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Liquid−Liquid Equilibria and Physical Properties of the Quaternary Systems Water + Caprolactam + Ammonium Sulfate + Benzene and Toluene

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Modeling of extraction operations for caprolactam requires an accurate description of the phase compositions and the physical properties of all liquid phases. Therefore experimental liquid−liquid equilibrium data were measured for the systems water (1) + caprolactam (2) + ammonium sulfate (3) + organic solvent (4) at 293 K, 313 K, and 333 K, where the organic solvent was either benzene or toluene. Furthermore, the physical properties, density and viscosity of the separate phases and the interfacial tension of the two-phase systems, were determined. The equilibrium phase composition data were correlated using the nonrandom two-liquid model. Density data were fitted via the concentration influence of the solutes and the thermal expansion coefficient. Viscosity data were correlated using the Dole−Jones equation for describing the influence of the solute concentration and the Guzman−Andrade equation for describing the influence of temperature. Interfacial tension data were described using the Szyzkowski and the Jasper equation for describing the influence of solute concentration and temperature. Excellent agreement was found between the measured data and developed correlations.

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 consisting of (65 to 70) mass % caprolactam, (1 to 1.5) mass % ammonium sulfate and water, is in equilibrium with a nearly saturated aqueous ammonium sulfate solution containing (1 to 1.5) mass % residual caprolactam. Both streams contain organic and inorganic impurities. After separation of the two phases, the caprolactam is recovered from each phase by solvent extraction, for which in industry currently benzene is often used as the organic solvent.[1−4] Several experimental studies on the ternary systems water + caprolactam + ammonium sulfate and water + caprolactam + benzene and the quaternary systems water + caprolactam + ammonium sulfate + benzene at 293 K already exist.[5−8] However, in most cases, the industrial caprolactam extraction is performed at elevated temperatures. Although the effect of temperature, in some cases combined with the effect of ammonium sulfate, has been measured,[2,9−14] data on liquid−liquid equilibrium (LLE) phase compositions covering all industrially applied concentrations and temperatures are limited. 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 processes.[4] Although the data for pure liquids and pure liquid−liquid systems have been reported,[4] the influence of caprolactam and ammonium sulfate on these physical properties is unknown.

Because of the growing awareness of the negative effects of benzene on health and environment and the resulting extremely strict legislation on the use of benzene,[15−17] toluene has been proposed and applied as an alternative solvent in several cases.[4,18−21] Experimental data on the system water + caprolactam + toluene at some temperatures are available,[22−24] but extensive data on phase compositions of the system water + caprolactam + ammonium sulfate + toluene at various temperatures are not reported, whereas physical properties are available for the pure liquids and the binary liquid−liquid system only.

The objective of this study was to determine the equilibrium phase compositions of the system water + caprolactam + ammonium sulfate + organic solvent, where the organic solvent was benzene or toluene, at 293 K, 313 K, and 333 K. The experimentally determined phase compositions were described using the nonrandom two-liquid (NRTL) model. Furthermore, density and viscosity data of the separate phases and interfacial tension data of the systems studied were determined and correlated.

Experimental Section

Chemicals. Toluene (purity > 99%) was supplied by Fluka (USA), benzene (purity > 99.5%) by Riedel de Haën (USA), ϵ-caprolactam (purity 99%) and ammonium sulfate (purity > 99%) by Sigma-Aldrich (USA), ethanol (purity 99.8%) and methanol (purity > 99.8%) by Merck (Germany), and 1-methyl-2-pyrrolidinone (purity 99%) by Acros (Belgium). All chemicals were used as received. MiliQ water was used in all experiments.

Equilibrium Measurements. The experimental setup consisted of an equilibrium cell, which had an inner chamber of about 55 mL. The cell was surrounded by a jacket for temperature control. The jacket was connected to a Julabo F12 heating/cooling bath (Julabo Labortechnik, Germany), and water was used as the heating/cooling fluid. The inner chamber had two sampling ports, one in the upper half and the other in the lower half of the cell,

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allowing sampling of both phases. The cell was placed on the plate of a multiple point magnetic stirrer (Variomag) and a magnetic bar (30 mm length) was used for agitation.

Equilibrium measurements were performed as follows. The organic solvent (20 mL, toluene or benzene) and 20 mL of an aqueous caprolactam solution were introduced in the vessel by a pipet. The caprolactam mass fraction in the initial aqueous solution was in the range from (0 to 60) mass %. After introduction of the solutions, the mixture was stirred for at least 45 min at 450 rpm at an alternating regime of 90 s stirring and 20 s pause. The time of agitation required to reach equilibrium was determined by measuring the change in caprolactam concentration for different stirring times and was found to be 25 min using the described regime. After equilibrium was reached, the mixture was left to settle for at least 1 h. During the agitation and settling, the temperature of the fluid in the vessels was kept constant at the required value with an uncertainty of 0.1 K. After the phases settled, a sample from the organic (100 μL) and two samples from the aqueous layer (both 20 μL) were taken with a syringe. Finally, a sample from the organic layer (1000 μL) was taken with a pipet. The 100 μL organic phase sample and one aqueous phase sample were diluted with 1000 μL of ethanol (in case of toluene as solvent) or methanol (in case of benzene as solvent). After that, 50 μL of the internal standard was added for determination of the caprolactam concentration in the organic solvent and of the concentrations of organic solvent and caprolactam in water. The second aqueous phase sample was diluted with 1000 μL of water. Of this solution, 50 μL was diluted 500 times for analytical determination of the ammonium sulfate concentration. The 1000 μL of the organic phase sample was used for analytical determination of the water concentration.

Density Measurements. Densities were determined for the ternary system water + caprolactam + ammonium sulfate and the binary systems benzene + caprolactam and toluene + caprolactam at 293 K, 313 K, and 333 K using a DMA 5000 automatic density meter (Anton Paar, Austria). Solutions of known composition (in mass fractions) were prepared and a sample was sucked up automatically via the SHx/SCx sample changer mode into the measuring cell, having a volume of 1 mL, and heated until the desired temperature with an uncertainty of 0.01 K. After measurement, the sample was ejected, whereas the cell was rinsed two times with water and acetone and finally it was dried with air for 2 min. The density was measured with an uncertainty of 1×10^{-2} kg·m^{-3}.

Viscosity Measurements. Kinematic viscosities were determined for the ternary system water + caprolactam + ammonium sulfate and the binary systems benzene + caprolactam and toluene + caprolactam at 293 K, 313 K, and 333 K using capillary Ubbelohde viscosimeters 501 13/Ic, having a capillary constant of 0.02887 mm^2·s^{-2} ± 0.65%, and 501 03/0c, having a capillary constant of 0.003162 mm^2·s^{-2} ± 0.65% (Schott, Germany). The capillaries were immersed in a Lauda 015T waterbath (Lauda, Germany), and the temperature was controlled using a Lauda E200 thermostat (Lauda, Germany) with an uncertainty of 0.1 K. Solutions of known composition (in mass fractions) were prepared, and a sample was sucked up in the capillary. The time needed for the meniscus of the sample to descend from the first to the second marker on the capillary was measured and corrected if necessary according to the kinetic energy correction tables supplied with the respective capillaries. Measuring ranges for both capillaries were (3−30) mm^2·s^{-1} and (0.3−3) mm^2·s^{-1}, respectively. The measurement uncertainty was 1×10^{-2} mm^2·s^{-1}.

Interfacial Tension Measurements. Interfacial tensions were determined of the ternary system water + caprolactam + toluene and the quaternary system water + caprolactam + ammonium sulfate + toluene at 293 K, 313 K, and 333 K using a Krüss K11 automatic tensiometer with a thermostated vessel (Wilten Physica, Belgium). The thermostated vessel was connected to a Julabo F12 heating/cooling bath (Julabo Labortechnik, Germany), and the temperature was controlled with an uncertainty of 1 K. Interfacial tensions were determined via the Du Noüy Ring method using a standard ring and corrected by the Huh & Mason method. The aqueous and organic phases were prepared at various precalculated equilibrium compositions (in mass fractions) and brought to the desired temperature in the waterbath. After cleaning, the ring was immersed in the light phase and the balance was set to zero. After removal of the light phase and cleaning of the ring, the sample vessel containing the heavy phase was placed in the thermostat vessel. The ring was placed above the surface, which was then searched for with a speed varying from (20 to 1) mm·min^{-1}. After detection, the ring was immersed to 3 mm in the heavy phase with a speed varying from (100 to 1) mm·min^{-1}. The heavy phase was covered with the light phase using a 10-mL pipet. The determination of the interfacial tension was performed at a speed varying from (2 to 0.2) mm·min^{-1} with a relaxation of 10% and the experiment was continued for 20 measurements or until a standard deviation of the last five values ≤ 0.3 mN·m^{-1}. The range applied for the experimental method settings covered aqueous caprolactam concentrations from (0 to 30) mass %. The measurement uncertainty was 0.3 mN·m^{-1} for low solute concentrations ($w_i < 0.10$) up to 1 mN·m^{-1} for high solute concentrations ($w_i > 0.20$).

