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Liquid−Liquid Equilibria of the Quaternary System Water + Caprolactam + 1-Octanol + Ammonium Sulfate

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Liquid−liquid equilibria of the quaternary system water + caprolactam + 1-octanol + ammonium sulfate at (25, 45, and 65) °C were determined. In our experiments, the distribution coefficient of caprolactam was usually higher than 1. With increasing temperature and salt content, the distribution coefficient of caprolactam increased. With increasing caprolactam content, the distribution coefficient became smaller. Compared to benzene, 1-octanol is nontoxic and has a much larger extraction capacity. Hence 1-octanol is a prospective substitute of benzene in caprolactam extraction. The extension of the Lyngby modified UNIFAC model was applied to represent the equilibrium data of systems without ammonium sulfate. $CH_2NHCOCH_2$ was defined as a new group, and new interaction parameters were determined from the equilibrium data of the ternary systems water + caprolactam + 1-octanol, water + caprolactam + 1-heptanol, water + caprolactam + benzene, and water + caprolactam + toluene. With the new interaction parameters, the equilibrium of the systems water + caprolactam + 1-heptanol + heptane and water + caprolactam + 1-heptanol + methyl cyclohexane were predicted. The prediction results agreed well with experimental value when the mass fraction of caprolactam is small.

Introduction

Caprolactam, an important industrial chemical, is mainly used to manufacture nylon 6 fiber and resin. The demands of caprolactam have risen steadily in recent years because of its polymers' merits.

There are several different methods to produce caprolactam, and the starting material may be benzene[1] or toluene.[2] After a Beckmann rearrangement, the crude caprolactam contains a high concentration of caprolactam, some ammonium sulfate, water, and impurities.[3] The impurities of caprolactam have a great influence on the polymerization process.[4] Even a small amount of impurity may significantly reduce the quality of caprolactam.[5] Therefore, the purification process is a key step to achieve high-quality caprolactam. On most occasions, extracting caprolactam from its crude product and the subsequent water stripping are the core of the purification process. More than 95 % of the impurities are removed in this process.[6] Hence it is very important to select a proper extractant to extract caprolactam. At present the most widely applied extractant is benzene. Toluene as the extractant is used in the Snia Viscosa Process.[2] There have been many studies on the equilibrium with benzene as the extractant.[7−10] Though the capacity of benzene to extract caprolactam is not very large, it increases rapidly when the concentration of caprolactam increases. At high concentration of caprolactam, the distribution coefficient can reach about 0.5, but benzene is recognized as a human leukaemogen.[11] It is urgent to find a harmless extractant with larger capacity for human safety reasons. Until now, many extractants have been investigated including carbon tetrachloride,[7,8] dichloroethane,[7] nitrobenzene,[8] cyclohexanol,[8] chloroform,[8] trichloroethylene,[8,12] toluene,[13] TBP,[14] 1-heptanol,[15] 2-heptanone,[16] ethers,[17] butyrates,[17] nonanone,[17] octanone,[17] and methylcyclohexanol.[17]

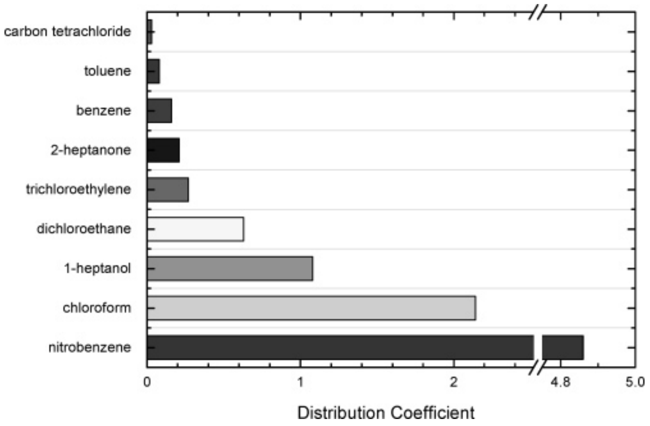

Figure 1. Distribution coefficients of caprolactam when using different extractants at 20 °C. The mass fraction of caprolactam is about 10 % in aqueous phase.

