Three-Liquid Phase Equilibria in Water + Benzene + Caprolactam + $(NH_4)_2SO_4$ Mixtures

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Liquid–liquid–liquid equilibrium (LLLE) data are reported for the water + benzene + caprolactam + ammonium sulfate system at 293.1 K, 313.1 K, and 328.1 K. The experiments show a distinct pattern of phase behavior with increasing salt concentration and temperature. The tricritical point of the system was not determined, but was estimated to be around 332 K. The results are modeled using a modification of the extended electrolyte NRTL model. The model was able to represent the LLLE data satisfactorily.

Introduction

In 1975, Lang and Widom published their well-known article on liquid–liquid–liquid equilibria (LLLE) in systems of water + benzene + ethanol + ammonium sulfate at atmospheric pressure (Lang and Widom, 1975). In that publication, equilibrium data are presented at different temperatures up to very close to the tricritical point, the temperature at which the three phases become identical. During experiments to determine the liquid–liquid phase behavior of water + benzene + caprolactam + ammonium sulfate systems, phase behavior similar to that for water + benzene + ethanol + ammonium sulfate systems was encountered.

The practical importance of LLLE is, for example, for the water + oil + surfactant systems in enhanced oil-recovery processes, where capillary forces in reservoir pores are reduced by surfactant flooding. Also, for improving the performance of an extraction process, understanding of the phase behavior of systems exhibiting three liquid phases can be essential (Garcia-Sanchez et al., 1996). Equilibria of three liquid phases can occur when two-liquid phase regions overlap. LLLE received considerable interest, mainly inspired by the possibility of a tricritical point, as a test for theories of critical phenomena. Despite this degree of interest, the amount of three-liquid phase equilibrium data is limited (Bocko, 1980). For electrolyte solutions, most LLLE data were determined for systems with surfactants (Kahlweit et al., 1988). However, some studies have been made for other electrolyte systems, showing three liquid phases: quaternary equilibrium data have been published for water + benzene + ethanol + ammonium sulfate (Lang and Widom, 1975), water + octane + 1-propanol + sodium chloride (Negahban et al., 1986), and water + caprolactam + heptanone + ammonium sulfate (Van Bochove et al., 2002). For these systems, the patterns of the three-liquid phase equilibria with increasing salt concentration are similar to those investigated by Knickerbocker et al. (1979, 1982) for a variety of water + hydrocarbon + alcohol + salt systems.

The phase-behavior pattern observed for LLLE in quaternary electrolyte solutions is a progression with increasing salt concentration from two liquid phases at low salt concentrations, a three-liquid phase region at higher salt concentrations, and again a two-liquid phase region at still higher salt concentrations. The three-phase region is limited by two critical tie-lines, where two of the three phases become identical. In this pattern, temperature or pressure (Sassen et al., 1989; Andersen et al., 1999) can play a role similar to that of the salt concentration. With increasing temperature, the size of the LLLE-region decreases. At a given pressure in a quaternary system, a point with a certain temperature and composition exists, where the three coexisting phases become identical. This is the tricritical point. Lang and Widom (1975) attempted to locate this tricritical point for the system water + benzene + ethanol + ammonium sulfate.

The amount of literature on the modeling of LLLE using an excess Gibbs energy model is quite limited. Negahban et al. (1986, 1988) applied the UNIQUAC model to correlate LLLE at 298.1 K in water + *n*-octane + 1-propanol + sodium chloride and water + *t*-butanol + tetradecane + NaCl systems,

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using a pseudoternary approach. Garcia-Sanchez et al. (1996) and Stateva et al. (2000) also used the UNIQUAC model to model LLLE of ternary and quaternary nonelectrolyte mixtures. Heidemann and Abdel-Ghani (2001) used the NRTL model to model LLLE in water + phenol + *n*-hexane.

In this article, LLLE are reported and modeled for the system water + benzene + caprolactam + ammonium sulfate in a temperature range of 293 K to 330 K. The system water + benzene + caprolactam + ammonium sulfate is of importance for the solvent-extraction process of caprolactam, the monomer of nylon. This extraction process is one of the many industrial processes in which a mixed-solvent electrolyte solution exists. In the extraction process of caprolactam, ammonium sulfate is present from very low concentrations up to concentrations near saturation. Modeling of the liquid–liquid equilibria in and simulation of these extraction processes is complicated by the inability of most electrolyte models to describe the nonideal behavior of a mixture of electrolyte and mixed solvent over a wide range of concentrations. Therefore, the availability of a model for mixed-solvent electrolyte solutions to describe liquid–liquid phase behavior is of great importance for industry. The development of such a model is the subject of the research project of which this work is part.