Chemical Analysis. The mass fraction of caprolactam in both the organic and the aqueous phases and of toluene in the aqueous phase was determined in a gas chromatograph, CP-3800 (Varian, USA), equipped with an EC-WAX column (30 m, 0.32 mm, 0.25 μm film thickness) using a flame ionization detector. During the analysis of caprolactam in the organic phase and of caprolactam and toluene or benzene in the aqueous phase, the column temperature was raised from 333 K to 343 K with an increment of 10 K·min^{-1} and then from 343 K to 523 K with an increment of 50 K·min^{-1}. The temperatures of the injector and detector were kept constant at 498 K and 523 K, respectively, using a pressure in the injector of 275 kPa with an initial flow of 14.2 mL·min^{-1} (in case of toluene as solvent) or with a constant flow of 5 mL·min^{-1} with an initial pressure of 97 kPa (in case of benzene as solvent). A split ratio of 10 was used. Helium was used as the carrier gas, and a sample of 0.3 μL was injected into the column. Quantification of caprolactam and toluene or benzene in the sample was done by using an internal standard method where 1-methyl-2-pyrrolidinone was used as the internal standard. A 10 mass % aqueous caprolactam solution was prepared and analyzed 4 times to test the repeatability and the uncertainty of the GC analysis. The mean value of 9.8 mass % is 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 using a Metrohm 733 IC Separation Center (Applikon, The Netherlands) connected to a Metrohm 709 IC Pump (Applikon, The Netherlands) and a Metrohm 732 IC Detector (Applikon, The Netherlands). The separation center was equipped

Table 1. Liquid−Liquid Equilibria of the Quaternary System Water (1) + Caprolactam (2) + Ammonium Sulfate (3) + Benzene (4) at 293 K, 313 K, and 333 K

organic phase				aqueous phase			
$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$
293 K							
0.04	0.00	0.00	99.96	99.87	0.00	0.00	0.13
0.09	1.53	0.00	98.38	90.28	9.51	0.00	0.21
0.18	4.02	0.00	95.80	81.03	18.60	0.00	0.37
0.42	8.24	0.00	91.34	71.13	28.20	0.00	0.67
0.71	10.90	0.00	88.39	61.66	37.00	0.00	1.34
1.20	16.20	0.00	82.60	51.08	45.90	0.00	3.02
2.39	23.60	0.00	74.01	39.53	53.40	0.00	7.07
0.04	0.00	0.00	99.96	94.85	0.00	5.07	0.08
0.14	2.47	0.00	97.39	84.60	9.39	5.85	0.16
0.38	7.39	0.00	92.23	76.15	18.50	5.16	0.19
0.80	13.20	0.00	86.00	66.91	27.40	5.01	0.68
1.70	20.30	0.00	78.00	57.14	36.00	5.07	1.79
2.08	22.70	0.00	75.22	54.97	37.60	5.21	2.22
0.06	0.00	0.00	99.94	84.77	0.00	15.20	0.03
0.40	8.46	0.00	91.14	76.46	7.95	15.50	0.09
1.61	19.50	0.00	78.89	69.29	15.70	14.70	0.31
0.06	0.00	0.00	99.94	60.00	0.00	40.00	0.00
3.13	32.20	0.00	64.67	58.53	0.57	40.90	0.00
8.32	51.10	0.00	40.58	56.59	0.61	42.80	0.00
11.00	55.90	0.00	33.10	58.48	0.72	40.80	0.00
13.80	58.90	0.00	27.30	59.85	0.85	39.30	0.00
313 K							
0.05	0.00	0.00	99.95	99.89	0.00	0.00	0.11
0.15	2.55	0.00	97.30	90.22	9.55	0.00	0.23
0.31	5.78	0.00	93.91	80.78	18.80	0.00	0.42
0.72	9.86	0.00	89.42	70.75	28.30	0.00	0.95
1.08	14.50	0.00	84.42	60.83	37.10	0.00	2.07
1.85	19.80	0.00	78.35	49.69	45.70	0.00	4.61
4.02	28.10	0.00	67.88	37.80	51.50	0.00	10.70
0.06	0.00	0.00	99.94	94.83	0.00	5.08	0.09
0.19	3.75	0.00	96.06	84.80	9.09	5.96	0.15
0.69	10.30	0.00	89.01	76.46	17.80	5.35	0.39
313 K (continued)							
1.67	17.90	0.00	80.43	67.53	26.50	5.06	0.91
3.74	27.30	0.00	68.96	57.83	34.50	5.15	2.52
4.88	31.30	0.00	63.82	55.72	35.80	5.33	3.15
0.09	0.00	0.00	99.91	84.97	0.00	15.00	0.03
0.83	11.60	0.00	87.57	77.14	6.97	15.80	0.09
3.93	28.50	0.00	67.57	71.35	12.70	15.70	0.25
0.05	0.00	0.00	99.95	60.20	0.00	39.80	0.00
3.29	31.90	0.00	64.81	59.40	0.60	40.00	0.00
9.30	50.00	0.00	40.70	58.53	0.67	40.80	0.00
10.80	55.70	0.00	33.50	57.82	0.68	41.50	0.00
13.70	58.00	0.00	28.30	59.56	0.84	39.60	0.00
333 K							
0.07	0.00	0.00	99.93	99.88	0.00	0.00	0.12
0.22	3.61	0.00	96.17	90.56	9.15	0.00	0.29
0.62	7.82	0.00	91.56	81.19	18.20	0.00	0.61
1.09	12.50	0.00	86.41	71.22	27.50	0.00	1.28
1.71	17.50	0.00	80.79	60.48	36.40	0.00	3.12
3.08	23.60	0.00	73.32	49.25	44.30	0.00	6.45
7.74	34.40	0.00	57.86	36.90	49.10	0.00	14.00
0.04	0.00	0.00	99.96	94.79	0.00	5.12	0.09
0.19	3.70	0.00	96.11	85.13	8.89	5.82	0.16
1.22	13.70	0.00	85.08	76.71	17.60	5.23	0.46
3.08	24.50	0.00	72.42	68.13	25.60	5.22	1.05
9.00	39.10	0.00	51.90	59.61	31.80	5.47	3.12
0.05	0.00	0.00	99.95	85.27	0.00	14.70	0.03
1.37	14.70	0.00	83.93	77.56	6.46	15.90	0.08
7.09	36.90	0.00	56.01	73.97	9.64	16.20	0.19
0.10	0.00	0.00	99.90	59.50	0.00	40.50	0.00
3.66	32.70	0.00	63.64	59.22	0.58	40.20	0.00
10.40	56.40	0.00	33.20	57.56	0.64	41.80	0.00
11.20	55.70	0.00	33.10	58.42	0.68	40.90	0.00
13.10	59.50	0.00	27.40	58.15	0.75	41.10	0.00

with a ICSep AN2 column (250 mm, 4.6 mm) (CETAC Technologies, USA). Sulfate was determined via conductivity measurement with chemical suppression. An eluent consisting of 1×10^{-3} mol·L^{-1} $NaHCO_3$ and 3.5×10^{-3} mol·L^{-1} Na_2CO_3 was used at a flow of 1200 μL·min^{-1}. A temperature of 308 K in the detector and a pressure of 800 kPa were applied. Quantification of the amount of sulfate was performed using Metrohm IC Metrodata for Windows 95 version 1.44 (Applikon, The Netherlands) and a calibration line of sodium sulfate. Sulfate was determined with an uncertainty of 0.01 mass %.