Some reported distribution coefficients of different extractants are shown in Figure 1.[8,9,15−17] Among above extractants, alcohols may be the preferable extractants with large capacity. But when the alcohol's carbon number is small, the mutual solubility between the two liquid phases will cause a loss of the solvent. Using mixed alcohols + alkanes solvents may be a good solution to the problem of solubility,[17] but the capacity of mixed solvents to caprolactam will decrease. Therefore, alcohols with long carbon chains may be a good choice. In this paper, 1-octanol is selected as the extractant. The phase compositions of the ternary system water + caprolactam + 1-octanol and the quaternary system water + caprolactam + 1-octanol + ammonium sulfate at (25, 45, and 65) °C are determined. The experimentally phase compositions in system of water + caprolactam + 1-octanol were described using the extension of the Lyngby modified UNIFAC model by defining new groups.

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Table 1. Liquid−Liquid Equilibria of the System Water (1) + Caprolactam (2) + 1-Octanol (3) + Ammonium Sulfate (4) at (25, 45, and 65) °C

	organic phase			aqueous phase			
t/°C	w_1	w_2	w_3	w_1'	w_2'	w_3'	w_4'
25	0.0488	0.0000	0.9512	1.0000	0.0000	0.0000	0.0000
	0.0779	0.1126	0.8095	0.8941	0.1021	0.0038	0.0000
	0.1103	0.1910	0.6987	0.8029	0.1939	0.0032	0.0000
	0.1334	0.2318	0.6349	0.7401	0.2520	0.0079	0.0000
	0.1867	0.3098	0.5035	0.6582	0.3285	0.0133	0.0000
	0.2146	0.3345	0.4509	0.6278	0.3451	0.0270	0.0000
	0.2691	0.3609	0.3700	0.5869	0.3711	0.0420	0.0000
	0.3179	0.3811	0.3009	0.5626	0.3827	0.0547	0.0000
	0.0687	0.0911	0.8402	0.8832	0.0557	0.0049	0.0562
	0.1076	0.1787	0.7137	0.8054	0.1369	0.0053	0.0524
	0.1186	0.2653	0.6161	0.7135	0.2218	0.0077	0.0570
	0.0659	0.1291	0.8050	0.8023	0.0356	0.0062	0.1560
	0.0943	0.2307	0.6750	0.7805	0.0667	0.0053	0.1475
	0.1445	0.3475	0.5080	0.7473	0.0987	0.0050	0.1490
	0.0805	0.3343	0.5852	0.6723	0.0123	0.0040	0.3113
	0.1215	0.4302	0.4483	0.6414	0.0137	0.0045	0.3404
45	0.0496	0.0000	0.9504	1.0000	0.0000	0.0000	0.0000
	0.0857	0.1353	0.7790	0.8997	0.0978	0.0025	0.0000
	0.1081	0.2052	0.6867	0.8257	0.1692	0.0052	0.0000
	0.1516	0.2708	0.5776	0.7551	0.2385	0.0065	0.0000
	0.2254	0.3246	0.4500	0.6833	0.2932	0.0235	0.0000
	0.2551	0.3461	0.3988	0.6512	0.3218	0.0270	0.0000
	0.3527	0.3763	0.2710	0.5783	0.3512	0.0705	0.0000
	0.0293	0.1062	0.8645	0.8900	0.0429	0.0030	0.0641
	0.0447	0.2092	0.7461	0.8320	0.0975	0.0035	0.0669
	0.0972	0.2998	0.6030	0.7750	0.1519	0.0049	0.0682
	0.1166	0.3754	0.5080	0.7305	0.1834	0.0056	0.0805
	0.0882	0.2542	0.6576	0.7623	0.0636	0.0032	0.1708
	0.1379	0.3660	0.4961	0.7593	0.0745	0.0039	0.1623
	0.0280	0.1618	0.8102	0.6653	0.0034	0.0050	0.3263
	0.0762	0.3498	0.5741	0.6468	0.0109	0.0036	0.3387
65	0.0500	0.0000	0.9500	1.0000	0.0000	0.0000	0.0000
	0.0587	0.0578	0.8834	0.9676	0.0295	0.0028	0.0000
	0.0985	0.1732	0.7283	0.8853	0.1105	0.0042	0.0000
	0.1218	0.2235	0.6547	0.8345	0.1591	0.0064	0.0000
	0.1723	0.2898	0.5378	0.7650	0.2236	0.0114	0.0000
	0.3434	0.3722	0.2844	0.5986	0.3299	0.0715	0.0000
	0.0675	0.1094	0.8230	0.8984	0.0360	0.0033	0.0624
	0.1036	0.2158	0.6806	0.8422	0.0903	0.0041	0.0634
	0.1815	0.3592	0.4593	0.7419	0.1651	0.0064	0.0866
	0.1397	0.3694	0.4909	0.7686	0.0652	0.0030	0.1633
	0.0519	0.1503	0.7978	0.5552	0.0002	0.0035	0.4410
	0.0761	0.2755	0.6484	0.6058	0.0037	0.0035	0.3870
	0.0736	0.3962	0.5302	0.5022	0.0050	0.0047	0.4881