In previous articles on this project, data were given for LLE in the water + 1-heptanol + caprolactam + ammonium sulfate system (Wijtkamp et al., 1999), and for the system water + 2-heptanone + caprolactam + ammonium sulfate (Van Bochove et al., 2002). The results were modeled using a modification of the extended electrolyte NRTL model (Van Bochove et al., 2000). In this article, the same model will be applied to both the experimental data published before and the three-liquid phase-equilibrium data reported here for the water + benzene + caprolactam + ammonium sulfate system.

Experimental Procedure

LLLE were determined experimentally in the range of 293 to 333 K. The caprolactam, obtained from DSM, had a minimum purity of 99.5%; the benzene (JT Baker) had a minimum purity of 99%, and the ammonium sulfate (Merck) had a minimum purity of 99.5%. The experimental procedure has been described elsewhere (Van Bochove et al., 2002) and will be discussed only briefly here.

The apparatus used, consisted of a stirred glass vessel with a thermostated water jacket and sample points for each phase. The vessel is shown in Figure 1. The temperature could be controlled to within 0.1 K. Liquid mixtures were prepared by weighing the pure components such that almost equal volumes could be expected for the different liquid phases. The mixtures were stirred for about 4 h and then allowed to settle until the three phases became completely clear, but for at least 12 h. (For some mixtures, the time to settle exceeded a week.) Consequently, samples were taken through the sealed sample ports using a syringe.

The benzene and caprolactam concentrations were determined by gas chromatography, using an HP 5890 Series II gas

Table 1. Liquid–Liquid–Liquid Equilibrium Data* for the Water (W) + Benzene (B) + Caprolactam (C) + Ammonium Sulfate (A) System at Different Temperatures

Temp. (K)	Exp. No.	Top Phase				Middle Phase				Bottom Phase			
		W	*B*	*C*	*A*	*W*	*B*	*C*	*A*	*W*	*B*	*C*	*A*
293.1	1	0.027	0.724	0.249	0.0000	0.582	0.019	0.332	0.066	0.67	0.0049	0.185	0.140
	2	0.028	0.720	0.252	0.0000	0.539	0.024	0.382	0.055	0.684	0.0032	0.151	0.162
	3	0.029	0.702	0.269	0.0000	0.519	0.027	0.402	0.052	0.689	0.0025	0.146	0.163
	4	0.031	0.691	0.278	0.0000	0.491	0.030	0.434	0.046	0.696	0.0020	0.128	0.174
	5	0.032	0.683	0.285	0.0000	0.471	0.038	0.455	0.035	0.695	0.0016	0.106	0.198
	6	0.036	0.664	0.300	0.0000	0.429	0.049	0.494	0.027	0.705	0.0009	0.0899	0.204
	7	0.042	0.638	0.320	0.0000	0.400	0.061	0.519	0.020	0.700	0.0007	0.0681	0.232
	8	0.046	0.625	0.329	0.0000	0.389	0.072	0.521	0.018	0.699	0.0006	0.0657	0.235
	9	0.050	0.616	0.334	0.0000	0.364	0.090	0.531	0.014	0.702	0.0005	0.0571	0.241
	10	0.058	0.587	0.356	0.0000	0.337	0.111	0.542	0.010	0.700	0.0005	0.0504	0.249
	11	0.059	0.580	0.361	0.0000	0.327	0.120	0.543	0.0094	0.704	0.0005	0.0480	0.248
	12	0.075	0.528	0.397	0.0000	0.284	0.156	0.553	0.0071	0.696	0.0004	0.0443	0.259
	13	0.091	0.477	0.431	0.0002	0.258	0.182	0.555	0.0054	0.703	0.0003	0.0422	0.254
	14	0.103	0.459	0.438	0.0002	0.240	0.200	0.555	0.0044	0.695	0.0003	0.0390	0.265
313.1	1	0.064	0.578	0.358	0.0000	0.543	0.032	0.366	0.059	0.620	0.0160	0.276	0.089
	2	0.072	0.562	0.366	0.0000	0.471	0.057	0.438	0.034	0.687	0.0029	0.177	0.133
	3	0.084	0.540	0.376	0.0000	0.438	0.077	0.464	0.021	0.688	0.0038	0.156	0.152
	4	0.087	0.536	0.378	0.0000	0.411	0.093	0.476	0.020	0.690	0.0045	0.149	0.156
	5	0.088	0.524	0.388	0.0001	0.391	0.100	0.490	0.019	0.696	0.0032	0.147	0.153
	6	0.092	0.515	0.393	0.0001	0.379	0.111	0.495	0.015	0.690	0.0033	0.122	0.185
	7	0.117	0.468	0.416	0.0001	0.328	0.150	0.512	0.010	0.708	0.0019	0.103	0.188
	8	0.149	0.393	0.457	0.0008	0.276	0.206	0.513	0.006	0.710	0.0019	0.104	0.185
328.1	1	0.147	0.417	0.434	0.0008	0.458	0.075	0.438	0.029	0.622	0.019	0.274	0.085
	2	0.156	0.383	0.460	0.0010	0.412	0.101	0.467	0.021	0.653	0.013	0.239	0.095
	3	0.174	0.348	0.476	0.0013	0.388	0.114	0.481	0.016	0.654	0.013	0.238	0.095
	4	0.203	0.295	0.500	0.0022	0.360	0.128	0.499	0.014	0.654	0.014	0.241	0.091
	5	0.225	0.258	0.515	0.0028	0.328	0.147	0.509	0.015	0.657	0.012	0.233	0.097
330.1	1	0.203	0.316	0.478	0.0028	0.453	0.052	0.457	0.039	0.595	0.026	0.315	0.063
	2	0.232	0.245	0.518	0.0045	0.420	0.067	0.490	0.023	0.603	0.025	0.306	0.065

