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Research Article

Impurity Distribution Behavior in Caprolactam Extraction with Environmentally Benign Mixed Solvents

In a previous study a solvent mixture of heptane containing 40 mass % heptanol was selected as an alternative in the industrial extraction of caprolactam to replace benzene, toluene, or chlorinated hydrocarbons. This work reports the equilibrium distribution ratio of caprolactam and four model impurities of organic nature, namely, cyclohexanone, aniline, n-methylcaprolactam, and cyclohexane-carboxamide, comparing the mixed solvents with toluene as a reference. The resulting phase equilibria were interpreted using the equilibrium stage model. Based on these calculations it was found that, compared to toluene, the co-extracted fraction of cyclohexanone and aniline was higher, that of n-methylcaprolactam was comparable, and that of cyclohexane-carboxamide was lower using the mixed solvent. Overall, the mixed solvent reduced the fraction of co-extracted impurities by almost 10 %.

Keywords: Caprolactam, Extraction, Phase equilibrium, Solvents, Impurities

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1 Introduction

Caprolactam is recovered by phase separation from the neutralized Beckmann rearrangement mixture, where both streams contain various impurities, followed by solvent extraction of the resulting crude caprolactam phase, the so-called forward extraction, and the aqueous ammonium sulfate layer [1, 2]. Currently, benzene, toluene, and chlorinated hydrocarbons are used as solvents in the caprolactam extraction process. Because of the negative effects on health and environment of these solvents and the resulting strict legislation, the need exists for an alternative solvent. In a previous study a mixed solvent composed of an alkane, being heptane or methylcyclohexane, and an alcohol, 40 mass % heptanol, was selected from an experimental screening procedure. The solvent mixture heptane + heptanol (40 mass %) was finally selected as a replacement solvent based on its beneficial physical properties, since the phase compositions of both candidate solvent mixtures are similar and the results are satisfying relative to conventional solvents [3].

The impurities entering the forward extraction process are remnants from the feedstock (benzene, toluene, phenol, cyclohexane, etc.), by-products formed in the reaction steps (oxidation, hydrogenation, dehydrogenation, Beckmann rearrangement, etc.), and/or additional compounds introduced in the different process steps (neutralization, extraction, etc.). They are of both inorganic and organic nature [1, 4, 5], of which mainly the latter are extracted along with caprolactam in the forward extraction [1].

The specifications for fiber-grade commercial caprolactam are severe, resulting in a required high purity (> 99.9 %). The impurities present in the crude caprolactam need therefore to be reduced to a very low level [1, 4, 6]. After the first separation step, which is the extraction, a series of purification steps, including chemical treatment and vacuum distillation, is applied to obtain the required purity [1]. Changing the solvent in the extraction process might result in a different impurity profile in the extract and therefore a different composition of the feed for the final purification, which needs to be identified before the implementation of the alternative solvent.

Therefore, in the present study the equilibrium distribution ratios of caprolactam and four model impurities of organic nature were studied at 293 K, 313 K, and 333 K in toluene as a reference solvent and in both alternative mixed solvents, in order to determine the effect of different solvent mixtures on the distribution ratio. The experimental conditions covered the industrial operating range with respect to the concentrations of caprolactam and ammonium sulfate. The phase equilibria results were interpreted using the equilibrium stage model for a conceptual extraction column design.

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2 Experimental Setup and Procedure

2.1 Model Impurities

In the crude caprolactam phase a large amount of impurities can be detected [5]. These are represented by four model impurities detected in crude caprolactam covering (I) impurities with low boiling points compared to caprolactam, (II) impurities with a moderate boiling point, (III) derivatives of caprolactam, and (IV) impurities with a boiling point higher than caprolactam. The selected model impurities were cyclohexanone (I) [4, 5], aniline (II) [4], n-methylcaprolactam (III) [4, 6], and cyclohexane-carboxamide (IV) [5], which are structures comparable to those used in other model studies [6]. The structural formulas of these model impurities are shown in Fig. 1.

