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Experimental Data and Thermodynamics Modeling (eNRTL and mUNIFAC) of the (Cyclohexane + Benzene + N,N-Dimethylformamide + Sodium Thiocyanate) Systems

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Abstract: This study investigates the liquid–liquid equilibrium (LLE) of a cyclohexane (1) + benzene (2) + [N,N-dimethylformamide + sodium thiocyanate] (3) system. Experimental tie-line data were obtained at 298.15 K and 318.15 K under atmospheric pressure (~101 kPa, Maringá, Paraná, Brazil) with varying sodium thiocyanate (NaSCN) concentrations in N, N-dimethylformamide (DMF) (3, 5, 8, and 16 wt%). The results contribute to determining the optimal operating conditions for the liquid–liquid extraction of cyclohexane/benzene mixtures. The Hand and Othmer–Tobias correlations confirm the consistency and accuracy of the experimental data. Furthermore, eNRTL and modified UNIFAC models were employed to correlate the experimental LLE data, achieving a root-mean-square deviation of less than 0.91%. The selectivity and distribution coefficients indicate a high efficiency of benzene distribution into the extract phase, suggesting a low solvent/feed ratio and fewer separation stages required for cyclohexane and benzene separation.

Keywords: liquid–liquid equilibrium; cyclohexane; benzene; NaSCN; eNRTL; mUNIFAC



Academic Editor: Luis M. Gandía

Received: 20 July 2024

Revised: 9 August 2024

Accepted: 26 August 2024

Published: 17 February 2025

Citation: Lenhare, S.; de Souza, B.F.B.; Miyasaki, F.V.; Zuber, A.; Arce, P.; Ferreira-Pinto, L.; Beneti, S.C.; Cardozo-Filho, L.; Zanette, A.F.

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ChemEngineering **2025**, *9*, 18.

<https://doi.org/10.3390/chemengineering9010018>

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1. Introduction

The separation of aromatic and aliphatic hydrocarbons (benzene and cyclohexane, respectively) is essential for the petrochemical industry. The separation process required the removal of unreacted benzene from the cyclohexane production stream. Cyclohexane is a raw material used to produce nylon resins, drugs, pesticides, and explosives [1]. However, separating these two compounds using conventional distillation is not viable because of the presence of a minimum-boiling azeotrope [2].

More complex distillation processes such as azeotropic and extractive distillation are used to separate benzene from cyclohexane. However, these processes incur high financial and energy costs [3–6].

Liquid–liquid extraction is an interesting alternative that involves separating these hydrocarbons using an extractive solvent [7]. The separation process is based on the immiscibility of liquids, in which the solute is distributed in the extract (rich in the extractive

solvent) and raffinate (rich in the main product) phases. A study of the liquid–liquid equilibrium is necessary to analyze the behavior of the extractive solvent and co-solvent in the mixture. For the combination to be effective for aromatic/aliphatic separation, the solvents must have good selectivity, regeneration, and low volatility. Solvents with low volatility provide better recovery yields when conventional distillation is used, thus separating them from the solute with greater ease and lower costs [6].

Aspi et al. [8] studied the addition of N,N-dimethylformamide (DMF) as an extractive solvent and found that the solvent had low selectivity in the hydrocarbon mixture. According to Wu et al. (2021) [9], the addition of salt to an aqueous non-electrolyte solution containing volatile compounds affects thermodynamic equilibrium. This can either increase or decrease the volatility of the non-electrolyte, and in extreme cases, lead to the formation of two liquid phases. These effects depend on the concentrations of both the salt and solute, as salt alters the general properties of the solvent. Upon dissolution, the salt can promote, destroy, or affect the interactions between the liquid components, thereby altering the selectivity of the system for one of the components.

Salt affects the solubility of organic compounds in phases where they are present at higher concentrations. The electrolyte “salts out” the organic solvent molecules, reducing the energy cost of the separation process [9]. When the mutual solubility decreased owing to the addition of salt, the two-phase region expanded. This effect is called “salting-out.” Conversely, when solubility increases, it is called “salting-in” and can be used to extract organic compounds from water [10].

Thiocyanate is considered a pseudo-halide because its reactions are analogous to those of halide ions [11]. Upon binding to alkali metals, salts are formed. Potassium (KSCN), sodium (NaSCN), and ammonium (NH_4SCN) thiocyanates are the most commonly used organic components owing to their high solubility in both water and polar organic solvents [12]. When dissolved in DMF, thiocyanate anions bind to hydrogen and cations bind to carbonyl oxygen. This structure hinders the interaction of aliphatic hydrocarbons with DMF molecules, increasing the selectivity of the saline solution and facilitating the separation of benzene from cyclohexane [13].

Therefore, the addition of an electrolyte to the mixture could significantly increase the selectivity for the separation of benzene and cyclohexane. The literature reports that the addition of thiocyanate electrolytes promotes good selectivity when combined as a co-solvent with N,N-dimethylformamide [2,14,15]. The addition of thiocyanate electrolytes indicates that liquid–liquid extraction is significantly more efficient when electrolytes are added to the extraction solvent. The use of a solvent consisting of the [DMF + NaSCN] complex is justified by its lower cost compared with ionic liquids.

Thus, the objective of this study was to analyze the liquid–liquid equilibrium behavior of a mixture of {cyclohexane (1) + benzene (2) + [DMF + NaSCN] (3)} by obtaining tie lines at temperatures of 298.15 K and 318.15 K, atmospheric pressure (~ 101 kPa, Maringá City, State of Paraná, Brazil), and different concentrations of NaSCN in DMF (3, 5, 8, and 16 wt%). The electrolyte non-Random Two-Liquids (eNRTL) and modified UNIQUAC Functional-group Activity Coefficients (mUNIFAC) were applied to correlate the experimental data of the liquid–liquid phase equilibrium.

2. Experimental Section

2.1. Materials

Cyclohexane (≥ 99.5 wt%, Sigma-Aldrich, Barueri, SP, Brazil), benzene (≥ 99.5 wt%, Dinâmica Química, Indaiatuba, SP, Brazil), N, N-dimethylformamide (≥ 99.5 wt%, Anidrol, Diadema, SP, Brazil), and sodium thiocyanate (≥ 99 wt%, Sigma-Aldrich, Barueri, SP, Brazil), all liquid reagents, were injected individually into the chromatograph confirming the

degree of purity specified by the manufacturers. All chemicals were used without further purification. Experimental values of the properties of the compounds (Table 1), were also compared with the ones obtained from the DIPPR database [16] and the literature [17–19].

Table 1. Compounds used in the modeling.

Compounds	CAS	MW (g·mol ^{−1})	Refractive Index		Density (g·cm ^{−3})	
			This Work	Literature	This Work	Literature
Cyclohexane	110-82-7	84.161	1.4232	1.4235 ^a	0.7732	0.7738 ^a
Benzene	71-43-2	74.114	1.4972	1.4974 ^a	0.8733	0.8736 ^a
N,N-dimethylformamide	68-12-2	73.095	1.4273	1.4279 ^b	0.9484	0.9488 ^b
Sodium thiocyanate	540-72-7	81.072 [19]	---	---	---	---

^a [18]; ^b [19].

2.2. Apparatus and Procedures for Equilibrium Liquid–Liquid

The experiments were carried out using glass-jacketed equilibrium cells with a capacity of 25 mL (internal volume) and connected to a thermostatic bath (FISATON, TE18, with an uncertainty of ± 0.1 K) at temperatures of 298.15 and 313.15 K to control the temperature through the circulation of water (Figure 1). The mass of the mixtures used for each experiment to determine the tie lines was obtained using an analytical balance (SHIMADZU, ATX224). The compositions of the mixtures were calculated by multiplying the Da mass fraction purities of each component. A magnetic stirrer was used to agitate the mixtures (IKA, RCT Basic) for 1 h after the temperature was established.

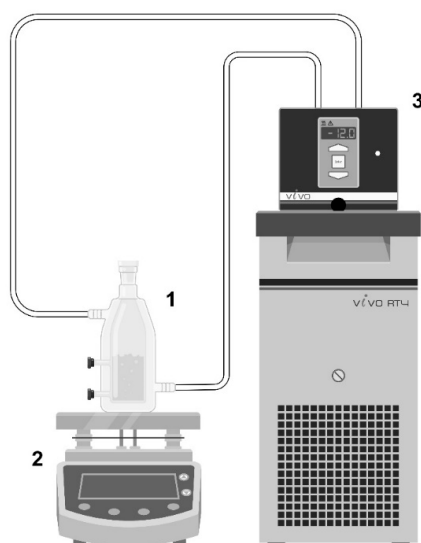


Figure 1. Experimental apparatus of the equilibrium cell: (1) cell equilibrium and (2) magnetic stirrer bar; (3) thermostatic bath.

