

Selection and evaluation of alternative solvents for caprolactam extraction

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Abstract

Because of the strict legislation for currently applied solvents in the industrial extraction of caprolactam, being benzene, toluene and chlorinated hydrocarbons, a need exists for alternative, environmentally benign solvents. An experimental screening procedure consisting of several steps was used to determine a suitable replacement solvent. (1) The distribution ratio of caprolactam was investigated at 293 K for an initial 10 mass% aqueous caprolactam solution; (2) the capacity and mutual solvent solubility were determined as function of the aqueous caprolactam concentration at equilibrium for solvents or solvent mixtures showing favourable capacities compared to benzene and toluene; (3) the equilibrium phase compositions for conditions covering the full industrial range were determined and correlated using the NRTL model for solvents or mixtures showing favourable characteristics compared to benzene and toluene; (4) the physical properties, being density and viscosity data of the separate phases and interfacial tension data of the liquid–liquid systems were determined and correlated for the remaining candidate solvents. It was found that the caprolactam distribution ratio increased with increasing solvent (mixture) polarity, characterized by a more polar active group (ether, ester, ketone and alcohol), decreasing carbon chain length of the polar solvent (C_{12} – C_6) or increasing polar solvent fraction in the mixture. Based on a high capacity, a low mutual solvent solubility and beneficial physical properties the solvent mixture of 40 mass% heptanol in heptane was finally selected as replacement solvent. Calculating the solvent to feed ratio (S/F) and the number of theoretical stages (NTS) needed to reach the industrially required raffinate concentrations, it was found that in the forward extraction the S/F is 3.0 for the mixed solvent and benzene, whereas the NTS is 5 and 9, respectively. In the back-extraction the S/F is 0.67 whereas the NTS is 10 and 5 for the solvent mixture and benzene, respectively.

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1. Introduction

Caprolactam, the monomer of nylon-6, is recovered from the Beckmann rearrangement mixture by neutralizing the reaction mixture with aqueous ammonia, which results in the formation of two liquid phases. The crude caprolactam phase consists of 65–70 mass% caprolactam, 1–1.5 mass% ammonium sulfate and water. This top layer is in equilibrium with a nearly saturated aqueous ammonium sulfate solution containing 1–1.5 mass% residual caprolactam. After separation of the two phases, the caprolactam is in industrial practise recovered from each phase by solvent extraction, for which currently benzene, toluene or chlorinated hydrocarbons are often used as the organic solvent [1,2].

Because of the negative effects on health and environment of these solvents and the resulting strict legislation [3–6],

the need exists to replace the currently used solvents in the caprolactam extraction process with an environmentally benign one. For a possible alternative solvent the system water + caprolactam + replacement solvent should show a capacity and a mutual solvent solubility comparable to those of the currently applied solvents or better [2]. Research on alternative solvents in literature is limited to 1-heptanol and 2-heptanone, where the influence of caprolactam and ammonium sulfate concentrations and temperature on the phase compositions is described [7,8]. For cyclohexanol, the binodal is determined at 293 K [9]. Furthermore, the equilibrium distribution of caprolactam is investigated as function of the carbon chain length for a series of linear alcohols (C_5 – C_8), but the experimental conditions were very limited [10]. These polar systems all show a favourable equilibrium distribution of caprolactam, but also a relatively high mutual solvent solubility compared to the currently used solvents. Non-polar solvents possess a low mutual solubility, but show a non-favourable capacity towards caprolactam [11].

The need for the replacement of solvents and the selection of substitute candidates is a result of strict environmental legisla-

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tion and/or the specific solvent properties that are required. This resulted in various studies on solvent selection procedures for the painting, cleaning and extraction industry [12,13], specific procedures for extraction processes [14,15] and selection procedures for other applications [16,17]. The selection of alternative solvents can be performed empirically, theoretically or experimentally. Empirical methods generally compare one or more properties of solvents to classify them and to assess the solvent capacity [18,19]. These methods, however, can only identify possible alternative solvent classes, but the selection of a specific solvent is not possible. Theoretical screening methods are based on a thermodynamic description of the investigated system. Here, solvent selection is based on the solute distribution ratio, selectivity and mutual solvent solubility of liquid–liquid systems, which can be calculated using various thermodynamic models [18–22]. For an overview of possible alternative solvents, the Hansen model was used by plotting the δ_p against the δ_h parameter for each solvent, representing the dipole and hydrogen bonding interactions of this solvent, respectively. The comparison of solvent characteristics relative to caprolactam, which is presented as (0,0), is shown in Fig. 1. Furthermore, the Unifac Dortmund model [18,20,22] was initially applied for the prediction of distribution and mutual solubility data. The activity coefficients used in the model are based on the data available in the Dortmund Data Bank. Using the resulting model, phase compositions were calculated for the systems water + caprolactam + benzene, toluene, 1-heptanol or cyclohexane at 293 K. The calculated and experimentally determined equilibrium caprolactam concentrations [7,23] are presented in Fig. 2.

In Fig. 1, it is shown that only alkanes are less polar than the current solvents, whereas several compounds with different functional groups are more polar. Furthermore, the influence of the structure of a molecule on the polarity is presented. From this figure, it can be concluded that no pure solvent is present with a polarity comparable to benzene or toluene. From literature, it is known that the more polar compounds show a larger capac-

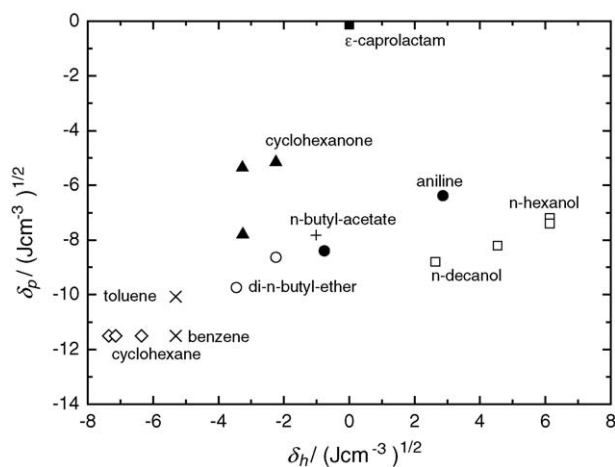


Fig. 1. Comparison of solvents based on their δ_p and δ_h Hansen solubility parameters relative to caprolactam as origin (0,0), for: x, current solvents; (●) amines; (○) ethers; (▲) ketones; (◇) alkanes; (+) esters; (□) alcohols.

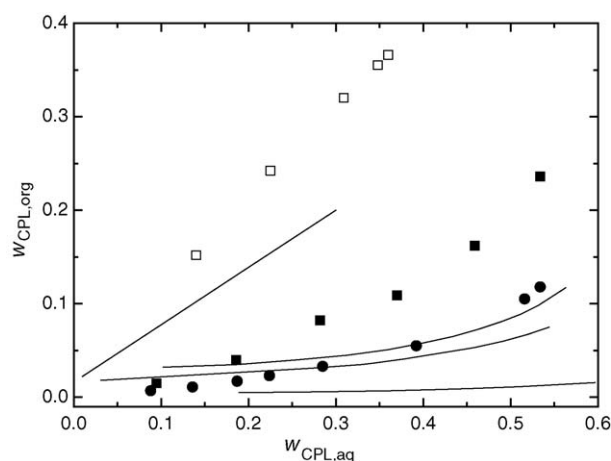


Fig. 2. Experimentally determined organic and aqueous equilibrium caprolactam concentrations at 293 K for: (■) benzene [23]; (□) 1-heptanol [7]; (●) toluene [23] and cyclohexane; and calculated values using the Unifac Dortmund model (lines).

ity towards caprolactam and a higher mutual solubility [7–10], which is shown in Fig. 2. The less polar compounds, the alkanes, show a lower capacity and mutual solubility. Therefore, solvents from both classes are expected to show the respective negative effects when investigated in the solvent selection process. However, both characteristics should at least be comparable to the currently used systems. Therefore, solvent mixtures containing a polar solvent and an alkane are investigated next to various pure solvents to combine the favourable and eliminate the negative properties of both solvent types [24].

