at higher cyclohexene concentrations. The Othmer-Tobias equation confirmed data consistency with r^2 values close to 1. UNIQUAC model showed superior performance with lower RMSD values compared to NRTL. This research demonstrates the potential of betaine-based DES as an environmentally friendly alternative for cyclohexene/cyclohexane separation in petrochemical processes.

Key words: deep eutectic solvent, distribution coefficient, liquid-liquid equilibrium, selectivity, correlation

1. Introduction

Cyclohexene and cyclohexane are crucial raw materials in the production of cyclohexanol and cyclohexanone, which serve as precursors for adipic acid and caprolactam-key components in nylon manufacturing [1,2]. The primary industrial method for producing these cyclic hydrocarbons is the catalytic hydrogenation of benzene [3]. This process yields a mixture of cyclohexene and cyclohexane, necessitating an effective separation technique. However, due to their closely related physical properties, such as relative volatilities and molecular geometries, conventional distillation is unsuitable for separating cyclohexene from cyclohexane [4]. One approach to overcome this challenge is reactive distillation in the presence of an entrainer, such as sulfolane, ethylene glycol, or water [5]. However, the high energy requirements and substantial initial capital investment associated with this method have prompted the development of new, economically feasible, and environmentally friendly separation techniques.

Ionic liquids have been applied as extracting agent in azeotropic distillation [6,7] and extraction [8,9] due to their low volatility, low flammability, and high thermal stability. However, significant barriers exist in applying ionic liquids to separation process, including complex synthesis procedures and concerns regarding environmental and human health impacts [10]. In efforts to replace ionic liquids, deep eutectic solvents (DESs) have gained attention in various applications, including extraction [11-13]. DESs offer several advantages over ionic liquids, including simpler synthesis, lower cost, and improved environmental compatibility [14]. Like ionic liquids, DESs can be tuned by varying their constituents. For DESs, their tunability can be achieved by altering the hydrogen bond donor (HBD), hydrogen bond acceptor (HBA), or the mole ratio of HBD to HBA.

Hydroxyl functional groups, particularly those in glycerol with its three hydroxyl groups, have been widely used as HBDs in DES formation. Among potential HBAs, betaine stands out as a nontoxic and readily biodegradable option. Unlike choline chloride, betaine is industrially obtained from renewable resources as a byproduct of sugar production [15]. These environmentally friendly properties make betaine-based DESs suitable for various applications. For instance, betaine-based DESs with diol acid and amine HBDs have shown promise as replacements for corrosive amine aqueous solution in carbon dioxide capture [16].

The selective extraction of cyclohexene by the betaine-glycerol DES arises from molecular-level interactions between the DES and hydrocarbons. Betaine, a zwitterionic compound, possesses both positively charged quaternary ammonium and negatively charged carboxylate groups, creating a polar microenvironment. Glycerol, with its three hydroxyl groups, forms an extensive hydrogen-bonding network with betaine, enhancing the DES's solvation power. Cyclohexene, with its -electrons from the double bond, engages in stronger dipole-induced dipole interactions with the polar DES compared to the nonpolar cyclohexane. Additionally, the DES's structured hydrogen-bond network preferentially stabilizes cyclohexene through weak but specific interactions, while cyclohexane's fully saturated lacks comparable affinity. This selectivity is further amplified by the DES's low viscosity at the 1:5 betaine-glycerol ratio, which facilitates

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mass transfer of cyclohexene into the extract phase [17].

Despite the promising properties of DESs, the application of betaine-based DESs for the separation of cyclohexene and cyclohexane has not been systematically explored. The novelty of this work lies in the comprehensive investigation of the liquid-liquid equilibria (LLE) of cyclohexene-cyclohexane mixtures with a betaine-glycerol DES (1:5 molar ratio) across a range of temperatures (303.2 K, 313.2 K, and 323.2 K). Unlike previous studies that focused on other DES compositions or hydrocarbon systems, this work demonstrates the unique capability of a betaine-glycerol DES to selectively extract cyclohexene from cyclohexane, supported by rigorous experimental data and thermodynamic modeling using both NRTL [18] and UNIQUAC [19] models. Furthermore, the research highlights the environmental and practical advantages of using betaine, a biodegradable and renewable hydrogen bond acceptor, over more commonly used but less sustainable alternatives such as choline chloride. Notably, the DES does not partition into the raffinate phase, minimizing solvent loss and contamination. The superior performance of the UNIQUAC model in correlating the experimental data further advances the thermodynamic understanding of DES-based separations.