Experimental Section

Chemicals. Caprolactam (>99.9 %) was kindly provided by Shijiazhuang Chemical Fiber Plant, SINOPEC. Ethanol (>99.7 %), 1-octanol (>99.8 %), ammonium sulfate (>99.0 %), and benzophenone (>99.8 %) were purchased from VAS Chemical Co., Ltd (China). All materials were used as received without any further purification.

Apparatus and Procedure. Liquid−liquid extraction experiments were carried out in a conical flask placed in a thermostat. The temperature could be controlled to within 0.1 K. After agitation for 10 h, the equilibrium state was considered to be reached. Then the liquid mixtures were allowed to settle for at least 10 h until the two phases separated completely. The caprolactam and 1-octanol concentrations in the organic and aqueous phase were measured by gas chromatography. The gas chromatography was HP 6890 plus, with a 25 m × 0.32 mm × 0.52 μm HP-FFAP column. The injected volume was 2 μL, and the sampling was performed using a split injection ratio of 1:10. The injection temperature was 250 °C. Detection was performed by a flame ionization detector operating at 300 °C. The column temperature was programmed at 120 °C, then heated to 230 °C at 60 °C·min^{-1}, and the final temperature was maintained for 4 min. The nitrogen flow through the column was 2.2 mL·min^{-1}. The gas flows through the detector were 400 mL·min^{-1} air, 40 mL·min^{-1} hydrogen, and 40 mL·min^{-1} nitrogen. The concentrations of ammonium sulfate were determined with an ion-selective electrode (501 Ammonia E., Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd., China). Only ammonium sulfate concentrations in aqueous phase were measured. Ammonium sulfate concentrations in the organic phase were assumed to be zero. The concentration of water was determined by a Mitsubishi moisturemeter (model CA-05). The injection volume is 10 μL and 30 μL for aqueous phase and organic phase, respectively. All the experiments were repeated three times. The uncertainties in the mass fractions were ± 0.0003 for caprolactam, ± 0.0006 for 1-octanol, ± 0.0007 for water, and ± 0.002 for ammonium sulfate. At (45 and 65) °C, when the mass of ammonium sulfate was high, the caprolactam content and 1-octanol content in aqueous phase was very low, so the relative experimental error was higher.

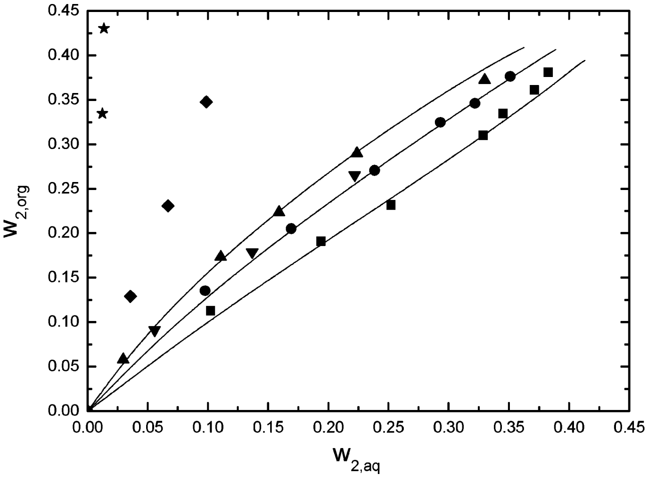

Figure 2. Organic equilibrium mass fraction of caprolactam as a function of the aqueous equilibrium mass fraction for the quaternary system water (1) + caprolactam (2) + 1-octanol (3) + ammonium sulfate (4): ■, 25 °C, 0 mass % ammonium sulfate; ●, 45 °C, 0 mass % ammonium sulfate; ▲, 65 °C, 0 mass % ammonium sulfate; ▼, 25 °C, 5 mass % ammonium sulfate; ◆, 25 °C, 15 mass % ammonium sulfate; ★, 25 °C, 30 mass % ammonium sulfate; solid lines, fitted equilibria according to the Lyngby modified UNIFAC model.