Ideally, solvent selection would be based on the prediction of phase compositions using the Unifac Dortmund model. From Fig. 2, it was concluded, however, that the results from the model were not accurate enough for solvent screening. It might be possible to improve the accuracy if specific experimental LLE data would be included in the fitting of the activity coefficients describing the studied system. This does, however, not guarantee the accuracy in the prediction of LLE data for new solvents. Furthermore, it needs to be considered that for the prediction of LLE data both the concentration and the temperature dependence have to be described by the activity coefficients. When predicting VLE and SLE, ideal behaviour (Raoult's law and ideal solubility, respectively) can be used as a starting point. For these phase equilibria the activity coefficient acts as a correction term only and the results are, therefore, in general more accurate than for predicted LLE. Hence, the available activity coefficients were used in the Unifac Dortmund model. The result obtained with this model resulted in the conclusion that the application of the Unifac Dortmund model was unsuitable in the solvent screening procedure for an alternative solvent (mixture) for the caprolactam extraction process. The screening was thus performed experimentally. Next to phase composition data, physical properties, being density and viscosity of the separate liquid phases and interfacial tension of the liquid–liquid system, are needed for the description of extraction equipment [2]. Therefore, these need to be determined for the selection of the final solvent (mixture), taking into account the influence of caprolactam.

The objective of this study was to select an alternative solvent (mixture) for the caprolactam extraction process based on the equilibrium distribution of caprolactam and mutual solvent solubility. These characteristics should at least be comparable to those of benzene, since this is industrially the most widely applied solvent, and to toluene, which is regarded as best alternative for benzene. The experimental solvent selection procedure consisted of four parts:

- (1) A one-point determination of the capacity of various solvents for caprolactam was performed to determine which solvents possess a favourable interaction with caprolactam. The equilibrium caprolactam distribution between the aqueous and (mixed) solvent phase was investigated at 293 K for an initial 10 mass% aqueous caprolactam solution as function of the active group of various polar compounds (alcohol, ketone, ester, ether), their carbon chain length (C_6 – C_{12}) and their concentration in a mixture with methylcyclohexane (MCH) or heptane. Solvents or solvent mixtures showing favourable capacities for caprolactam compared to benzene and toluene were selected.
- (2) For these (mixed) solvents, the capacity and mutual solvent solubility were determined as function of the equilibrium aqueous caprolactam concentration ($w_{CPL,aq} = 0.0$ – 0.5) at 293 K, since the amount of caprolactam has strong effect on the distribution ratio. Solvents or mixtures showing a favourable equilibrium caprolactam distribution and mutual solubility compared to benzene and toluene were selected.
- (3) For the remaining alternatives, the equilibrium phase compositions of the system water + caprolactam + ammonium sulfate + (mixed) solvent were determined at 293, 313 and 333 K, covering the full industrial range. The experimentally determined phase compositions were described using the NRTL model.
- (4) Physical properties, being density and viscosity data of the separate phases and interfacial tension data of the remaining liquid–liquid systems were determined, since the operation of the extraction process is influenced by them. The density data were correlated using a linear effect of the solute mass fraction and a temperature effect that is described with the volumetric expansion coefficient. Viscosities were described with the (extended) Dole–Jones and the Guzman–Andrade equation. The interfacial tension was correlated via the Szyzkowski isotherm and the Jasper equation [23]. Finally, the best candidate solvent was determined.

The first two steps form the solvent screening part and steps 3 and 4 form the solvent characterization part of the selection procedure.

2. Experimental set-up and procedure

2.1. Equilibrium measurements

The following procedure was followed to obtain experimental data [23]. The used apparatus consisted of a stirred glass vessel surrounded by a thermostated jacket. The temperature

inside the vessel was controlled to within 0.1 K by a waterbath 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 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.

2.2. Chemicals

All chemicals were used as received. These are: ϵ -caprolactam (purity 99%), ammonium sulfate (purity >99%), di-propyl-ether (purity >99%), propyl-butyrate (purity 99%), 2-heptanone (purity 99%), 5-nonanone (purity 98%), methylcyclohexane (purity >99%) by Sigma–Aldrich (USA), butyl-butyrate (purity >98%) and *n*-heptane (purity >99%) by Merck (Germany), di-hexyl-ether (purity >97%), di-butyl-ether (purity >99%) by Fluka (Germany) and di-pentyl-ether (purity 99%), 3-octanone (purity 99%), 2-methylcyclohexanol (purity 99%) and 1-heptanol (purity 98%) by Acros (Belgium). MilliQ water was used in all experiments.

2.3. Physical properties measurements

Densities, kinematic viscosities and the interfacial tension were determined as function of caprolactam concentration at 293, 313 and 333 for the selected (mixed) solvents and the ternary systems water + caprolactam + solvent (mixture), respectively. Solutions or pre-calculated equilibrium systems of known composition (in mass fractions) were prepared and the physical properties determined. The density and kinematic viscosity data were measured with an uncertainty of $1 \times 10^{-2} \text{ kg m}^{-3}$ and $1 \times 10^{-2} \text{ mm}^2 \text{ s}^{-1}$. The interfacial tension was determined with an uncertainty of 0.3 mN m^{-1} for low solute concentrations ($w_{CPL,org} < 0.02$) up to 1 mN m^{-1} for high solute concentrations ($w_{CPL,org} > 0.02$), respectively [23].

2.4. Chemical analysis

The mass fraction of caprolactam in both the organic and the aqueous phase was determined by gas chromatography, as were the mass fraction(s) of the solvent(s) in the aqueous phase and of the polar solvent in the organic phase (in case of a solvent mixture). The same analytical method was applied for each (mixed) solvent, except for the temperature profile and column pressure, which were optimised for each system. A 10 mass% aqueous caprolactam solution was prepared and analysed four times. The mean value of 9.8 mass% was found with an uncertainty of 0.2 mass% (determined as standard deviation). The mass fraction of ammonium sulfate in the aqueous phase was determined by ion chromatography with an uncertainty of 0.01 mass%. The

mass fraction of water in the organic phase was measured by coulometric Karl Fischer determination with an uncertainty of 0.005 mass% [23].

2.5. Data analysis

Using the described analytical methods, the amount of solute and the mutual solvent solubility (in mass fractions) were determined in the organic and aqueous phase with the described uncertainties. The mass fraction of water in the aqueous phase and of the (non-polar) solvent in the organic phase was finally determined using a mass balance. The mass fraction of ammonium sulfate in the organic phase was assumed to be negligible. The distribution ratio of a solute i , $K_{D,i}$, is defined as the ratio of the determined solute mass fractions in the organic phase, $w_{i,org}$, and in the aqueous phase, $w_{i,aq}$, at equilibrium:

$$K_{D,i} = \frac{w_{i,org}}{w_{i,aq}} \quad (1)$$

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

3. Solvent screening results

3.1. Step 1: one-point capacity determination

The first step in the solvent selection procedure was to determine which solvents possess a favourable interaction with caprolactam indicating which solvents might be a replacement for benzene and toluene. Therefore the caprolactam distribution ratio, $K_{D,CPL}$, of the systems water + caprolactam + (mixed) solvent were measured as function of the equilibrium polar solvent mass fraction in the organic phase for an initial 10 mass% aqueous caprolactam solution at 293 K. The results are shown in Fig. 3 and are compared with the equilibrium distribution ratio

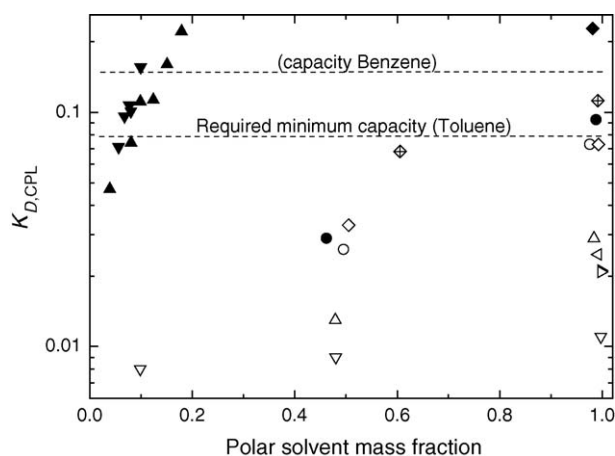


Fig. 3. Equilibrium distribution ratio of caprolactam, $K_{D,CPL}$, as function of the polar solvent mass fraction in MCH at 293 K and $w_{CPL,aq} = 0.10$ initially for: (∇) di-hexylether; ($>$) di-butylether; ($<$) di-pentylether; (Δ) di-propylether; (\circ) butyl-butylate; (\bullet) propyl-butylate; (\diamond) nonanone; (\blacklozenge) octanone; (\blacklozenge) heptanone; (\blacktriangledown) methylcyclohexanol; (\blacktriangle) heptanol; (—) benzene and toluene as reference.

for benzene and toluene at comparable conditions [23]. It was found that the amount of caprolactam extracted increased with an increasing polarity of the organic phase. This was shown by an increase of the distribution ratio at higher polar solvent concentrations, for solvents with shorter carbon chain lengths, which trend was observed in literature before [10], and for solvents with a more polar active group.