The procedure included adding known masses of the two components to the equilibrium cell and titrating the mixture with a third component. Cyclohexane and benzene were mixed and titrated with a DMF (DMF + NaSCN) solution. This is known as the cloud point method [20,21]. The tie lines were determined for different proportions of the selected components. The compositions of the two phases were selected to determine the tie line, keeping the molar ratio between cyclohexane and benzene constant and changing the proportion of the DMF solution. Cyclohexane and benzene were added to equilibrium cells at known concentrations. Then, DMF was added to the mixture to obtain different compositions of the overall phase and measure the tie lines. Predetermined mixtures were agitated with a magnetic stirrer and allowed to stand for 6 h. After this process, the

formation of two phases with well-defined interfaces is observed. Samples from each phase were collected for subsequent quantifications.

The samples were injected in triplicate into a gas chromatograph (Agilent, Model GC 7890) equipped with an FID detector and a DB-WAX capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μ m) and split injection at a 1:80 ratio. The column temperature was 353.15 K for 1 min, programmed to increase at 40 K $\cdot$ min $^{-1}$ to 513.15 K, and maintained for 5 min. The injector and detector temperatures were 513.15 K at 523.15 K, respectively. With a flow of H₂ (carrier gas) for 1.2 mL $\cdot$ min $^{-1}$ and 35 mL $\cdot$ min $^{-1}$ for N₂ (auxiliary gas). For the flame detector, 35 and 300 mL $\cdot$ min $^{-1}$ for H₂ and synthetic air, respectively. At least three measurements were performed for each sample and phase. Mass balances were determined based on the total system mass, phase, and overall composition. Owing to their low volatility (T = 323.15 K) and NaSCN degradability, they were not detected, and the mass fractions were calculated using the mass conservation law according to Yang et al. [15].

The method of normalizing the corrected areas was used to determine the compositions of the areas, according to the methodology described by Song et al. [14]. Standard mixtures were prepared and analyzed according to the method described by Grob [22]. Using the values of the standard and analysis areas, it was possible to determine the mass fractions of the compounds in the two phases formed in ELL.

2.3. Quality Test of the Experimental Data

The Hand [23] (Equation (1)) and Othmer–Tobias [21] (Equation (2)) correlations were used because a consistency test cannot evaluate the tie-line data.

$$\ln\left(\frac{w_3^I}{w_1^I}\right) = A + B \ln\left(\frac{w_3^{II}}{w_2^{II}}\right) \quad (1)$$

$$\ln\left(\frac{1 - w_1^I}{w_1^I}\right) = A' + B' \ln\left(\frac{1 - w_2^{II}}{w_2^{II}}\right) \quad (2)$$

where w_1^I is the cyclohexane mass fraction in the raffinate phase, w_3^I is the DMF mass fraction in the raffinate phase, w_3^{II} is the DMF mass fraction in the extract phase, and w_2^{II} is the mass fraction of benzene in the extract phase. Parameters A and B are from the Hand correlation and parameters A' and B' are from the Othmer–Tobias correlation. The correlation factor, R^2 , indicates the reliability of the experimental data [24–28].

2.4. Distribution Coefficient and Selectivity

The distribution coefficient (D) and selectivity for benzene in the DMF solution (S) were calculated (Equations (3) and (4)) to evaluate the extraction performance of the extractants in the aqueous phase.

$$D = \frac{w_2^{II}}{w_2^I} \quad (3)$$

$$S = \left(\frac{w_2^{II}}{w_2^I}\right) / \left(\frac{w_1^{II}}{w_1^I}\right) \quad (4)$$

where w is the mass fraction; subscripts 1 and 2 refer to cyclohexane and benzene, respectively; and superscripts I and II refer to the raffinate and extract phases, respectively.

3. Thermodynamic Modeling

Following the criterion of phase equilibrium, the fugacity of component I in liquid phase 1 ($\hat{f}_i^{L1}$) must be equal to the fugacity of the same component in liquid phase 2 ($\hat{f}_i^{L2}$), at constant pressure and temperature [29,30], as shown in Equation (5).

$$\hat{f}_i^{L1}(T, P, x_1^{L1}, x_2^{L1}, \dots, x_n^{L1}) = \hat{f}_i^{L2}(T, P, x_1^{L2}, x_2^{L2}, \dots, x_n^{L2}) \quad (5)$$

Under equilibrium, the fugacity of component i can be expressed by the activity coefficient i in both the liquid phases. The fugacities of the pure components in both liquid phases are the same, and Equation (6) assumes a rigorous format for the liquid–liquid phase equilibrium, as shown in Equation (7).

$$x_i^{L1} \gamma_i^{L1}(T, P, x_1^{L1}, x_2^{L1}, \dots, x_n^{L1}) f_i^0(T, P) = x_i^{L2} \gamma_i^{L2}(T, P, x_1^{L2}, x_2^{L2}, \dots, x_n^{L2}) f_i^0(T, P) \quad (6)$$

$$x_i^{L1} \gamma_i^{L1}(T, P, x_1^{L1}, x_2^{L1}, \dots, x_n^{L1}) = x_i^{L2} \gamma_i^{L2}(T, P, x_1^{L2}, x_2^{L2}, \dots, x_n^{L2}) \quad (7)$$

To calculate the activity coefficient, mainly as a function of temperature and mixture composition, local composition models, such as electrolyte non-Random Two-Liquids (eNRTL) and modified UNIQUAC Functional-group Activity Coefficients (mUNIFAC), were applied to correlate the experimental data of the liquid–liquid phase equilibrium.

3.1. eNRTL Model

The electrolyte NRTL model uses an infinitely diluted aqueous solution as the reference state for ions. It adopts the Born Equation to transform the reference state of ions from an infinitely diluted mixed-solvent solution to an infinitely diluted aqueous solution [31]. This model was reduced to the well-known NRTL model when the electrolyte concentration was zero [32].

The eNRTL model, developed by Chen et al. [33], considers the contributions of the activity coefficient of a species in solution, an NRTL-type local composition contribution, γ_i^{LC} , and a contribution to the Pitzer-extended Debye–Hückel, γ_i^{PDH} , which can be used for molecular or ionic species. In this study, the activity coefficient of the solute, which is used to calculate the Pitzer-extended Debye–Hückel contribution, is as follows (Equation (8)):

$$\ln \gamma_i^{PDH} = \frac{2A_\phi I_\chi^{2/3}}{1 + \rho^* I_\chi^{1/2}} \quad (8)$$

where ρ^* is the closest approach parameter, a ϕ is the Debye–Hückel parameter, and I_χ is the ionic strength on the molar scale. Parameters were calculated using the method described by Maia et al. [34]. The resulting equation for the activity coefficient is given by (Equation (9)):

$$\ln \gamma_i = \ln \gamma_i^{LC} + \ln \gamma_i^{PDH} \quad (9)$$

3.2. mUNIFAC Model

The mUNIFAC model [35] is based on empirical modifications of UNIFAC [36,37]. The activity coefficient expression predicted by the mUNIFAC model was calculated from the sum of the combinatorial and residual components (Equation (7)). However, the difference from the original UNIFAC was based on modification of the contribution. The original UNIFAC combinatorial part modified in the Dortmund model (mUNIFAC) is a 3/4 exponent used to calculate the volume fraction [38]. A comprehensive explanation of semi-empirical models and their equations were presented in [31,39,40].

4. Results and Discussion

4.1. Experimental Data

The experimental ternary LLE data obtained for the {cyclohexane (1) + benzene (2) + [DMF + NaSCN] (3)} system at 298.15 and 313.15 K at atmospheric pressure (~101 kPa)

are presented in Table 2 (tie lines and overall composition) and shown in Figures 2–5. The accuracy and precision of the experimental data were evaluated using type-A uncertainty, which was calculated using the standard deviation of analytical measurements [41]. The uncertainties in the equilibrium compositions ranged from (0.07 to 0.33)% by mass for cyclohexane, (0.05 to 0.42)% for benzene, and (0.03 to 0.56)% for the [DMF + NaSCN] solution. The relative deviations for both temperatures in all the evaluated systems were less than 0.5%.