The mass fraction of water in the organic phase was measured by coulometric Karl Fischer determination with a Metrohm 652 KF Coulometer (Applikon, The Netherlands), where controlled-current potentiometry with two platinum indicator electrodes was used for determination of the end-point, which was fixed at 250 mV. In the reaction vessel, 200 mL of Hydranal-AK anode-liquid (Riedel-de Haën, USA) was transferred, and in the generation electrode, 5 mL Hydranal CK-G cathode liquid from an ampule (Riedel-de Haën, USA) was placed. When water was present at the start, iodine was automatically generated until equilibrium was reached. For determination of water in a sample, a fixed amount of sample was added to the Hydranal-AK liquid, whereas iodine was automatically generated until the end point was reached. Water was determined with an uncertainty of 0.005 mass %.

Data Analysis. By use of 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 toluene or benzene in the organic phase was finally determined using mass balance. The mass fraction of ammonium sulfate in the organic phase was assumed to be negligible. This assumption was based on the results of Huan et al.,[14] where a very small amount of ammonium sulfate (AS) was detected in the organic phase near the phase boundary. The amount detected was $w_{AS} < 0.004$ at the highest amounts of caprolactam (CPL) and water (W) in the organic phase ($w_{CPL,org} = 0.52$ and $w_{W,org} = 0.23$) at 333 K. In the determination of the physical properties, the phase compositions were directly calculated from the weighted amounts and, in case of interfacial tension measurements, from the determined phase equilibria.

Results and Data Correlation

Equilibrium Experiments. Tables 1 and 2 present the LLE data of the systems water + caprolactam + ammonium sulfate + benzene and toluene, respectively, at 293 K, 313 K, and 333 K. The determined phase equilibrium data for the described systems were correlated with the classical NRTL model using the approach of de Haan and Niemann.[12] This model was reported to provide a good representation of the experimental LLE data for the ternary and quaternary systems water + caprolactam + ammonium sulfate + benzene at 293 K, 313 K, and 333 K, when ammonium sulfate was treated as a fully dissociated pseudocomponent and the nonrandomness parameter was determined in the fitting procedure and not set at the default value of 0.2 or 0.3.[12] This approach results, however, in values for α_{ij} that are physically unrealistic and reduces the NRTL model to a fit procedure. The NRTL electrolyte model[25] or the extended NRTL electrolyte model[14,26] are capable of describing LLE and even LLLE systems con-

Table 2. Liquid−Liquid Equilibria of the Quaternary System Water (1) + Caprolactam (2) + Ammonium Sulfate (3) + Toluene (4) at 293 K, 313 K, and 333 K

organic phase				aqueous phase			
$100w_1$	$100w_2$	$100w_3$	$100w_4$	$100w_1$	$100w_2$	$100w_3$	$100w_4$
293 K							
0.04	0.08	0.00	99.87	98.54	1.20	0.00	0.26
0.06	0.28	0.00	99.66	95.38	4.41	0.00	0.21
0.07	0.69	0.00	99.25	90.99	8.79	0.00	0.22
0.08	1.14	0.00	98.78	86.13	13.63	0.00	0.24
0.10	1.69	0.00	98.21	81.07	18.69	0.00	0.24
0.12	2.31	0.00	97.57	77.19	22.40	0.00	0.41
0.16	3.27	0.00	96.57	70.97	28.51	0.00	0.52
0.28	5.46	0.00	94.26	59.69	39.20	0.00	1.11
0.58	10.49	0.00	88.93	45.41	51.58	0.00	3.01
0.79	11.81	0.00	87.40	41.16	53.44	0.00	5.40
3.26	24.93	0.00	71.82	17.41	60.21	0.00	22.38
0.05	0.09	0.00	99.87	93.70	1.02	5.10	0.18
0.06	0.51	0.00	99.44	90.77	4.00	5.03	0.20
0.07	1.24	0.00	98.69	85.65	9.16	4.98	0.22
0.17	3.63	0.00	96.21	75.19	19.24	5.07	0.50
0.31	7.02	0.00	92.67	63.77	30.46	5.05	0.73
0.50	10.62	0.00	88.88	53.08	40.45	5.00	1.46
0.04	0.40	0.00	99.56	59.96	0.14	39.86	0.04
0.05	0.86	0.00	99.09	59.76	0.18	40.02	0.04
0.06	1.24	0.00	98.70	60.13	0.21	39.60	0.06
0.15	4.59	0.00	95.26	59.02	0.39	40.58	0.01
0.37	10.16	0.00	89.47	57.13	0.54	42.32	0.01
0.72	14.87	0.00	84.41	56.95	0.58	42.44	0.02
0.65	14.55	0.00	84.80	58.73	0.61	40.65	0.00
1.30	20.55	0.00	78.15	59.16	0.93	39.90	0.01
2.88	29.96	0.00	67.16	59.61	0.97	39.35	0.06
313 K							
0.06	0.10	0.00	99.84	98.80	0.99	0.00	0.21
0.07	0.49	0.00	99.44	95.56	4.24	0.00	0.20
0.12	1.09	0.00	98.79	91.33	8.47	0.00	0.20
0.15	2.68	0.00	97.17	81.50	18.14	0.00	0.36
0.23	4.59	0.00	95.17	70.73	28.60	0.00	0.67
0.37	7.37	0.00	92.26	59.40	39.16	0.00	1.44
0.75	12.41	0.00	86.84	45.70	50.50	0.00	3.80
1.17	14.45	0.00	84.38	40.48	51.12	0.00	8.39
4.48	26.36	0.00	69.16	17.63	56.27	0.00	26.10
313 K (continued)							
0.05	0.15	0.00	99.80	93.80	0.98	5.07	0.16
0.08	1.11	0.00	98.81	89.09	5.87	4.84	0.20
0.11	1.68	0.00	98.21	86.51	8.35	4.98	0.16
0.28	4.92	0.00	94.80	75.89	18.87	4.83	0.41
0.59	8.61	0.00	90.80	65.91	27.70	4.85	1.55
0.80	12.79	0.00	86.41	55.62	37.58	5.16	1.63
0.06	0.47	0.00	99.47	59.72	0.12	40.16	0.00
0.06	0.93	0.00	99.00	60.35	0.17	39.45	0.03
0.08	1.31	0.00	98.61	59.82	0.20	39.92	0.05
0.16	4.06	0.00	95.78	57.96	0.28	41.72	0.04
0.48	11.09	0.00	88.43	59.22	0.65	40.13	0.00
1.42	20.67	0.00	77.91	58.93	0.81	40.25	0.01
2.92	31.03	0.00	66.05	59.46	0.82	39.70	0.02
333 K							
0.06	0.15	0.00	99.79	98.73	0.96	0.00	0.32
0.08	0.83	0.00	99.09	94.84	5.01	0.00	0.15
0.11	2.29	0.00	97.60	88.46	11.12	0.00	0.42
0.19	3.84	0.00	95.97	80.77	18.79	0.00	0.44
0.32	6.38	0.00	93.31	68.89	30.08	0.00	1.04
0.49	9.48	0.00	90.03	58.13	40.00	0.00	1.87
1.05	13.38	0.00	85.57	49.91	44.78	0.00	5.31
3.63	24.35	0.00	72.02	24.08	52.54	0.00	23.38
0.05	0.24	0.00	99.71	93.64	0.91	5.04	0.41
0.09	1.42	0.00	98.49	89.92	5.07	4.81	0.21
0.16	3.11	0.00	96.73	84.65	9.92	5.06	0.37
0.80	12.68	0.00	86.52	62.50	31.35	4.97	1.17
1.20	17.57	0.00	81.23	55.46	37.14	5.30	2.10
0.06	0.48	0.00	99.46	60.98	0.10	38.92	0.00
0.07	0.97	0.00	98.96	60.56	0.13	39.30	0.01
0.08	1.37	0.00	98.54	60.56	0.16	39.27	0.02
0.18	4.26	0.00	95.56	56.97	0.26	42.77	0.00
0.37	8.86	0.00	90.77	56.24	0.39	43.35	0.01
0.51	10.92	0.00	88.57	59.03	0.57	40.39	0.00
1.46	21.77	0.00	76.77	59.42	0.73	39.82	0.03
3.10	32.22	0.00	64.68	58.06	0.78	41.13	0.03

taining salts, but these models are more complicated. The classical NRTL model using the described approach is, however, a simple and direct model available in ASPEN Plus. Applying the classical NRTL model in fitting phase composition data of the quaternary systems described here provided a calculation tool, which was sufficiently accurate for our purposes of extraction column modeling. The binary interactions were calculated using eq 1[25]