2. Experimental Section

2-1. Chemicals and DESs preparation

Cyclohexene, cyclohexane, and glycerol used had a purity greater than 99.0%, while betaine had a minimum purity of 98%, as shown in Table 1 and Fig. 1. Dimethyl sulfoxide-d6 (DMSO-d6) and deuterated chloroform ($CDCl_3$) with a minimum purity of 99.5 atom % D were used to analyze the extract and raffinate phase, respectively. All chemicals were purchased from Sigma-Aldrich and used as received. DES was prepared by using glycerol as an HBD and betaine as an HBA with mole ratio of 5 to 1 in a 500 mL round flask at 353 K. The synthesized DES was analyzed using a ^{1}H NMR (JNM-LAMDA, 300 MHz, Jeol, Inc., Japan) spectrometer.

Table 1. Chemicals* used in this study

Compound	CAS number	Purity (wt%)
cyclohexane	110-82-7	≥ 99%
cyclohexene	110-83-8	≥ 99.5%
betaine	107-43-7	≥ 98%
glycerol	56-81-5	≥ 99.5%
DMSO-d6	2206-27-1	99.5 atom % D
$CDCl_3$	865-49-6	99.5 atom % D

*All chemicals were purchased from Sigma-Aldrich Inc.

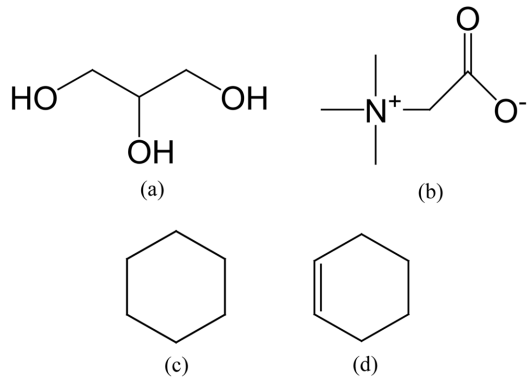

Fig. 1. Chemical structures of (a) glycerol (b) betaine (c) cyclohexane (d) cyclohexene.

2-2. Experimental procedure and analysis method

A known amount (~15 g) of DES was measured using an analytical balance (Shimadzu ATX 224, Japan) with an accuracy of $\pm 1\times10^{-4}$ g in a 50 cm^3 round flask containing cyclohexene and cyclohexane to prepare several mixtures at different mole fractions of each compound. They were added into a temperature-controlled glass vessel under vigorous mixing for several hours and held for a few hours to obtain equilibrium. A ^{1}H NMR spectrometer was used to quantitatively analyze each compound in both phases at least three times, as we did earlier [9,11,20].

The LLE data were experimentally measured at 303.2 K, 313.2 K and 323.2 K using the tie-line method. The proton peak in cyclohexane appearing at 1.3-1.4 was used to determine the amount of cyclohexane in each phase. Similarly, two-proton peak in cyclohexene in both the raffinate and extract phases appearing at 5.6-5.7 ppm was used for quantitative analysis. The hydroxyl peak in glycerol appearing at 4.4-4.9 ppm was used for quantitative analysis of DES.

3. Results and Discussion

3-1. Experimental LLE Data and Phase Behavior

Liquid-liquid equilibrium (LLE) data for the ternary system of cyclohexane, cyclohexene, and DES were determined at atmospheric pressure and three temperatures: 303.2 K, 313.2 K, and 323.2 K. The detailed results are presented in Table 2. Notably, no DES peaks were detected in the raffinate phase at any temperature, indicating that the DES remains almost entirely in the extract phase. This immiscibility is a significant advantage, as it minimizes solvent loss and contamination in the raffinates, simplifying downstream processing and solvent recovery [21,22].

The LLE experimental data of the ternary systems were measured at three temperatures, 303.2 K, 313.2 K, and 323.2 K. The distribution coefficient (D_i) for each component i and the selectivity (S) for cyclohexene were calculated using Eqs. (1) and (2), respectively:

$$D_i = \frac{x_i^{II}}{x_i^{I}} \tag{1}$$

$$S = \frac{D_1}{D_2} \tag{2}$$

where x_i^I and x_i^{II} are the mole fractions of each component i in the raffinate phase (I) and the extract phase (II), respectively. Subscripts 1 and 2 refer to cyclohexene and cyclohexane, respectively.