Table 2. (Liquid + liquid) equilibrium data for the {cyclohexane (1) + benzene (2) + [DMF + NaSCN] (3)} system at 298.15 K and 313.15 K, normal atmospheric pressure ($P = 0.1$ MPa), where w is the weight fraction ^a and D_2 is distributions coefficient of benzene and S is selectivity.

T (K)	Overall Composition			Experimental (Tie Lines)						D ₂	S
				Cyclohexane Rich-Phase			DMF Rich-Phase				
	w ₁ ^b	w ₂ ^b	w ₃ ^b	w ₁ ^b	w ₂ ^b	w ₃ ^b	w ₁ ^b	w ₂ ^b	w ₃ ^b		
298.15	NaSCN = 3 wt%										
	0.4581	0.4280	0.1138	0.8463	0.0820	0.0717	0.0959	0.0678	0.8363	0.83	7.31
	0.4209	0.4144	0.1647	0.7660	0.1422	0.0917	0.0924	0.1200	0.7881	0.84	7.05
	0.3682	0.4109	0.2209	0.7199	0.1687	0.1114	0.1248	0.1529	0.7223	0.91	5.22
	NaSCN = 5 wt%										
	0.4906	0.4096	0.0998	0.8340	0.1090	0.0570	0.0960	0.0898	0.8142	0.82	7.21
	0.4677	0.3725	0.1598	0.7558	0.1699	0.0743	0.1209	0.1509	0.7282	0.89	5.53
	0.4240	0.3630	0.2130	0.6893	0.2136	0.0971	0.1362	0.2040	0.6598	0.96	4.81
	0.3952	0.3259	0.2789	0.5937	0.2864	0.1199	0.1742	0.2683	0.5575	0.94	3.24
	NaSCN = 8 wt%										
	0.4858	0.4566	0.0576	0.8827	0.0658	0.0515	0.0771	0.0580	0.8649	0.88	10.10
	0.4695	0.4271	0.1033	0.8217	0.1236	0.0547	0.0959	0.0824	0.8217	0.67	5.74
	0.4407	0.4006	0.1587	0.7419	0.1923	0.0658	0.1233	0.1226	0.7541	0.64	3.83
	0.4134	0.3714	0.2152	0.6664	0.2561	0.0775	0.1440	0.1787	0.6773	0.70	3.27
	NaSCN = 16 wt%										
	0.4683	0.4549	0.0768	0.8341	0.1035	0.0624	0.0455	0.0516	0.9029	0.52	9.18
	0.4307	0.4383	0.1310	0.7293	0.2019	0.0688	0.0478	0.0771	0.8751	0.50	5.83
	0.3904	0.4156	0.1940	0.6566	0.2638	0.0796	0.0455	0.1169	0.8376	0.38	6.40
	0.2918	0.4637	0.2545	0.5556	0.3632	0.0812	0.0439	0.1474	0.8087	0.44	5.12
313.15	NaSCN = 3 wt%										
	0.4041	0.4328	0.1631	0.7689	0.1014	0.1297	0.1172	0.0863	0.7973	0.84	5.54
	0.3547	0.4279	0.2174	0.6350	0.1889	0.1761	0.1315	0.1605	0.7091	0.85	4.10
	0.3093	0.3921	0.2986	0.5480	0.2547	0.1973	0.2077	0.2131	0.5806	0.84	2.22
	NaSCN = 5 wt%										
	0.4906	0.4096	0.0998	0.7814	0.0993	0.1203	0.0902	0.0892	0.8204	0.89	7.82
	0.4677	0.3725	0.1598	0.7022	0.1751	0.1226	0.0944	0.1585	0.7480	0.90	6.75
	0.4240	0.3630	0.2130	0.6476	0.2256	0.1282	0.1237	0.2021	0.6753	0.90	4.72
	0.3952	0.3259	0.3000	0.5620	0.3130	0.1254	0.1313	0.2828	0.5882	0.90	3.95
	NaSCN = 8 wt%										
	0.4697	0.4368	0.0934	0.8003	0.1114	0.0892	0.0819	0.0814	0.8384	0.73	7.20
	0.4194	0.4164	0.1641	0.7161	0.1821	0.1027	0.0875	0.1457	0.7686	0.79	6.63
	0.3767	0.3875	0.2358	0.6247	0.2658	0.1123	0.1027	0.2172	0.6813	0.82	5.03
	0.3335	0.3465	0.3199	0.5373	0.3363	0.1281	0.1112	0.3060	0.5828	0.91	4.42
	NaSCN = 16 wt%										
	0.4523	0.4574	0.0903	0.8112	0.0973	0.0915	0.0757	0.0847	0.8410	0.86	9.34
	0.4131	0.4137	0.1732	0.7197	0.1811	0.0992	0.0835	0.1592	0.7582	0.88	7.67
	0.3605	0.3806	0.2590	0.6128	0.2750	0.1122	0.0878	0.2433	0.6715	0.88	6.23
	0.3038	0.3575	0.3387	0.5161	0.3730	0.1109	0.0892	0.3276	0.5853	0.88	5.18

The estimated standard error was $\leq 1\%$. ^a Standard uncertainties u are $u(T) = 0.5$ K, $u(P) = 1$ kPa, $u(w) \leq 0.6$ wt%.

^b w_1 : mass fraction of cyclohexane; w_2 : mass fraction of benzene; w_3 : mass fraction of DMF.

4.2. Quality Test of the LLE Data

Before submitting the LLE experimental data to thermodynamic modeling, it was necessary to analyze the quality of the data. Quality tests of the experimental values were

performed using the Othmer–Tobias [21] and Hand [23] methods. The fitting parameters and regression coefficients (R^2) for each temperature are presented in Table 3. As shown, regression coefficients above 0.98 were obtained for all datasets. This indicated the reliability of the experimental LLE data obtained in this study.

Table 3. Hand and Othmer–Tobias correlation results.

T (K)	Hand R^2	A	B	T (K)	Othmer–Tobias R^2	A'	B'
NaSCN 3 wt%				NaSCN 3 wt%			
298.15	0.9913	0.6172	−0.9287	298.15	0.9999	−0.8363	0.4846
313.15	0.9811	0.7197	−0.2038	313.15	0.9959	−1.0064	1.1536
NaSCN 5 wt%				NaSCN 5 wt%			
298.15	0.9898	0.7412	−1.0875	298.15	0.9932	−0.9293	0.5088
313.15	0.9856	0.2543	−1.3235	313.15	0.9946	−0.7353	0.4125
NaSCN 8 wt%				NaSCN 8 wt%			
298.15	0.9887	0.5154	−1.4809	298.15	0.9904	−1.0489	0.9555
313.15	0.9935	0.4582	−1.1491	313.15	0.9985	−0.7738	0.4786
NaSCN 16 wt%				NaSCN 16 wt%			
298.15	0.9972	0.5701	−0.9693	298.15	0.9813	−1.1416	1.7481
313.15	0.9823	0.384	−1.3253	313.15	0.9948	−0.8366	0.5061

In Figure 2, the Hand and Othmer–Tobias equations are represented for both temperatures and four salt compositions. As shown in Table 3, the R^2 values were close to 1.00. This is corroborated in Figure 2, where linear behavior for both equations (2 A and 2 B) can be observed.