The equilibrium distribution ratio of caprolactam with toluene as solvent, presented as the dashed line in Fig. 3, was taken as minimal required capacity for a solvent. From Fig. 3, it could be concluded that several solvents or solvent mixtures showed an acceptable to favourable distribution ratio relative to toluene. These solvents were heptanone, which was already known to possess a too high mutual solvent solubility [8], propyl-butylate, octanone and the solvent mixtures with methylcyclohexanol and heptanol as polar components. Therefore, the latter three solvents were further investigated.

3.2. Step 2a: capacity and mutual solubility determination of candidate solvents at 293 K as function of the caprolactam concentration

From the phase composition data of the systems water + caprolactam + ammonium sulfate + benzene or toluene [23], it is known that the caprolactam concentration has a strong influence on the equilibrium distribution ratio. Temperature and ammonium sulfate concentration affect the distribution ratio as well, because of their influence on the water–caprolactam hydrogen bond and the salting-out effect, respectively. However, it is expected that the latter two effects will influence all systems in a comparable way. Therefore, the second step in the solvent selection procedure was the determination of the equilibrium distribution ratio of caprolactam and the mutual solvent solubility as function of the aqueous caprolactam concentration at 293 K for octanone, 15 mass% heptanol in MCH and 12 mass% methylcyclohexanol in MCH. The aqueous caprolactam concentration at equilibrium varied from (0 to 55) mass%. The results are shown in Fig. 4 as function of the equilibrium aqueous caprolactam concentration and compared to the values for benzene and toluene.

In Fig. 4, it can be seen that for all solvents the capacity at high caprolactam concentrations was below that of toluene, although the capacities were favourable at low caprolactam concentrations. Therefore, an alternative solvent needs to be found with an increased capacity at high caprolactam concentrations compared to those of the studied candidate solvents.

3.3. Step 2b: capacity and mutual solubility determination of alcohol mixtures at 293 K as function of the caprolactam concentration

According to Fig. 3, the caprolactam distribution ratio can be increased for solvents with a specific active group by using a shorter carbon chain length or a higher fraction in the solvent mixture. Of the candidate solvents, octanone was already used as pure solvent, while heptanone was known to possess

a too high mutual solvent solubility [8]. For the alcohol mixtures shown in Fig. 3, however, the polar solvent fraction could be increased further. It was, therefore, investigated whether the alcohol concentration could be increased such that at high caprolactam concentrations a capacity comparable to benzene and toluene was obtained, without increasing the mutual solvent solubility too much. The loss of alcohol to the aqueous phase for the methylcyclohexanol–MCH system was, however, already 1.5 mass% at $w_{\text{CPL,eq}} = 0.2$ and an alcohol fraction of 10 mass% in the organic phase. Therefore it was expected that at higher alcohol and caprolactam concentrations the mutual solubility would be too high for this system. For the system heptanol–MCH it was, therefore, investigated whether the alcohol content could be increased to obtain a suitable capacity and mutual solvent solubility for aqueous caprolactam concentrations up to 50 mass% at equilibrium.

The caprolactam distribution ratio as function of the aqueous caprolactam concentration at 293 K for initial alcohol concentrations of 5, 15, 20, 30 and 40 mass% in the organic phase is shown in Fig. 5.

In accordance to the results shown in Fig. 3, it was found that the amount of caprolactam extracted to the organic phase increased strongly with the amount of alcohol in the organic phase. In comparison to the distribution ratio in benzene and toluene, a mixed solvent with an initial heptanol content of 40 mass% showed a comparable and a higher extraction capacity, respectively, at high caprolactam concentrations. At low concentrations, the distribution coefficient of caprolactam is higher compared to both solvents. The alcohol concentration was not increased further, since that would result in a further increase of the mutual solvent solubility, next to an increase of the caprolactam distribution ratio. Based on Fig. 5, the solvent mixture consisting of 40 mass% heptanol in MCH was selected as candidate alternative solvent for benzene and toluene. This candidate solvent mixture was investigated further.

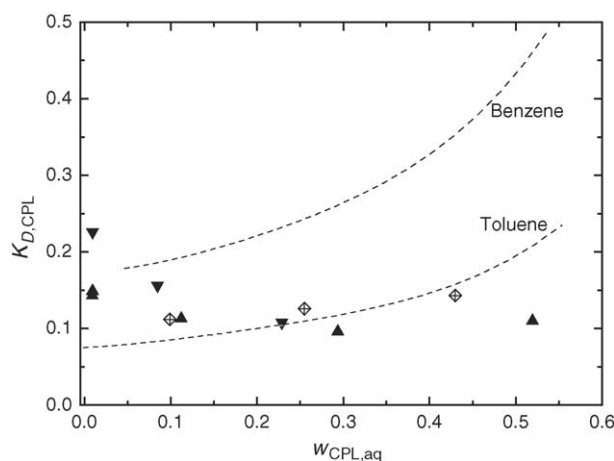


Fig. 4. Equilibrium distribution ratio of caprolactam, $K_{D,CPL}$, as function of the aqueous caprolactam concentration at equilibrium, $w_{\text{CPL,eq}}$, at 293 K for: \diamond , octanone; \blacktriangle , 15 mass% heptanol in MCH; \blacktriangledown , 12 mass% methylcyclohexanol in MCH; (–) benzene and toluene as reference.

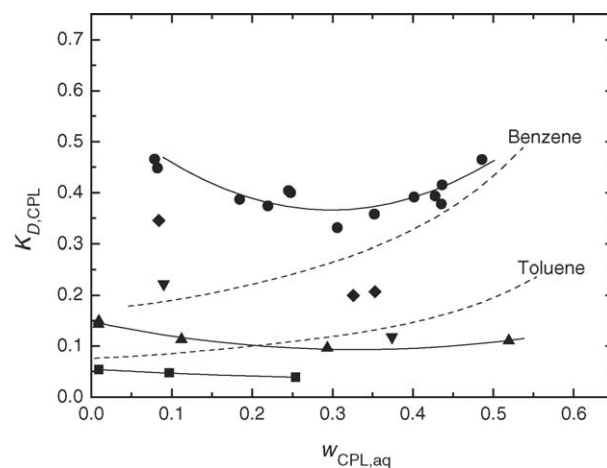


Fig. 5. Equilibrium distribution ratio of caprolactam, $K_{D,CPL}$, as function of the aqueous caprolactam concentration at equilibrium, $w_{\text{CPL,eq}}$, at 293 K for heptanol–MCH mixtures having initial heptanol mass fractions of: \blacksquare 0.05; \blacktriangle 0.15; \blacktriangledown 0.20; \blacklozenge 0.30; \bullet 0.40; (–) benzene and toluene as reference.

4. Solvent characterization: results and data correlation

4.1. Step 3a: phase compositions of the candidate system for conditions covering the industrial range

The third step in the solvent selection procedure was to determine whether the remaining solvent, 40 mass% heptanol in MCH, showed acceptable characteristics for conditions covering the full industrial range. Therefore, equilibrium phase compositions of the system water + caprolactam + ammonium sulfate + (mixed) solvent were determined at 293, 313 and 333 K. From the phase compositions using the solvent mixtures heptanol + MCH and methylcyclohexanol + MCH, it is known that the molecular structure influences the system properties. Therefore, the influence of the alkane structure on system behaviour was determined by replacing methylcyclohexane with heptane to investigate a possible optimisation of the candidate solvent. Tables 1 and 2 present the liquid–liquid equilibrium data of the systems water (1) + caprolactam (2) + ammonium sulfate (3) + methylcyclohexane (4) + heptanol (5), respectively heptane (4) + heptanol (5), at 293, 313 and 333 K. The determined phase diagrams at 293 K of the ternary systems water + caprolactam + solvent, where the solvent represents the combined mass fractions of MCH + heptanol and heptane + heptanol, are presented in Fig. 6, relative to benzene (a) and toluene (b).