As illustrated in Fig. 2, D_1 values increased with increasing mole fraction of cyclohexene in the raffinate phase but decreased with increasing temperature. For instance, at a mole fraction of cyclohexene

Table 2. LLE data, distribution coefficient of ethanol (D_1), and selectivity (S) for the systems cyclohexene (1) - cyclohexane (2) – DES (3) at 303.2 K, 313.2 K, and 323.2 K

cyclohexene (1) - cyclohexane (2) – DES (3) at 303.2 K

Raffinate Phase		Extract Phase				
x_1^I	x_2^I	x_1^{II}	x_2^{II}	x_3^{II}	D_1	S
0.3088	0.6912	0.0046	0.0078	0.9876	0.015	1.3
0.6242	0.3758	0.0239	0.0125	0.9636	0.038	1.2
0.7556	0.2444	0.0402	0.0056	0.9543	0.053	2.3
0.7856	0.2144	0.0530	0.0024	0.9446	0.067	6.0
0.8142	0.1858	0.0529	0.0028	0.9443	0.065	4.3

cyclohexene (1) - cyclohexane (2) – DES (3) at 313.2 K

Raffinate Phase		Extract Phase				
x_1^I	x_2^I	x_1^{II}	x_2^{II}	x_3^{II}	D_1	S
0.3624	0.6376	0.0013	0.0024	0.9963	0.004	1.0
0.4307	0.5693	0.0023	0.0013	0.9964	0.005	2.3
0.5211	0.4789	0.0043	0.0014	0.9943	0.008	2.8
0.7758	0.2242	0.0337	0.0026	0.9637	0.043	3.7
0.8095	0.1905	0.0416	0.0015	0.9569	0.051	6.5

cyclohexene (1) - cyclohexane (2) – DES (3) at 323.2 K

Raffinate Phase		Extract Phase				
x_1^I	x_2^I	x_1^{II}	x_2^{II}	x_3^{II}	D_1	S
0.5202	0.4798	0.0005	0.0018	0.9977	0.001	0.3
0.5901	0.4099	0.0025	0.0003	0.9972	0.004	5.8
0.6072	0.3928	0.0004	0.0033	0.9963	0.001	0.1
0.6656	0.3344	0.0041	0.0005	0.9954	0.006	4.1
0.8232	0.1768	0.0193	0.0006	0.9801	0.023	6.9
0.8324	0.1676	0.0211	0.0011	0.9777	0.025	3.9

The standard uncertainties u are u(T) = 0.1 K, u(P) = 1 kPa, $u(x_i^I) = 0.017$ and $u(x_i^{II}) = 0.009$.

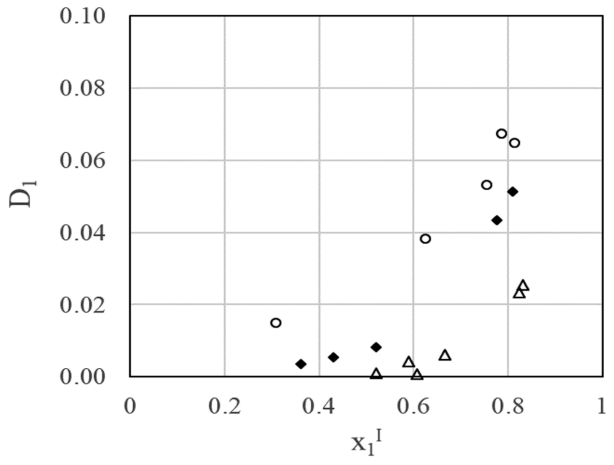

Fig. 2. Distribution coefficient of cyclohexene (D_1) as a function of cyclohexene mole fraction (x_1^I) in the raffinate phase in a ternary system of cyclohexene (1) + cyclohexane (2) + DES (3) at 303.2 K (○), 313.2 K (◆), and 323.2 K (△).