Results and Discussion

Table 1 shows the results of the experimental liquid−liquid equilibrium (LLE) data for the quaternary system water + caprolactam + 1-octanol + ammonium sulfate. The mass fraction of each component was calculated from

$$w_i = \frac{m_i}{\sum_{i=1}^{4} m_i} \tag{1}$$

where m_i means the mass of component i. In Figure 2, it was noted that at higher temperatures the solubility of caprolactam in the organic phase increased to a larger extent than the solubility in the aqueous phase. When the mass fraction of caprolactam is small, the distribution coefficient is larger than 1. With increasing mass fraction of caprolactam, the capacity of caprolactam in the organic phase increases to a smaller extent than in the aqueous phase. An increasing salt concentration in the aqueous phase results in a salting out of caprolactam into the organic phase. From the literature, it is known that the

Table 2. Group Division and Group Parameters

group	$CH_2NHCOCH_2$	CH_3	CH_2	CH	OH	ACH	AC	H_2O
$(z/2)Q_k$	2.424	0.848	0.540	0.228	1.200	0.400	0.120	1.400
R_k	2.6527	0.9011	0.6744	0.4469	1.0000	0.5313	0.3652	0.9200
caprolactam	1	0	3	0	0	0	0	0
1-octanol	0	1	7	0	1	0	0	0
1-heptanol	0	1	6	0	1	0	0	0
water	0	0	0	0	0	0	0	1
heptane	0	2	5	0	0	0	0	0
methyl cyclohexane	0	1	5	1	0	0	0	0
benzene	0	0	0	0	0	6	0	0
toluene	0	1	0	0	0	5	1	0

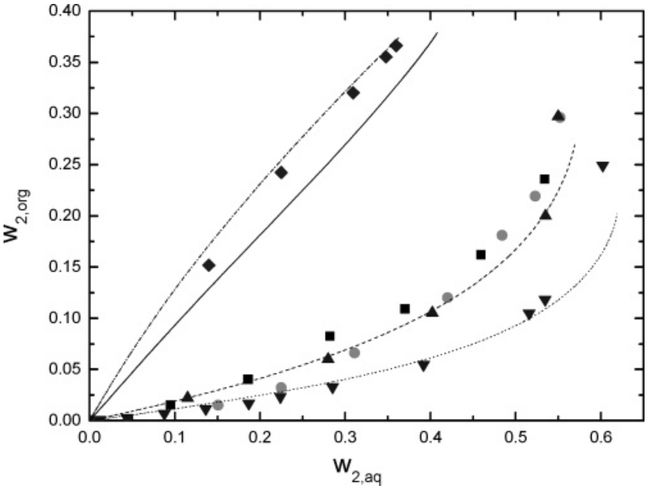

Figure 3. Organic equilibrium mass fraction of caprolactam as a function of the aqueous equilibrium mass fraction at 20 °C for the systems water (1) + caprolactam (2) + benzene (3): ■, reported by ref 9; ●, reported by ref 7; ▲, reported by ref 8; water (1) + caprolactam (2) + toluene (4): ▼, reported by ref 9; water (1) + caprolactam (2) + 1-heptanol (5): [diaf2], reported by ref 15. Dashed line, dotted line, and dashed−dotted line are fitted equilibria according to the Lyngby modified UNIFAC model for benzene, toluene, and 1-heptanol systems, respectively. Solid line is the predicted results of the system water (1) + caprolactam (2) + 1-octanol (6) at 20 °C.