*All data are given as weight fractions.

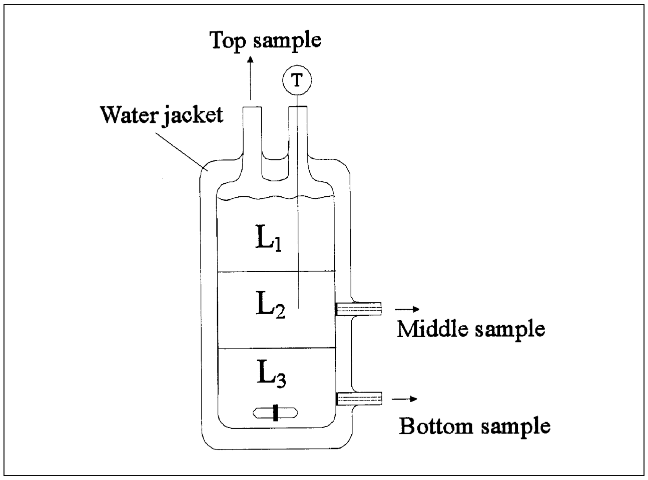

Figure 1. Vessel used for the measurements of LLLE.

chromatograph with a 30 m × 0.53 mm DB5 (J&W Scientific) column. Toluene (Janssen Chimica, 99.5%) was taken as the internal calibration standard and methanol (Merck, 99.5%) was used for the dilution. For the determination of the water content, Karl-Fischer analysis was used with a Mettler DL 35 Karl-Fisher Titrator with Hydranal Titrant 2 or Hydranal Titrant 5 (Riedel de Haën) as titrant and Hydranal solvent (Riede de Haën) as the solvent. Ammonium sulfate contents were determined by photometric titration using a Mettler DL 21 Titrator. The titrant was a 0.005 mole L^{-1} barium perchlorate solution in 2-propanol/water (Merck) and thorin (Merck), 0.2 wt % in water, was used as an absorption indicator. The samples were diluted with 2-propanol (Baker Analyzed, 99%).

The average relative error in the weight fractions was around 1% for benzene, 2% for caprolactam, 1.5% for water, and around 3% for ammonium sulfate, based on a 95% confidence interval.

Experimental Results

The results for the LLLE measurements are given in Table 1. The experiments were carried out at 293.1 K, 313.1 K, 328.1 K, and 330.1 K. At 332 K only two-liquid phase equilibria were found; at 330.1 K only two LLLE could be determined. The time needed to get a full phase separation increased dramatically with increasing temperature or at concentrations approaching those of a critical tie-line. Some of the results are depicted in Figures 2 to 5. A quaternary system at constant temperature and pressure can be represented by a tetrahedron. In Figure 2, the tetrahedron is given with the curve formed by the phase compositions at 293.1 K. In addition some of the three-phase triangles are given. For a better picture of the progression of the LLLE region with salt concentration, the salt-free projection of the LLLE at 293.1 K is given in Figure 3. In Figures 4 and 5 the same projections are given for the equilibrium data at 313.1 K and 328.1 K.