In these figures, the calculated phase compositions are shown as well. The data were correlated with the classical NRTL model using the approach of de Haan and Niemann [25]. This method was already successfully applied in the description of the phase compositions of the quaternary systems water + caprolactam + ammonium sulfate + benzene and toluene at 293–333 K with ASPEN Plus 11.1 [23]. For the solvent mixtures the influence of ammonium sulfate on the system behaviour was experimentally determined, but it was not fitted, since there were not enough data points available. For the description of the quaternary systems

Table 1

Liquid–liquid equilibria of the systems water (1) + caprolactam (2) + ammonium sulfate (3) + methylcyclohexane (4) + heptanol (5) at 293, 313 and 333 K

Organic phase				Aqueous phase				
$100 \cdot w_1$	$100 \cdot w_2$	$100 \cdot w_4$	$100 \cdot w_5$	$100 \cdot w_1$	$100 \cdot w_2$	$100 \cdot w_3$	$100 \cdot w_4$	$100 \cdot w_5$
293 K								
1.58	3.67	57.77	36.99	92.04	7.88	0.00	0.02	0.07
2.00	7.14	51.63	39.23	81.53	18.45	0.00	0.00	0.02
2.53	9.91	52.23	35.32	75.10	24.54	0.00	0.04	0.32
4.00	16.83	48.50	30.67	55.57	42.76	0.00	0.18	1.49
4.27	22.59	43.43	29.71	51.04	48.59	0.00	0.01	0.36
3.20	13.49	57.75	33.64	72.25	21.61	5.84	0.04	0.26
313 K								
1.78	4.52	56.75	36.95	92.43	7.31	0.00	0.20	0.06
1.19	9.07	49.85	39.89	81.23	18.74	0.00	0.00	0.02
1.45	12.16	53.46	32.93	77.33	22.25	0.00	0.02	0.40
2.93	11.53	49.12	36.42	69.97	29.53	0.00	0.08	0.42
–	12.45	–	36.29	67.12	31.97	0.00	0.24	0.67
4.89	18.70	46.26	30.15	55.97	41.53	0.00	0.32	2.18
1.78	7.67	64.72	38.20	86.05	7.89	5.94	0.02	0.10
3.69	15.11	52.64	32.50	75.62	17.40	6.70	0.02	0.26
333 K								
1.75	4.73	56.24	37.29	92.89	6.92	0.00	0.12	0.07
3.54	14.09	48.47	33.89	77.54	21.93	0.00	0.02	0.51
3.15	12.50	55.30	34.58	72.92	26.50	0.00	0.08	0.50
–	15.57	–	37.04	67.08	32.23	0.00	0.08	0.67
5.74	20.24	45.75	28.27	55.45	41.23	0.00	0.49	2.84
5.27	27.15	39.00	28.59	50.35	48.88	0.00	0.02	0.75
1.70	8.43	63.46	38.98	87.05	6.59	6.22	0.03	0.11
3.72	18.55	54.36	33.56	76.42	16.21	6.97	0.06	0.34
8.36	27.29	36.65	24.71	70.60	22.35	5.60	0.48	0.97

water + caprolactam + MCH + heptanol and heptane + heptanol, the systems were simplified to water + caprolactam + solvent. The interactions for the resulting ternary systems, expressed by the five NRTL parameters for all component pairs, were deter-

mined from the corresponding ternary phase equilibrium data via data regression using ASPEN Plus 11.1. Since it was found that the phase compositions of both mixed solvents were almost comparable, these parameters were used for the description of

Table 2

Liquid–liquid equilibria of the systems water (1) + caprolactam (2) + ammonium sulfate (3) + heptane (4) + heptanol (5) at 293, 313 and 333 K

Organic phase				Aqueous phase				
$100 \cdot w_1$	$100 \cdot w_2$	$100 \cdot w_4$	$100 \cdot w_5$	$100 \cdot w_1$	$100 \cdot w_2$	$100 \cdot w_3$	$100 \cdot w_4$	$100 \cdot w_5$
293 K								
2.20	4.29	48.43	45.08	92.12	7.68	0.00	0.04	0.16
1.99	7.18	48.09	42.74	83.70	16.24	0.00	0.00	0.06
3.58	10.94	44.09	41.38	74.74	24.78	0.00	0.05	0.43
3.17	12.41	48.03	36.40	65.25	34.61	0.00	0.00	0.13
5.41	17.82	40.57	36.20	54.41	42.98	0.00	0.26	2.35
313 K								
2.27	5.35	44.64	47.74	92.68	7.13	0.00	0.03	0.16
2.15	8.30	50.60	38.96	86.74	13.16	0.00	0.00	0.10
4.11	11.92	41.71	42.26	75.75	23.59	0.00	0.10	0.56
3.73	15.89	42.45	37.93	71.30	34.94	0.00	0.00	0.16
6.23	19.65	39.36	34.76	52.52	43.40	0.00	0.45	3.63
5.27	18.85	47.95	27.93	51.87	47.19	0.00	0.02	0.93
333 K								
1.32	1.35	52.32	45.01	97.60	2.07	0.00	0.32	0.01
5.06	16.67	38.23	40.04	76.40	22.71	0.00	0.12	0.77
4.19	18.49	39.47	37.85	71.75	27.92	0.00	0.00	0.32
6.38	23.53	34.66	35.43	52.67	41.51	0.00	0.76	5.06
6.27	27.09	39.16	27.48	52.00	46.85	0.00	0.03	1.13

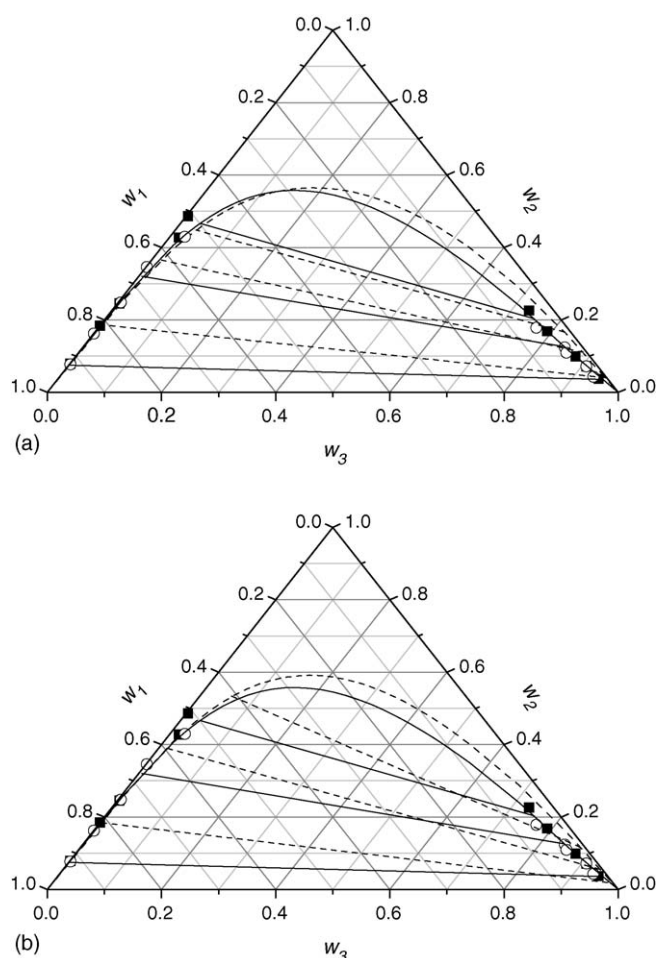


Fig. 6. Equilibrium phase compositions (in mass fractions) at 293 K for the ternary systems water (1) + caprolactam (2) + solvent (3) for the solvents: (■) 40 mass% heptanol in MCH; (○) 40 mass% heptanol in heptane; (—) NRTL fit solvent; (---) NRTL fit benzene (a) and toluene (b) as reference.

both solvent mixtures. The solvent was defined as a pseudo-component with a mass based average molecular weight and a density that was determined experimentally. The values of the fitted NRTL parameters are listed in Table 3. In the fitting procedure, initially the literature values for the CPL + water interaction [23] were used, but eventually the interaction parameters were fitted in order to obtain a good description. The different interaction parameters for CPL + water compared to those for the systems water + caprolactam + ammonium sulfate + benzene or toluene are the result of the simplified description of the stud-

Table 3

Fitted NRTL interaction parameters for the description of liquid–liquid phase equilibria of the systems water + caprolactam (CPL) + solvent at (293–333) K, where the solvent is methylcyclohexane–heptanol (40 mass% initially) or heptane–heptanol (40 mass% initially)

Binary parameter	α_{ij}	a_{ij}	a_{ji}	b_{ij} (K)	b_{ji} (K)
CPL + water [23]	0.300	24.89	−6.166	−6123	1147
CPL + water	0.300	273.8	−10.21	−6123	2282
CPL + solvent	0.300	−5.056	109.5	1170	4400
Water + solvent	0.200	−16.52	0.227	7444	338.9

ied quaternary systems as ternary systems. Furthermore, ternary interactions play a role, whereas the NRTL model assumes binary interactions only. The uncertainty in the fitted data was described with the average absolute deviation (AAD) between the experimental and fitted phase compositions at equal aqueous phase caprolactam concentrations. For the MCH + heptanol and the heptane + heptanol systems the AAD for the caprolactam mass fractions in the organic phase was 8.7×10^{-3} and 1.6×10^{-2} , for water in the organic phase the AAD was 4.9×10^{-3} and 7.8×10^{-3} , and the AAD for solvent in the aqueous phase was 1.6×10^{-2} and 1.3×10^{-2} , respectively.

