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Extraction of Aromatic Hydrocarbons from Light Petroleum Fractions with Lactam Solvent

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Abstract

The investigation and modeling of phase equilibrium in the extraction of aromatics from naphtha reformate using N-(β-cyanoethyl)-ε-caprolactam (NCECL) and water were conducted using the ASPEN HYSYS Program. The extraction process was studied at various temperatures (50, 70, 95, 110, and 125°C) and different proportions of water in the NCECL solvent (2%, 5%, and 8% by weight). The solvent-to-feed ratio was maintained at 2:1, and the concentration of aromatics in the feed remained constant at 42.71% by weight. Experimental results were compared to predictions made using the UNIFAC method. Successful predictions were made for the aromatic extraction capacity from reformation, processing index, solvent power, and solvent selectivity. The impact of water-content and temperature on selectivity, solubility, and distribution coefficient was investigated, and the equilibrium data was used to calculate the values of the distribution coefficient and selectivity. A low root mean square deviation value was obtained, and the experimental and calculated extract yields were determined under the best operating conditions, considering the specified temperature and water content. The optimal operating conditions were found to be a temperature of 50°C and a water content of 2%, resulting in extract yields of 52.77% and 56.80% for the experimental and calculated values, respectively.

Keywords: Phase equilibrium; Modeling; Aromatic solvent extraction; Liquid-liquid extraction; Aspen Hysys program

1. Introduction

Recently, green processes have been seriously required in large-scale production in the aromatics industry, due to the rapid growth in the global demand for aromatics and emphasis on environmental protection [1, 2]. Benzene, toluene, and xylene (BTX) are essential raw materials utilized in the petrochemical sector and can be used to produce pharmaceuticals, rappers, resins, detergents, Oxygenates, and synthetic fibers [3,4]. The implementation of liquid-liquid extraction has made it possible to separate aromatics from other hydrocarbon categories, facilitating the simultaneous extraction of BTX aromatics with minimal non-aromatic contaminants from various reformed naphtha [5-7]. The choice of solvents for aromatic extraction can vary significantly, and the development of solvent mixtures that can accommodate different feedstocks and product ranges is an ongoing area of research [8,9]. While the commercial-scale recovery of aromatic hydrocarbons through liquid liquid extraction with selective solvents has been practiced for several decades, new solvents continue to be introduced and patented, indicating that the search for the ideal solvent is still ongoing [10-15].

Liquid–liquid equilibrium (LLE) data are critical for designing and optimizing processes for extracting aromatics. The LLE data for the extraction of aromatics by sulfolane were obtained using the COSMO-RS model [16]. Among the various water-soluble derivatives of ε-caprolactam, N-(β-cyanoethyl)-ε-caprolactam (NCECL) is the most effective solvent for aromatic hydrocarbon extraction from reformate [17,18]. NCECL was initially synthesized and manufactured by Cuiban and his team [19]. Liquid-liquid equilibrium data can be obtained through experimental methods or calculated using appropriate mathematical models [20-24]. In this study, the liquid-liquid equilibrium measurements were conducted between a mixture of NCECL, water, and naphtha reformate to extract aromatics from the reformate. Gas chromatography was employed to determine the composition of the reformate feed and the extract and raffinate phases. In the UNIFAC-original model, group interaction parameters require accurate equilibrium data [25,26]. The experimental findings were compared to the predictions generated by the Aspen Hysys software using the UNIFAC method. To the best of our knowledge, the successful synthesis of N-(β-cyanoethyl)-ε-caprolactam (NCECL) and its use as solvent extract with water, and naphtha reformate to extract aromatics from the reformate with the liquid-liquid equilibrium measurements have not been reported.

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2.Materials and methods 2.1 Materials

ε-caprolactam (99% purity, Sigma–Aldrich), acrylonitrile (99% purity, Sigma–Aldrich), sodium hydroxide (98% purity, Sigma–Aldrich), sulfuric acid (98% purity), and calcium chloride (99.99% purity, Sigma–Aldrich). The hydrocarbons used were n-hexane, benzene, n-heptane, cyclohexane, isooctane (2,2,4-trimethyl pentane), toluene, ethylbenzene, and p-xylene. These chemicals were obtained from Sigma–Aldrich and used without further purification. Gas chromatography analysis confirmed their purity to be above 99.0%.

