

Selection and Evaluation of a New Extractant for Caprolactam Extraction*

GONG Xingchu (龚行楚), LÜ Yangcheng (吕阳成), LI Mu (李牧), MA Xuefeng (马雪峰), NI Qianyin (倪前银) and LUO Guangsheng (骆广生)**
The State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Abstract Mixed solvent of 1-octanol and cyclohexane with 60% (by mass) 1-octanol content was selected as a new extractant for caprolactam extraction. Compared with benzene or toluene, the new extractant has larger extraction capacity and much lower toxicity. Although the extraction capacity of the new extractant is smaller than that of pure 1-octanol, 1-octanol solubility of the new extractant in aqueous phase is much smaller. Because of its physical properties of lower density, lower viscosity, and higher interfacial tension, the new extractant performed much better phase separation ability than pure 1-octanol. The new extractant showed certain selectivity when dealing with lactam oil. The mixed solvent of 1-octanol and cyclohexane with 60% (by mass) 1-octanol content is a promising extractant for caprolactam extraction.

Keywords caprolactam, extraction, octanol, cyclohexane

1 INTRODUCTION

Caprolactam, an important chemical raw material is mainly used to manufacture nylon 6 fiber and resin. In industry, the crude caprolactam, also named lactam oil, contains a high concentration of caprolactam, some ammonium sulfate, water, and impurities [1]. Extraction of caprolactam from its crude product and the subsequent water stripping are the core of the purification process. Most of the impurities are removed in this process. At present, the most widely applied extractant is benzene [2, 3]. There have been many studies on the equilibrium with benzene as the extractant [4–10]. Using benzene as the extractant, it is possible to obtain extraction capacity close to trichloroethylene, but the extraction selectivity is much higher [11]. However, benzene is recognized as a human leukemogen. It is urgently required to find a harmless extractant with larger capacity for human safety reasons. In our previous work [12], 1-octanol was selected as one of the preferable extractants with much larger capacity than benzene or toluene [6, 13, 14]. But with increasing caprolactam content in aqueous phase, the solubility of 1-octanol in aqueous phase increases significantly [12]. Accordingly, it is difficult to get high concentration caprolactam solution (mass fraction >30%) in the water stripping process, otherwise the 1-octanol loss in raffinate will become serious. It indicates that more water has to be evaporated and more energy has to be cost to get pure caprolactam.

In van Delden *et al.*'s work, 40% 1-heptanol in heptane was selected as a substitute solvent [15]. Because of the existence of amide group in molecular structure of caprolactam, there is hydrogen bond existing between water and caprolactam in caprolactam aqueous solution, which results in very large solubility in water. In Fig. 1, extractants with higher polarity or shorter carbon chain lengths have larger extraction

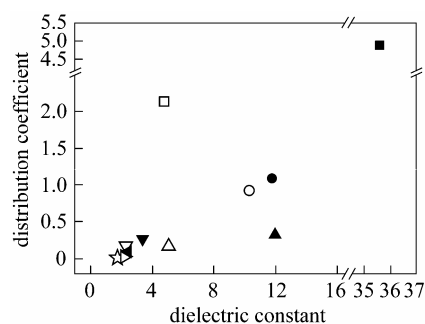


Figure 1 Extractants' dielectric constant and distribution coefficient when caprolactam content in aqueous phase is about 10% [4, 7, 8, 15–18]

▽ benzene; ◇ carbon tetrachloride; ● 1-heptanol; ■ nitrobenzene; ○ 1-octanol; ▼ trichloroethylene; ◄ toluene; △ butyl acetate; □ chloroform; ☆ heptane; ▲ 2-heptanone

capacity to caprolactam, such as alcohols, chloroform, and nitrobenzene. But solubilities of alcohols in aqueous phase are large, especially when caprolactam concentration is high. If the mixed extractant of alcohol+alkane is applied, the alcohol will distribute between aqueous phase and the alkane, which leads to the decrease of solubility in aqueous phase. But with the addition of alkane, the polarity of organic phase decreases, which results in the decrease in extraction capacity. In van Delden *et al.*'s work, because of high solubility of 1-heptanol in aqueous phase, the mass content of 1-heptanol in the mixed solvent cannot be higher than 50%. Compared with pure 1-heptanol [16], the mixed solvent's extraction capacity reduces dramatically due to low 1-heptanol content in the mixed solvent.