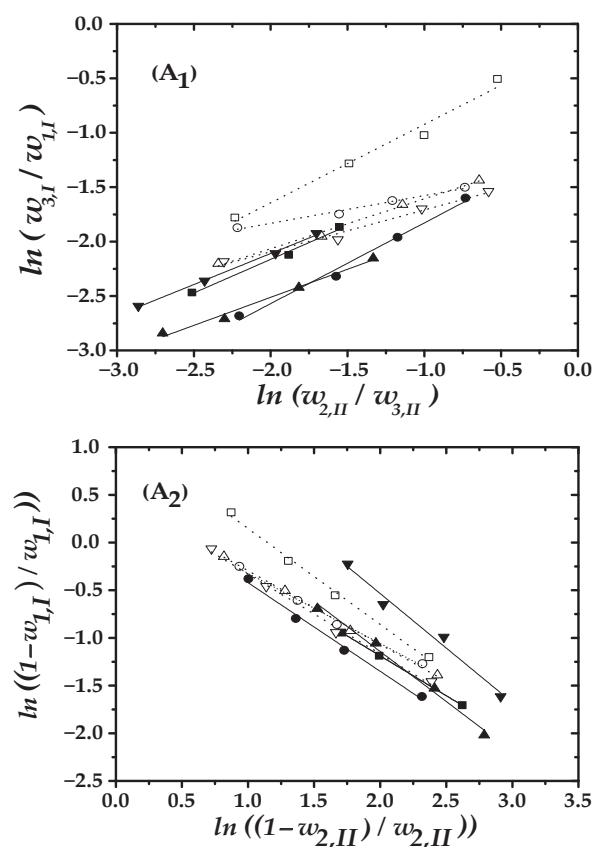


Figure 2. Correlations for the ternary {cyclohexane (1) + benzene (2) + [DMF + NaSCN (16 wt%)] (3)} system for different weight fractions of the NaSCN in DMF at T = 298.15 K [(■) 3 wt%; (●) 5 wt%; (▲) 8 wt%; (▼) 16 wt%] and T = 313.15 K [(□) 3 wt%; (○) 5 wt%; (△) 8 wt%; (▽) 16 wt%]: (A₁): Hand and (A₂) Othmer–Tobias.

4.3. Separation Factor and Distribution Coefficient

Figures 3–5 show the selectivity and distribution coefficients (D_1 and D_2) against benzene and cyclohexane compositions in the diluent phase (raffinate), respectively. It is important to note that the relationship between these parameters was almost linear in all cases, at different temperatures and salt compositions.

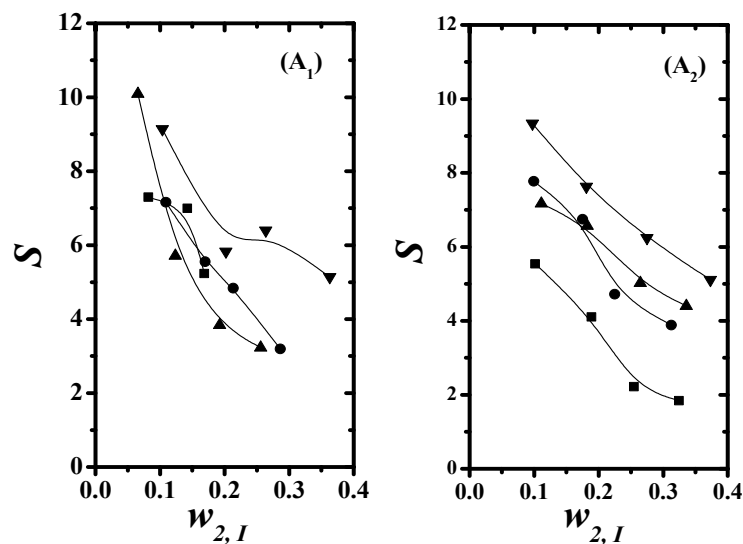


Figure 3. Selectivity coefficient (S) of benzene in the raffinate phase (I) at temperatures (A₁) $T = 298.15$ K and (A₂) $T = 313.15$ K for different weight fractions of the NaSCN in DMF: (■) 3 wt%; (●) 5 wt%; (▲) 8 wt%; (▼) 16 wt%.

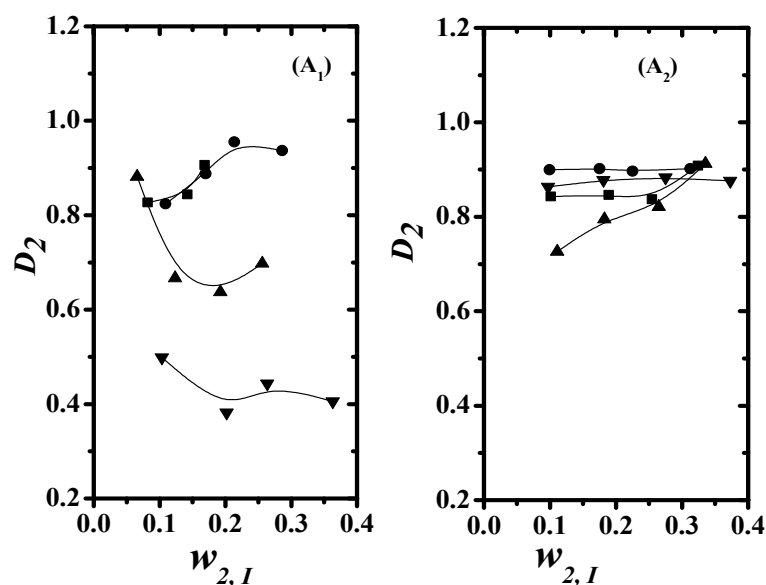


Figure 4. Distribution coefficient (D_2) of benzene in the raffinate phase (I) at temperatures (A₁) 298.15 K and (A₂) 313.15 K for different weight fractions of the NaSCN in DMF: (■) 3 wt%; (●) 5 wt%; (▲) 8 wt%; (▼) 16 wt%.

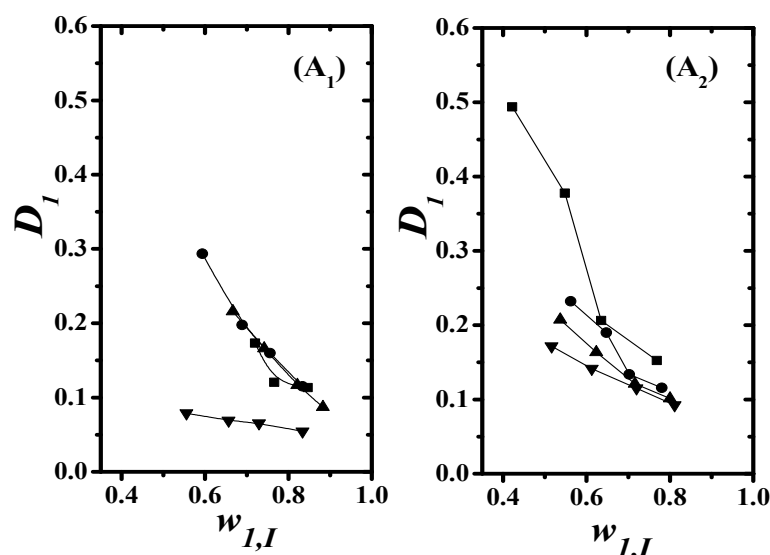


Figure 5. Distribution coefficient (D_1) of cyclohexane in the raffinate phase (I) at temperatures (**A₁**) 298.15 K and (**A₂**) 313.15 K for different weight fractions of NaSCN in DMF: (■) 3 wt%; (●) 5 wt%; (▲) 8 wt%; (▼) 16 wt%.

The values obtained for the selectivity (see Table 2) were similar to those obtained by Dong et al. [20]. For all evaluated systems, the selectivity values were higher than 1, indicating that the DMF solution (DMF + NaSCN) was preferably solubilized in the extract phase (rich in solvent) and could separate the cyclohexane/benzene mixture.

4.4. Thermodynamic Modeling Results

Table 4 presents the temperature-dependent binary interaction parameters (energies) as functions of temperature $\Delta g_{ij}/R$ for the eNRTL model. The non-randomness parameters α for the eNRTL model obtained for the interactions of components i and j are presented in Table 5.

Table 4. Binary interaction parameters, $\Delta g_{ij}/R$, for the eNRTL model.

i/j	Cyclohexane	Benzene	DMF	NaSCN
Cyclohexane	0.00	$-2142.55 + 162.17/T$	$-1740.34 + 89.72/T$	$-2382.48 + 102.30/T$
Benzene	$-1928.41 + 281.92/T$	0.00	$-1506.45 + 85.07/T$	$-1805.82 + 113.35/T$
DMF	$-2675.23 + 153.38/T$	$-1510.28 + 162.20/T$	0.00	$-1865.22 + 236.37/T$
NaSCN	$-2341.74 + 336.75/T$	$-1845.33 + 160.48/T$	$-1592.74 + 226.27/T$	0.00

Table 5. Non-randomness parameter for the eNRTL model.

i	j	α_{ij}
Cyclohexane	Benzene	0.2845
Cyclohexane	DMF	0.2941
Cyclohexane	NaSCN	0.3654
Benzene	DMF	0.2748
Benzene	NaSCN	0.3241
DMF	NaSCN	0.3514

The mUNIFAC model requires geometric and interaction parameters to predict LLE using the group contribution method. The parameters of the mUNIFAC group are listed in Table 6. The groups and subgroups were obtained from the cyclohexane, benzene, DMF, and NaSCN structures. The mUNIFAC interaction parameters for these groups are presented in Table 7. All parameters were obtained from a study by Gmehling et al. [35].