Table 3. Representation of Experimental Data Using the Extension of Lyngby Modified UNIFAC

t/°C	$W_{caprolactam}$	data sets	$10^4\ \sigma$	results type	data source
Water + Caprolactam + 1-Octanol					
25	0−0.3827	8	3.10	correlation	this work
45	0−0.3763	7	3.92	correlation	this work
65	0−0.3722	6	2.73	correlation	this work
Water + Caprolactam + 1-Heptanol					
20	0−0.3663	6	5.65	correlation	15
40	0−0.3436	6	6.24	correlation	15
60	0−0.3416	7	5.74	correlation	15
Water + Caprolactam + Benzene					
20	0−0.552	8	0.86	correlation	7
20	0−0.5340	7	0.55	correlation	9
40	0−0.5150	7	0.50	correlation	9
60	0−0.4910	7	1.30	correlation	9
Water + Caprolactam + Toluene					
20	0−0.6021	11	0.27	correlation	9
40	0−0.5627	9	2.83	correlation	9
60	0−0.5254	8	4.00	correlation	9
25	0.022−0.536	3	1.92	correlation	13
Water + Caprolactam + 1-Heptanol + Heptane					
20	0−0.4298	5	5.52	prediction	17
40	0−0.4719	6	28.4	prediction	17
60	0−0.4685	5	46.4	prediction	17
Water + Caprolactam + 1-Heptanol + Methyl Cyclohexane					
20	0−0.4859	5	46.1	prediction	17
40	0−0.4153	5	2.59	prediction	17
60	0−0.4888	5	9.38	prediction	17

extractants with higher polarity show a larger capacity toward caprolactam and a higher mutual solubility.[17] Our results verified this. In Figure 3, although the extraction capacity of 1-octanol is a little smaller than 1-heptanol, it is much larger than benzene and toluene. Even when the mass fraction of caprolactam is high, the capacity of 1-octanol is about 2 times that of benzene. The extraction capacity of 1-octanol is also larger than the mixed solvents of 1-heptanol and alkanes mentioned by van Delden et al.[17] As a widely used solvent, 1-octanol is economical to use and is a good alternative to benzene. However, in practice the effect of higher mutual solubility and a higher boiling point of 1-octanol as compared to benzene will affect the evaporative separations in the solvent recovery steps. The higher solvent polarity of 1-octanol will affect the impurity distribution behavior.[18] These influences deserve further research.

Modeling and Prediction

The UNIFAC method is a powerful tool for the prediction of liquid−liquid phase equilibrium,[19] especially for extension to systems containing similar groups. Dortmund modified UNIFAC[20] was applied to the prediction of the distribution of caprolactam by van Delden[17] et al., but the accuracy was not satisfactory. The efforts made in predicting the partition coefficient of some biochemicals by Kuramochi et al.[21] showed that the Lyngby modified UNIFAC[22] exhibited better prediction capability than the original UNIFAC, LLE UNIFAC, or Dortmund modified UNIFAC. We used the Lyngby modified UNIFAC model for prediction of the distribution of caprolactam in systems without ammonium sulfate. Herein, we defined $CH_2NHCOCH_2$ as a new group. All defined groups and their parameters are listed in Table 2. z is the lattice coordination number. Q_k and R_k are the surface area parameter and the volume parameter for group k, respectively. In these groups, the additive property is tenable for the structural parameters.[23] Meanwhile, $(z/2)Q_k$ and R_k of similar groups are nearly the same. Therefore $(z/2)Q_k$ and R_k of $CH_2NHCOCH_2$ can be obtained as follows:

$$((z/2)Q, R)_{CH_2NHCOCH_2} = ((z/2)Q, R)_{CH_2CO} + ((z/2)Q, R)_{CH_2NH} \qquad (2)$$

The $(z/2)Q_k$ and R_k of other groups were taken from the literature.[22] The divisions of the components are also listed in Table 2. As in the Lyngby modified UNIFAC, cyclic CH_2 and linear CH_2 are not distinguished here. Toluene is composed of 5 ACH, 1 AC, and 1 CH_3 as the Lyngby modified UNIFAC recommended.[22]

New binary interaction parameters were evaluated with the experimental data in the ternary systems of water + caprolactam + 1-octanol, water + caprolactam + 1-heptanol, water +