Compared with 1-heptanol, 1-octanol has smaller solubility in water and more similarity in polarity with alkanes. Hence, 1-octanol may be more favorable in making mixed solvent with alkanes for extraction of caprolactam. In this article, alkanes were selected for

Received 2007-12-28, accepted 2008-06-06.

* Supported by the National Natural Science Foundation of China (20490200, 20525622) and the National Basic Research Program of China (2007CB714302).

** To whom correspondence should be addressed. E-mail: gsluo@tsinghua.edu.cn

the additive solvent in 1-octanol. The extraction capacity of the mixture of 1-octanol and alkane was determined and described using the extension of Lyngby modified UNIFAC model [19]. Then, optimized mass ratio of 1-octanol in the mixed solvent is recommended. Finally, the phase separation ability and selectivity when using the new extractant is discussed.

2 EXPERIMENTAL

2.1 Chemicals

Caprolactam (>99.9%) and lactam oil was kindly provided by Shijiazhuang Chemical Fiber Plant, SINOPEC. Ethanol (>99.7%), 1-octanol (>99.8%), cyclohexane (>99.5%), hexane (>95.0%), heptane (>99.0%), octane (>98.0%), and 1-pentanol (>99.9%) were purchased from VAS Chemical Co., Ltd. (China). All materials were used as received without any further purification.

2.2 Experimental

Liquid-liquid extraction experiments were carried out in a conical flask placed in a thermostat. The temperature could be controlled within 0.1 K. After agitation for 10 h, the equilibrium state was considered to be reached. The liquid mixtures were then allowed to settle for at least 10 h until the two phases separated completely. The caprolactam concentrations in the organic and aqueous phase were measured by a gas chromatography. The gas chromatography was an HP 6890 plus, with a 25 m×0.32 mm×0.52 μ m HP-FFAP column. Samples with a volume of 150 μ l were taken out from two phases. 1-Pentanol was used as the internal standard sample. Samples and 1-pentanol were diluted with ethanol in a 10 ml volumetric flask for determination. The injected volume was 2 μ l, and the sampling was performed using a split injection ratio of 1 : 10. The injection temperature was 250°C. Detection was performed using a flame ionization detector operating at 250°C. The column temperature was programmed at 60°C for 2 min, and then heated to 230°C at 40°C·min⁻¹, and the final temperature was maintained for 3 min. The nitrogen flow through the column was 2.2 ml·min⁻¹. The gas flows through the detector were as follows: 400 ml·min⁻¹ air, 40 ml·min⁻¹ hydrogen, and 40 ml·min⁻¹ nitrogen. The water content was determined using a Mitsubishi moisturemeter (Model CA-05). The absorbance of caprolactam solution at 290 nm was measured by the spectrophotometry method (Agilent 8453, Agilent). Viscosity of caprolactam concentrations was measured using a viscosity meter (NDJ-5S, Shanghai Jingtian Electronic Machine Co., Ltd.). Interfacial tension was determined using a Contact Angle System (OCAH200, Dataphysics).

3 RESULTS AND DISCUSSION

3.1 Selection of alkane

In van Delden's work, alkane content in the mix-

ture of alcohol and alkane affected its extraction capacity [15]. Generally, smaller alkane content leads to larger extraction capacity. But alkanes' species also affected the extraction capacity of the mixed solvent. Accordingly, it is important to select an alkane, which does smaller negative effect on extraction capacity. In our experiments, mixed solvents of 1-octanol+cyclohexane (MS1), 1-octanol+hexane (MS2), 1-octanol+heptane (MS3), and 1-octanol+octane (MS4) were prepared by mixing 1-octanol and alkanes equally in mass, respectively. 15 ml mixed solvents mentioned above contacted 15 ml aqueous solution with 8% caprolactam at 25°C, respectively. Their extraction capacities were determined and distribution coefficients are plotted in Fig. 2. It can be found that MS1 has the largest extraction capacity. Considering both the boiling point and price, cyclohexane was selected as additive solvent.