Table 6. Group volume (R_k) and surface (Q_k) parameters.

Group	Subgroup	R_k	Q_k
CH ₂	CH	0.4469	0.2280
ACH	ACH	0.5313	0.4000
DMF	DMF	3.0856	2.7360
Na ⁺ (*)	Na	3.0000	3.0000
SCN ⁻ (**)	SCN	1.9446	1.1752

(*) reference [42]; (**) reference [43].

Table 7. mUNIFAC group interaction parameters.

m	N	a_{mn} (K)	b_{mn}	c_{mn} (K ⁻¹)	a_{nm}	c_{nm} (K ⁻¹)
CH	ACH	1142.8	−4.410	0.001041	−1468.3	0.000841
CH	DMF	1840.4	−3.293	0.002021	−88.6	0.000124
CH	Na+	2845.1	−0.465	0.00	−317.3	0.00
CH	SCN ⁻	2664.3	−0.834	0.00	−181.6	0.00
ACH	DMF	−1251.6	2.342	0.001521	158.3	0.000074
ACH	Na+	2338.7	−0.335	0.00	−109.8	0.00
ACH	SCN ⁻	2603.5	−0.636	0.00	−201.5	0.00
DMF	Na+	2412.0	−0.841	0.00	−175.6	0.00
DMF	SCN ⁻	2674.3	−0.556	0.00	−181.1	0.00

The binary and group interaction parameters for the eNRTL and mUNIFAC models were obtained by minimizing the objective function represented by Equation (10) using the Levenberg–Marquardt algorithm [44].

$$OF = \sum_{k=1}^D \sum_{j=1}^{N_k} \left[\frac{(T_{j,k}^{exp} - T_{j,k}^{calc})^2}{\sigma_{T_{j,k}}} + \left\{ \sum_{i=1}^{C_k-1} \left[\frac{(x_{i,j,k}^{exp} - x_{i,j,k}^{calc})^2}{\sigma_{x_{i,j,k}}} \right] \right\} \right] \quad (10)$$

where D is the number of datasets, N_k and C_k are the number of data points and components in dataset k, respectively, T is the temperature, x is the mole fraction in the extract phase, and σ is the observed standard deviation.

The experimental liquid–liquid equilibrium data were correlated with the estimated binary and group interaction parameters. The results were expressed in terms of the mean deviations between the experimental and calculated compositions for both phases (Equation (11)) are listed in Table 8.

Table 8. Mean deviations between the experimental and calculated compositions for the {cyclohexane + benzene + [DMF + NaSCN]} system for several NaSCN compositions.

T (K)	NaSCN (wt%)	ARD (%)	
		eNRTL	mUNIFAC
298.15	3	0.38	0.75
	5	0.51	0.81
	8	0.64	0.86
	16	0.41	0.91
313.15	3	0.36	0.81
	5	0.34	0.76
	8	0.48	0.80
	16	0.43	0.78

$$ARD(\%) = 100 \sqrt{\frac{\sum_{j=1}^{N_k} \sum_{i=1}^{C_k-1} \left[(x_{i,j}^{I,exp} - x_{i,j}^{I,calc})^2 + (x_{i,j}^{II,exp} - x_{i,j}^{II,calc})^2 \right]}{2N_k C_k}} \quad (11)$$

To illustrate the LLE behavior of the correlated models, Figures 6–9 plot the tie lines in terms of the mass fractions of the ternary mixture for several mass fractions of NaSCN, at 298.15 and 313.15 K, respectively.

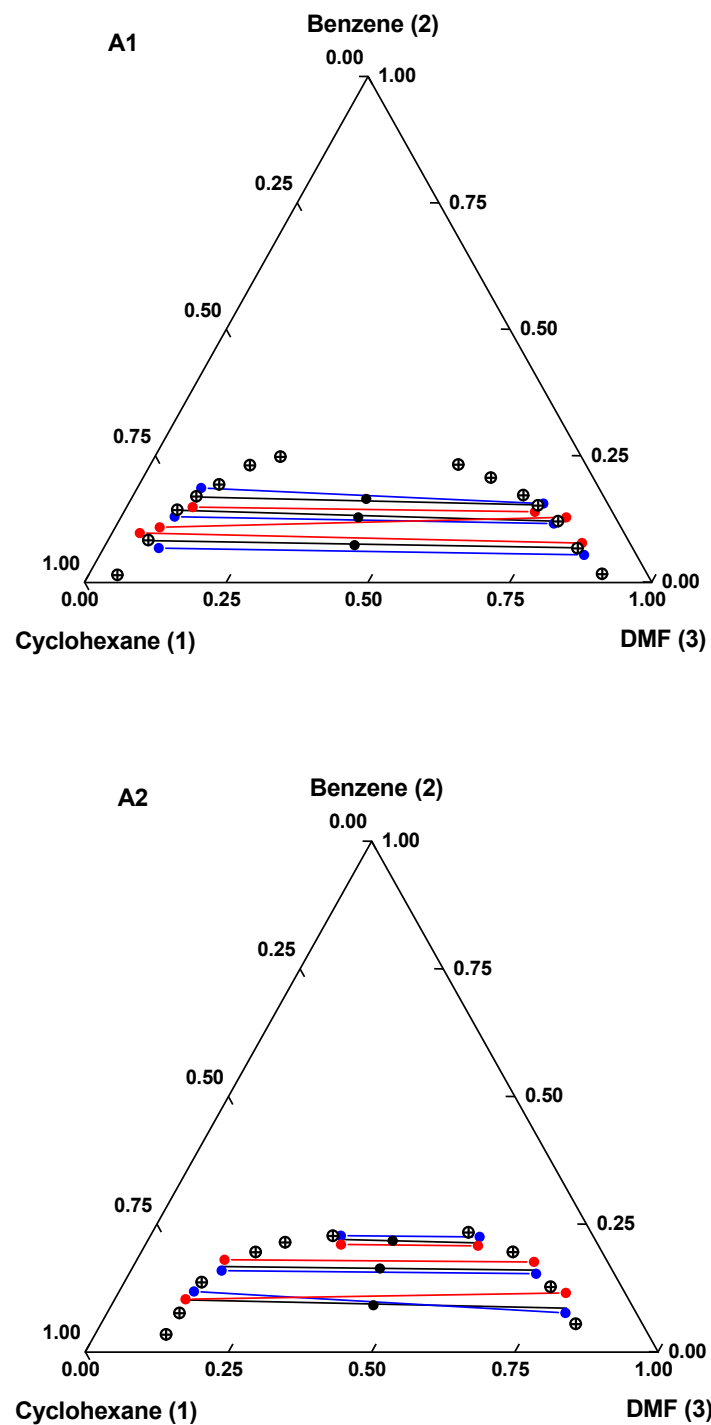


Figure 6. (Liquid + liquid) equilibrium data for the {cyclohexane (1) + benzene (2) + [DMF + NaSCN (3 wt%)] (3)} system at temperatures (A₁) 298.15 K and (A₂) 313.15 K: (⊕) binodal curve; (●) global composition; (—) experimental tie lines; (—●) calculated (mUNIFAC) tie lines; (—●) calculated (eNRTL) tie lines.