2-2 Synthesized of N-(β-cyanoethyl)-ε-caprolactam (NCECL)

The synthesis of NCECL was carried out following a previously described method [18]. Simply, the synthesis process involved dissolving ε-caprolactam (56.5g, 0.5mol) in warm toluene (approximately 140mL, at a temperature of around 60°C) in a three-neck flask equipped with a Dean-Stark trap, dropping funnel, mechanical stirrer, and a condenser with a CaCl$_2$ tube. While stirring, solid NaOH (0.2g, 0.005mol) was added to the mixture and refluxed. After cooling to 15°C, acrylonitrile (33.8mL, 27.2g, and 0.5mol) was gradually added while continuing to stir. The reaction mixture was then heated to 50°C for 1h, cooled down, and neutralized using concentrated sulfuric acid with phenolphthalein as an indicator. The resulting mixture was filtered, and distilled, yielding colorless crystals of N-(β-cyanoethyl)ε-caprolactam with a 90% weight yield. The physical properties of NCECL are presented in Table (1), and its structure is depicted in Figure (1). For the extraction experiments, various runs were conducted at different extraction temperatures (50, 70, 95, 110, and 125°C) using NCECL as the solvent with varying proportions of water (2%, 5%, and 8% by weight). The solvent-to-feed ratio was kept constant at 2:1, and the concentration of aromatics in the feed remained consistent at 42.71% by weight.

Table (1) The physical properties of N-(β-cyanoethyl)-ε-caprolactam

Properties	Value
Chemical formula	C9H14N2O
Molecular weight	166.22
Purity by GC, wt.%	99.36
Appearance	Solid,Colorless crystal
Melting point	35-35.5°C
Moisture (Karle -Fisher), %	0.2
Freezing point (NCECL +2% water)	17°C
Boiling point (2.7 torr)	155°C
Latent heat of vaporization, KJ/kg at 140°C	90
Flashpoint (open cup)	183°C
Density, g/cm3 at 40°C	1.069
Viscosity, CP (2.5 % water at 40°C)	30.6
Specific heat (liquid), kcal/kg at 28°C (NCECL +5% water)	0.4952
Surface tension at 23°C, dyn/cm	56.8
Interfacial tension at 30°C (NCECL +5% water)	3
Dipole moment, D	4.36
Dielectric constant at 35°C	38.2
Solubility	Soluble in water and most organic solvents but not in alkanes

2.3. Extraction of aromatics

Batch extraction operations were conducted using a stainless-steel mixer-settler apparatus with a capacity of 600 cm^3. Figure (2) illustrates the employed batch mixer-settler apparatus for the extraction process. The operating temperature was regulated by circulating paraffin oil through a jacket surrounding the extractor, utilizing a thermostatic bath. A stirring period of 60 minutes and a settling time of 60 minutes was performed (to ensure perfect mixing and complete separation).

A level glass was installed to observe the extract and raffinate phases, with a cooling condenser attached to prevent product loss. During the phase separation process, nitrogen was introduced to maintain constant pressure and prevent the vaporization of more volatile components as the extractor emptied. The sampling vials were used to collect the two phases, and Molecular sieves, type 5A were used to eliminate any residual water from the samples before analysis. A Chrom pack CP9001 gas chromatograph was utilized, equipped with a WCOT fused silica column measuring 50 m in length and 0.32 mm in internal

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diameter, alongside an FID detector. The analysis was conducted at a temperature of 573K, with an inlet pressure set at 35 kPa. The column was coated with CB silica (5CB, DF=1.2μm), and the splitter injection temperature matched the oven temperature at 573K. The oven temperature programming involved two distinct ranges.

The first range encompassed temperatures between 318K and 393K, with a gradual increase of 8K per minute. The duration for this range was from 5 minutes at the start to 15 minutes at the end. The second range spanned temperatures from 393K to 533K, with a steeper rise of 15K per minute. The initial time for this range was 15 minutes, and it concluded at 17 minutes.The concentrations of compounds in the extract and raffinate phases, determined through GC analysis, were presented as weight percentages. These percentages were converted into mole fractions to facilitate comparison with predicted values. Tables (3-8) display the measured and calculated values of the liquid-liquid equilibrium in the Naphtha Reformate + NCECL - Water system at different water concentrations and temperatures. The distribution coefficients K_A, K_{NA}, and selectivity β were calculated.

The calculation of the extract yield was determined based on material balance using the following formula:

Extract yield, $E = X_{AE} (E) / X_{AR} (F)$ (1)

Where:

E represents the amount of the extract phase in moles.

F represents the amount of the initial Feed in moles.