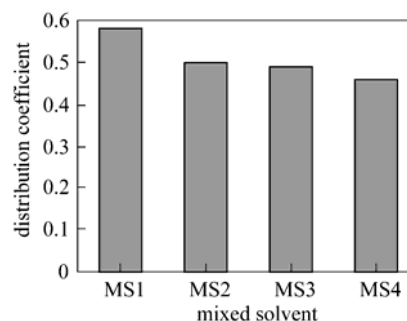


Figure 2 Comparison of different mixed solvents in extraction capacity

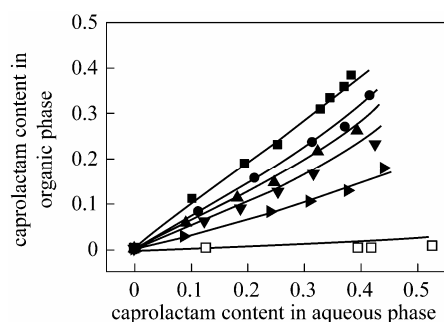
3.2 Selection of 1-octanol/cyclohexane ratio

Mixed solvents of 1-octanol+cyclohexane with different 1-octanol mass ratios were used to extract caprolactam from its aqueous solutions at 25°C. Caprolactam concentrations in two phases were measured, and the results are listed in Table 1. W_{org} and W_{aq} indicate caprolactam mass fraction in organic phase and aqueous phase, respectively. In Fig. 3, extraction results using 1-octanol as the extractant are also plotted for comparison [12]. It is obvious that cyclohexane has a very small extraction capacity. The amount of caprolactam extracted to the organic phase is strongly affected by the content of 1-octanol in the organic phase. The higher the 1-octanol content in the mixed solvent is, the larger the extraction capacity is. The 1-octanol solubility in the aqueous phase was determined when the caprolactam mass content in the aqueous phase was about 40%. For 50%, 60%, and 70% 1-octanol content in the mixed solvents, the results are 0.7%, 1.3%, and 2.1%, respectively. Considering higher 1-octanol solubility in the aqueous phase leads to larger extractant loss in raffinate, the mixed solvent with 60% 1-octanol content is selected as the preferable extractant.

The caprolactam distribution between two phases at 35°C and 45°C was determined, and the results are listed in Table 2. The influence of temperature on the experimental and calculated caprolactam distribution in two phases is shown in Fig. 4. The caprolactam

Table 1 Caprolactam distribution in the system water+caprolactam+1-octanol+cyclohexane at 25°C

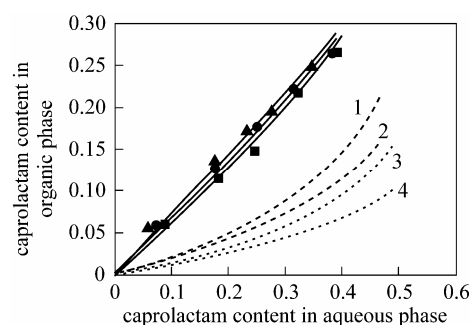
Mass content of 1-octanol in mixed solvents/%	W_{org}	W_{aq}
0	0.0030	0.1267
	0.0037	0.3948
	0.0047	0.4178
	0.0075	0.5264
	0.0084	0.5870
	0.0297	0.0883
	0.0848	0.2392
33.3	0.1058	0.3087
	0.1281	0.3763
	0.1814	0.4405
	0.0637	0.1237
	0.0906	0.1885
	0.1286	0.2536
	0.1670	0.3155
50	0.2329	0.4244
	0.0585	0.0891
	0.1139	0.1834
	0.1473	0.2468
	0.2172	0.3235
	0.2645	0.3920
	0.0846	0.1116
60	0.1559	0.2133
	0.2402	0.3132
	0.2721	0.3735
	0.3389	0.4152
70		

**Figure 3** Distribution of caprolactam when using a solvent mixture of 1-octanol and cyclohexane at 25°C (Dots refer to experimental results. Lines refer to calculation results) ■ 1-octanol; ● 1-octanol 70%; ▲ 1-octanol 60%; ▼ 1-octanol 50%; ▴ 1-octanol 33.3%; □ cyclohexane

distribution with benzene or toluene as the extractant is also plotted in Fig. 4. It can be concluded that the caprolactam concentration in the organic phase is increased considerably when temperature increases, which is caused by the weakening of the water-caprolactam

Table 2 Caprolactam distribution at 35°C and 45°C when using mixed solvent with 60% 1-octanol content

Temperature/°C	W_{org}	W_{aq}
35	0.0579	0.0746
	0.1264	0.1773
	0.1766	0.2521
	0.2216	0.3140
	0.2635	0.3855
45	0.0555	0.0596
	0.1349	0.1766
	0.1719	0.2322
	0.1935	0.2766
	0.2473	0.3465

**Figure 4** Distribution of caprolactam when using the new extractant at 25°C, 35°C, and 45°C (Dots refer to experimental results. Lines refer to calculation results) ■ new extractant, 25°C; ● new extractant, 35°C; ▲ new extractant, 45°C; 1—benzene, 45°C; 2—benzene, 25°C; 3—toluene, 45°C; 4—toluene, 25°C

hydrogen bond. For the new extractant, the extraction capacity is larger than benzene and toluene at all caprolactam concentrations and all temperatures.