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \qquad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad \alpha_{ij} = \alpha_{ji} \tag{1}$$

where G_{ij} and τ_{ij} are NRTL parameters, which are calculated via the nonrandomness parameter α_{ij} and the parameters a_{ij} and b_{ij} /K. The five NRTL parameters (α_{ij}, a_{ij}, a_{ji}, b_{ij} /K, and b_{ji} /K) for all component pairs were determined via data regression using ASPEN Plus 11.1. Initial values for the solvent−solvent interactions were determined from binary solubility data.[27] The interactions for the ternary system, and after initial regression also the solvent−solvent interactions, were determined from the ternary phase equilibria data. Interactions of all components with ammonium sulfate were determined from the quaternary phase equilibrium data. In the determination of the interactions with ammonium sulfate, it was found that the value of the nonrandomness parameter was critical for obtaining a good description of the system, which was also concluded by de Haan and Niemann.[12] The values of the fitted parameters are listed in Table 3. Experimental and calculated phase compositions of the ternary systems water + caprolactam + benzene and toluene at 293 K are presented in parts a and b of Figure 1. In this figure, the data measured for the system water + caprolactam + benzene are compared to those reported by Tettamanti et al.[6] It can be concluded that all data are in good agreement. The figure shows, furthermore, that the two-phase region for both solvents is comparable and well correlated by the NRTL model. The uncertainty in the fitted data was described with an average absolute deviation (AAD). For the benzene systems without and with ammonium sulfate, respectively, the AAD for the caprolactam mass fractions in both phases combined was 4.6×10^{-3} and 6.9×10^{-3}, the AAD for water in the organic phase was 1.7×10^{-3} and 8.7×10^{-3}, the AAD for benzene in the aqueous phase was 2.4×10^{-3} and 2.7×10^{-3}, and the AAD for ammonium sulfate in the aqueous phase was 9.0×10^{-3}. For the

Table 3. Fitted NRTL Interaction Parameters for the Description of LLE of the Systems Water (1) + Caprolactam (CPL) (2) + Ammonium Sulfate (AS) (3) + Solvent (4) at (293 to 333) K, Where the Solvent Is Benzene or Toluene

binary parameter	α_{ij}	a_{ij}	a_{ji}	b_{ij} /K	b_{ji} /K
water + benzene	0.200	2.280	2.272	1340	359.2
water + toluene	0.200	0.479	4.383	1963	−428.3
CPL + benzene	0.300	−6.050	1.139	1242	432.6
CPL + toluene	0.300	−6.965	3.159	1657	−327.3
CPL + water	0.300	24.89	−6.166	−6123	1147
CPL + AS	0.0063	45.90	23.56	3016	−24105
water + AS	0.118	3.682	−15.88	1921	2245
benzene + AS	−0.260	−6.203	7.363	307.9	−629.3
toluene + AS	−0.294	2.384	−14.24	−2345	4845

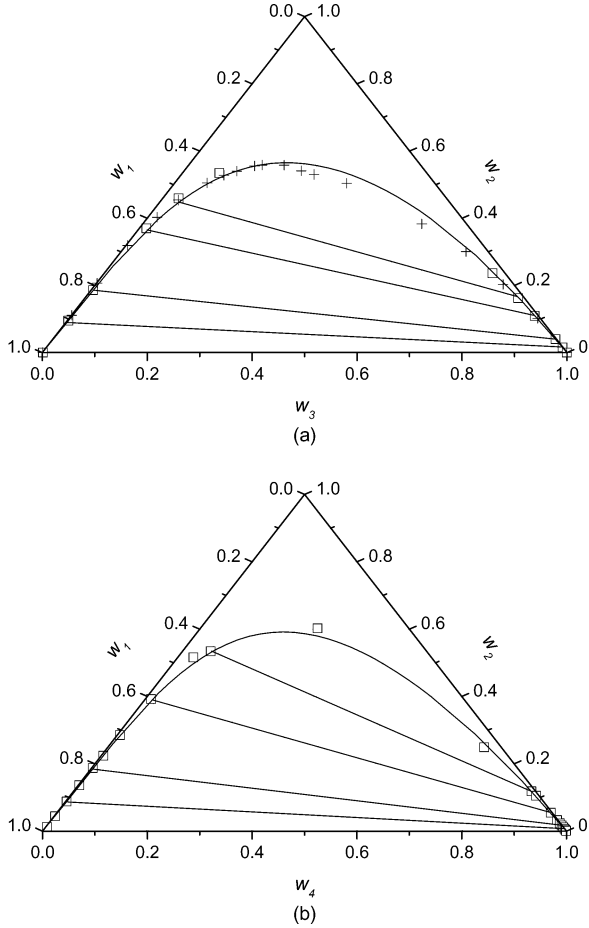


Figure 1. Equilibrium phase compositions (mass fractions) for the ternary systems water (1) + caprolactam (2) + benzene (3) (a) and toluene (4) (b) at 293 K: □, this work; +, Tettamanti et al.;[6] solid line, fitted values according to the NRTL model.

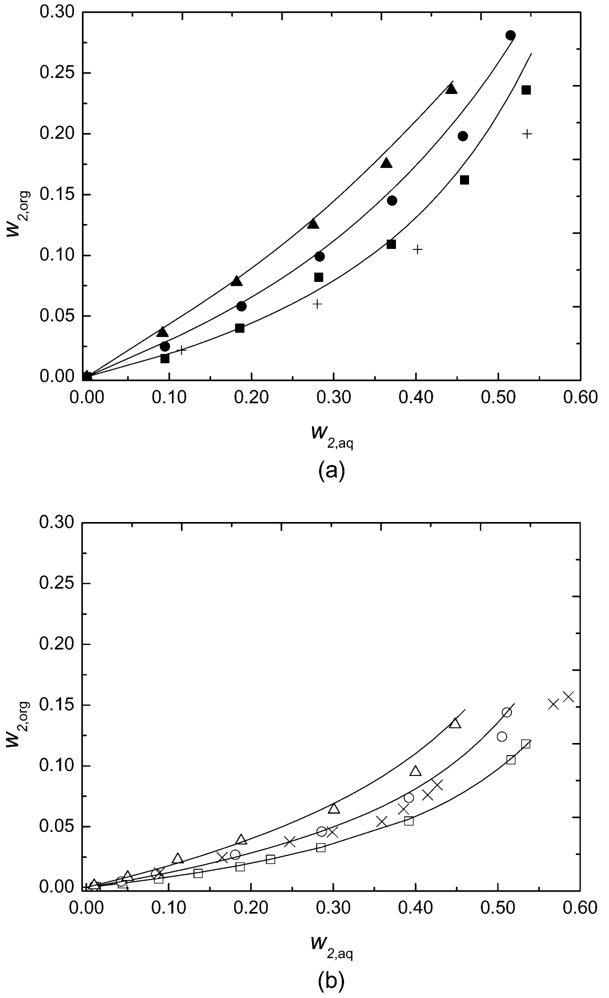


Figure 2. Organic equilibrium mass fraction of caprolactam as a function of the aqueous equilibrium mass fraction for the ternary system water (1) + caprolactam (2) + benzene (3) (a): ■, 293 K; ●, 313 K; ▲, 333 K; +, 293 K reported by Tettamanti et al.;[6] solid line, fitted equilibria according to the NRTL model; for the ternary system water (1) + caprolactam (2) + toluene (3) (b): □, 293 K; ○, 313 K; △, 333 K; ×, 313 K reported by Pajak et al.;[20] solid line, fitted equilibria according to the NRTL model.

toluene systems without and with ammonium sulfate, respectively, the AAD for the caprolactam mass fractions in both phases combined was 3.7×10^{-3} and 2.4×10^{-3}, the AAD for water in the organic phase was 2.1×10^{-3} and 2.3×10^{-3}, the AAD for toluene in the aqueous phase was 3.0×10^{-3} and 3.7×10^{-3}, and the AAD for ammonium sulfate in the aqueous phase was 1.6×10^{-3}. The influence of temperature on the experimental and calculated equilibrium data for caprolactam for both ternary systems is shown in parts a and b of Figure 2. The data for the benzene system at 293 K are compared to literature data reported by Tettamanti et al.,[6] whereas the data for the toluene system at 313 K are compared to literature data reported by Pajak et al.[20] From this figure, it can be concluded that the measured data show good agreement with the literature data and that the temperature influence on the caprolactam distribution is represented well by the NRTL model for both solvents. It is clearly shown that for both solvents the caprolactam concentration in the organic phase is increased considerably at elevated temperatures and that the caprolactam concentration in the organic phase is always higher for benzene than for toluene at equal conditions. The influence of ammonium sulfate on the experimental and fitted equilibrium data for caprolactam for both ternary systems is presented in parts a and b of Figure 3. It shows that the influence of ammonium sulfate on the caprolactam distribution is fitted well with the NRTL model. From parts a and b of Figure 3, it can be concluded that addition of ammonium sulfate to the system causes considerable salting out of caprolactam for both solvents, resulting in significant changes of the caprolactam distribution between the two liquid phases. The caprolactam concentration in the organic phase is, however, still always higher for benzene than for toluene at equal conditions. For the 15 mass % ammonium sulfate system with benzene and the 5 mass % ammonium sulfate system with toluene. A three liquid-phase equilibrium region was observed at caprolactam concentrations higher than the presented experimental range in Tables 1 and 2. This appearance of three-phase equilibria for the quaternary system water + caprolactam + ammonium sulfate + benzene at 293 K, 313 K, and 333 K was studied and fitted in more detail by van Bochove et al.[14,26] However, three-phase equilibria do not occur in the industrial caprolactam extraction process and were therefore not investigated further here. The three-phase systems disappeared when going to the 40 mass % ammonium sulfate systems.