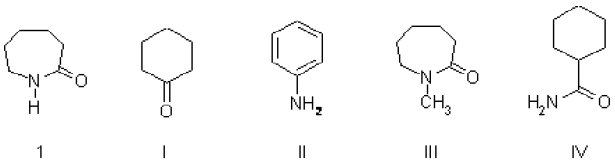

Figure 1. Structural formulas of: 1 caprolactam; I cyclohexanone; II aniline; III n-methylcaprolactam; IV cyclohexane-carboxamide.

2.2 Equilibrium Measurements

The following procedure was followed to obtain experimental data [7]. The used apparatus consisted of a stirred glass vessel surrounded by a thermostat jacket. The temperature inside the vessel was controlled to within 0.1 K by a water bath that was connected to the jacket. A sample point was present for each phase. The cell was placed on the plate of a multiple point magnetic stirrer and a magnetic bar was used for agitation. Liquid mixtures were prepared by weighing the pure components, such that almost equal volumes of 20 mL were obtained for both liquid phases. The initial mass fraction of caprolactam in the aqueous phase ranged from $w_{\mathrm{CPL,aq}} = 0.3$–$0.7$ and the initial organic heptanol mass fraction was $w_{\mathrm{heptanol,org}} = 0.4$. To the aqueous mixture 0.5 mass % of each impurity was added and 1.5 mass % ammonium sulfate if required. The mixtures were stirred for at least 45 min to be sure that equilibrium was reached and then allowed to settle for at least 1 h after which the phases were completely separated. Then samples were taken from both phases with a syringe. The samples were diluted and prepared for analysis. The determined equilibrium data were interpreted using the distribution ratio, $K_{\mathrm{D,i}}$ [3], which is defined as the ratio of the determined solute mass fractions in the organic phase, $w_{\mathrm{i,org}}$, and in the aqueous phase, $w_{\mathrm{i,aq}}$, at equilibrium:

$$K_{\mathrm{D,i}} = \frac{w_{\mathrm{i,org}}}{w_{\mathrm{i,org}}} \tag{1}$$

This distribution ratio represents the capacity of a solvent system for the extraction of caprolactam and was used for interpretation and evaluation of the experimental results.

2.3 Chemicals

All chemicals were used as received. These are: ε-caprolactam (purity 99 %), ammonium sulfate (purity > 99 %), methylcyclohexane, and n-methylcaprolactam (purity 99 %) from Sigma-Aldrich (USA), 1-heptanol (purity 98 %) and cyclohexane-carboxamide (purity 97 %) from Acros (Belgium), cyclohexanone (purity > 99 %), aniline (purity > 99.5 %), and n-heptane (purity > 99 %) from Merck (Germany). MilliQ water was used in all experiments.

2.4 Chemical Analysis

The mass fraction of caprolactam and the impurities in both the organic and the aqueous phase was determined by gas chromatography [3, 7]. The same analytical procedure was applied for both phases and each solvent. An aqueous mixture containing 0.5 mass % of the four impurities was analyzed four times with an uncertainty of 0.01 mass %. The mass fraction of ammonium sulfate in the aqueous phase was determined via ion chromatography [7] and the amount of ammonium sulfate distributed in the organic phase was assumed to be negligible.

3 Experimental Results and Discussion

3.1 Toluene

In Fig. 2 the results are shown for the distribution ratio of all four model impurities and caprolactam with toluene as a benchmark solvent at 293 K and 333 K. The data measured are compared with the equilibrium distribution ratio for toluene under similar conditions.