From Fig. 6, it can be concluded that the amount of water in the organic phase for both solvents is slightly higher than for benzene and toluene. Consequently, the two-phase region for both alternative solvents is slightly smaller than for the currently used solvents. The presented tie-lines show that both solvent mixtures possess a favourable caprolactam distribution ratio compared to benzene and especially toluene at 293 K. The experimentally determined equilibrium distribution data of caprolactam for both alternative solvents are compared at 293 and 333 K in Fig. 7. It is shown that replacing MCH by heptane has a negligible effect on the distribution ratio of caprolactam, which was the basis for the simplification to describe both solvent mixtures with the same NRTL interaction parameters.

The influence of temperature on the experimental and calculated caprolactam distribution ratio for MCH + heptanol is shown in Fig. 8 relative to benzene and toluene.

From Fig. 8, it can be concluded that the caprolactam concentration in the organic phase is increased considerably at elevated temperatures, which is caused by the weakening of the water–caprolactam hydrogen bond. For the mixed solvent the caprolactam distribution coefficient is higher than for benzene at low caprolactam concentrations ($w_{\text{CPL,aq}} < 0.3$) and comparable to benzene at high caprolactam concentrations ($w_{\text{CPL,aq}} > 0.3$), whereas it is always higher compared to toluene.

The influence of ammonium sulfate on the measured equilibrium distribution of caprolactam for the MCH + heptanol system

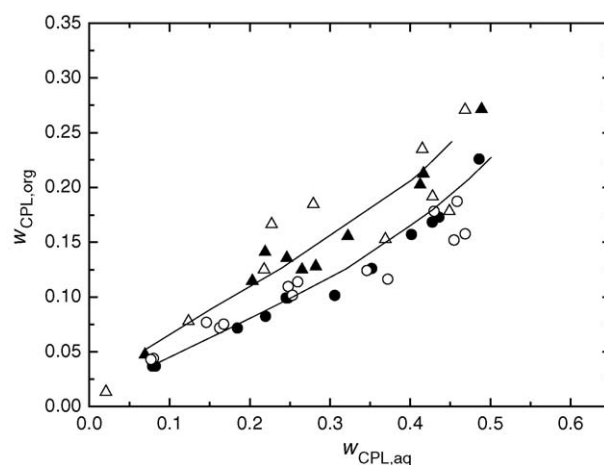


Fig. 7. The equilibrium organic caprolactam concentration as function of the equilibrium aqueous caprolactam concentration for 40 mass% heptanol in MCH at: (●) 293 K; (▲) 333 K; for 40 mass% heptanol in heptane at: (○) 293 K; (△) 333 K; (---) NRTL fit solvent.

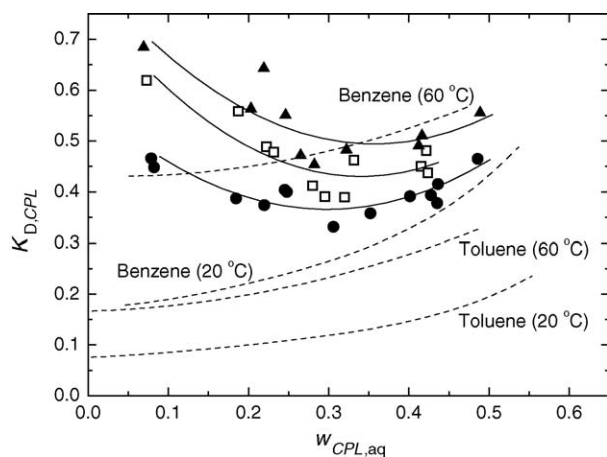


Fig. 8. Equilibrium distribution ratio of caprolactam, $K_{D,CPL}$, as function of the aqueous caprolactam concentration at equilibrium, $w_{CPL,aq}$, for 40 mass% heptanol in MCH at: (●) 293 K; (□) 313 K; (▲) 333 K; (---) NRTL fit solvent; (---) benzene and toluene as reference.

is presented in Fig. 9 relative to benzene. For clarity reasons toluene was omitted from the graph. The ammonium sulfate concentration used was about 6 mass% at equilibrium, since the concentration in the forward extraction varies from about 1 to 4 mass% from the entrance to the exit of the column, respectively.

From Fig. 9, it can be concluded that addition of ammonium sulfate to the system causes considerable salting out of caprolactam. The presence of ammonium sulfate results, therefore, in an absolute change of the caprolactam distribution ratio. This is comparable to the observation for the quaternary systems water + caprolactam + ammonium sulfate + benzene and toluene [23]. The caprolactam concentration in the organic phase is, however, still higher for the mixed solvent than for benzene and toluene at equal conditions. For the mixed solvent, a three liquid phase equilibrium region was observed for the 6 mass% ammo-

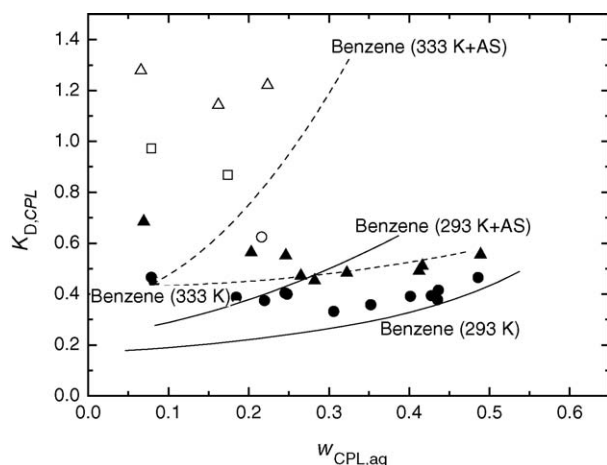


Fig. 9. Equilibrium distribution ratio of caprolactam, $K_{D,CPL}$, as function of the aqueous caprolactam concentration at equilibrium, $w_{CPL,aq}$, for 40 mass% heptanol in MCH at: (●) 293 K; (▲) 333 K; and with 6 mass% ammonium sulfate (AS) at: (○) 293 K; (□) 313 K; (△) 333 K; benzene with 5 mass% AS as reference at: (---) 293 K; (---) 333 K.

niun sulfate system and caprolactam concentrations higher than the presented experimental range in Table 1. This three-phase system was also observed for a 15 mass% ammonium sulfate system with benzene and a 5 mass% ammonium sulfate system with toluene [23]. For the mixed solvent system, however, the three-phase region was observed at lower caprolactam concentrations compared to toluene, which results in a smaller two-phase region. This presents in practise, however, no problem, since the highest ammonium sulfate concentration in the forward extraction is found at the exit of column. At this point, the caprolactam concentration is the lowest.

From the obtained results in step 3 it can be concluded that the candidate solvent mixtures, 40 mass% heptanol in MCH or heptane, show comparable phase diagrams and capacities towards caprolactam. Compared to benzene and toluene, the solubility of water in the organic phase is slightly higher and the solvent mixtures show a favourable capacity, especially at lower caprolactam concentrations. In presence of ammonium sulfate the caprolactam distribution ratio is increased, because of the salting-out effect, but this effect plays a comparable role for all solvents. The effect of the application of a solvent mixture in the forward and back-extraction process on the process lay-out was described via the number of theoretical stages (NTS) and the required solvent to feed ratio (S/F).

4.2. Step 3b: calculation of the number of theoretical stages

Using the presented results in Figs. 7 and 8, the solvent to feed ratio, S/F, and the number of theoretical stages, NTS, for the forward and back-extraction of caprolactam was calculated for both candidate solvents, 40 mass% heptanol in MCH or heptane, and compared to benzene. The process was based on the industrial DSM process lay-out [1,24]. Since the equilibrium distribution for both solvent systems is comparable, the results apply to both the MCH and heptane system. In the forward extraction of caprolactam, a 70 mass% aqueous caprolactam phase is extracted at 313 K with an organic solvent. The solvent to feed ratio for both benzene and the mixed solvent was chosen at $S/F = 3.0$, since the minimum solvent to feed ratio for the mixed solvent and benzene was calculated as $(S/F)_{min} = 2.0$ and 1.9, respectively. The fraction of caprolactam remaining in the raffinate after extraction is shown in Fig. 10(a) as function of the number of equilibrium stages. It was thereby assumed that there was no mutual solubility of the solvents, that no ammonium sulfate was present in the feed stream and that the extraction of the aqueous ammonium sulfate layer, which is present in the industrial process [1,24], was not considered. In the back-extraction, the caprolactam rich organic phase from the forward extraction is re-extracted at 313 K with water as solvent. Using the extract concentration from the forward extraction, $w_{CPL,extract} = 0.189$, the minimum solvent to feed ratio needed for the back-extraction process at 313 K was calculated for both the mixed solvent and benzene at $(S/F)_{min} = 0.45$. Therefore, using 1.5 times this amount, $S/F = 0.67$ was selected for both solvents. The fraction of caprolactam remaining in the raffinate after extraction is shown in Fig. 10(b) as function of the amount of equilibrium stages.