X_{AE} is the total mole fraction of the aromatic components in the extract phase.

X_{AR} is the total mole fraction of the aromatic components in the raffinate phase using commonly employed formulas [27].
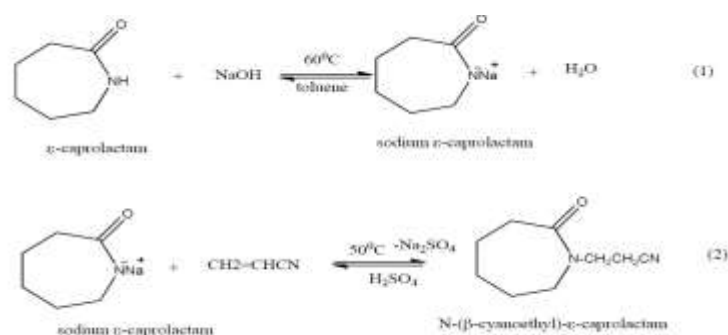

Figure 1. The proposed chemical reaction for of N-(β-cyanoethyl)-ε-caprolactam synthesis.

3. Results and discussion

The laboratory-prepared synthetic naphtha reformate utilized in the experiments was created by blending pure hydrocarbons. It possesses a boiling range of 64-145°C and a density of 0.7644 g/cm³ at 20°C. The composition of the synthetic naphtha reformate, as determined through gas chromatography analysis, is provided in Table (2), including the account of functional groups present in each component.

3.1. Critical solution temperature

The critical temperature for a solution, which refers to the temperature at which complete mixing of the two phases occurs, was measured. This was accomplished by preparing a known feed to solvent ratio mixture in a conical flask equipped with a magnetic stirrer, placed on a hot plate. The solution was heated gradually while closely monitoring its temperature. The critical temperature of the solution was identified as the point where all turbidity disappeared, indicating complete mixing. The critical temperatures of solution for N-(β-cyanoethyl)-ε-caprolactam (NCECL) at different water compositions and solvent-feed ratios are illustrated in Figure (3). The data presented in Figure (3) illustrates how the critical solution temperatures change. It's evident that as the amount of water in the solvent increases, the critical solution temperature also rises. As a consequence, separating the two liquid phases becomes more straightforward, and the extraction temperature increases as well. Conversely, when the solvent-to-feed ratio is increased, the critical solution temperature decreases. This implies that achieving separation between the liquid phases becomes challenging, especially at elevated temperatures when using high solvent to-feed ratios. Consequently, longer settling times were necessary for situations involving high solvent-to-feed ratios. For all extraction processes, the temperatures employed were at least 20°C lower than the critical solution temperature. This precaution was taken to ensure the successful formation of two distinct liquid phases.
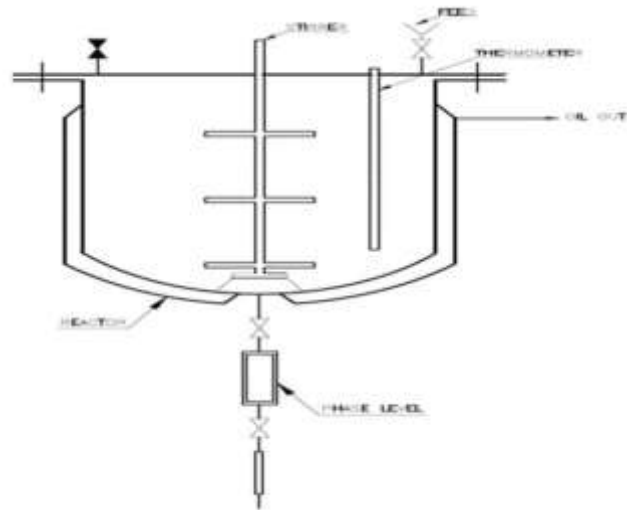
Figure 2. Batch mixer –settler apparatus for extraction process.

Table (2) the composition of the reformate and the number of functional UNIFAC groups in each of its constituents [17]

Component	Mass %	Number of UNIFAC groups in each component						
		CH_3	CH_2	CH	C	ACH	$ACCH_3$	ACCH2
Benzene	14.28	0	0	0	0	6	0	0
Toluene	19.31	0	0	0	0	5	1	0
Ethyl benzene	1.94	1	0	0	0	5	0	1
p-xylene	6.98	0	0	0	0	4	2	0
Hexane	31.80	2	4	0	0	0	0	0
Cyclohexane	3.92	0	6	0	0	0	0	0
Heptane	21.31	2	5	0	0	0	0	0
Iso-Octane	0.46	5	1	1	1	0	0	0

Figure 3. Critical solution temperatures for the naphtha reformate with aqueous NCECL solvent.