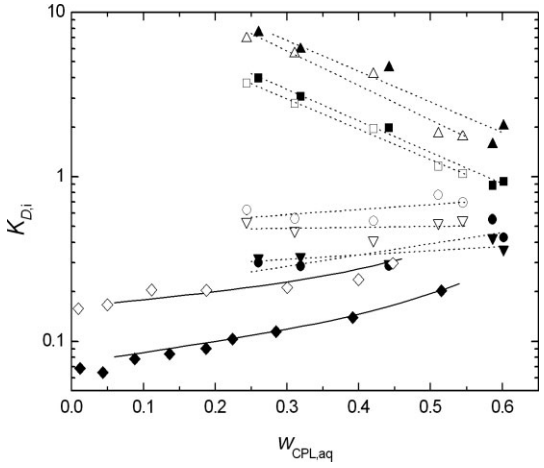

Figure 2. Equilibrium distribution ratio as a function of $w_{\mathrm{CPL,aq}}$ with toluene as a solvent at 293 K: ◆ caprolactam; ■ aniline; ● n-methylcaprolactam; ▲ cyclohexanone; ▼ cyclohexane-carboxamide; at 333 K: corresponding open symbols; and: — NRTL fit of the distribution ratio of caprolactam [7]; - - trend lines.

From Fig. 2 it can be seen that all impurities at both temperatures showed a distribution ratio higher than the distribution ratio of caprolactam. Furthermore, the model impurities show different behavior in the liquid-liquid system due to differences in the chemical structure. n-Methylcaprolactam, as a derivative of caprolactam, and cyclohexane-carboxamide, because of the strong amide-water interaction, both showed low distribution ratios that increased slightly with an increasing concentration of caprolactam in the aqueous phase, which is comparable to the behavior of caprolactam itself. The less polar aniline and cyclohexanone showed high distribution ratios that decreased with increasing concentrations of caprolactam. The dependence of the distribution ratios on the amount of caprolactam present in the system is explained by the fact that both phases become more alike at higher concentrations of caprolactam. An increasing temperature resulted in a slight increase of the distribution ratios for n-methylcaprolactam and cyclohexane-carboxamide, which is the same trend as that for caprolactam, while the distribution ratios for aniline and cyclohexanone decreased. This first observation is explained by the weakening of hydrogen bond formation in the aqueous phase with increasing temperature, whereas in this phase the repelling forces to non-polar organic components decrease, explaining the latter observation.

In the crude lactam phase 1–1.5 mass % ammonium sulfate is present. It is known that its presence increases the distribution ratio of caprolactam because of the salting-out effect (precipitation due to high salt concentrations). The influence of this effect on the distribution ratio of the impurities was investigated at 293 K, 313 K, and 333 K by addition of an initial amount of 1.5 mass % ammonium sulfate to the above aqueous mixture before extraction. This resulted in equilibrium concentrations of 1.5–2.0 mass %. The impurity distribution ratio at 313 K, with and without ammonium sulfate, is shown in Fig. 3, compared to caprolactam.

From Fig. 3 it can be concluded that with ammonium sulfate present the distribution ratio of the impurities seems to increase slightly. Similar to caprolactam the increase is caused by salting out. The effect shown in this figure is, however, not very large and will therefore not be investigated further in this study, although it should be taken into account for detailed process design. Furthermore, it can be seen that all trends observed were similar to those already shown in Fig. 2, which was also the case for the determined temperature effect.

3.2 Mixed Solvents

Whether and how the impurity distribution ratio changes when applying both selected mixed solvents, being heptane + heptanol (40 mass %) and methylcyclohexane + heptanol (40 mass %) is shown in Fig. 4 for temperatures of 293 K, 313 K, and 333 K.

In Fig. 4 it can be seen that, as for toluene, the impurity distribution ratio is comparable or higher than the distribution ratio of caprolactam in both mixed solvents. Furthermore, it is shown that the impurity distribution ratio was similar for both mixed solvents used. The solvent mixture heptane + heptanol (40 mass %) was selected as a candidate solvent based on its beneficial physical properties, since the distribution ratio of caprolactam and the mutual solvent solubility were similar for both solvents [3]. As the impurity distribution ratio is equal for both solvent mixtures as well, the previously selected