There are numerous impurities in crude caprolactam, such as aniline, cyclohexanone, and methylcaprolactam. Compared with caprolactam, some impurities have similar molecular structures, for example, methylcaprolactam. They are difficult to be separated from caprolactam in industry. The UNIFAC model has been proved to be a powerful tool for the prediction of liquid-liquid phase equilibrium, especially for extension to systems containing similar groups [6]. In our previous work, new group of $\text{CH}_2\text{NHCOCH}_2$ was defined and new interaction parameters were calibrated based on the equilibrium results of the systems of water+caprolactam+1-octanol, water+caprolactam+1-heptanol, water+caprolactam+benzene, and water+caprolactam+toluene [12]. The calibrated results showed good agreement with experimental data. Therefore, the Lyngby modified UNIFAC model is applied for the description of equilibrium of caprolactam extraction system. The defined groups are listed in Table 3. The volume parameters, surface parameters, and interaction parameters of UNIFAC groups are taken from Ref. [12]. The calculation results are plotted in Fig. 3 and Fig. 4. The calculated results fit the experimental results well.

Table 3 Group divisions in UNIFAC model

	CH ₂ NHCOCH ₂	CH ₃	CH ₂	OH	H ₂ O	ACH	AC
caprolactam	1	0	3	0	0	0	0
1-octanol	0	1	7	1	0	0	0
water	0	0	0	0	1	0	0
cyclohexane	0	0	6	0	0	0	0
benzene	0	0	0	0	0	6	0
toluene	0	1	0	0	0	5	1

3.3 Phase separation

Physical properties such as density, viscosity, and interfacial tension of the liquid-liquid system influence the operation of extraction process [15]. Therefore, these physical properties of caprolactam extraction systems with 1-octanol and the new extractant were determined at room temperature. The density data of the systems 1-octanol+caprolactam and new extractant+caprolactam are plotted in Fig. 5. The density increases with increasing caprolactam mass fraction for all solvents. It can be observed that the new extractant has lower density, which results in a larger density difference with the aqueous phase. Therefore, application of the new extractant will lead to a larger driving force for phase separation, which is beneficial for extraction operation.

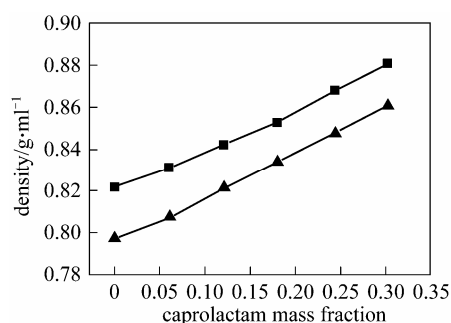
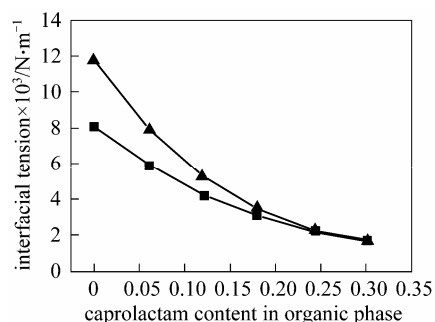
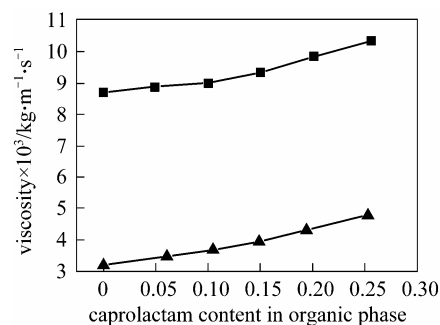
**Figure 5** The comparison of density
■ 1-octanol; ▲ new extractant

Figure 6 shows the comparison in interfacial tension of the new extractant and 1-octanol. It is obvious that the interfacial tension decreases with increasing caprolactam concentration for two extractants. Com-

**Figure 6** The comparison of interfacial tension
■ 1-octanol; ▲ new extractant

pared with 1-octanol, the interfacial tension of the new extractant is higher, especially when caprolactam content is not very large. Higher interfacial tension will help to obtain phase separation more quickly.