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Table (3) Experimental LLE of the Naphtha Reformate + NCECL 2% Water at S:F=2
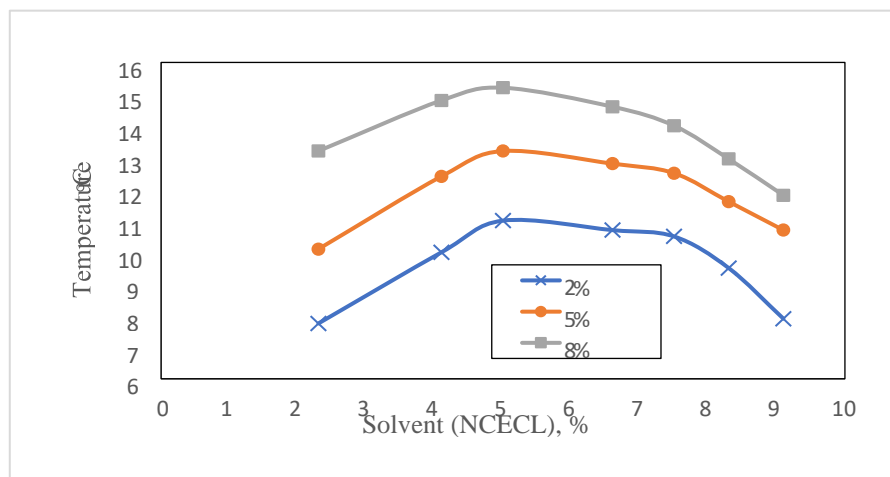
Component	T=50°C		T=70°C		T=95°C	
	X_E	X_R	X_E	X_R	X_E	X_R
Benzene	0.0338	0.0726	*0.0342*	0.0709	0.0313	0.0663
Toluene	0.0456	0.981	*0.0462*	0.0958	0.0460	0.0894
Ethyl Benzene	0.0045	0.0098	0.0046	0.0096	0.0043	0.0089
P-Xylene	0.0164	0.0353	0.0167	0.0345	0.0151	0.0322
Hexane	0.0330	0.4046	0.0430	0.4016	0.0508	0.3907
Cyclohexane	0.0034	0.0418	0.0044	0.0413	0.0052	0.0404
Heptane	0.0224	0.2745	0.0292	0.2723	0.0345	0.2651
Iso -Octane	0.0005	0.0058	0.0006	0.0058	0.0007	0.0056
Water	0.0051	0.0028	0.0045	0.0022	0.0041	0.0017
NCECL	0.8353	0.0547	0.8166	0.0660	0.8080	0.0997

Table (4) Predicted LLE of the Naphtha Reformate + NCECL 2% Water at S:F=2

Component	T=50°C		T=70°C		T=95°C	
	X_E	X_R	X_E	X_R	X_E	X_R
Benzene	0.0159	0.0549	*0.0198*	0.0580	0.0298	0.0547
Toluene	0.0210	0.721	*0.0205*	0.0722	0.0301	0.0722
Ethyl Benzene	0.0063	0.0065	0.0060	0.0066	0.0056	0.0066
P-Xylene	0.0164	0.0239	0.0150	0.0240	0.0141	0.0241
Hexane	0.0398	0.4223	0.0376	0.4419	0.0581	0.4438
Cyclohexane	0.0050	0.0379	0.0111	0.0377	0.0052	0.0374
Heptane	0.0195	0.3481	0.0204	0.3248	0.0272	0.3211
Iso -Octane	0.0017	0.0012	0.0005	0.0006	0.0042	0.0048
Water	0.0025	0.0060	0.0031	0.0062	0.0037	0.0064