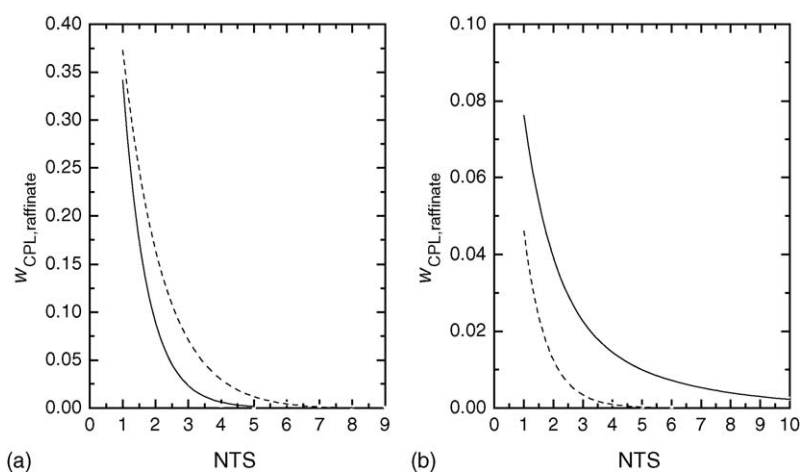


Fig. 10. Caprolactam raffinate fraction at 313 K as function of NTS used in the forward extraction (a) and back-extraction with water (b) for: (–) 40 mass% heptanol in MCH or heptane and (---) benzene.

From Fig. 10(a), it was concluded that in the forward extraction the mixed solvent with $\text{NTS}=5$ needs only half of the NTS in order to reach the required raffinate concentration of $w_{\text{CPL,raffinate}} = 5 \times 10^{-4}$ relative to benzene under comparable conditions. In Fig. 10(b), it can be seen that this trend is reverse. This behaviour can be understood from Fig. 8, where it is shown that at high caprolactam concentrations the behaviour of the mixed solvents and benzene is more or less comparable, whereas at low concentrations the caprolactam distribution ratio is higher for the mixed solvent compared to benzene.

In the industrial process, however, 1–1.5 mass% ammonium sulfate is present in the feed stream of the forward extraction and from Fig. 9 it was concluded that the caprolactam distribution ratio increases in presence of ammonium sulfate. However, since this effect plays a comparable role for all solvents, it will affect only the absolute calculated S/F and NTS values. The mixed solvents will, however, still require a solvent to feed ratio comparable to benzene, but much less theoretical stages. The mass fraction of ammonium sulfate in the organic phase is assumed to be negligible and has therefore no influence on the back-extraction.

It can be concluded from the obtained experimental results, the calculated solvent to feed ratios and the required theoretical stages that both solvent mixtures present good alternatives for benzene and toluene. As a result of these, both mixed solvents are characterized further by determination of their physical properties.

4.3. Step 4: physical properties of the candidate system for conditions covering the industrial range

Physical properties, being density and viscosity of the separate liquid phases and interfacial tension of the liquid–liquid system, influence the operation of extraction equipment. The driving force for phase separation, flow characteristics and drop size are, amongst others, a result of these properties. The density and viscosity data for the systems water + ammonium sulfate + caprolactam, benzene + caprolactam and toluene + caprolactam are described in lit-

erature [23], where the mass fraction of ammonium sulfate in the organic phase was assumed to be negligible. Therefore, the density and viscosity data of the systems mixed solvent + caprolactam were determined and compared to those of benzene and toluene. In literature, the interfacial tension data of the systems water + caprolactam + ammonium sulfate + toluene was investigated as well [23]. It was found that the combined influence of the caprolactam and ammonium sulfate concentrations on the interfacial tension could be described using the caprolactam concentration in the organic phase. The interfacial tension of the systems water + caprolactam + mixed solvent were thus determined and compared to those of toluene. In the correlation of the physical properties, only caprolactam was considered a solute and a mixed solvent was treated as one compound.

4.3.1. Density

In Table 4, the results are given for the density data of the systems 40 mass% heptanol in MCH + caprolactam and 40 mass% heptanol in heptane + caprolactam at 293, 313 and 333 K. The

Table 4
Densities of the systems alkane (1) + heptanol (2) + caprolactam (3) at 293, 313 and 333 K, where the alkane is methylcyclohexane or heptane

$100 \cdot w_2$	$100 \cdot w_3$	$10^{-3} \rho \text{ (kg m}^{-3}\text{)}$		
		293 K	313 K	333 K
Methylcyclohexane system				
0.00	0.00	0.7692	0.7517	0.7341
100.00	0.00	0.8232	0.8084	0.7936
40.11	0.00	0.7894	0.7736	0.7566
38.22	4.71	0.7989	0.7824	0.7658
36.50	9.00	0.8078	0.7916	0.7751
33.91	15.45	0.8218	0.8058	0.7894
Heptane system				
0.00	0.00	0.6838	0.6667	0.6491
39.51	0.00	0.7333	0.7168	0.7000
37.35	5.48	0.7462	0.7298	0.7131
35.65	9.79	0.7568	0.7403	0.7238
33.58	15.02	0.7699	0.7534	0.7370

presented density data were correlated using a linear effect of the solute mass fraction and the volumetric expansion coefficient [23]:

$$\frac{\rho_{i,T}}{\rho_{0,293}} = \frac{1}{1 + \alpha \cdot (T - 293)} + \sum_i \frac{A_i \cdot w_i}{1 + \alpha \cdot (T - 293)^{b_i}} \quad (2)$$

where $\rho_{i,T}$ (kg m^{-3}) is the density for given mass fractions w of solute i in the solvent at the system temperature T (K), $\rho_{0,293}$ (kg m^{-3}) is the density of pure solvent ($w_i = 0$) at the reference temperature of 293 K, A_i is an adjustable parameter describing the influence of the mass fraction of solute i on the mixture volume, α (K^{-1}) is the volumetric thermal expansion coefficient, and b_i is an adjustable parameter describing the influence of the temperature on the mixture volume expansion as result of the addition of solute i . In case of $b_i = 1$, the temperature influence simplifies to the standard volumetric thermal expansion expression. The coefficients A_i , b_i and α (K^{-1}) were determined by minimization of the standard error in fitting the density data for various amounts of solute at 293, 313 and 333 K using the program Origin 6.0. The determined parameters are shown in Table 7. The average of the ratio of the measured and calculated density data and its standard deviation is $1.000 \pm 8 \times 10^{-4}$ and $1.000 \pm 7 \times 10^{-4}$ for the MCH and heptane systems, respectively. Experimental and calculated density data for the ternary systems MCH + heptanol + caprolactam and heptane + heptanol + caprolactam as function of the caprolactam mass fraction at 293 and 333 K are presented in Fig. 11 relative to the calculated data for the binary system benzene + caprolactam [23].

Fig. 11 shows that for all solvents the density at different temperatures increases linearly with increasing solute mass fraction, while an increase of the temperature resulted in a decrease of the density. It can be seen that the benzene system has the highest density, whereas the heptane + heptanol system has the lowest. A lower density results in a larger density difference with the aqueous phase and, therefore, in a larger driving force for phase separation, which is beneficial for extraction operation. Com-

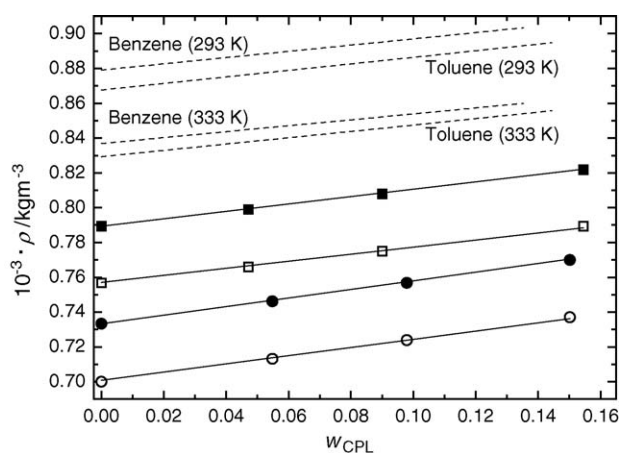


Fig. 11. Densities as a function of the caprolactam mass fraction, w_{CPL} , of the systems 40 mass% heptanol in MCH or heptane + caprolactam at 293 K for: (■) MCH; (●) heptane; and at 333 K for: (□) MCH; (○) heptane; (—) fitted densities of both systems; (---) benzene and toluene as reference.