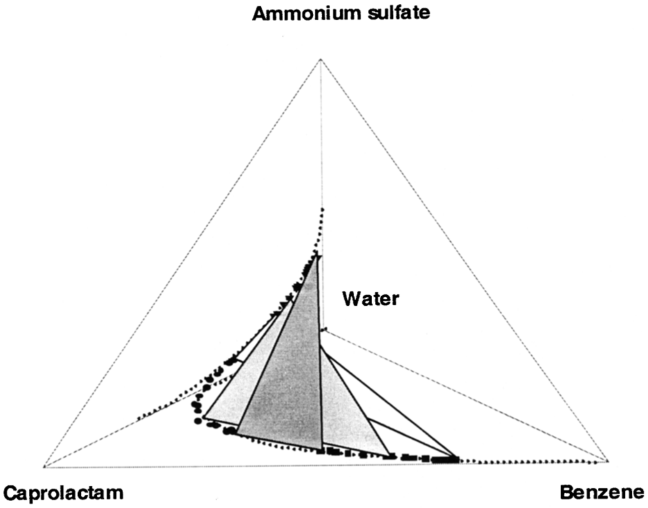

Figure 2. Top (■), middle (▼), and bottom (●) phase compositions and some tie-triangles of LLLE in the water + benzene + caprolactam + ammonium sulfate system at 293.1 K.

Dotted lines give the binodal curves for the ternary system.

Comparison of Figures 3 to 5 shows the influence of temperature on the region where LLLE exist, and gives an idea of the location of the tricritical point. The figures illustrate how the three-phase triangles move, with increasing salt concentration, from one critical tie-line, where the bottom and middle phase are identical, to the second critical tie-line, where the middle and top phase become identical and merge. The size of the LLLE region decreases as the temperature increases. At higher temperatures, the three-phase region is found at lower overall salt concentrations, and the range of salt concentrations in which three-phase equilibria occur is decreasing. To illustrate the influence of temperature and salt concentration on the size and location of the three-phase region, Figure 6 contains the overall salt concentrations at which LLLE occur at 293.1 K, 313.1 K, 328.1 K, and 330.1 K. Figure 6 can be used to estimate the tricritical point. Here, it is

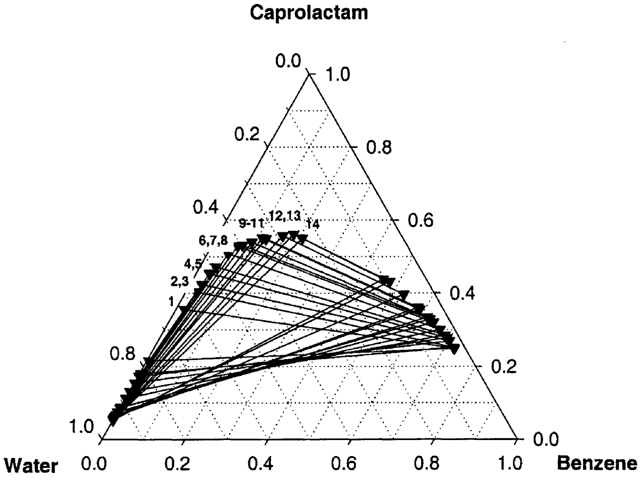

Figure 3. Salt-free projection of experimental LLLE for the water + benzene + caprolactam + ammonium sulfate system at 293.1 K.

Labels refer to the LLLE data in Table 1.

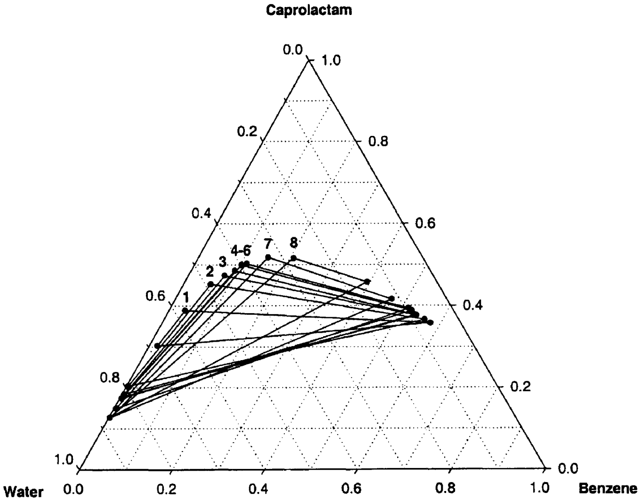

Figure 4. Salt-free projection of experimental LLLE for the water + benzene + caprolactam + ammonium sulfate system at 313.1 K.