Table (5)   LLE of the Naphtha Reformate + NCECL 5% Water at S: F=2

Component	T=50 °C		T=70°C		T=95°C		T=110°C	
	XE	XR	X^E	XR	X^E	X^R	X^E	X^R
BENZENE	0.03033	0.0819	0.0263	0.0690	0.0261	0.0675	0.0314	0.077
TOLUENE	0.0409	0.1107	0.0354	0.0933	0.0353	0.0912	0.0425	0.1039
ETHYL BENZENE	0.00409	0.0111	0.0035	0.0093	0.0035	0.0092	0.0043	0.0104
P-XYLENE	0.01478	0.0398	0.0128	0.0336	0.0128	0.0328	0.0153	0.0374
HEXANE	0.0194	0.395	0.0271	0.4088	0.0359	0.3928	0.0438	0.3923
CYCLOHEXANE	0.00205	0.04081	0.0028	0.0422	0.0038	0.0406	0.0046	0.0405
HEPTANE	0.01310	0.2681	0.0184	0.2774	0.0243	0.2672	0.0297	0.2661
ISO -OCTANE	0.00028	0.00569	0.0004	0.0059	0.0005	0.0057	0.0006	0.0057
WATER	0.0069	0.0031	0.0059	0.0027	0.0052	0.0021	0.0041	0.0016
NCECL	0.8682	0.0437	0.8674	0.0578	0.8526	0.0899	0.8237	0.0651

Table (6) Predicted LLE of the Naphtha Reformate + NCECL 5% Water at S: F=2

Component	T=50 °C		T=70°C		T=95°C		T=110°C	
	XE	XR	X^E	XR	X^E	X^R	X^E	X^R
BENZENE	0.0166	0.0552	0.0234	0.0552	0.0179	0.055	0.0211	0.0550
TOLUENE	0.0220	0.0719	0.0251	0.0719	0.0237	0.0720	0.0223	0.0720
ETHYL BENZENE	0.0065	0.0112	0.0063	0.0076	0.0071	0.00635	0.0064	0.0067
P-XYLENE	0.0156	0.0233	0.0083	0.0234	0.01570	0.0236	0.0169	0.0238
HEXANE	0.0360	0.4007	0.0454	0.4359	0.0493	0.4459	0.0514	0.4393
CYCLOHEXANE	0.0049	0.0386	0.0045	0.0385	0.0047	0.0383	0.0043	0.0381
HEPTANE	0.0163	0.3348	0.0168	0.3367	0.0189	0.3271	0.0223	0.3323
ISO -OCTANE	0.0045	0.0345	0.0006	0.0005	0.0006	0.0005	0.0005	0.0006
WATER	0.0017	0.0055	0.0024	0.0056	0.0027	0.0058	0.0027	0.0058
NCECL	0.8759	0.0243	0.8672	0.0247	0.8594	0.0255	0.8521	0.0264

Table (7) Experimental LLE of the Naphtha Reformate + NCECL 8% Water at S: F=2

Component	T=50 °C		T=70°C		T=95°C		T=125°C	
	XE	XR	X^E	XR	X^E	X^R	X^E	X^R
BENZENE	0.0274	0.0782	0.0277	0.0734	0.0306	0.0746	0.0346	0.0734
TOLUENE	0.0370	0.1057	0.0373	0.0992	0.0413	0.1007	0.0466	0.0991
ETHYL BENZENE	0.0037	0.0106	0.0037	0.0099	0.0041	0.0101	0.0047	0.0099
P-XYLENE	0.0133	0.0380	0.0135	0.0356	0.0148	0.0362	0.0168	0.0356
HEXANE	0.0180	0.4060	0.0241	0.4098	0.0298	0.3928	0.0406	0.3786
CYCLOHEXANE	0.0019	0.0419	0.0025	0.0422	0.0030	0.0405	0.0043	0.0390
HEPTANE	0.0123	0.2753	0.0164	0.2779	0.0203	0.2664	0.0276	0.2569
ISO -OCTANE	0.0003	0.0058	0.0003	0.0060	0.0004	0.0057	0.0005	0.0055
WATER	0.0081	0.0037	0.0067	0.0031	0.0061	0.0023	0.0048	0.0021
NCECL	0.878o	0.0348	0.8678	0.0429	0.8496	0.0707	0.8195	0.0999

3.2. Investigating the impact of water-content and temperature on selectivity, solubility, and distribution coefficient
Water mixed with NCECL to enhance its selectivity. As water and NCECL are all polar solvents, water is soluble in NCECL and very difficult to dissolve in hydrocarbons. Upon examining the critical solution temperatures of the naphtha reformate with an aqueous NCECL solvent, it becomes evident that an increase in water concentration within the solvent leads to an elevation in the critical solution temperature. As the proportion of water in NCLCL increases (from 2 to 8 vol.%) the immiscible area in which solvent extraction is operating increases, so that feeds containing increasingly larger proportions of aromatics can be extracted and higher purity of extracted aromatics can be obtained as shown in Figure (3). The addition of water to NCECL serves as an effective method to enhance its selectivity. Both water and NCECL are categorized as polar solvents, which means that water can readily dissolve in NCECL but faces significant challenges when it comes to dissolving in hydrocarbons. This characteristic makes water an ideal candidate for improving the separation and extraction processes involving NCECL.