Density. In Table 4, the results are given for the density data of the systems water + caprolactam + ammonium sulfate, benzene + caprolactam, and toluene + caprolactam at 293 K, 313 K, and 333 K. The presented density data were correlated using eq 2, which represents a linear effect

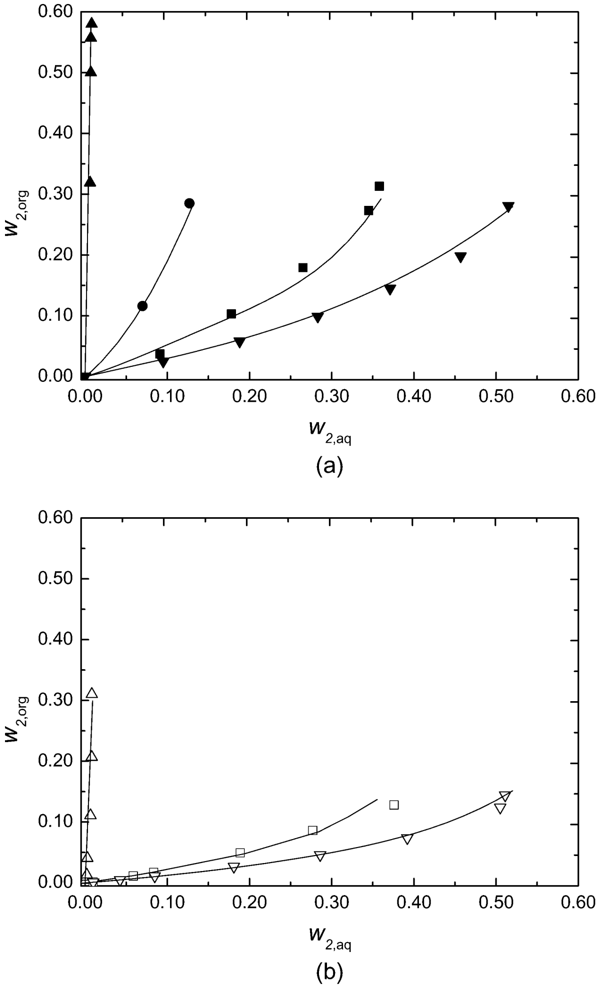


Figure 3. Organic equilibrium mass fraction of caprolactam as a function of the aqueous equilibrium mass fraction for the quaternary system water (1) + caprolactam (2) + ammonium sulfate (3) + benzene (4) (a) at 313 K: ▼, 0 mass % ammonium sulfate; ■, 5 mass %, ●, 15 mass %; ▲, 40 mass %; solid line, fitted equilibria according to the NRTL model; and for the quaternary system water (1) + caprolactam (2) + ammonium sulfate (3) + toluene (4) (b) at 313 K: ▽, 0 mass % ammonium sulfate; □, 5 mass %; △, 40 mass %; solid line, fitted equilibria according to the NRTL model.

Table 4. Densities of the Systems Solvent (1) + Caprolactam (2) + Ammonium Sulfate (3) at 293 K, 313 K, and 333 K, Where the Solvent Is Water, Benzene, or Toluene

		$10^{-3}\rho$/kg·m^{-3}		
$100w_2$	$100w_3$	293 K	313 K	333 K
		Water System[a]		
0.00	0.00	0.9984	0.9924	0.9833
10.31	0.00	1.0070	0.9994	0.9892
20.31	0.00	1.0165	1.0069	0.9948
29.99	0.00	1.0256	1.0140	1.0008
39.92	0.00	1.0344	1.0210	1.0064
50.29	0.00	1.0428	1.0279	1.0116
60.08	0.00	1.0495	1.0337	1.0170
0.00	4.96	1.0276	1.0210	1.0119
0.00	10.02	1.0569	1.0498	1.0401
0.00	19.96	1.1141	1.1065	1.0982
0.00	30.13	1.1724	1.1647	1.1551
0.00	39.82	1.2269	1.2198	1.2126
9.93	4.99	1.0357	1.0277	1.0174
19.98	5.00	1.0447	1.0349	1.0232
30.10	4.99	1.0534	1.0417	1.0288
39.38	5.04	1.0609	1.0477	1.0337
		Benzene System[b]		
0.00		0.8790	0.8580	0.8358
4.84		0.8872	0.8661	0.8447
9.21		0.8947	0.8739	0.8528
13.53		0.9020	0.8815	0.8608
		Toluene System[c]		
0.00		0.8676	0.8483	0.8293
5.14		0.8773	0.8574	0.8386
9.38		0.8852	0.8650	0.8463
14.44		0.8948	0.8741	0.8557

[a] Water (1) + caprolactam (2) + ammonium sulfate (3). [b] Benzene (1) + caprolactam (2). [c] Toluene (1) + caprolactam (2).

Table 5. Fitted Parameters for the Description of Densities According to Eq 2 of the Systems Solvent (1) + Caprolactam (CPL) (2) + Ammonium Sulfate (AS) (3) at 293 K, 313 K, and 333 K, Where the Solvent Is Water, Benzene, or Toluene

	water[a]	benzene[b]	toluene[c]
$\rho_{0,293}$ /kg·m^{-3}	998.4	879.0	867.6
A_{CPL} /kg·m^{-3}	0.086	0.204	0.216
b_{CPL}	2	1	1
A_{AS} /kg·m^{-3}	0.580		
b_{AS}	1		
α/K^{-1}	0.366×10^{-3}	1.26×10^{-3}	1.15×10^{-3}

[a] Water (1) + caprolactam (2) + ammonium sulfate (3). [b] Benzene (1) + caprolactam (2). [c] Toluene (1) + caprolactam (2).

of the solute mass fraction and a temperature effect that is described with the volumetric expansion coefficient[4]

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

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 the case of $b_i = 1$, the temperature influence simplifies to the standard volumetric thermal expansion expression.[28] The coefficients A_i, b_i, and the volumetric thermal expansion coefficient were determined by minimization of the standard error in fitting the density data for various amounts of solute at 293 K, 313 K, and 333 K using the program Origin 6.0. The determined parameters are shown in Table 5. The average of the ratio of the measured and calculated density data and its standard deviation is $0.9999 \pm 8 \times 10^{-4}$, $1.0000 \pm 3 \times 10^{-4}$ and $1.0001 \pm 8 \times 10^{-4}$ for the water, toluene, and benzene systems, respectively. Experimental and calculated density data for the binary systems water + caprolactam, benzene + caprolactam, and toluene + caprolactam as a function of the caprolactam mass fraction, for the binary system water + ammonium sulfate as function of the ammonium sulfate mass fraction, and for the ternary system water + caprolactam + ammonium sulfate as function of the caprolactam concentration at 293 K and 333 K are presented in Figure 4. Comparison of the calculated and experimental results shows that the experimental data are very well represented by eq 2. Figure 4 shows that for all solvents and all solutes the density increases linearly with increasing solute mass fraction. This increase is equal at different temperatures, except for the binary and ternary