Labels refer to the LLLE data in Table 1.

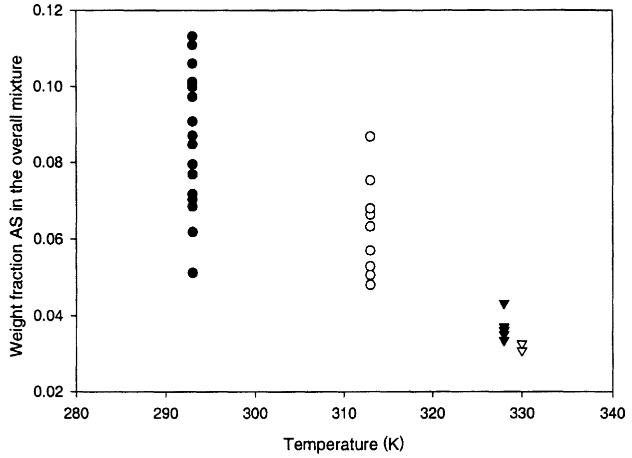

Figure 6. Overall salt concentrations for the experiments in Table 1.

Data are given in weight fractions.

estimated to be around 332 K, and the overall weight fraction of ammonium sulfate to be around 0.027. Experimentally, no LLLE were found at 332 K or higher.

Thermodynamic Model

The model that was used to correlate the experimental data is a modification of the electrolyte NRTL (Chen and Evans, 1986; Aspen Technology, 1998). The modified extended electrolyte NRTL (Van Bochove et al., 2000) differs from the model of Chen in the way the solution properties are treated and in the addition of a Brønsted–Guggenheim contribution, as used by Christensen et al. (1983) and suggested by Liu and Watanasiri (1996). The model has been applied successfully to liquid–liquid equilibria in water + solvent + caprolactam + ammonium sulfate and has been shown capable of representing three-liquid phase equilibria (Van Bochove et al., 2002). It has not been used yet to model LLLE at different temperatures, simultaneously with the corresponding ternary and quaternary liquid–liquid equilibria, which is the aim of the current work.

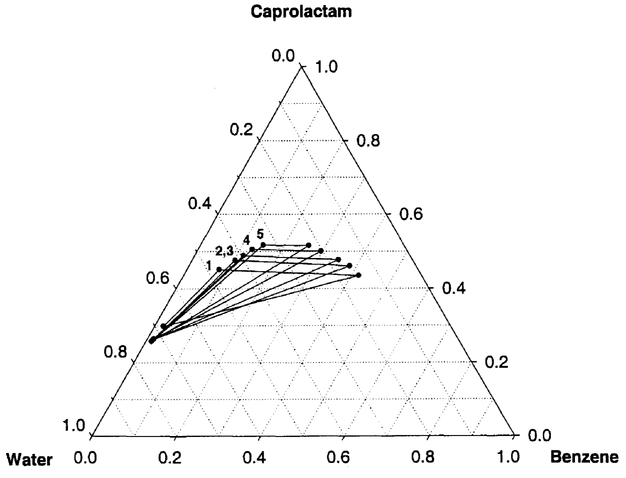

Figure 5. Salt-free projection of experimental LLLE for the water + benzene + caprolactam + ammonium sulfate system at 328.1 K.

Labels refer to the LLLE data in Table 1.

The extended electrolyte NRTL model for the excess Gibbs energy is given in the Appendix. The model is constructed from four contributions: a local composition contribution (the NRTL model), an electrostatic contribution [the Pitzer–Debye–Hückel (PDH) model], a Born contribution, and a Brønsted–Guggenheim (BG) contribution. The activity coefficients are constructed in the same way

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{NRTL}} + \ln \gamma_i^{\mathrm{PDH}} + \ln \gamma_i^{\mathrm{BG}} + \ln \gamma_i^{\mathrm{Born}} \qquad (1)$$

In the derivation of the activity coefficients, the dependence of the solution properties in the electrostatic contribution on the solvent composition was taken into account. The Born contribution was used to change the reference state in the PDH model from infinite dilution in the mixed-solvent to infinite dilution in water. The Brønsted–Guggenheim contribution was added and modified, in particular to improve the representation of systems with a plait point, as in the liquid–liquid equilibria of the ternary system, water + caprolactam + ammonium sulfate. The original electrolyte NRTL (Chen et al., 1986) fails here in the closure of the binodal line. A more extensive description of the model has been given elsewhere (Van Bochove et al., 2000).