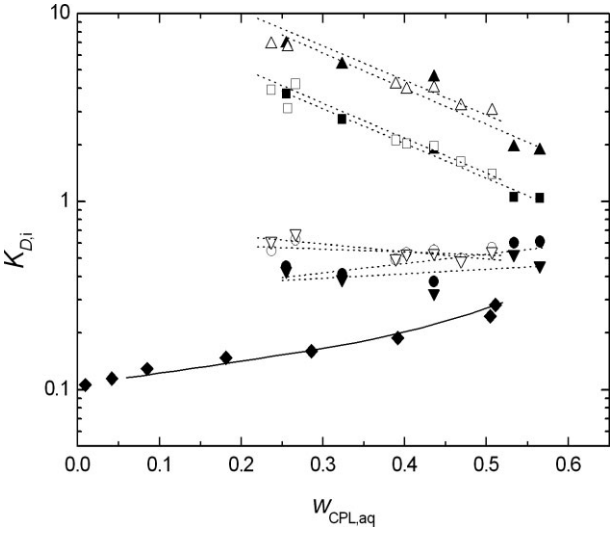

Figure 3. Equilibrium distribution ratio as a function of $w_{CPL,aq}$ with toluene as a solvent at 313 K: ◆ caprolactam; ■ aniline; ● n-methylcaprolactam; ▲ cyclohexanone; ▼ cyclohexane-carboxamide; and with 1.5 mass % ammonium sulfate: corresponding open symbols; and: — NRTL fit of the distribution ratio of caprolactam [7]; - - trend lines.

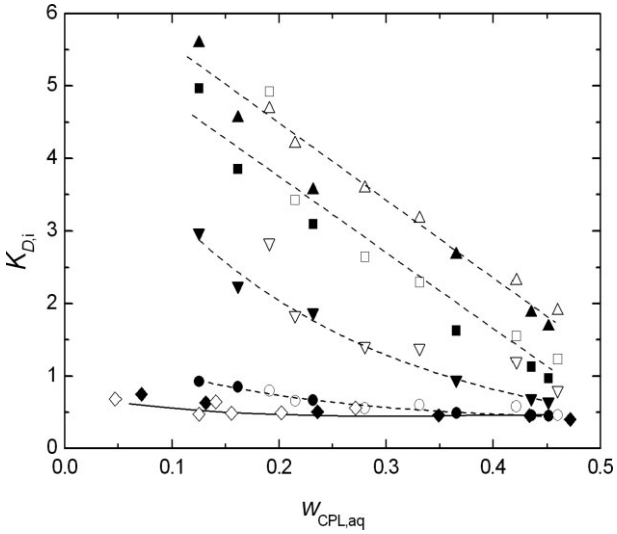

Figure 4. Equilibrium distribution ratio as a function of $w_{CPL,aq}$ with heptane + heptanol (40 mass %) as a solvent at 313 K: ◆ caprolactam; ■ aniline; ● n-methylcaprolactam; ▲ cyclohexanone; ▼ cyclohexane-carboxamide; and for methylcyclohexane + heptanol (40 mass %): corresponding open symbols; and: — NRTL fit of the distribution ratio of caprolactam [7]; - - trend lines.