Table 5

Kinematic viscosities of the systems alkane (1) + heptanol (2) + caprolactam (3) at 293, 313 and 333 K, where the alkane is methylcyclohexane or heptane

100 · w ₂	100 · w ₃	10 ⁶ ν (m ² s ^{−1})		
		293 K	313 K	333 K
Methylcyclohexane system				
0.00	0.00	0.95	0.75	0.61
100.00	0.00	8.52	4.59	2.72
39.70	0.00	1.84	1.30	0.97
37.61	5.27	1.99	1.40	1.03
35.59	10.34	2.16	1.50	1.11
33.77	14.95	2.36	1.64	1.19
Heptane system				
0.00	0.00	0.60	0.50	0.43
40.30	0.00	1.25	0.94	0.72
38.18	5.25	1.36	1.01	0.78
36.34	9.82	1.46	1.07	0.82
34.13	15.30	1.61	1.17	0.89

parison of the calculated and experimental results shows that the experimental data are represented very well.

4.3.2. Viscosity

In Table 5, the results are shown for the kinematic viscosity data of the systems 40 mass% heptanol in MCH + caprolactam and 40 mass% heptanol in heptane + caprolactam at 293, 313 and 333 K. The presented viscosity data were correlated using the (extended) Dole–Jones equation [23]:

$$\frac{\nu_{i,T} \cdot \rho_{i,T}}{\nu_{0,T} \cdot \rho_{0,T}} = \frac{\eta_{i,T}}{\eta_{0,T}} = 1 + A_{\text{DJ},T} \cdot \sqrt{c_i} + B_{\text{DJ},T} \cdot c_i + D_{\text{DJ},T} \cdot c_i^{F_{\text{DJ},T}} \quad (3)$$

where $\nu_{i,T}$ ($\text{m}^2 \text{s}^{-1}$) and $\eta_{i,T}$ ($\text{kg m}^{-1} \text{s}^{-1}$) are the kinematic and dynamic viscosities for a given concentration c (mol L^{-1}) of solute i at the system temperature T (K), $\nu_{0,T}$ ($\text{m}^2 \text{s}^{-1}$) and $\eta_{0,T}$ ($\text{kg m}^{-1} \text{s}^{-1}$) are the kinematic and dynamic viscosities for the pure solvent (c_i (mol L^{-1}) = 0)) at the system temperature T (K), A_{DJ} ($\text{L}^{1/2} \text{mol}^{-1/2}$) accounts for the ion–ion interaction, B_{DJ} (L mol^{-1}) accounts for ion–solvent interaction (in case of an electrolyte solution) or solvent–solvent interaction and viscosity difference of pure solvents (in case of a mixture of solvents), D_{DJ} ($\text{L}^F \text{mol}^{-F}$) is an adjustable parameter, which extends the validity of the empirical expression from 0.1 mol L^{-1} up to $1\text{--}2 \text{ mol L}^{-1}$ in combination with parameter F_{DJ} , which is generally set to $F_{\text{DJ}} = 2$. The electrolyte ion–ion interaction, expressed in parameter A_{DJ} , is zero for non-electrolyte solutes and was, therefore, neglected. The temperature influence on the pure solvent viscosity was described by the Guzman–Andrade equation:

$$\frac{\nu_{0,T} \cdot \rho_{0,T}}{\nu_{0,293} \cdot \rho_{0,293}} = \frac{\eta_{0,T}}{\eta_{0,293}} = \exp \left(B_{\text{AG}} \cdot \left(\frac{1}{T} - \frac{1}{293} \right) \right) \quad (4)$$

where $\nu_{0,293}$ ($\text{m}^2 \text{s}^{-1}$) and $\eta_{0,293}$ ($\text{kg m}^{-1} \text{s}^{-1}$) are the kinematic and dynamic viscosities of the pure solvent at the reference temperature of 293 K and B_{AG} (K) represents the Andrade–Guzman coefficient. In binary solutions, the Dole–Jones coefficients B_{DJ} and D_{DJ} can be determined graphically from the lin-

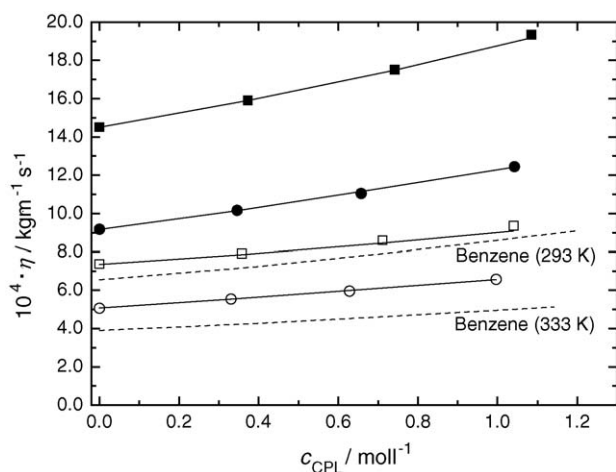


Fig. 12. Dynamic viscosities as a function of the caprolactam concentration, c_{CPL} , of the systems 40 mass% heptanol in MCH or heptane + caprolactam at 293 K for: (■) MCH; (●) heptane; and at 333 K for: (□) MCH; (○), heptane; (—) fitted densities of both systems; (---) benzene as reference.

ear relation between $(B_{\text{DJ}} + D_{\text{DJ}} \cdot c_i)$ and c_i , according to Eq. (3) when $F_{\text{DJ}} = 2$. This method was found to be valid for all caprolactam solutions. The remaining coefficients were determined by minimization of the standard error in fitting the viscosity data for various amounts of solute at 293, 313 and 333 K using the program Origin 6.0. The determined parameters are listed in Table 7. The average of the ratio of the fitted and measured viscosity data and its standard deviation for the Dole–Jones and Guzman–Andrade equation is $0.99 \pm 1 \times 10^{-2}$ and $1.00 \pm 4 \times 10^{-3}$ for the MCH and heptane systems, respectively. Experimental and fitted dynamic viscosity data for the systems MCH + heptanol + caprolactam and heptane + heptanol + caprolactam as function of the caprolactam concentration at 293 and 333 K are presented in Fig. 12 relative to the calculated data for the binary system benzene + caprolactam [23]. For clarity reasons, the values for toluene were omitted, since the viscosity data for benzene and toluene are almost comparable.

Fig. 12 shows that for all solvents and all solutes the viscosity increases with increasing solute concentration, but the increase is lower at elevated temperatures. Furthermore, it can be seen that an increase of temperature results in a decrease of viscosity and that the benzene system has the lowest viscosity, followed by the heptane + heptanol system. If a liquid is the continuous phase during extraction operation, a lower viscosity is favourable, because it results in a reduced resistance for drops travelling. If a liquid is dispersed, a lower viscosity results in a decrease in the required power input for drop break-up. Comparison of the calculated and experimental results shows that the experimental data are very well represented with the (extended) Dole–Jones and the Andrade–Guzman equations.

4.3.3. Interfacial tension

In Table 6, the results are shown for the interfacial tension data of the systems water + caprolactam + 40 mass% heptanol in MCH and water + caprolactam + 40 mass% heptanol in heptane at 293, 313 and 333 K. The presented interfacial tension data

Table 6

Interfacial tensions dependent on the aqueous (aq) and organic (org) caprolactam concentrations of the systems water (1) + caprolactam (2) + alkane (3) + 1-heptanol (4) at 293, 313 and 333 K, where the alkane is methylcyclohexane or heptane