A constant temperature, constant pressure multiphase flash routine was programmed to calculate the LLLE. The algorithm was based on the work of Koak (1997), and the group of Heidemann (Andersen et al., 1999; Phoenix and Heidemann, 1998). They used a nested approach. In the inner loop the fugacity coefficients are assumed constant and the mole balance is solved by multidimensional Newton–Raphson iteration. In the outer loop the fugacity coefficients are updated and chemical equilibrium is calculated by the use of the direct substitution method. The tangent plane distance criterion of Michelsen (1982) was implemented as a stability test to determine the number of phases.

The binary interaction parameters were obtained from regressions using the Levenberg–Marquardt method. Best results were obtained by regressing the LLLE data first. The liquid–liquid equilibria of the quaternary system and ternary subsystems and the mean ionic activity coefficients of water + ammonium sulfate could then be represented with no or only minor adjustments of the binary interaction parameters. The objective function used is given in Eq. 2, where x can be weight fractions and/or mole fractions, nd is the number of data points, np is the number of phases, and nc is the number of components

$$F_{\mathrm{OBJ}} = \sum_{k}^{nd} \sum_{p}^{np} \sum_{i}^{nc} \left[\left(x_{kpi}^{\exp} - x_{kpi}^{\mathrm{calc}} \right)^2 \right] \tag{2}$$

The polynomials provided by Perry (1997) were used for the densities of the pure solvents; the solution dielectric constant was calculated from the pure component data (Lide, 1995) by solvent-free weight fractions. The Born radii were taken from the article by Rashin and Honig (1985).

Modeling Results

The modeling was carried out with a large number of data sets, including three sets of LLLE data: the system water + benzene + caprolactam + ammonium sulfate; the system water + benzene + ethanol + ammonium sulfate; and the system water + 2-heptanone + caprolactam + ammonium sulfate. Initially, the normal temperature dependence of the NRTL interaction parameters ($\tau = A/T$) was used. Accurate results could be obtained by regressions with data sets at only one temperature, but a subsequent application of the parameters found to represent all the data in the measured temperature range failed. It appeared impossible to model the LLLE at the different temperatures simultaneously, without changing the temperature dependence of the binary interaction parameters. Hence, the interaction parameters are now calculated by

$$\tau_{ij} = \frac{\tau_{ij}^0 + \tau_{ij}^1 (T - 293.15)}{T} \tag{3}$$

The results for the various systems are tabulated in Table 2 and depicted in Figures 7 and 8. The average deviations given in Table 2 were calculated by Eq. 4. The binary interaction parameters obtained from the regressions are presented in Table 3

$$\Delta x = \sqrt{\frac{\sum_k \sum_p \sum_i \left(x_{kpi}^{\exp} - x_{kpi}^{\mathrm{calc}} \right)^2}{nc \times np \times nd}} \tag{4}$$

Table 2. Experimental Equilibrium Data of Ternary and Quaternary Systems with Water, Caprolactam, Solvents, and Ammonium Sulfate (AS), Using the Modified Extended Electrolyte NRTL

Type	System	T (K)	Calculations Δx (%)	Δw (%)	Source*
LLE	Water + benzene + caprolactam	293	0.9	0.7	1
		313	1.6	1.2	1
		333	2.5	2.9	1
	Water + 1-heptanol + caprolactam	293	0.8	1.9	2
		313	1.5	2.5	2
		333	0.9	2.1	2
	Water + 2-heptanone + caprolactam	293	2.4	1.8	3
		313	1.7	1.4	3
		333	1.4	1.6	3
	Water + caprolactam + AS	293	0.9	2.7	4
		313	0.8	2.6	4
		328	0.6	0.9	4
	Water + benzene + caprolactam + AS	293	0.9	0.6	1
		313	1.1	1.4	1
		333	1.6	1.4	1
	Water + 1-heptanol + caprolactam + AS	293	0.5	0.9	2
		313	0.7	1.4	2
		333	0.9	2.1	2
	Water + 2-heptanone + caprolactam + AS	293	1.0	1.4	3
		313	0.8	1.5	3
LLLE	Water + 2-heptanone + caprolactam + AS	293	1.5	2.3	3
	Water + benzene + caprolactam + AS	293	1.3	2.4	5
		313	2.1	4.1	5
		328	1.9	4.1	5
	Water + benzene + ethanol + AS	294	2.6	3.8	6
		317	4.0	4.6	6
Gamma**	Water + AS	298	0.3		7

*Source of data: 1 = De Haan and Niemann (1999); 2 = Wijtkamp et al. (1999); 3 = Van Bochove et al. (2002); 4 = Haase (1998); 5 = this publication; 6 = Lang and Widom (1975); 7 = Robinson and Stokes (1959).