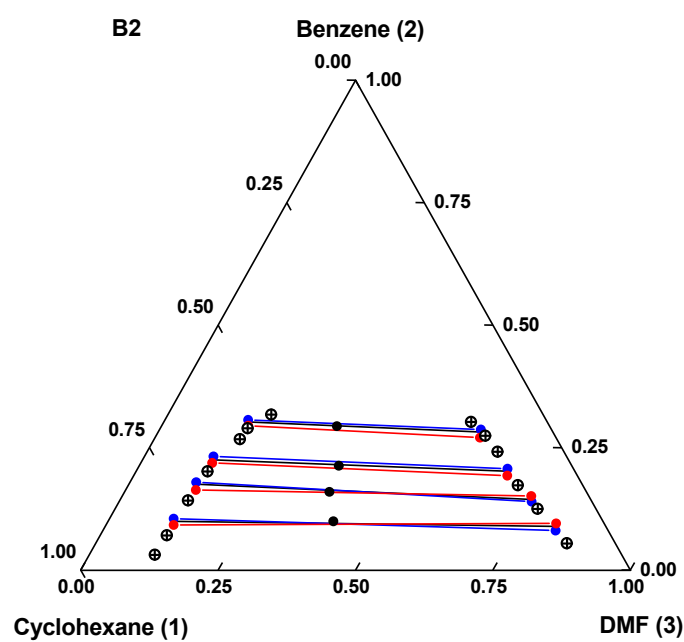
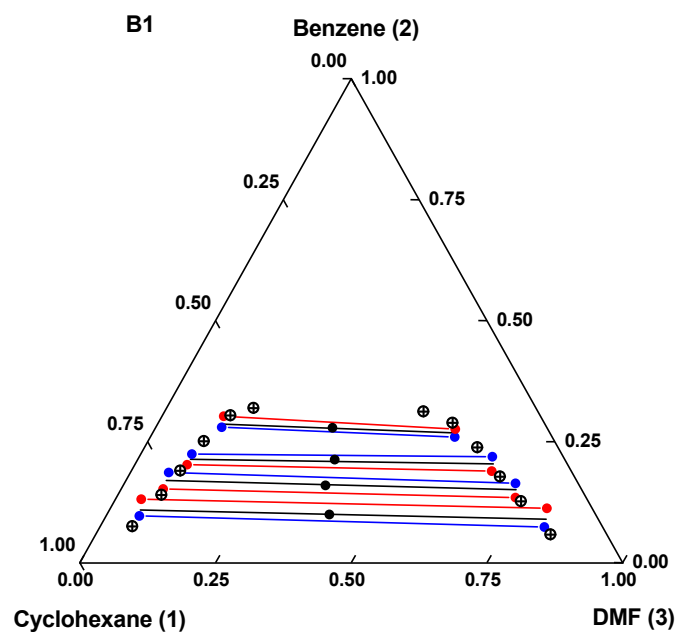


Figure 7. (Liquid + liquid) equilibrium data for the {cyclohexane (1) + benzene (2) + [DMF + NaSCN (5 wt%)] (3)} system at temperatures (**B₁**) 298.15 K and (**B₂**) 313.15 K: (⊕) binodal curve; (●) global composition; (—) experimental tie lines; (—●—) calculated (mUNIFAC) tie lines; (—●—) calculated (eNRTL) tie lines.

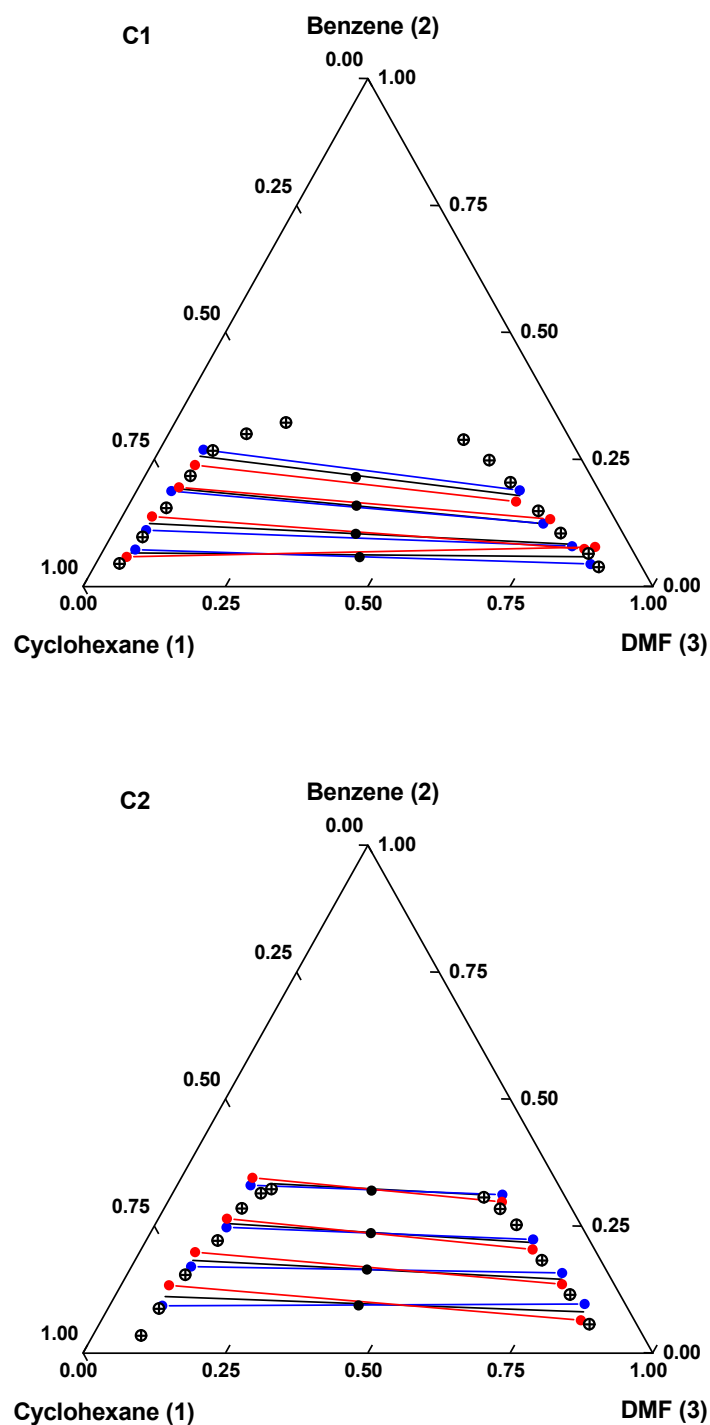


Figure 8. (Liquid + liquid) equilibrium data for the {cyclohexane (1) + benzene (2) + [DMF + NaSCN (8 wt%)] (3)} system at temperatures (C₁) 298.15 K and (C₂) 313.15 K: (⊕) binodal curve; (●) global composition; (—) experimental tie lines; (—●—) calculated (mUNIFAC) tie lines; (—●—) calculated (eNRTL) tie lines.

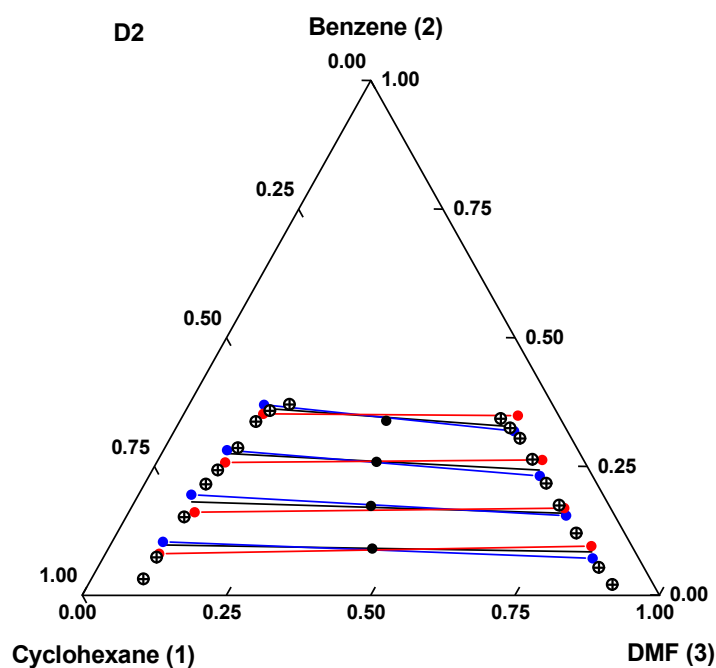
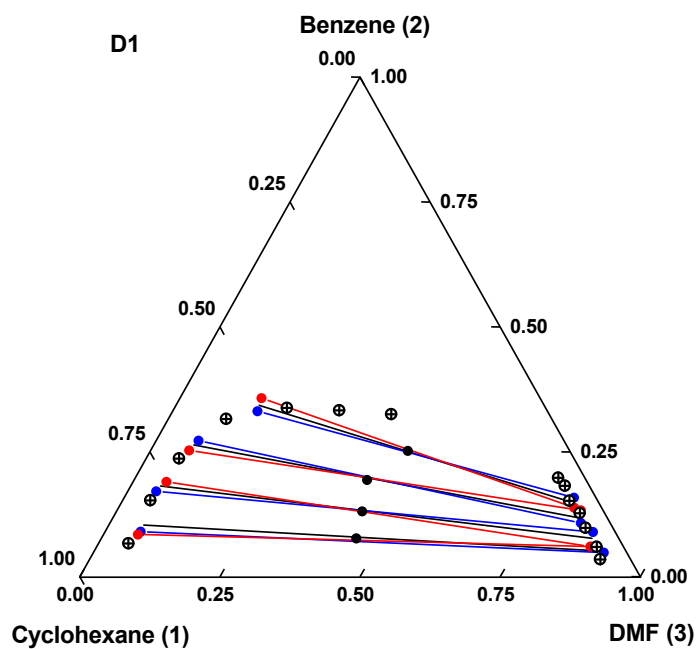