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Table (8) Predicted LLE of the Naphtha Reformate + NCECL 8% Water at S:F=2

Component	T=50 °C		T=70°C		T=95°C		T=125°C	
	XE	XR	X^E	XR	X^E	X^R	X^E	X^R
BENZENE	0.0116	0.0554	0.0146	0.0553	0.0212	0.0553	0.0201	0.0552
TOLUENE	0.0315	0.0713	0.0299	0.0715	0.0281	0.0717	0.0266	0.0718
ETHYL BENZENE	0.0059	0.0094	0.0059	0.0089	0.0061	0.0085	0.0062	0.0080
P-XYLENE	0.0103	0.0237	0.0098	0.0228	0.0093	0.0230	0.0174	0.0320
HEXANE	0.0300	0.4490	0.0312	0.4301	0.0355	0.4479	0.0452	0.4340
CYCLOHEXANE	0.0039	0.0390	0.0041	0.0389	0.0046	0.0388	0.0044	0.0386
HEPTANE	0.0136	0.3248	0. 0144	0.3442	0.0152	0.3256	0.0280	0.3304
ISO -OCTANE	0.0006	0.0005	0.0006	0.0052	0.0005	0.0006	0.0006	0.0005
WATER	0.0041	0.0050	0.0038	0.0052	0.0036	0.0053	0.0039	0.0055
NCECL	0.8885	0.0219	0.8857	0.0226	0.8759	0.0233	0.8476	0.0240

In the context of the critical solution temperatures for the naphtha reformation when combined with an aqueous NCECL solvent, it becomes evident that the concentration of water in the solvent plays a crucial role. The critical solution temperature is elevated with an increase in the water concentration. Essentially, this means that the ability of the solvent to dissolve or separate components from the naphtha reformate is significantly influenced by the amount of water present. By studying the impact of water concentration on the immiscible area, which refers to the region where solvent extraction occurs, we can observe a compelling trend. As the proportion of water in NCECL increases, ranging from 2 to 8 vol.%, the immiscible area expands. This expansion enables the extraction of feeds that contain progressively larger proportions of aromatics. As a result, the extracted aromatics exhibit higher purity levels, offering enhanced separation and purification capabilities. Figure (3) provides a visual representation of these findings, illustrating the relationship between water concentration, immiscible area, and the purity of extracted aromatics. To gain insights into the interactions between NCECL and water, as well as various molecular groups such as CH_3, CH_2, CH, C, ACH, $ACCH_2$, and $ACCH_3$, we benefited from phase equilibria data from ternary systems involving paraffin/aromatic/NCECL.

 These interactions were quantified using parameters generated from reference [17], which serves as a valuable source of experimental data and insights into the behavior of these systems. While we encountered some deviations between the phase equilibria predictions and the actual experimental results, we utilized the percentage root mean square deviation (RMSD) as a metric to estimate and quantify these discrepancies. This approach allowed us to evaluate the accuracy of the predictions and refine our understanding of the system's behavior. The interaction parameters for NCECL with water and various groups (CH_3, CH_2, CH, C, ACH, $ACCH_2$, and $ACCH_3$) were derived from the phase equilibria data of paraffin/aromatic/NCECL ternary systems found in reference [17]. Although the phase equilibria predictions exhibited some deviations from the experimental results, the RMSD was utilized to estimate these deviations. Calculating the RMSD between the experimental and predicted values is a crucial step in evaluating the accuracy of a model or method. In this particular case, the RMSD is determined using a formula that takes into account the differences between the experimental and calculated mole fractions of individual components.By summing these differences and dividing them by the number of components, the RMSD provides a quantitative measure of the overall deviation between the experimental and predicted values. These values represent the deviations between experimental and predicted data in these respective phases, considering different temperatures and water concentrations. The presented RMSD values provide insights into the level of agreement between the experimental and predicted results.