**Mean ionic activity coefficients, given as average relative deviations (%).

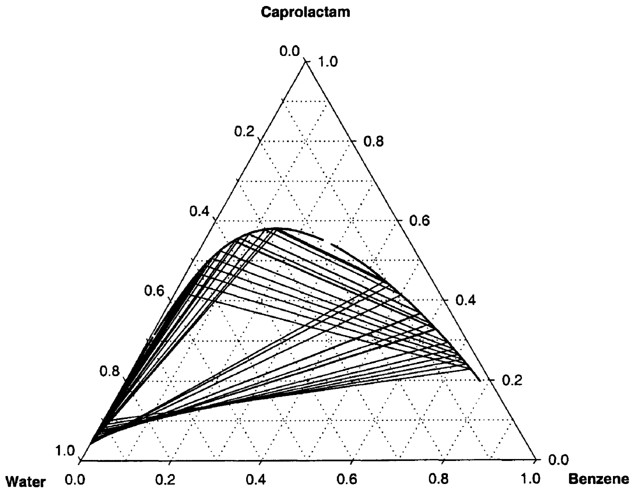

Figure 7. Salt-free projection of calculated LLLE and phase composition curve for the water + benzene + caprolactam + ammonium sulfate system at 293.1 K.

LLLE were calculated with the overall compositions of the triangles in Figure 3.

Table 3. NRTL Binary Interaction Parameters* for the Systems in Table 2

Component 1	Component 2	τ_{12}^{0}	τ_{21}^{0}	τ_{12}^{1}	τ_{21}^{1}	β_{12}^{AS}
Water	Benzene	1,793.3	713.2	1.16	−0.782	
Water	1-Heptanol	1,876.1	−77.5	3.067	−1.398	
Water	2-Heptanone	1,569.8	216.1	2.289	0.685	
Water	Ethanol	309.2	−188.2	2.398	−0.403	839.5
Water	Caprolactam	1,195.5	−662.2	2.318	−0.851	368.2
Benzene	Caprolactam	−276.0	235.8	2.026	−1.652	
1-Heptanol	Caprolactam	−794.6	1,015.1	−6.263	19.15	
2-Heptanone	Caprolactam	28.0	−38.1	−4.396	0.908	
Benzene	Ethanol	461.9	−158.2	−9.107	−0.127	
Water	$(NH_4)_2SO_4$	2,922.1	−1384.7	2.647	−2.05	
Benzene	$(NH_4)_2SO_4$	3,529.8	3,440.8	24.81	−0.52	
1-Heptanol	$(NH_4)_2SO_4$	1,158.1	1,068.0	−2.749	−6.053	
2-Heptanone	$(NH_4)_2SO_4$	804.1	1,133.2	4.016	20.95	
Ethanol	$(NH_4)_2SO_4$	1,169.3	1,653	2.561	−8.276	
Caprolactam	$(NH_4)_2SO_4$	537.8	3,167.4	5.446	−52.98	

*All nonrandomness factors (α) are fixed at 0.20 as used for LLE by Chen et al. (1986), except those for solvent + caprolactam, which were fixed at 0.30 for a better representation of the experimental data.

The results of the modeling show that, using the temperature dependency of Eq. 3, it was possible to get a good representation of the experimental data. This is not only valid for the equilibrium data presented in this work, but also for other experimental data on liquid demixing of similar systems, including LLLE data. The model could not be used to calculate the tricritical point, because the temperature dependence of the NRTL interaction parameters is not described accurately enough. The model is not able to give a quantitative representation of the decrease in the size of the three-liquid phase region.