Figure 9. (Liquid + liquid) equilibrium data for the {cyclohexane (1) + benzene (2) + [DMF + NaSCN (16 wt%)] (3)} system at temperatures (**D₁**) 298.15 K and (**D₂**) 313.15 K: (⊕) binodal curve; (●) global composition; (—) experimental tie lines; (—●) calculated (mUNIFAC) tie lines; (—●) calculated (eNRTL) tie lines.

The ternary figures show that the miscibility region of the systems at the two temperatures studied (298.15 K and 313.15 K) increased when the concentration of NaSCN was high. In general, the greater the amount of salt, the lower is the amount of DMF solution (DMF + NaSCN) required to extract the cyclohexane/benzene system.

5. Conclusions

LLE experimental data were obtained for the cyclohexane (1) + benzene (2) + [DMF + NaSCN] (3) system at 298.15 and 318.15 K and atmospheric pressure. The experimental data indicate that the phase behavior of the system is type I (only one binodal curve). The quality tests were performed using the Hand and Othmer–Tobias correlations, which indicated that the observed experimental tie-line data were coherent and accurate. For thermodynamic modeling, the eNRTL and mUNIFAC activity models and the gamma–gamma approach were used to correlate the experimental data. The models correlated satisfactorily with the LLE experimental data, with a root-mean-square deviation of < 0.91%. The parameters of the selectivity and distribution coefficient showed values in the order of their highest value of 10.1 and a distribution coefficient very close to 0.9, which indicates a good distribution of benzene for the extract phase, providing a low solvent/feed ratio and decreasing the stages for the separation between cyclohexane and benzene. It is also important to highlight the influence of temperature on benzene separation. When the temperature was 298.15 K, the degree of extraction was slightly better than at 313.15 K, which is due to the higher values of the selectivity coefficients, also called separation factors.

It is necessary for a subsequent regeneration of the solvent (after extraction) and post-purification of the target component. Because DMF forms an azeotrope with cyclohexane, it is recommended to use an azeotropic distillation process by adding another component to generate a new, lower-boiling azeotrope that is heterogeneous (e.g., producing two immiscible liquid phases).

Author Contributions: Conceptualization, L.C.-F., A.F.Z. and S.C.B.; methodology, F.V.M., A.F.Z., S.C.B., S.L. and B.F.B.d.S.; software, A.Z. and P.A.; formal analysis, L.C.-F., A.F.Z., S.C.B., L.F.-P. and P.A.; data curation, L.C.-F., A.F.Z. and S.C.B.; writing—original draft preparation, S.L. and B.F.B.d.S.; writing—review and editing, L.C.-F., A.F.Z., S.C.B., L.F.-P. and P.A.; visualization, L.F.-P. and P.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article and further inquiries can be directed to the corresponding authors.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Li, Q.; Jia, B.; Wang, L.; Yan, M.; Liu, H.; Yu, Y. Liquid-Liquid Equilibrium for Ternary Systems of Water + 2,2,3,3-Tetrafluoro-1-Propanol + Isopropyl Ether/Tert-Butyl Methyl Ether at 298.2, 308.2 K. *J. Chem. Thermodyn.* **2018**, *124*, 32–37. [\[CrossRef\]](#)
2. Dong, H.; Yang, X.; Zhang, J. Liquid–Liquid Equilibria for Benzene + Cyclohexane + N, N -Dimethylformamide + Potassium Thiocyanate. *J. Chem. Eng. Data* **2010**, *55*, 3972–3975. [\[CrossRef\]](#)
3. LUE, S. Pervaporation of Benzene/Cyclohexane Mixtures Using Ion-Exchange Membrane Containing Copper Ions. *J. Membr. Sci.* **2004**, *240*, 149–158. [\[CrossRef\]](#)
4. Peng, F.; Lu, L.; Hu, C.; Wu, H.; Jiang, Z. Significant Increase of Permeation Flux and Selectivity of Poly(Vinyl Alcohol) Membranes by Incorporation of Crystalline Flake Graphite. *J. Membr. Sci.* **2005**, *259*, 65–73. [\[CrossRef\]](#)
5. Garcia Villaluenga, J.P.; Tabe-Mohammadi, A. A Review on the Separation of Benzene/Cyclohexane Mixtures by Pervaporation Processes. *J. Membr. Sci.* **2000**, *169*, 159–174. [\[CrossRef\]](#)
6. Wang, R.; Wang, J.; Meng, H.; Li, C.; Wang, Z. Liquid–Liquid Equilibria for Benzene + Cyclohexane + 1-Methyl-3-Methylimidazolium Dimethylphosphate or + 1-Ethyl-3-Methylimidazolium Diethylphosphate. *J. Chem. Eng. Data* **2008**, *53*, 1159–1162. [\[CrossRef\]](#)