In Fig. 7, the viscosity increases with increasing caprolactam content for the two extractants. Furthermore, it can be observed that the new extractant system has lower viscosity at all caprolactam concentrations. If a liquid is the continuous phase during extraction operation, a lower viscosity is favorable because it results in a reduced resistance for traveling of drops. This will be helpful for phase separation.

**Figure 7** The comparison of viscosity
■ 1-octanol; ▲ new extractant

The new extractant and 1-octanol were used to extract caprolactam from lactam oil with phase ratio equal to 1, respectively. After stirring for 3 h, the two systems were settled for phase separation. For the new extractant, phase separation reached in 10 min. For 1-octanol, phase separation was not observed in 30 min. It verified the improvement of new extractant in phase separation ability.

3.4 Selectivity

There are several quality indexes to describe the impurity content in caprolactam product, such as permanganate number, volatile bases, and caprolactam solution's absorbance at 290 nm. Because absorbance of caprolactam solution at 290 nm of final product is considered to be directly related to intermediate product after the extraction process, this index is selected to describe the impurity content. The new extractant was used to extract equal volume lactam oil at room temperature. After extraction, the extract was separated. The caprolactam concentration and absorbance in the extract were then measured. 20 ml extract was back extracted with different volume water. After back extraction, the caprolactam concentration and absorbance of two phases were determined. The results are listed in Table 4. When using more water in stripping, caprolactam concentration and absorbance in two phases decreased. But to the organic phase, absorbance value decreased in a smaller content than caprolactam concentration. It indicates that the new extractant can remain with some impurities in organic phase. When small amount of water is applied, the absorbance in aqueous phase could reach a high value, which maybe much higher than the absorbance value

Table 4 Extraction results when dealing with lactam oil

Water volume/ml	Phase	Caprolactam concentration/g·L ⁻¹	Absorbance
2	extract	302.7	1.061
	organic	229.1	0.564
	aqueous	400.0	2.075
5	organic	190.5	0.455
	aqueous	339.0	1.483
10	organic	129.4	0.416
	aqueous	275.1	0.953
20	organic	95.73	0.398
	aqueous	194.7	0.585

in extract. It indicates some impurities extracted from lactam oil are preferred to concentrating in aqueous phase. Therefore, a water washing process is recommended before water stripping process [20]. The water washing process can remove considerable impurities with little loss of caprolactam, and a higher selectivity can be obtained in the extraction process.

4 CONCLUSIONS

1-Octanol is considered as a low toxic extractant with large capacity for caprolactam mass extraction. But after back extraction, caprolactam mass content in the aqueous phase is difficult to reach 30% for the high solubility of 1-octanol in aqueous phase. In order to reduce the solubility of 1-octanol in the aqueous phase, cyclohexane was selected as the additive solvent, which has less negative effect on extraction capacity compared with other alkanes investigated. The extraction capacities of the mixture of 1-octanol and cyclohexane with different 1-octanol content were measured at 25°C. Considering to control the solubility of 1-octanol in the aqueous phase in an acceptable range, mixed solvents with 60% 1-octanol content was recommended as the new extractant for caprolactam extraction. Caprolactam distribution between two phases using the new extractant at 35°C and 45°C was also determined. It was found that the new extractant has larger extraction capacity than benzene or toluene at all experimental temperatures. The equilibrium results were described using Lyngby modified UNIFAC model and the calculated results agreed well with experimental results. Compared with 1-octanol, the new extractant performed much better phase separation ability when directly dealing with lactam oil. The reasons include lower density, lower viscosity, and higher interfacial tension. The new extractant also showed certain selectivity in back extraction process. After extraction, a water washing process is recommended before water stripping process to improve extraction selectivity.