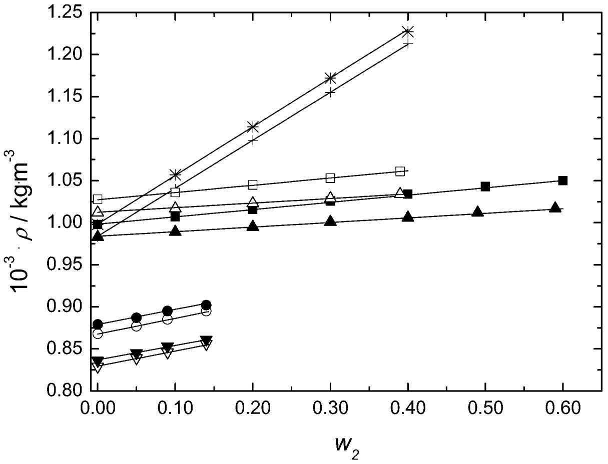


Figure 4. Densities as a function of the solute concentration of the binary systems water (1) + caprolactam (2): ■, 293 K; ▲, 333 K; of benzene (1) + caprolactam (2): ●, 293 K; ▼, 333 K; of toluene (1) + caprolactam (2): ○, 293 K; ▽, 333 K; of water (1) + ammonium sulfate (2): *, 293 K; +, 333 K; and of the ternary system water (1) + caprolactam (2) + ammonium sulfate (3) at 5 mass % ammonium sulfate: □, 293 K; △, 333 K; solid line, fitted values according to eq 2.

solutions containing water and caprolactam, where the density increase with a higher solute mass fraction was lower at elevated temperatures. From the figure, it can furthermore be seen that an increase of the temperature resulted in a decrease of density. From the results for the binary water + caprolactam and ternary water + caprolactam + ammonium sulfate solutions, it was concluded that the influence of solute mass fraction on the density was additive.

Viscosity. In Table 6, the results are shown for the kinematic viscosity data of the systems water + caprolactam + ammonium sulfate, benzene + caprolactam, and toluene + caprolactam at 293 K, 313 K, and 333 K. The presented viscosity data were correlated using the (extended) Dole−Jones equation as shown in eq 3, which is capable of correlating the influence of solute concentration on the viscosity for both electrolyte solutions[29] as well as for nonelectrolyte mixtures[30,31]

$$\frac{\nu_{i,T}\rho_{i,T}}{\nu_{0,T}\rho_{0,T}} = \frac{\eta_{i,T}}{\eta_{0,T}} = 1 + A_{\mathrm{DJ},T}\sqrt{c_i} + B_{\mathrm{DJ},T}c_i + D_{\mathrm{DJ},T}c_i^{F_{\mathrm{DJ},T}} \tag{3}$$

where $\nu_{i,T}$ /m^2·s^{-1} and $\eta_{i,T}$ /kg·m^{-1}·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, $\nu_{0,T}$ /m^2·s^{-1} and $\eta_{0,T}$ /kg·m^{-1}·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} /L$^{1/2}$·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} /L$^{\mathrm{F}}$·mol$^{-\mathrm{F}}$ is an adjustable parameter, which extends the validity of the empirical expression from 0.1 mol·L^{-1} up to (1 to 2) mol·L^{-1} [29,30] in combination with parameter F_{DJ}, which is generally set to $F_{\mathrm{DJ}} = 2$. The electrolyte ion−ion interaction, expressed in parameter A_{DJ}, is zero for nonelectrolyte solutes[30,31] and shows an influence for electrolyte solutes up to concentrations of c_i /mol·L^{-1} = 0.05.[29] Since NH_4^+ and SO_4^{2-} concentrations in this study reached up to (3 to 6) mol·L^{-1}, the effect of parameter A_{DJ} was neglected.

Table 6. Kinematic Viscosities of the Systems Solvent (1) + Caprolactam (2) + Ammonium Sulfate (3) at 293 K, 313 K, and 333 K, Where the Solvent Is Water, Benzene, or Toluene

		$10^6\nu$/m^2·s^{-1}		
$100w_2$	$100w_3$	293 K	313 K	333 K
		Water System[a]		
0.00	0.00	1.02	0.67	0.48
10.00	0.00	1.44	0.88	0.61
19.93	0.00	1.96	1.16	0.77
30.05	0.00	2.74	1.56	1.00
39.92	0.00	4.04	2.12	1.31
50.29	0.00	5.98	2.88	1.69
60.08	0.00	9.36	4.15	2.28
0.00	5.06	1.08	0.72	0.53
0.00	10.00	1.13	0.77	0.56
0.00	19.72	1.29	0.90	0.67
0.00	31.62	1.69	1.15	0.86
0.00	40.01	2.07	1.46	1.06
10.28	4.97	1.52	0.95	0.67
19.88	5.00	2.14	1.28	0.87
30.03	5.03	3.17	1.78	1.17
39.38	5.04	4.72	2.50	1.56
		Benzene System[b]		
0.00		0.75	0.58	0.47
5.05		0.82	0.63	0.51
9.49		0.89	0.68	0.54
14.98		1.01	0.76	0.60
		Toluene System[c]		
0.00		0.68	0.55	0.46
5.14		0.75	0.60	0.50
9.76		0.84	0.65	0.54
14.97		0.94	0.73	0.59

[a] Water (1) + caprolactam (2) + ammonium sulfate (3). [b] Benzene (1) + caprolactam (2). [c] Toluene (1) + caprolactam (2).

The temperature influence on the pure solvent viscosity was described by the Guzman−Andrade equation as shown in eq 4[28]

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

where $\nu_{0,293}$ /m^2·s^{-1} and $\eta_{0,293}$ /kg·m^{-1}·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 linear relation between ($B_{\mathrm{DJ}} + D_{\mathrm{DJ}}c_i$) and c_i, according to eq 3 when $F_{\mathrm{DJ}} = 2$.[30] This method was found to be valid for all caprolactam solutions but not for aqueous ammonium sulfate solutions. Since the NH_4^+ and SO_4^{2-} ions were always present in the same ratio, their separate influence could not be distinguished. In the determination of the Dole−Jones parameters for the NH_4^+ and SO_4^{2-}, ions it was therefore assumed that ammonium sulfate is fully dissociated and that the influence of all solutes is additive. The parameters B_{DJ} for the NH_4^+ and SO_4^{2-} ions and the temperature influence on these parameters were taken from literature.[29] The remaining Dole−Jones coefficients, D_{DJ} for both ions, were determined by minimization of the standard error in fitting the viscosity data for various amounts of solute at 293 K, 313 K, and 333 K using the program Origin 6.0. The Andrade−Guzman coefficient for the pure solvents was also determined using this approach. As expected from literature,[29−31] a temperature influence on the Dole−Jones parameters was observed both from the graphical interpretation as from the fitting method. The temperature

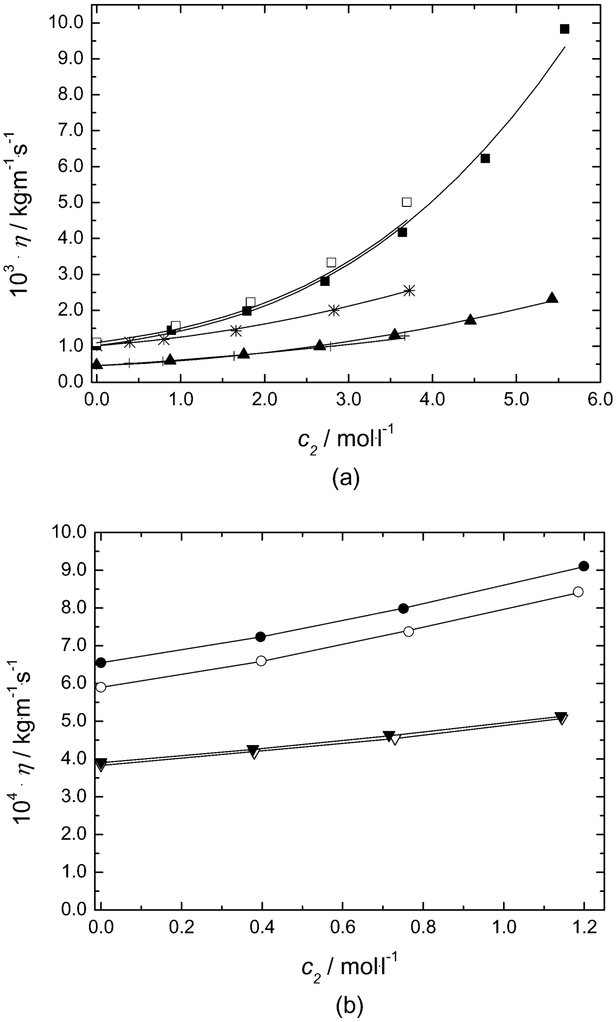
Table 7. Fitted Parameters for the Description of Dynamic Viscosities According to Eqs 3 and 4 of the Systems Solvent (1) + Caprolactam (CPL) (2) + Ammonium Sulfate (3) at 293 K, 313 K, and 333 K, Where the Solvent Is Water, Benzene, or Toluene