7. García, J.; García, S.; Torrecilla, J.S.; Oliet, M.; Rodríguez, F. Separation of Toluene and Heptane by Liquid–Liquid Extraction Using z-Methyl-N-Butylpyridinium Tetrafluoroborate Isomers (Z = 2, 3, or 4) at T = 313.2 K. *J. Chem. Thermodyn.* **2010**, *42*, 1004–1008. [\[CrossRef\]](#)
8. Aspi, K.K.; Surana, N.M.; Ethirajulu, K.; Vennila, V. Liquid–Liquid Equilibria for the Cyclohexane + Benzene + Dimethylformamide + Ethylene Glycol System. *J. Chem. Eng. Data* **1998**, *43*, 925–927. [\[CrossRef\]](#)
9. Wu, X.; Wu, J.; Wang, S.; Gao, J.; Xu, D.; Zhang, L.; Wang, Y. Liquid–Liquid Equilibrium for Ternary Systems (Ethyl Acetate/Isopropyl Acetate + 2,2-Difluoroethanol + Water) at 298.15 and 308.15 K. *J. Chem. Eng. Data* **2021**, *66*, 1399–1405. [\[CrossRef\]](#)
10. Santos, F.S.; d'Ávila, S.G.; Aznar, M. Salt Effect on Liquid–Liquid Equilibrium of Water+1-Butanol+acetone System: Experimental Determination and Thermodynamic Modeling. *Fluid Phase Equilib.* **2001**, *187–188*, 265–274. [\[CrossRef\]](#)
11. Patai, S. (Ed.) *Saul Patai Cyanates and Their Thio Derivatives*; John Wiley & Sons, Ltd.: Chichester, UK, 1977; Volume 2, ISBN 9780470771532.
12. McCullough, J.P.; Scott, D.W.; Waddington, G. Thermodynamics of Organic Sulfur Compounds. In *Organic Sulfur Compounds*; Kharasch, N., Ed.; Elsevier: Amsterdam, The Netherlands, 1961; Volume 1, pp. 20–29.
13. Fernanda Bonfim de Souza, B.; Lenhare, S.; Cristaldo Heck, S.; Zuber, A.; Beneti, S.C.; Zanette, A.F.; Filho, L.C. COSMO Study on the Heptane–Toluene–DMF/DEG-KSCN Liquid–Liquid Equilibrium System. *Ind. Eng. Chem. Res.* **2022**, *61*, 653–659. [\[CrossRef\]](#)
14. Song, S.; Lin, C.; You, N. Phase Equilibria Study of the (Benzene + Cyclohexane + N,N-Dimethylformamide + Potassium Thiocyanate) Quaternary Systems. *Fluid Phase Equilib.* **2014**, *376*, 154–158. [\[CrossRef\]](#)
15. Yang, X.; Fu, Y.; Zhang, X.; Dong, H.; Wang, Y.; Yue, G.; Liu, J. Liquid–Liquid Equilibria of Benzene + Cyclohexane + N,N-Dimethyl Acetamide + Ammonium Thiocyanate at 298.15 K and Atmospheric Pressure. *J. Chem. Eng. Data* **2015**, *60*, 971–975. [\[CrossRef\]](#)
16. Wilding, W.V.; Rowley, R.L.; Oscarson, J.L. DIPPR® Project 801 Evaluated Process Design Data. *Fluid. Phase Equilib.* **1998**, *150–151*, 413–420. [\[CrossRef\]](#)
17. Lemmon, E.W.; McLinden, M.O.; Friend, D.G. *Thermophysical Properties of Fluid Systems*; Linstrom, P.J., Mallard, W.G., Eds.; NIST Standard Reference Database Number 69; NIST Chemistry WebBook: Gaithersburg, MD, USA, 1998.
18. Martínez-Reina, M.D.; Amado-González, E. Refraction Indexes and Density for Binary Mixtures of Heptane with Cyclohexane, Benzene and Toluene at 293.15, 298.15, 303.15 K. *Orinoquia* **2012**, *16*, 110–120. [\[CrossRef\]](#)
19. Qiu, D.; Tang, J.; Li, S.; Zhai, Q.; Jiang, Y.; Hu, M. Solubility, Density and Refractive Index of Formamide/N-Methylformamide/N,N-Dimethylformamide + Rb₂SO₄ + H₂O Ternary Systems at 283.2, 298.2 and 313.2 K. *J. Chem. Thermodyn.* **2022**, *175*, 106907. [\[CrossRef\]](#)
20. Dong, H.; Yang, X.; Yue, G.; Zhang, W.; Zhang, J. (Liquid + liquid) Equilibria for Benzene + cyclohexane + N,N-Dimethylformamide + sodium Thiocyanate. *J. Chem. Thermodyn.* **2013**, *63*, 169–172. [\[CrossRef\]](#)
21. Othmer, D.; Tobias, P. Liquid-Liquid Extraction Data—The Line Correlation. *Ind. Eng. Chem.* **1942**, *34*, 693–696. [\[CrossRef\]](#)
22. Grob, R.L.; Barry, E.F. *Modern Practice of Gas Chromatography*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2004; ISBN 0471229830.
23. Hand, D.B. Dimeric Distribution. *J. Phys. Chem.* **1929**, *34*, 1961–2000. [\[CrossRef\]](#)
24. Imahara, H.; Minami, E.; Saka, S. Thermodynamic Study on Cloud Point of Biodiesel with Its Fatty Acid Composition. *Fuel* **2006**, *85*, 1666–1670. [\[CrossRef\]](#)
25. Brandani, V.; Chianese, A.; Rossi, M. Ternary Liquid-Liquid Equilibrium Data for the Water-Ethanol-Benzene System. *J. Chem. Eng. Data* **1985**, *30*, 27–29. [\[CrossRef\]](#)
26. Follegatti-Romero, L.A.; Oliveira, M.B.; Batista, F.R.M.; Batista, E.A.C.; Coutinho, J.A.P.; Meirelles, A.J.A. Liquid–Liquid Equilibria for Ternary Systems Containing Ethyl Esters, Ethanol and Glycerol at 323.15 and 353.15K. *Fuel* **2012**, *94*, 386–394. [\[CrossRef\]](#)
27. Mesquita, F.M.R.; Evangelista, N.S.; de Sant'Ana, H.B.; de Santiago-Aguiar, R.S. Liquid–Liquid Equilibrium for the Glycerol + Alcohol + Coconut Biodiesel System at Different Temperatures and Atmospheric Pressure. *J. Chem. Eng. Data* **2012**, *57*, 3557–3562. [\[CrossRef\]](#)
28. Oliveira, M.B.; Barbedo, S.; Soletti, J.I.; Carvalho, S.H.; Queimada, A.J.; Coutinho, J.A. Liquid–Liquid Equilibria for the Canola Oil Biodiesel+ ethanol+ glycerol System. *Fuel* **2011**, *90*, 2738–2745. [\[CrossRef\]](#)
29. Walas, S.M. *Phase Equilibria in Chemical Engineering*, 1st ed.; Butterworth-Heinemann: Oxford, UK, 1984; ISBN 9781483145082.
30. Sandler, S.I. *Chemical, Biochemical and Engineering Thermodynamics*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2006.
31. Gmehling, J.; Kleiber, M.; Kolbe, B.; Rarey, J. *Chemical Thermodynamics for Process Simulation*; Wiley: Hoboken, NJ, USA, 2019; ISBN 9783527343256.
32. Renon, H.; Prausnitz, J.M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144. [\[CrossRef\]](#)
33. Chen, C.-C.; Britt, H.I.; Boston, J.F.; Evans, L.B. Local Composition Model for Excess Gibbs Energy of Electrolyte Systems. Part I: Single Solvent, Single Completely Dissociated Electrolyte Systems. *AIChE J.* **1982**, *28*, 588–596. [\[CrossRef\]](#)

34. Maia, F.M.; Rodríguez, O.; Macedo, E.A. LLE for (Water+ionic Liquid) Binary Systems Using [Cxmim][BF₄] (X=6, 8) Ionic Liquids. *Fluid Phase Equilib.* **2010**, *296*, 184–191. [[CrossRef](#)]
35. Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178–193. [[CrossRef](#)]
36. Fredenslund, A.; Jones, R.L.; Prausnitz, J.M. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* **1975**, *21*, 1086–1099. [[CrossRef](#)]
37. Gaube, J. A. Fredenslund, J. Gmehling, and P. Rasmussen: *Vapor-Liquid equilibria using UNIFAC a group-contribution method*. Elsevier Scientific Publishing Company, Amsterdam, Oxford, New York 1977. 380 Seiten, Preis: \$ 59.75, Dfl 146,-. *Berichte Der Bunsenges. Für. Phys. Chem.* **1978**, *82*, 551. [[CrossRef](#)]
38. Aznar, M.; Telles, A.S. Prediction of Electrolyte Vapor-Liquid Equilibrium by UNIFAC-Dortmund. *Braz. J. Chem. Eng.* **2001**, *18*, 127–137. [[CrossRef](#)]
39. Vera, J.H. Molecular thermodynamics of fluid-phase equilibria by John M. Prausnitz, Rüdiger N. Lichtenthaler and Edmundo Comes de Azevedo, Third Edition, 1999; Prentice Hall PTR, Upper-Saddle River, New Jersey 07458, xxiii + 860 pages; price \$131.95 CND; ISBN 0-13-977745-8. *Can. J. Chem. Eng.* **2000**, *78*, 429–430. [[CrossRef](#)]
40. Michelsen, M.L.; Møllerup, J.M. *Thermodynamic Models: Fundamentals & Computational Aspects*, 2nd ed.; Tie-Line Publications: Holte, Denmark, 2007; ISBN 87-989961-3-4.
41. Taylor, B.N.; Kuyatt, C.E. *Guidelines for the Evaluation and Expression of Uncertainty in NIST Measurement Results Technical Note 1297 for NIST*; NIST: Gaithersburg, MD, USA, 1994.
42. Macedo, E.A.; Skovborg, P.; Rasmussen, P. Calculation of Phase Equilibria for Solutions of Strong Electrolytes in Solvent—Water Mixtures. *Chem. Eng. Sci.* **1990**, *45*, 875–882. [[CrossRef](#)]
43. Roughton, B.C.; Christian, B.; White, J.; Camarda, K.V.; Gani, R. Simultaneous Design of Ionic Liquid Entrainers and Energy Efficient Azeotropic Separation Processes. *Comput. Chem. Eng.* **2012**, *42*, 248–262. [[CrossRef](#)]
44. Arce, P.F.; Guimarães, D.H.P.; de Aguirre, L.R. Experimental Data and Prediction of the Physical and Chemical Properties of Biodiesel. *Chem. Eng. Commun.* **2019**, *206*, 1273–1285. [[CrossRef](#)]

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