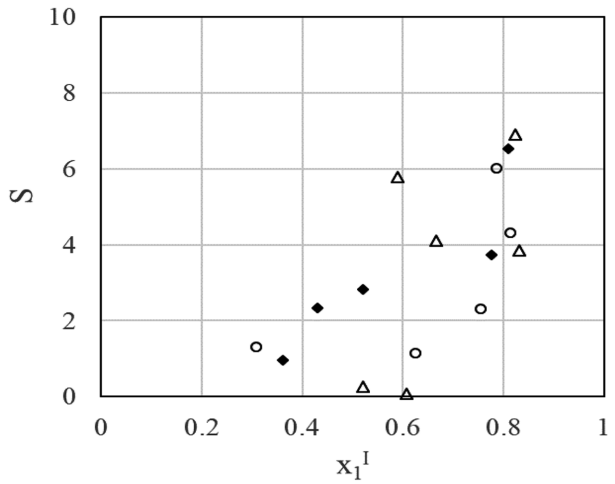

Fig. 3. Selectivity (S) as a function of cyclohexene mole fraction (x_1^I) in the raffinate phase in a ternary system of cyclohexene (1) + cyclohexane (2) + DES (3) at 303.2 K (○), 313.2 K (◆), and 323.2 K (△).

in the raffinate phase of approximately 0.8, D_1 was 0.06 at 303.2 K and about 0.02 at 323.2 K. This trend suggests that higher temperatures reduce the affinity of the DES for cyclohexene, likely due to weakened hydrogen bonding or other specific interactions at elevated temperatures. Selectivity (S) values exceeded unity at higher cyclohexene concentrations, confirming the DES's ability to preferentially extract cyclohexene 1over cyclohexane under these condition, as shown in Fig. 3. However, selectivity was less than one at lower cyclohexene concentrations, indicating that effective separation is most feasible at higher feed concentrations of cyclohexene.

Table 3. Parameters and coefficients (r^2) of Othmer-Tobias equation

Temperature (K)	a	b	r^2
303.2	5.6234	1.4386	0.9795
313.2	3.7276	0.7156	0.9769
323.2	4.1001	00.6359	0.9886

3-2. Consistency test

The reliability of the experimental LLE data was evaluated using the Othmer-Tobias equation. Eq. 3 represents the Othmer-Tobias equation:

$$\ln\left(\frac{1-w_2^I}{w_2^I}\right) = a + b\ln\left(\frac{1-w_3^{II}}{w_3^{II}}\right) \tag{3}$$

where, w_2^I and w_3^{II} represent the mass fractions of cyclohexene in the raffinate phase and DES in the extract phase, respectively. Table 3 displays the parameters a and b, along with the correlation coefficient r^2 at different temperatures. The r^2 values approaching 1 indicate high consistency with the experimental data.

3-3. Comparative insights and mechanistic interpretation

Compared to other DESs and extractive agents reported in the literature, the betaine-glycerol DES demonstrates unique advantages. Previous studies on choline chloride-based DESs and other DESs for hydrocarbon separation have shown that selectivity and distribution coefficients generally decrease with increasing temperature, consistent with the present findings [23,24]. This property not only reduces solvent loss but also addresses concerns about product purity and environmental impact.

The observed decrease in distribution coefficient with temperature can be attributed to the weakening of hydrogen bonding and van der Waals interactions between cyclohexene and the DES at higher temperatures. The higher selectivity at elevated cyclohexene concentrations suggests that the DES's extraction mechanism may involve specific interactions that are more effective when cyclohexene is abundant, possibly due to cooperative effects among cyclohexene molecules within the solvent microenvironment.

3-4. Data correlation

The liquid-liquid equilibria for a ternary system are defined by Eq. 4:

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \tag{4}$$

where γ_i is the activity coefficient of each component in the ternary system. The NRTL and UNIQUAC models were used to correlate the experimentally measured LLE data. The NRTL equation for the activity coefficient is given by Eq. 5.

$$\ln\gamma_i = \frac{\sum_{j=1}^{n} x_j \tau_{ji} G_{ji}}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k}\left(\tau_{ij} - \frac{\sum_{m=1}^{n} x_m \tau_{mj} G_{mj}}{\sum_{k=1}^{n} G_{kj} x_k}\right) \tag{5}$$

where,

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{6}$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} \tag{7}$$

In this study α was set to 0.2, as is commonly performed in literature [18]. Common practice adopts this value by default in non-electrolyte system analysis [25].

The UNIQUAC model for the activity coefficient is given by Eq. 8:

$$\ln\gamma_i = \ln\frac{\phi_i}{x_i} + \left(\frac{z}{2}\right) q_i \ln\frac{\Theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j - q_i \ln\left(\sum_j \theta_j \tau_{ji}\right) + q_i - q_i \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \tag{8}$$

where,

$$l_i = \left(\frac{z}{2}\right)(r_i - q_i) - (r_i - 1) \tag{9}$$

$$\Theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{10}$$

$$\phi = \frac{r_i x_i}{\sum_j r_j x_j} \tag{11}$$

$$\tau_{ij} = \exp\left(-\frac{u_{ij} - u_{jj}}{RT}\right) \tag{12}$$

The lattice coordination number, z, was set to 10. Structural parameters (r_i and q_i) for each compound are presented in Table 4 [26].