The RMSD was determined using the following formula:

$$RMSD = \sqrt{\frac{\sum_{i=1}^{n}(x_{iexp}-x_{icalc})^2}{n}}100 \qquad (2)$$

 In this equation, the RMSD represents the deviation in the extract phase, summed over all temperatures and water oncentrations. The variable n represents the number of components, while x_{iexp} and x_{ical} denote the measured and calculated mole fractions of individual components, respectively. The overall RMSD for the extract phase was found to be 0.098 mol.%, while for the raffinate phase, it was 0.264 mol.%. Specifically, at 8% water concentration, the RMSD values were 0.0739 and 0.2499 for the extract and raffinate phases, respectively. These values are indicated in Table (9).

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Table (9) Summary of root mean square deviation between measured and predicted composition of phases for the extraction with NCECL at
S/F 2/1.

Water %	Temperature C	Extract RMSD	Raffinate RMSD
2	50	0.1053	0.2784
	70	0.1085	0.2422
	95	0.0646	0.2685
5	50	0.1045	0.2948
	70	0.2480	0.2371
	95	0.0701	0.2806
	110	0.0839	0.3040
8	50	0.0715	0.2639
	70	0.0764	0.2601
	95	0.0636	0.1493
	125	0.0840	0.3266

Furthermore, the solvent power (P), is an important parameter in extraction processes. The solvent power is estimated by combining the mole fractions of the aromatic in the extract phase (X_{AE}) and the mole fractions of the non-aromatic components in the extract phase (X_{NAE}). This calculation allows for an assessment of the ability of the solvent to dissolve hydrocarbons, which is crucial in extraction applications. To assess the solvent power (P) in the extract, a formula was used:

$$P = X_{AE} + X_{NAE}$$

(3)

The main objective of employing various solvents for extracting naphtha reformate is to optimize the quantity of aromatics present in the extract. Therefore, it is essential to investigate a significant property known as the relative concentration increase of total aromatic components (TA). This property signifies the rise in the aromatic content within the extract phase compared to the original feed, on the other hand, provides information about the relative efficiency of the extraction process. It is determined by considering the mole fraction of the aromatic in the extract phase (X_{AE}), the mole fraction of the solvent in the extract phase (X_{SE}), and the sum of the mole fractions of the aromatic components in the feed (X_{AF}). This calculation enables the evaluation of the extraction process's performance in terms of solute extraction efficiency. Table (10) presents solubility properties for both experimental and predicted data. Notably, the values of β and TA decrease with increasing temperature, while KA and P increase for both experimental and predicted data.

The percentage relative concentration increases of total aromatic components (TA%) was determined using the following equation:

$$TA\% = (X_{AE}/((1-X_{SE})) - X_{AF}))/X_{AF}$$ (4)

The processing solvent index (PSI) was estimated using the equation:

$$PSI\% = (\beta)(P)(KA)(\%TA)$$ (5)

The processing solvent index (PSI) is introduced as an estimation derived from β, P, KA, and TA, which provides a comprehensive assessment of the extraction process. The PSI is calculated by multiplying these parameters, reflecting the combined effects of solute-solvent interactions, solvent power, and extraction efficiency. The PSI% values are used as a quantitative indicator to determine the optimal conditions for the extraction process, considering factors such as water content and temperature. By utilizing the solvent index to select the optimal water content and temperature, it was observed that the highest PSI values were 21.22 and 18.35 for experimental values at 5% and 2% water content, respectively, with a temperature of 50°C. Considering the thermal stability of the solvent, a water content of 2% at 50°C may be preferred.

The results displayed in Figure (4) indicate that the calculated extract yield values are consistently higher than the experimental values, regardless of temperature and water content. As temperature increases, both calculated and experimental yields also increase, while they decrease with higher water content. It is worth noting that the yields for both experimental and calculated data are higher with 2% water content compared to 5% and 8%. Considering the solvent's degradation at higher temperatures [17], it is advisable to operate at a temperature of 50°C and water content of 2%, which yielded 52.77% and 56.80% for experimental and calculated values, respectively.

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Table (10) Values properties for extraction based on experimental and predicted data