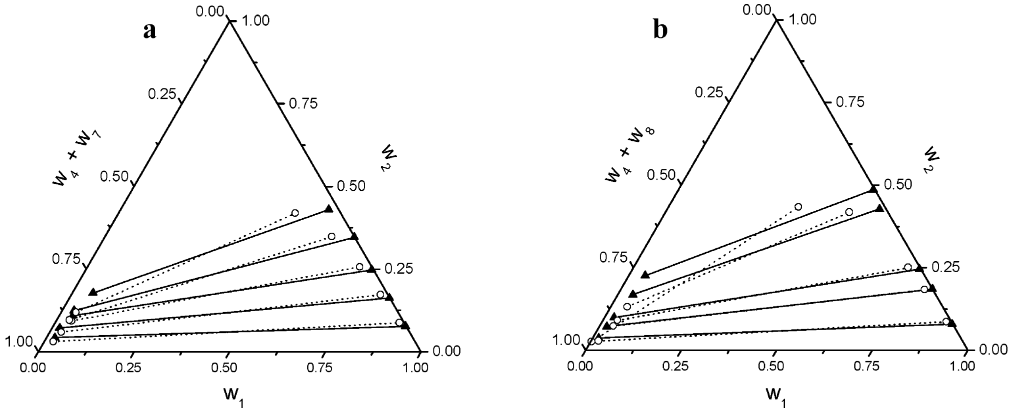

Figure 4. Equilibrium phase compositions (mass fractions) for the systems water (1) + caprolactam (2) + 1-heptanol (3) + heptane (4) at 20 °C reported by van Delden et al.[17] (a); water (1) + caprolactam (2) + 1-heptanol (3) + methyl cyclohexane (5) at 20 °C reported by van Delden et al.[17] (b). Solid lines and ▲ refer to experimental data. Dotted lines and ○ refer to calculations.

Table 4. Interaction Parameters of UNIFAC Groups

group *i*	group *j*	$a_{ij,1}$	$a_{ij,2}$
$CH_2NHCOCH_2$	CH_2	302.7	1.790
$CH_2NHCOCH_2$	ACH	304.4	−1.194
$CH_2NHCOCH_2$	OH	450.7	3.214
$CH_2NHCOCH_2$	H_2O	−250.2	−2.117
CH_2	$CH_2NHCOCH_2$	252.5	−8.581
ACH	$CH_2NHCOCH_2$	38.37	−3.667
OH	$CH_2NHCOCH_2$	−305.0	−7.188
H_2O	$CH_2NHCOCH_2$	218.5	−2.433

caprolactam + benzene, and water + caprolactam + toluene by minimizing the following objective function:

$$F(a_{ij,1}, a_{ij,2}) = \sum \left| w_o^{\mathrm{exp}} - w_o^{\mathrm{calc}} \right| = \min \qquad (3)$$

where w_o means the mass fraction of all the components. A total of 100 data sets were used during the correlation process. The range of system temperatures and composition is shown in Table 3. The correlation results are listed in Table 4. Other binary interaction parameters were taken from the literature. With the determined interaction parameters, we predicted the distribution of caprolactam in the quaternary systems water + caprolactam + 1-heptanol + heptane and water + caprolactam + 1-heptanol + methyl cyclohexane at different temperatures. The calculation results are plotted in Figures 2 to 4. The deviations (σ), defined as

$$\sigma = \sqrt{\sum_1^{\mathrm{nc}} \sum_1^{\mathrm{nd}} (w_o^{\mathrm{exp}} - w_o^{\mathrm{calc}})^2 / (\mathrm{nc} \times \mathrm{nd})} \qquad (4)$$

are also listed in Table 3. The summation of the number of components and data points is abbreviated as nc and nd, respectively. As seen from Figures 2 and 3 and Table 3, the correlation results showed good agreement with experimental data. In Figure 4 and Table 3, predicted results agreed well with experimental value when the mass fraction of caprolactam is small. But at higher caprolactam concentrations, significant deviations appear.

Conclusions

Liquid−liquid equilibriums of the quaternary system water + caprolactam + 1-octanol + ammonium sulfate at (25, 45, and 65) °C were determined. With increasing temperature or salt content, the solubility of caprolactam in the organic phase increases to a greater extent than the solubility of caprolactam in the aqueous phase. The increasing of caprolactam content results in lower extraction capacity of 1-octanol. In our experiments, the distribution coefficient of caprolactam is larger than 1 at most occasions. With a view of mutual solubility, extraction capacity, and price, 1-octanol is a good alternative of benzene.

To represent the equilibrium data, the extension of the Lyngby modified UNIFAC model was applied. $CH_2NHCOCH_2$ was defined as a new group, and its volume and area constants were derived. New interaction parameters were obtained by fit to the equilibrium data. The prediction results agreed well with experimental value when the mass fraction of caprolactam is small.

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