$100 \cdot w_{2,\text{aq}}$	$100 \cdot w_{2,\text{org}}$	$100 \cdot w_{4,\text{org}}$	$10^3 \gamma \text{ (N m}^{-1}\text{)}$
Methylcyclohexane system at 293 K			
1.03	0.65	39.87	9.5
2.66	1.46	39.36	8.3
5.10	2.50	38.98	7.9
10.24	4.39	38.22	5.3
Heptane system at 293 K			
0.99	0.72	39.61	9.5
2.51	1.63	39.60	8.8
4.97	2.93	38.73	7.2
8.87	4.80	40.82	5.6
$100 \cdot w_{4,\text{org}}$	$10^3 \gamma \text{ (N m}^{-1}\text{)}$		
	293 K	313 K	333 K
Methylcyclohexane system (no caprolactam present)			
0.00	49.0	47.2	44.8
39.80	12.3	11.4	12.4
100.00	7.3	8.3	8.1
Heptane system (no caprolactam present)			
0.00	50.0	48.6	46.0
40.25	11.5	11.3	12.4

were correlated using the Szyzkowski isotherm, where the concentration influence of caprolactam on the interfacial tension of the system was described via the organic caprolactam concentration [23]:

$$\gamma_{i,T} = \gamma_{0,T} \cdot \left[1 - B_{\text{SZ}} \cdot \ln \left(\frac{c_i}{A_{\text{SZ}}} + 1 \right) \right] \quad (5)$$

where $\gamma_{i,T}$ (N m^{−1}) is the interfacial tension for a given concentration c (mol L^{−1}) of solute i at system temperature T (K), $\gamma_{0,T}$ (N m^{−1}) the interfacial tension for the system without solute present (c_i (mol L^{−1}) = 0) at system temperature T (K) and A_{SZ} (mol L^{−1}) and B_{SZ} are the so-called Szyzkowski adsorption coefficients. For all temperatures, the determined interfacial tension of both solvent systems without caprolactam varied between (11.3 and 12.4) mN m^{−1}. This is probably due to a combined effect of the interfacial tension decrease with increasing temperature for the binary systems water + MCH and water + heptane, the parabolic dependence of the interfacial tension on temperature for the binary system water + heptanol [26] and finally the experimental accuracy. Therefore, an average value of $\gamma_{0,T}$ (N m^{−1}) = 11.9 mN m^{−1} at all temperatures for both ternary solvent systems water + 40 mass% heptanol in MCH or heptane was used for the correlation of interfacial tension data. The determined parameters are shown in Table 7. The average of the ratio of the fitted and measured interfacial tension data and its standard deviation for the Szyzkowski equation is $1.0 \pm 6.5 \times 10^{-2}$ and $1.0 \pm 4.3 \times 10^{-2}$ for the MCH and heptane systems, respectively. Experimental and calculated interfacial tension data for the systems water + caprolactam + 40 mass% heptanol in MCH or heptane are presented in Fig. 13

Table 7

Fitted parameters for the description of densities, dynamic viscosities and interfacial tensions of the systems alkane + heptanol + caprolactam (CPL) and water + alkane + heptanol + CPL, respectively, at 293, 313 and 333 K, where the alkane is methylcyclohexane or heptane

Parameters	Methylcyclohexane system	Heptane system
Density		
$\rho_{0,293}$ (kg m ⁻³)	789.4	733.3
A_{CPL} (kg m ⁻³)	0.269	0.337
b_{CPL}	1	1
α (K ⁻¹)	1.07×10^{-3}	1.16×10^{-3}
Dynamic viscosity		
$\eta_{0,293}$ (kg m ⁻¹ s ⁻¹)	1.45×10^{-3}	0.92×10^{-3}
$B_{DJ} = k_1 (T - 273) + k_2$		
CPL	$k_1 = -15.2 \times 10^{-4}$ $k_2 = 0.2660$	$k_1 = -5.0 \times 10^{-4}$ $k_2 = 0.2968$
$D_{DJ} = m_1 (T - 273) + m_2$		
CPL	$m_1 = 2.2 \times 10^{-4}$ $m_2 = 0.0614$	$m_1 = -5.9 \times 10^{-4}$ $m_2 = 0.0591$
B_{AG} (K)	1659	1334
Interfacial tension		
A_{SZ} (mol l ⁻¹)	6.3×10^{-2}	
B_{SZ}	0.294	

as function of the organic caprolactam concentration at 293 K relative to the calculated interfacial tension data of the ternary system water + caprolactam + toluene at 293 K [23].

Fig. 13 shows that the interfacial tension decreased with increasing caprolactam concentration for the ternary and quaternary systems. Furthermore, it can be seen that at high organic caprolactam concentrations the interfacial tension of all systems is comparable. With a decreasing concentration, the interfacial tension of the toluene system increases exponentially, whereas it increases slightly for the mixed solvent systems. This lower

interfacial tension at low caprolactam concentrations compared to toluene is favourable, because it results in a smaller drop size and therefore a larger interfacial area at equal power input. Comparison of the calculated and experimental results shows that the experimental data are very well represented with the Szyzkowski equation.

5. Conclusion

Possible alternative solvents for the replacement of benzene and toluene in the caprolactam extraction process were screened using the Hansen solubility model and the Unifac Dortmund model. An indication of alternative solvent groups was obtained using the Hansen model. The results obtained with the Unifac Dortmund model supported the trends found in the Hansen model, but were, however, not accurate enough for in depth solvent selection. Solvent screening was therefore performed experimentally.

In the solvent screening part, it was found that the caprolactam distribution ratio increased with increasing solvent (mixture) polarity, characterized by a more polar active group (ether, ester, ketone and alcohol), decreasing carbon chain length (C₁₂–C₆) or increasing polar solvent fraction in the mixture. Based on a high capacity and a low mutual solvent solubility, the mixture 40 mass% heptanol in methylcyclohexane was selected as candidate replacement solvent. In the solvent characterisation, liquid–liquid equilibrium phase compositions were determined using the candidate solvent at the full concentration and temperature range of the industrial process. Data were determined for the two-phase systems, where three liquid phases were observed for systems at 6 mass% of ammonium sulfate. The influence of alkane structure on phase compositions was observed to be negligible by replacing methylcyclohexane with heptane, resulting in 40 mass% heptanol in heptane being selected as second candidate solvent. The phase equilibria were correlated with the classical NRTL model. A good representation was obtained for both systems, where the mixed solvent was treated as a pseudo-component. This approach resulted in a simple and directly applicable model in ASPEN Plus 11.1.

Since the phase compositions of both alternative solvent mixtures are comparable, they result in similar required S/F and NTS values. For the forward extraction the S/F is 3.0 for the mixed solvent and benzene, whereas the NTS is 5 and 9, respectively. In the back-extraction the S/F is 0.67 whereas the NTS is 10 and 5 for the solvent mixture and benzene, respectively.

Since the phase compositions for both solvent mixtures are comparable, the final solvent selection was based on the physical properties. The density of the 40 mass% heptanol in heptane mixture is the lowest of the candidate and currently used solvents, resulting in the largest driving force for phase separation. Density data were correlated well using a linear relation for the solute concentration influence and the volumetric thermal expansion coefficient. The viscosity for 40 mass% heptanol in heptane is slightly higher compared to benzene and toluene, but for 40 mass% heptanol in MCH it is much higher. An increased viscosity of the continuous phase in an extraction column results in higher drag coefficients for drops. A more viscous dispersed

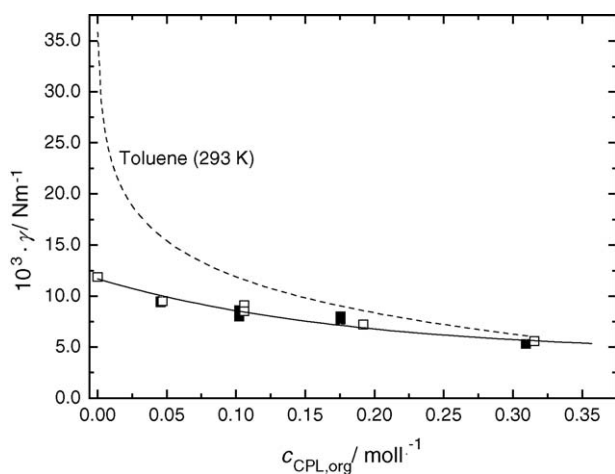


Fig. 13. Interfacial tension as a function of the organic caprolactam concentration, $C_{CPL,org}$, of the systems water + caprolactam + 40 mass% heptanol in MCH or heptane at 293 K for: (■) MCH; (□) heptane; (–) fitted interfacial tension of both systems; (–) toluene as reference.

phase requires a higher power input to achieve drop break-up. Viscosity data were correlated using the extended Dole–Jones equation and the Andrade–Guzman equation. The interfacial tension of both systems is comparable, but lower than for benzene and toluene. This results in a smaller drop size and, therefore, a larger interfacial area at equal power input. Interfacial tension data were fitted with the Szyzkowski equation via the organic caprolactam concentration, which resulted in good fits. Because of its favourable density and viscosity characteristics 40 mass% heptanol in heptane was selected as replacement solvent.

The impact on the environment is influenced positively by using the selected solvent. This is illustrated by the fact that benzene, as carcinogenic component, or toluene, as experimental teratogenic component, is removed from the process. Another example is the LD₅₀ (oral, rat) value, which is 930 and 636 mg kg⁻¹ for benzene and toluene, respectively, while it is >15,000 and 3250 mg kg⁻¹ for heptane and heptanol, respectively [27].

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