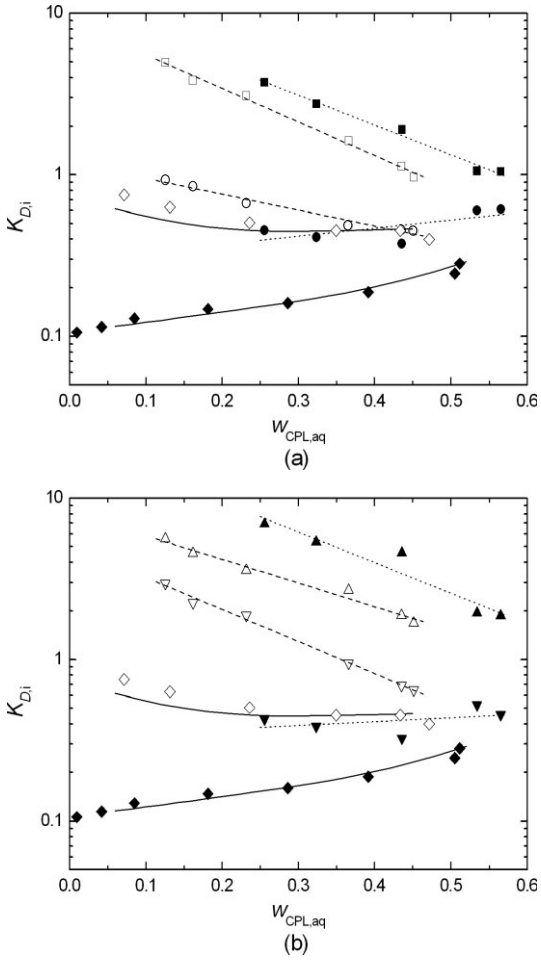

Figure 5. Equilibrium distribution ratio as a function of $w_{CPL,aq}$ with toluene as a solvent at 313 K: ◆ caprolactam; ■ aniline (a); ● n-methylcaprolactam (a); ▲ cyclohexanone (b); ▼ cyclohexane-carboxamide (b); and for heptane + heptanol (40 mass %): corresponding open symbols; and: — NRTL fit of the distribution ratio of caprolactam [3, 7]; -- trend lines for toluene; – – trend lines for mixed solvent.

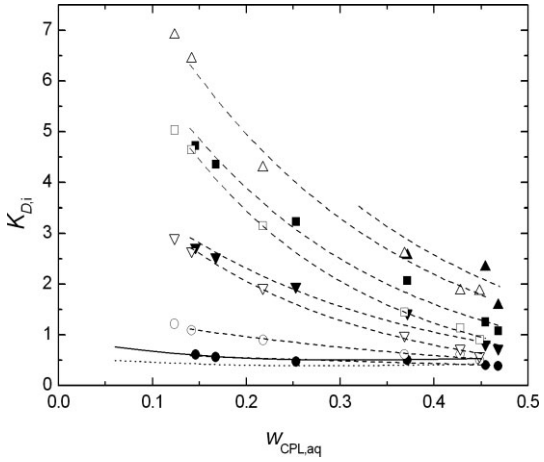

Figure 6. Equilibrium distribution ratio as a function of $w_{CPL,aq}$ with heptane + heptanol (40 mass %) as a solvent at 293 K: ■ aniline; ● n-methylcaprolactam; ▲ cyclohexanone; ▼ cyclohexane-carboxamide; and at 333 K: corresponding open symbols; – – trend lines; and NRTL fit of the distribution ratio of caprolactam [3, 7]: -- 293 K; — 333 K.

solvent was investigated further as best alternative solvent for the extraction of caprolactam.

The caprolactam and impurity distribution ratio for heptane + heptanol (40 mass %) at 313 K are shown in Figs. 5(a) and 5(b), and compared to those in toluene.

From Fig. 5 it can be seen that the distribution ratio for some impurities differed compared to the distribution in toluene. The equilibrium data for aniline and n-methylcaprolactam were more or less comparable to those in toluene showing a slight decrease and increase, respectively, but the distribution ratio of cyclohexanone decreased strongly, whereas the distribution ratio of cyclohexane-carboxamide increased significantly. From the equilibrium distribution ratio of caprolactam it is known that it is higher for the mixed solvents compared to toluene because of the presence of heptanol, which is capable of hydrogen bond formation. This influence also seems to be valid for n-methylcaprolactam and especially for cyclohexane-carboxamide, while aniline and particularly cyclohexanone are repelled by the more polar organic phase.

In Fig. 6 the influence of the temperature on the impurity distribution ratio is shown using heptane + heptanol (40 mass %) as solvent relative to the fitted distribution ratio of caprolactam.