	Dole−Jones Parameters		
	$\eta_{0,293}$ /kg·m^{-1}·s^{-1}		
	1.02×10^{-3} [a]	0.66×10^{-3} [b]	0.59×10^{-3} [c]
	$B_{DJ} = k_1(T - 273) + k_2$		
SO_4^{2-}	$k_1 = 19.8 \times 10^{-4}$		
	$k_2 = 0.1570$ [d]		
NH_4^+	$k_1 = 7.8 \times 10^{-4}$		
	$k_2 = -0.0282$ [d]		
CPL	$k_1 = -29.3 \times 10^{-4}$	$k_1 = -2.8 \times 10^{-4}$	$k_1 = -15.8 \times 10^{-4}$
	$k_2 = 0.3960$	$k_2 = 0.2388$	$k_2 = 0.2944$
	$D_{DJ} = m_1(T - 273) + m_2$; $F_{DJ} = 2$		
SO_4^{2-}	$m_1 = -3.0 \times 10^{-4}$		
	$m_2 = -1.4628$		
NH_4^+	$m_1 = -0.7 \times 10^{-4}$		
	$m_2 = 0.3843$		
CPL	$m_1 = -10.2 \times 10^{-4}$	$m_1 = -7.7 \times 10^{-4}$	$m_1 = -3.0 \times 10^{-4}$
	$m_2 = 0.1353$	$m_2 = 0.0929$	$m_2 = 0.0892$
	$D_{DJ} = m_1(T - 273) + m_2$; $F_{DJ} = n_1(T - 273) + n_2$		
CPL	$m_1 = 4.9 \times 10^{-4}$		
	$m_2 = 0.0555$		
	$n_1 = -1.5 \times 10^{-2}$		
	$n_2 = 2.960$		
B_{AG} /K	1943 [e]	1266	1048

[a] Water (1) + caprolactam (2) + ammonium sulfate (3). [b] Benzene (1) + caprolactam (2). [c] Toluene (1) + caprolactam (2). [d] On the basis of literature data.[29] [e] On the basis of literature data.[4]

influence was assumed to be linear. The determined parameters are listed in Table 7, where the Dole−Jones parameters determined for caprolactam are based on the combined data of the aqueous caprolactam solution and the aqueous ammonium sulfate solution containing caprolactam. All parameters were initially determined for data at c_i /mol·L^{-1} < 3 and $F_{DJ} = 2$. The average of the ratio of the fitted and measured viscosity data and its standard deviation for the Dole−Jones equation is $0.96 \pm 7.0 \times 10^{-2}$, $1.001 \pm 3.7 \times 10^{-3}$, and $1.000 \pm 3.8 \times 10^{-3}$ for the water, toluene, and benzene systems, respectively.

Since it appeared that the description of the viscosity data using the Dole−Jones equation showed a large deviation at caprolactam concentrations of c_i /mol·L^{-1} > 3, eq 3 was adjusted for the description of caprolactam solutions in order to ensure the validity over an extended concentration range. The determined values for parameters B_{DJ} and B_{AG} were kept constant, but the values for the parameters D_{DJ} and F_{DJ} were determined by minimization of the standard error in fitting the viscosity data for various amounts of caprolactam at 293 K, 313 K, and 333 K using the program Origin 6.0. The determined parameters are listed in Table 7, where these parameters are obtained from the combined data of the aqueous caprolactam solution and the aqueous ammonium sulfate solution containing caprolactam. The average of the ratio of the fitted and measured viscosity data and its standard deviation for the Dole−Jones equation is $0.99 \pm 4.5 \times 10^{-2}$ for the water system. Experimental and fitted dynamic viscosity data for the binary systems water + caprolactam, benzene + caprolactam, and toluene + caprolactam and the ternary solution water + caprolactam + ammonium sulfate as functions of the caprolactam concentration and for the binary system water + ammonium sulfate as a function of the ammonium sulfate concentration at 293 K and 333 K are presented in parts a and b of Figure 5. Comparison of the calculated and experimental results shows that the experimental data are very well represented with the modified extended Dole−Jones and the Andrade−Guzman equations. Figure 5 shows that for all solvents and all solutes the viscosity increases with increasing solute concentration, but the increase is lower at elevated temperatures. Obviously, it can be seen that an increase of temperature results in a decrease of viscosity.



(a)

(b)

Figure 5. Dynamic viscosities as a function of solute concentration of the binary systems water (1) + caprolactam (2): ■, 293 K; ▲, 333 K; of water (1) + ammonium sulfate (2): *, 293 K; +, 333 K; of the ternary solution water (1) + caprolactam (2) + ammonium sulfate (3): □, 293 K; solid line, fitted values according to eqs 3 and 4 (a) and of the binary systems benzene (1) + caprolactam (2): ●, 293 K; ▼, 333 K; and toluene (1) + caprolactam (2) (b): ○, 293 K; ▽, 333 K; solid line, fitted values according to eq 3 and 4.

Interfacial Tension. In Table 8, the results are shown for the interfacial tension of the system water + caprolactam + ammonium sulfate + organic solvent at 293 K, 313 K, and 333 K, where the organic solvent is benzene or toluene. The presented interfacial tension data were correlated using the Szyzkowski isotherm as described in eq 5[32]

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

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

Table 8. Interfacial Tensions Dependent on the Aqueous (aq) and Organic (org) Solute Concentrations of the Systems Water (1) + Caprolactam (2) + Ammonium Sulfate (3) + Toluene (4) at 293 K, 313 K, and 333 K

$100w_{2,\text{aq}}$	$100w_{3,\text{aq}}$ [a]	$100w_{2,\text{org}}$	$10^3\gamma$/N·m^{-1}
	293 K		
0.00	0.00	0.00	35.7
0.00	5.00	0.00	36.4
0.00	9.38	0.00	36.7
0.00	17.33	0.00	37.1
0.00	19.96	0.00	37.8
0.00	22.45	0.00	37.7
0.00	34.72	0.00	38.9
0.00	36.95	0.00	39.2
0.00	40.02	0.00	40.0
2.50	0.00	0.17	22.4
5.41	0.00	0.37	18.0
9.87	0.00	0.74	15.2
14.92	0.00	1.27	11.4
21.77	0.00	2.18	10.0
29.95	0.00	3.55	7.3
33.08	0.00	4.15	5.7
2.54	5.05	0.28	20.3
5.04	4.99	0.60	17.2
10.08	5.03	1.42	11.1
15.09	5.00	2.44	9.1
20.05	5.00	3.67	7.8
25.12	5.02	5.14	5.8
30.25	5.00	6.85	4.8
	313 K		
0.00	0.00	0.00	34.9
0.00	5.00	0.00	35.2
0.00	9.97	0.00	35.9
0.00	20.05	0.00	37.0
0.00	30.77	0.00	38.7
0.00	36.95	0.00	38.5
0.00	40.02	0.00	39.2
2.67	0.00	0.32	20.6
5.34	0.00	0.64	17.0
9.95	0.00	1.27	13.3
14.96	0.00	2.05	10.3
19.90	0.00	2.92	8.3
29.66	0.00	4.96	5.3
2.55	4.99	0.43	19.8
5.09	5.03	0.93	15.5
10.09	5.00	2.11	10.8
15.17	4.98	3.57	8.8
20.15	5.00	5.26	5.9
	333 K		
0.00	0.00	0.00	33.4
0.00	5.00	0.00	33.8
0.00	9.98	0.00	34.6
0.00	20.07	0.00	35.6
0.00	29.24	0.00	37.3
0.00	40.02	0.00	37.5
2.63	0.00	0.48	19.6
5.06	0.00	0.92	17.1
9.85	0.00	1.85	11.9
19.32	0.00	3.91	8.2
23.33	0.00	4.86	7.0
2.56	5.02	0.69	18.0
5.11	4.99	1.45	14.6
9.86	5.03	3.05	9.6
15.11	5.00	5.10	6.7

[a] $100w_{3,\text{org}}$ assumed to be zero.