| Water content (%)	Temp. °C)	K_A exp.	K_A calc.	Select. exp.	Select. calc.	P exp.	P cal.	TA exp.%	TA calc.%	PSI exp.	PSI calc.
2%	50	0.4650	0.3786	5.70	4.65	0.1595	0.1257	43.40	9.45	18.35	2.09
	70	0.4825	0.3812	4.51	4.41	0.1789	0.1309	30.44	7.62	11.85	1.68
	95	0.4914	0.5050	3.78	4.30	0.1879	0.1743	18.47	5.2	6.45	1.97
5%	50	0.3700	0.3756	7.55	4.92	0.1249	0.1224	60.81	15.06	21.22	3.41
	70	0.3800	0.3991	5.71	4.81	0.1267	0.1304	38.37	11.79	10.55	2.95
	95	0.3870	0.4105	4.24	4.54	0.1422	0.1379	24	7.74	5.60	1.99
	110	0.4100	0.4235	3.66	4.37	0.1722	0.1452	24.75	11.59	6.39	3.11
8%	50	0.3500	0.3711	7.45	6.28	0.1139	0.1074	56.95	25. 10	16.91	6.28
	70	0.3770	0.3798	6.40	6.14	0.1255	0.1105	46.27	23.90	14.01	6.15
	95	0.4100	0.4082	5.40	5.95	0.1443	0.1205	42.01	22.62	13.42	6.62
	125	0.4710	0.4209	4.39	4.32	0.1757	0.1485	33.83	8.52	12.29	2.30
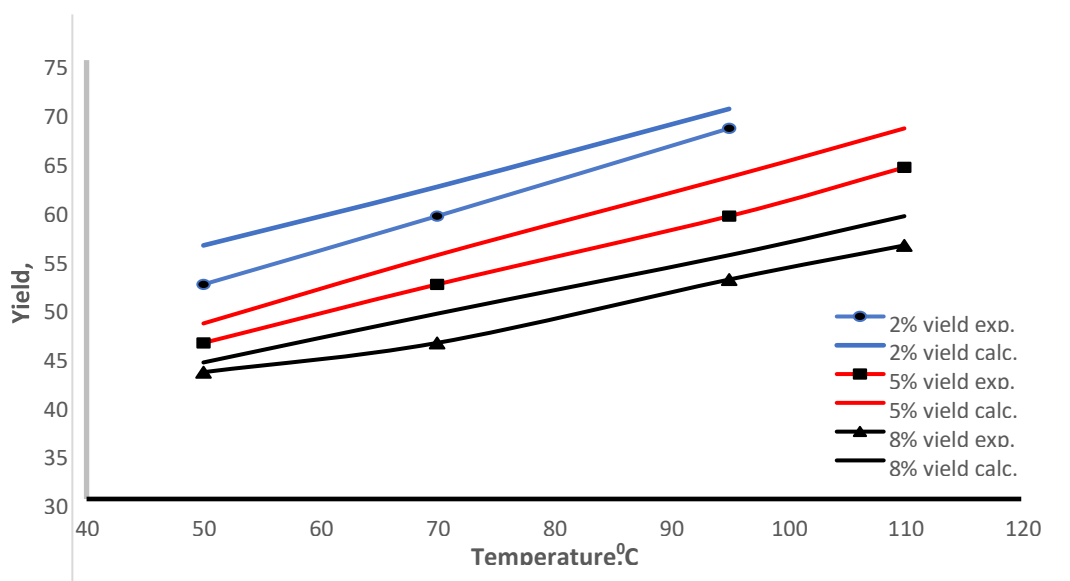
Figure 4. Measured and predicted yields of aromatics in the extract using NCECL at different temperatures, water compositions, and 2:1 solvent ratio.

4. Conclusion

Ternary liquid-liquid equilibrium data for the naphtha reformate, N-(β-cyanoethyl)-ε-caprolactam (NCECL), and water system were investigated using the ASPEN HYSYS Version 11 Program. The experiments were conducted at temperatures of 50, 70, 95, 110, and 125°C, with varying water content (2%, 5%, and 8% by weight). The results indicate that the aqueous NCECL solvent shows great potential for the extraction of aromatics from naphtha reformation. The phase behavior of multi-component systems containing the aqueous NCECL solvent can be accurately predicted using the UNIFAC prediction method.

Among the different water compositions tested, the extraction efficiency was found to be highest when using an aqueous NCECL solvent with 2% water content within the temperature range of 50 to 125°C. Specifically, the most suitable operating conditions were determined to be a temperature of 50°C and a water content of 2%, resulting in extract yields of 52.77% and

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56.80% for the experimental and calculated values, respectively. A root means square deviation (RMSD) of 0.098 mol.% was determined for the extract phase, encompassing all temperatures and water concentrations. In the raffinate phase, the RMSD was found to be 0.264 mol.%. When the water content reached 8%, the RMSD values decreased even further to 0.0739 and 0.2499 for the extract and raffinate phases respectively. These computed values exhibit excellent concurrence with the experimental data, showcasing strong agreement.

5. Conflicts of interest
"There are no conflicts to declare"

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