It can be seen in Fig. 6 that the distribution ratio decreases with increasing temperature for aniline and cyclohexanone, whereas it increases for n-methylcaprolactam, as was the case with toluene. The presented influence can be explained by the lower hydrogen bonding strength at elevated temperatures. Furthermore, the non-polar organic compounds are less repelled by the aqueous phase.

For cyclohexane-carboxamide, however, a decrease of the equilibrium distribution was observed, which was the opposite effect compared to that in toluene. From Fig. 5 it was concluded that the presence of heptanol in the organic phase resulted in a strong increase of the cyclohexane-carboxamide distribution relative to toluene. Apparently, the interaction of cyclohexane-carboxamide with heptanol is strong compared to the interaction with water. At elevated temperatures, the strength of the hydrogen bond with water, but especially heptanol, decreases and non-polar organic compounds are less repelled by the aqueous phase. Therefore, the equilibrium distribution of cyclohexane-carboxamide decreased with an increasing temperature for the mixed solvent.

Finally it can be seen that the distribution ratio of the impurities is comparable or higher than that of caprolactam, as was also the case in toluene.

3.3 Equilibrium Calculations

Using equilibrium data and the solvent-to-feed ratio, S/F, the number of theoretical stages, NTS, needed for the extraction

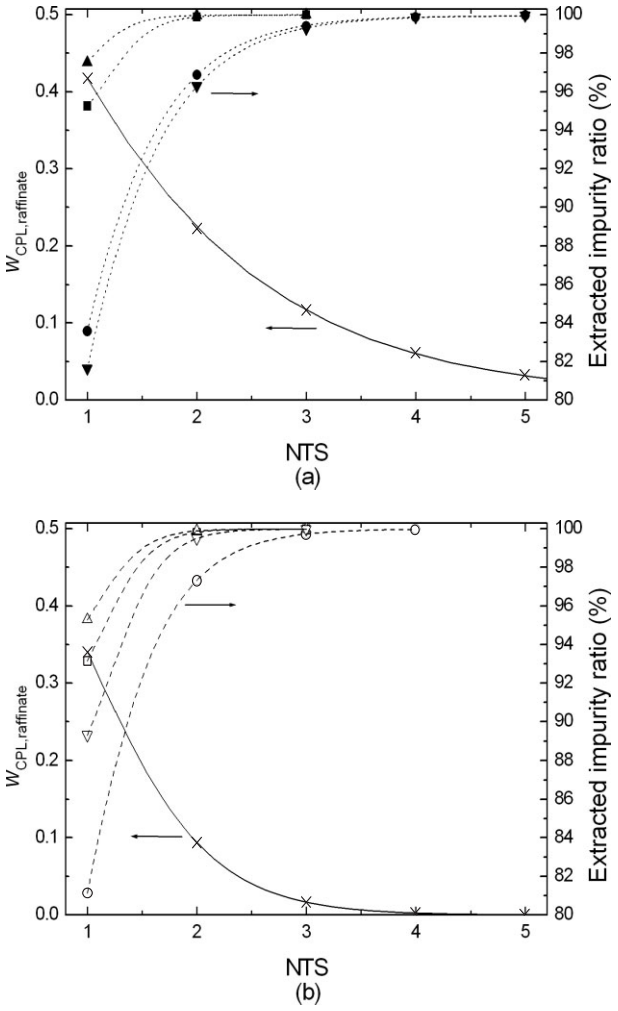

Figure 7. Calculated concentration of caprolactam in the raffinate as a function of the NTS with toluene (a) and heptane + heptanol (40 mass %) (b) as a solvent in the forward extraction: × caprolactam; — trend line; and the extracted impurity ratios (a): ■ aniline; ● n-methylcaprolactam; ▲ cyclohexanone; ▼ cyclohexane-carboxamide; -- trend line; and (b): corresponding open symbols; – – trend line.

of caprolactam according to the industrial DSM process layout [1] with toluene and the proposed best solvent mixture heptane + heptanol (40 mass %) was calculated. Furthermore the fraction of impurities extracted was calculated. In the calculations the influence of the extracted fraction of caprolactam on the mass flows was taken into account, but the influence of the impurities was assumed negligible. Furthermore, it was assumed that there was no mutual solubility of both phases and that no ammonium sulfate was present in the feed stream, while the extraction of the aqueous ammonium sulfate layer, which is present in the reference process, was not taken into account.