Binary interaction parameters for both models were determined by minimizing the objective function (O.F.) defined in Eq. 13 using the differential evolution function in SciPy, known for finding the global minimum of a multivariate function [27].

$$O.F. = \min \sum_{i=1}^{c}\sum_{j=1}^{t}\sum_{k=1}^{p} [(x_{ij}^{exp} - x_{ij}^{cal})^2]^k \tag{13}$$

where i, j, k, c, t, p, exp, and cal represent each component, tie-line, phase, number of chemical components, number of tie-lines, number of phases, and experimental and calculated equilibrium data, respectively. The root mean square deviation (RMSD) was used to test the accuracy of the correlation, as defined in Eq. 14.

$$\mathrm{RMSD} = \sqrt{\frac{\sum_{i=1}^{c}\sum_{j=1}^{t}[(x_{ij}^{I,exp} - x_{ij}^{I,cal})^2 + (x_{ij}^{II,exp} - x_{ij}^{II,cal})^2]}{6t}} \tag{14}$$

RMSD values for the NRTL and UNIQUAC models at three

Table 4. UNIQUAC structural parameters r and q for compounds

Compound	r	q
Cyclohexene	3.9159	4.4246
Cyclohexane	4.2816	5.1810
Glycerol	5.881	4.4497
Betaine	4.8282	5.5902
DES*	5.4615	4.6398

*The structural parameters r and q for DES were determined by $r = \sum x_i r_i$ and $q = \sum_i x_i q_i$, where, x_i is the mole fraction of glycerol and betaine.[i]

Table 5. NRTL binary interaction parameters and RMSD for cyclohexene (1), cyclohexane (2), and DES (3) system at 303.2 K-323.2 K

i-j	Δg_{ij} (J/mol)	Δg_{ji} (J/mol)	a	RMSD
		T = 303.2 K		
1-2	-2.9927	-0.4501		
1-3	4.3893	0.2237	0.2	0.007725
2-3	4.1595	0.4649		
		T = 313.2 K		
1-2	-3.8884	2.3809		
1-3	4.9431	1.1010	0.2	0.007360
2-3	4.6416	1.7294		
		T = 323.2 K		
1-2	4.7161	-2.3887		
1-3	4.8048	2.5123	0.2	0.004836
2-3	4.511	2.5848		

Table 6. UNIQUAC binary interaction parameters and RMSD for cyclohexene (1), cyclohexane (2), and DES (3) system at 303.2 K-323.2 K

i-j	U_{ij} (J/mol)	U_{ji} (J/mol)	RMSD
		T = 303.2 K	
1-2	3.3312	7.2251	
1-3	2.0333	5.1947	0.000886
2-3	2.2194	2.9886	
		T = 313.2 K	
1-2	8.6344	7.1813	
1-3	0.1307	5.6171	0.001161
2-3	9.9931	1.7849	
		T = 323.2 K	
1-2	6.9992	9.8256	
1-3	6.2483	5.8073	0.001058
2-3	3.4043	6.2716	

temperatures are listed in Tables 5 and 6, respectively. The values closed to 0 suggest exceptional regression results for both models. The UNIQUAC model demonstrated smaller RMSD values than the NRTL model at all temperatures, indicating its superior performance in describing the liquid-liquid phase equilibria of the ternary mixture. For instance, at 303.2 K, the RMSD for the UNIQUAC model was 0.000886, compared 0.007725 for the NRTL model. This suggests that the UNIQUAC model more accurately captures the molecular interactions in the system, likely due to its explicit consideration of molecular size and shape parameters. The strong agreement between experimental and calculated tie-lines (Fig. 4) further supports the reliability of the models and the underlying data.

However, extending these models to predict phase behavior at higher concentration introduces significant uncertainties. The fixed α parameter (0.2) in NRTL may inadequately represent nonrandomness in concentrated systems, where cyclohexene-DES interactions dominate. The UNIQUAC model's structural parameters (r and q in Table 4) assume constant molecular geometry. At high cyclohexene concentrations, conformational changes in the DES could invalidate these assumptions, reducing prediction accuracy.