T/K, $\gamma_{0,T}$ /N·m^{-1} is 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 so-called Szyzkowski adsorption coefficients. The concentration influence of ammonium sulfate on the interfacial tension was described via the aqueous ammonium sulfate concentration, since ammonium sulfate was assumed not to be present in the organic phase. The concentration influence of caprolactam on the interfacial tension of the ternary system was described either via the aqueous or the organic caprolactam concentration. Both methods resulted in a good fit. For the quaternary system, an influence of both solutes on the interfacial tension was expected, based on experimental data for the ternary systems as shown in Table 8, although the influence of ammonium sulfate would be small compared to caprolactam. Salting out of caprolactam caused by the presence of ammonium sulfate would result in a large influence however. The water + caprolactam + ammonium sulfate + toluene system was therefore described as the ternary caprolactam system, where the concentration influence was based on the organic caprolactam concentration, assuming that the influence of caprolactam and the salting-out effect would cover almost fully the influence of both solutes on the interfacial tension. The temperature influence on the interfacial tension of the system without solute present was described by the Jasper correlation as shown in eq 6[28]

$$\gamma_{0,T} = \gamma_{0,293} - A_J(T - 293) \qquad (6)$$

where $\gamma_{0,293}$ /N·m^{-1} is the interfacial tension of the system without solute present (c_i /mol·L^{-1} = 0) at the reference temperature of 293 K and A_J /N·m^{-1}·K^{-1} represents the Jasper coefficient. The adsorption and Jasper coefficients were determined by minimization of the standard error in fitting the interfacial tension data for various amounts of solute at 293 K, 313 K, and 333 K using the program Origin 6.0. The determined parameters are shown in Table 9, where the results showed a temperature influence on the caprolactam adsorption coefficients. The averages of the ratio of the fitted and measured interfacial tension data and its standard deviation are $1.00 \pm 1.1 \times 10^{-2}$, $1.02 \pm 9.1 \times 10^{-2}$, and $0.98 \pm 1.0 \times 10^{-1}$ for the systems water + ammonium sulfate toluene, water + caprolactam + toluene, and water + caprolactam + ammonium sulfate + toluene, respectively. Experimental and calculated interfacial tension data for the ternary system water + caprolactam + toluene as function of the organic caprolactam concentration and water + ammonium sulfate + toluene as function of the aqueous ammonium sulfate concentration and for the quaternary system water + caprolactam + ammonium sulfate + toluene as function of the organic caprolactam concentration at 293 K and 333 K are presented in Figure 6. Comparison of the calculated and experimental results shows that the experimental data are very well represented with the Szyzkowski and the Jasper equations. Figure 6 shows that for the ternary system water + ammonium sulfate + toluene the interfacial tension increased with solute concentration, where it decreased for the ternary and quaternary systems containing caprolactam. The figure illustrates furthermore the opposite behavior with temperature, since the interfacial tension decreases with increasing temperature for the binary system water + toluene and the ternary system water + ammonium sulfate + toluene as expected from the Jasper equation. It increases, however, with increasing temperature for the ternary and quaternary systems containing caprolactam. The reason for this behavior can probably be found in the increase of the caprolactam distribution ratio with increasing temperature as presented in part b of Figure 2. At equal organic caprolactam concentrations, this change results in decreasing aqueous caprolactam concentrations with increasing temperature. These lower aqueous caprolactam concentrations have an effect on the interfacial tension. The combined effect of temperature and the phase compositions at that temperature then results in the increase of the interfacial tension with increasing temperature. Figure 6

Table 9. Fitted Parameters for the Description of Interfacial Tension Data Based on the Organic (org) Caprolactam (CPL) and Aqueous (aq) Ammonium Sulfate (AS) Concentration According to Eqs 5 and 6 of the Systems Water (1) + Caprolactam (2) + Ammonium Sulfate (3) + Toluene (4) at 293 K, 313 K, and 333 K

	$\gamma_{0,293}$ /N·m^{-1}	A_J /N·m^{-1}·K^{-1}
water + toluene	35.8×10^{-3}	5.75×10^{-5}
	A_{SZ} /mol·L^{-1}	B_{SZ}
CPL$_{org}$	$-5.8 \times 10^{-4} + 7.63 \times 10^{-5}(T - 273)$	$0.125 + 9.06 \times 10^{-4}(T - 273)$
AS$_{aq}$	5.1	-2.15×10^{-1}

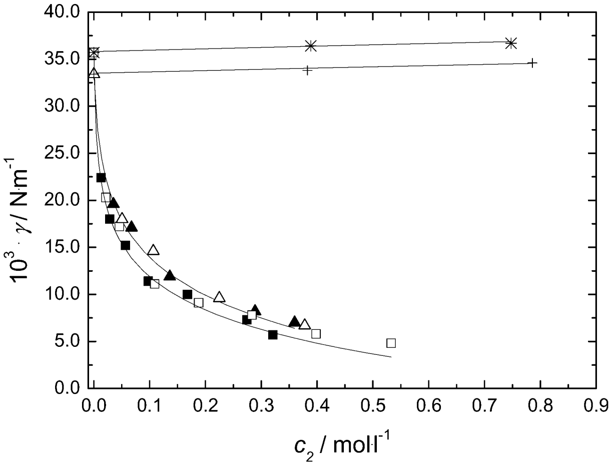


Figure 6. Interfacial tension data of the ternary systems water (1) + caprolactam (2) + toluene as function of the organic caprolactam concentration: ■, 293 K; ▲, 333 K; of water (1) + ammonium sulfate (2) + toluene (3) as function of the aqueous ammonium sulfate concentration: *, 293 K; +, 333 K; of the quaternary system water (1) + caprolactam (2) + ammonium sulfate (3) + toluene (4) as function of the organic caprolactam concentration: □, 293 K; △, 333 K; solid line, model fits according to eqs 5 and 6.

shows also that the experimental interfacial tension data for the ternary system water + caprolactam + toluene and the quaternary system water + caprolactam + ammonium sulfate + toluene were comparable at equal equilibrium organic caprolactam concentrations, which supports the assumption that the interfacial tension of the quaternary system could be described as the ternary system water + caprolactam + toluene, where the influence of ammonium sulfate was taken into account via the salting-out effect on the equilibrium distribution of caprolactam.

Conclusions

LLE phase compositions for the quaternary system water + caprolactam + ammonium sulfate + solvent, where the solvent was benzene or toluene, and density, viscosity, and interfacial tension data for the respective phases were determined at 293 K, 313 K, and 333 K, covering the full concentration and temperature range as present in the industrial process. Data were determined for the two liquid phase systems, where three liquid phases were observed for the benzene and toluene system at, respectively, 15 mass % and 5 mass % of ammonium sulfate. The measured data showed good agreement with results reported in the literature by Tettamanti et al.[6] and Pajak et al.[20]

Phase equilibria were correlated with the classical NRTL model, and a good representation was obtained for both ternary and quaternary systems, when ammonium sulfate was treated as a fully dissociated pseudocomponent and the nonrandomness parameter was determined in the fitting procedure and not set at the default value of 0.2 or 0.3. This approach resulted in a simple and direct applicable model in ASPEN Plus 11.1, although the developed model by van Bochove et al.[26] and applied in Huan et al.[14] might give an even better representation and holds also the possibility of describing LLLE data. Three-phase systems, however, do not occur in the industrial caprolactam extraction process and were therefore not further investigated here.

Density data were correlated well using a linear relation for the solute concentration influence, whereas the volumetric thermal expansion coefficient is used to describe the temperature influence on the system. Viscosity data were correlated using the adapted Dole−Jones equation for the concentration influence, taking into account the temperature influence on the Dole−Jones parameters. The Andrade−Guzman equation was used to accurately describe the temperature influence on the viscosity of the pure solvents. Interfacial tension data were fitted with the Szyzkowski equation and the Jasper equation for the temperature influence on the binary system. The concentration influence on ternary systems was described via the aqueous ammonium sulfate concentration and both the aqueous and organic caprolactam concentration, which resulted in good fits. The concentration influence on the quaternary system, however, was described via the organic caprolactam concentration assuming that the influence of caprolactam and the salting-out effect would cover almost fully the influence of both solutes on the interfacial tension. A temperature influence on the caprolactam Szyzkowski coefficients was observed, but for ammonium sulfate, this influence was not clearly present. A good representation of the interfacial tension for all systems was obtained using this approach.

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