REFERENCES

- van Delden, M.L., Drumm, C., Kuipers, N.J.M., de Haan, A.B., "Impurity distribution behavior in caprolactam extraction with environmentally benign mixed solvents", *Chem. Eng. Technol.*, **29**, 1221–1226 (2006).
- Xie, F.Y., Zhu, M.Q., Liu, J.Q., He, C.H., "Extraction of caprolactam from aqueous ammonium sulfate solution in pulsed packed column using 250Y Mellapak packings", *Chin. J. Chem. Eng.*, **10**, 677–680 (2002).
- Xie, F.Y., "Extraction of caprolactam in the (NH₄)₂SO₄ aqueous solution using pulsed column with various inner parts", *Chem. Ind. Eng. Progr.*, **21**, 922–925 (2002).
- van Delden, M.L., Kuipers, N.J.M., De Haan, A.B., "Liquid-liquid equilibria and physical properties of the quaternary systems water+caprolactam+ammonium sulfate+benzene and toluene", *J. Chem. Eng. Data*, **49**, 1760–1770 (2004).
- Zhou, H., van Bochove, G.H., de Loos, T.W., "Three-liquid phase equilibria in water+benzene+caprolactam+(NH₄)₂SO₄ mixtures", *AIChE J.*, **49**, 745–752 (2003).
- Gong, X.C., Lu, Y.C., Luo, G.S., "Distribution coefficient of caprolactam and methyl caprolactam using benzene or toluene as extractants: Experiments and prediction", *Chin. J. Chem. Eng.*, **15**, 463–467 (2007).
- Morachevskii, A.G., Sabinin, V.E., "Solubility diagrams for the ternary systems caprolactam-water-benzene, caprolactam-water-carbon tetrachloride, and caprolactam-water-dichloroethane", *J. Appl. Chem.*, **33**, 1755–1758 (1960).
- Tettamanti, K., Nogradi, M., Sawinsky, J., "Equilibria of the ternary system caprolactam/water/organic solvent, in the liquid state", *Period. Polytech. Chem. Eng.*, **4**, 201–218 (1960).
- Xie, F., "Liquid-liquid equilibria of caprolactam-H₂O-(NH₄)₂SO₄-C₆H₆ system at low caprolactam concentrations", *Chem. Ind. Eng. Progr.*, **21**, 839–841 (2002).
- Liu, J.Q., Xie, F.Y., He, C.H., Zhu, M.Q., "Recovery of caprolactam from waste water in caprolactam production using pulsed-sieve-plate extraction column", *Chin. J. Chem. Eng.*, **10**, 371–373 (2002).
- Glazko, I.L., Druzhinina, Y.A., Levanova, S.V., "Performance and selectivity of organic solvents in extraction of caprolactam from lactam oil", *Russ. J. Appl. Chem.*, **80**, 941–944 (2007).
- Gong, X.C., Lu, Y.C., Zhang, Y.N., Gao, M.Y., Luo, G.S., "Liquid-liquid equilibria of the quaternary system water+caprolactam+1-octanol+ammonium sulfate", *J. Chem. Eng. Data*, **52**, 851–855 (2007).
- Zhenleznova, N.I., Popov, D.M., Kanakina, S.V., "Phase equilibrium in the caprolactam-toluene-water system", *J. Appl. Chem. USSR*, **58**, 1900–1903 (1986).
- Pajak, M., Piotrowicz, J., Skrzypinski, W., "Extraction of caprolactam in packed columns", *Przem. Chem.*, **71**, 107–110 (1991).
- van Delden, M.L., Kuipers, N.J.M., de Haan, A.B., "Selection and evaluation of alternative solvents for caprolactam extraction", *Sep. Purif. Technol.*, **51**, 219–231 (2006).
- Wijtkamp, M., van Bochove, G.H., de Loos, T.W., Niemann, S.H., "Measurements of liquid-liquid equilibria of water+ε-caprolactam+electrolyte+organic solvent systems", *Fluid Phase Equilib.*, **158-160**, 939–947 (1999).
- van Bochove, G.H., Krooshof, G.J.P., de Loos, T.W., "Two- and three-liquid phase equilibria in the system water+2-heptanone+caprolactam+ammonium sulfate: Experiments and modeling", *Fluid Phase Equilib.*, **194-197**, 1029–1044 (2002).
- Tettamanti, K., Nogradi, M., "The influence of ammonium sulphate on the distribution of caprolactam in the water/trichloro ethylene system", *Period. Polytech. Chem. Eng.*, **5**, 15–23 (1960).
- Larsen, B., Rasmussen, P., Fredenslund, A., "A modified UNIFAC group-contribution model for prediction of phase equilibria and heats of mixing", *Ind. Eng. Chem. Res.*, **26**, 2274–2286 (1987).
- Alessi, V., Penzo, R., Slater, M.J., Tessari, R., "Caprolactam production: A comparison of different layouts of the liquid-liquid extraction section", *Chem. Eng. Technol.*, **20**, 445–454 (1997).