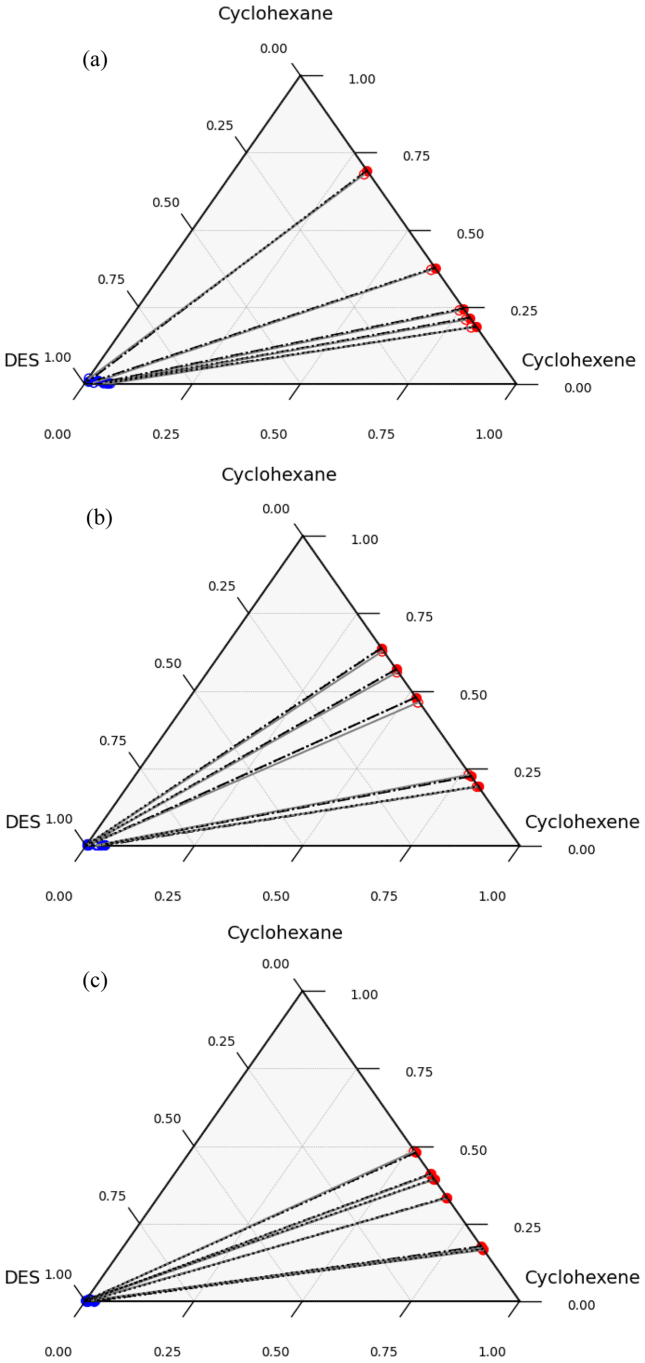

Fig. 4. (a) Tie-lines of the cyclohexene (1) + cyclohexane (2) + DES (3) at 303.2 K. (b) Tie-lines of the cyclohexene (1) + cyclohexane (2) + DES (3) at 313.2 K. (c) Tie-lines of the cyclohexene (1) + cyclohexane (2) + DES (3) at 323.2 K. Solid line: experimental tie-lines; dashed line: correlated (NRTL model) tie-lines; dotted line: correlated (UNIQUAC model) tie-lines. Closed symbols represent experimental values; open symbols represent correlated values.

4. Conclusions

The study investigated the liquid-liquid equilibria (LLE) of a ternary system of cyclohexene, cyclohexane, and betaine-based deep eutectic solvents (DES) at temperatures 303.2 K, 313.2 K,

and 323.2 K. DESs were synthesized with betaine and glycerol, offering an environmentally friendly and economically feasible separation method. Experimental LLE data, analyzed using NRTL and UNIQUAC models, confirmed their reliability and consistency. The results showed that cyclohexene can be effectively separated from cyclohexane using betaine-based DES, with the UNIQUAC model demonstrating higher accuracy than the NRTL model. This study highlights the potential of betaine-based DESs as a sustainable alternative for separating cyclohexene and cyclohexane, reducing energy consumption and initial capital investment associated with conventional methods. The findings encourage further exploration and development of DESs for various industrial applications, emphasizing their role in promoting environmentally friendly processes and innovative solutions.

Acknowledgements

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