In the forward extraction of caprolactam a 70 mass % aqueous caprolactam phase is extracted at 313 K with an organic solvent. The S/F ratios for toluene and the mixed solvent were calculated as S/F = 5.0 and 3.0, respectively, which is equal to 1.5 times the minimum S/F ratio for both. In Fig. 7 the fraction of impurities extracted along with caprolactam is shown as a function of the NTS for toluene (a) and the mixed solvent (b). It can be seen that for both solvents all impurities (100 %) are present in the extract after NTS = 5 and 4, respectively. Furthermore in this figure, the caprolactam raffinate concentration is shown as a function of the NTS. It was calculated that the mixed solvent with NTS = 5 only needs one half of the NTS in order to reach the required raffinate concentration of $w_{CPL,raffinate} < 5 \cdot 10^{-4}$ relative to toluene under equal conditions. Based on these calculated values of NTS it can therefore be concluded that for both solvents in the forward extraction process the total fraction of impurities, 100 %, is present in the extract. This can be explained by the fact that all impurities possess a distribution coefficient higher than caprolactam.

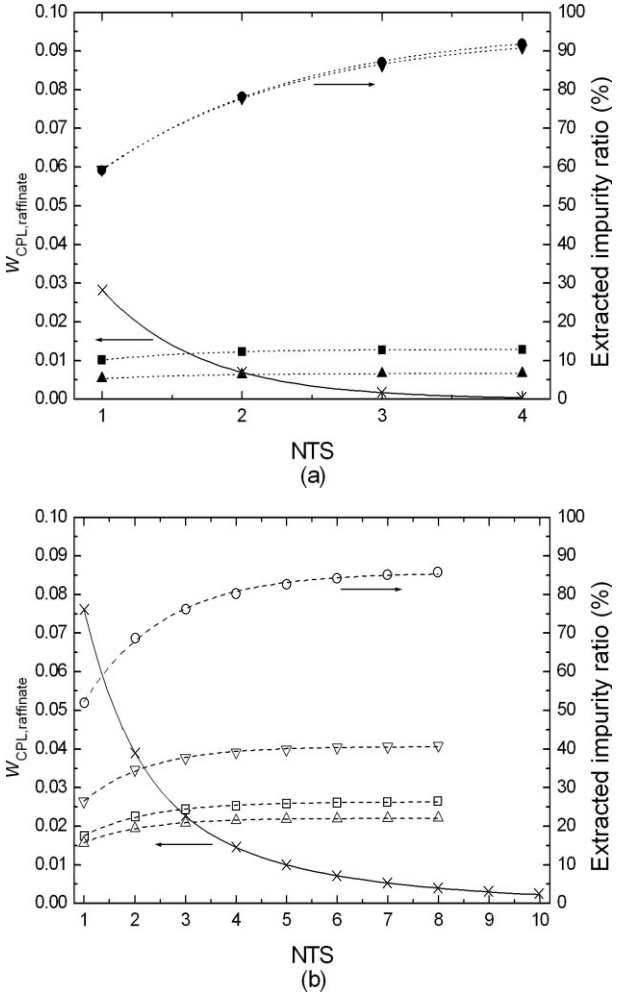

Figure 8. Calculated concentration of caprolactam in the raffinate as a function of the NTS with toluene (a) and heptane + heptanol (40 mass %) (b) as feed phase in the back-extraction: ○ caprolactam; — trend line; and the extracted impurity ratio (a): ■ aniline; ● n-methylcaprolactam; ▲ cyclohexanone; ▼ cyclohexane-carboxamide; -- trend line; and (b): corresponding open symbols; – – trend line.

Table 1. Calculated extracted impurity ratio for toluene and mixed solvent as feed in the back-extraction.

	Cyclohexanone	Aniline	n-Methyl-caprolactam	Cyclohexane-carboxamide	Total
Toluene	6.7 %	12.9 %	92.0 %	91.0 %	50.6 %
Mixed solvent	22.2 %	26.5 %	85.9 %	40.9 %	43.9 %

In the back-extraction the caprolactam-rich organic phase from the forward extraction is re-extracted at 313 K with water as a solvent. Using the extract concentration from the forward extraction, $w_{CPL,extract}$ = 0.123 and 0.189 for toluene and the mixed solvent, respectively, the minimum S/F ratio was calculated at $(S/F)_{min}$ = 0.26 and 0.45, respectively, resulting in S/F = 0.39 and 0.67 for toluene and the mixed solvent. The calculated raffinate fraction of caprolactam as a function of the amount of equilibrium stages is shown in Figs. 8(a) and 8(b) for toluene and the solvent mixture, respectively. Furthermore the extracted impurity ratio is presented as a function of the amount of equilibrium stages.

From Fig. 8 it can be concluded that the trend shown for the required amount of equilibrium stages for caprolactam extraction is reversed. This behavior can be understood from the equilibrium distribution ratio of caprolactam, which is higher for the mixed solvent compared to toluene. This results, furthermore, in a reduced amount of mixed solvent required in the forward extraction, while in the back-extraction the toluene process can operate with a lower S/F ratio. Since, however, the amount of toluene used in the forward extraction is 1.7 times higher than the amount of mixed solvent and the S/F ratio for the toluene process in the back-extraction is 1.7 times lower, the absolute amount of water required in the back-extraction is similar for both processes. Furthermore, in the back-extraction the distribution coefficient in the solvent is favorable for caprolactam and since the distribution coefficients differ for the impurities and is different for each impurity in the different solvents according to Fig. 5, different profiles are calculated. The resulting impurity amount in the extract of the back-extraction compared to the initial amount fed in the forward extraction using toluene and heptane + heptanol (40 mass %) is shown in Tab. 1.

From Tab. 1 it can be seen that the amount of cyclohexanone and aniline extracted with the mixed solvent is higher than that in toluene. This can be understood from Fig. 5, where it is shown that the equilibrium distribution of these impurities is higher for toluene. In the back-extraction, both impurities are therefore extracted in a larger amount by the aqueous solvent phase from the mixed solvent feed. For cyclohexane-carboxamide the opposite trend can be seen, since the equilibrium distribution is lower for toluene. The equilibrium distribution of n-methylcaprolactam is comparable for both solvents and therefore the extracted amount by the water phase is also comparable. Overall, the mixed solvent reduced the fraction of co-extracted impurities with almost 10 %.

4 Conclusions

For the model impurities, cyclohexanone, aniline, n-methyl-caprolactam, and cyclohexane-carboxamide, at all conditions, it was found that the distribution in the organic phase was higher compared to that of caprolactam. Furthermore, it can be concluded that changing the alkane structure in the mixed solvent from heptane to methylcyclohexane did not influence the impurity distribution ratio. Salting out caused by the presence of an initial 1.5 mass % of ammonium sulfate was determined for the toluene system, but the effect on the impurity distribution ratio was not large. The temperature influence was measured, but the effect differed depending on the solvent system and chemical structure of the impurities.

Using the equilibrium stages model, the fraction of model impurities present in the extract of the back-extraction was calculated for toluene and the mixed solvent. The model impurities cyclohexanone and aniline were present in a higher ratio using the mixed solvent. For n-methylcaprolactam the fraction was comparable to toluene. Cyclohexane-carboxamide was present in a significantly lower amount compared to toluene. Overall it can be concluded that the fraction of impurities co-extracted with toluene was higher than with the new environmentally benign mixed solvent.

Acknowledgements

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