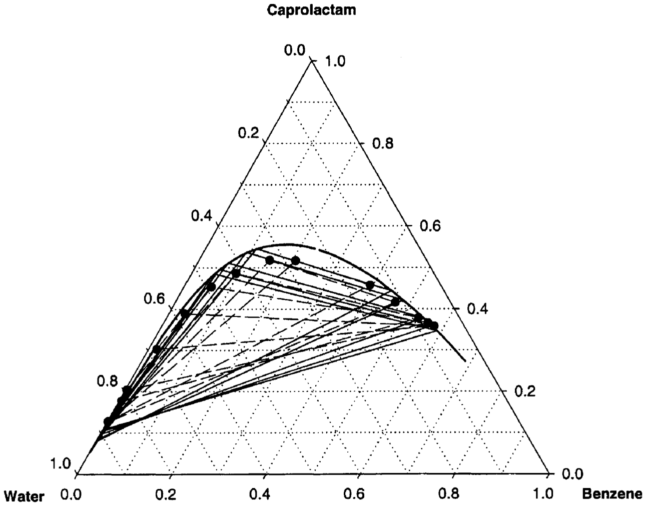

Figure 8. Salt-free projection of selected experimental (dashed lines, ●) and calculated (solid lines) LLLE and the calculated phase composition curve (bold) for the water + benzene + caprolactam + ammonium sulfate system at 313.1 K.

Conclusions

The experimental data given here for the system water + benzene + caprolactam + ammonium sulfate, illustrate the phase pattern as discussed in the literature for other systems, in particular the system water + benzene + ethanol + ammonium sulfate, and explained in detail by Rowlinson and Swinton (1982): the two ternary subsystems, water + solvent + caprolactam and water + caprolactam + ammonium sulfate, form two of the four triangular faces of the tetrahedron by which the quaternary system is represented (Figure 2). By adding salt to the critical point of the first ternary system, the critical point moves to the interior of the tetrahedron. When solvent is added to the second ternary system, its critical point is also moved to the interior. The critical points at different salt or solvent concentrations are points of a critical line. The two critical lines can form a continuous curve from one face to another. In this case, one two-liquid phase region is found, and a continuous transition is found for the slope of the LLE tie-lines from one triangular face or ternary subsystem to the other one. If the quaternary system (water + benzene + ethanol or caprolactam + ammonium sulfate) is below its tricritical point, the two critical lines do not meet, but have an endpoint. At this endpoint, the two critical phases are in equilibrium with a third phase. The tie-lines, thus formed are the two critical tie-lines that bound the three-phase region. Between the two endpoints, there is a stack of three-phase triangles. The compositions of the LLLE follow the three-phase composition curve. A progression with salt concentration from two liquid phases to three liquid phases and again to two liquid phases is characteristic of this and similar systems.

As the temperature increases, the range of concentrations showing three liquid phases grows much smaller. At 328.1 K and 330.1 K, the LLLE are only found in a narrow range of salt concentrations. These observations are comparable to those for the system water + benzene + ethanol + ammonium sulfate (Lang and Widom, 1975).

The extended electrolyte NRTL model was applied to represent the experimental data, including LLLE of three different quaternary systems. Satisfactory results can be obtained if a two-parameter function of temperature is used for the binary interaction parameters. Even then, the decrease in the size of the three-phase region represents major difficulties to the model. Despite this shortcoming, the results are considered to be good enough to motivate further study: As far as is known by the authors, no other model in the literature has been applied before to this kind of system, and especially not with data sets of LLLE of different systems at different temperatures simultaneously.

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Notation

F_{OBJ} = optimization function
nc = number of components
nd = number of data points
np = number of phases
w_i = weight fraction
x_i = mole fraction
T = temperature

Greek letters

β_{ij} = Brønsted−Guggenheim interaction parameter
γ_i = activity coefficient component i
Δ = mean average deviation
τ_{ij} = binary interaction parameter

Subscripts and superscripts

BG = Brønsted−Guggenheim
Born = Born contribution
calc = calculated value
exp = experimental value
NRTL = NRTL contribution
PDH = Pitzer−Debye−Hückel contribution

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Appendix: Modified Extended Electrolyte NRTL Model

Local composition contribution

$$\frac{G^E}{RT} = \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_j}{\sum_k X_k G_{km}} + X_c \frac{\sum_j X_j G_{jc} \tau_{jc}}{\sum_k X_k G_{kc}} + X_a \frac{\sum_j X_j G_{ja} \tau_{ja}}{\sum_k X_k G_{ka}} - x_c \ln(\gamma_c^\infty) - x_a \ln(\gamma_a^\infty)$$

where

$$X_j = C_j x_j \quad \left(C_j = Z_j \text{ for ions; } C_j = 1 \text{ for solvents} \right)$$

$$\alpha_{jc} = \alpha_{ja} = \alpha_{cj} = \alpha_{aj} = \alpha_{j,ca}$$

$$\tau_{jc} = \tau_{ja} = \tau_{j,ca}$$

$$\tau_{cj} = \tau_{aj} = \tau_{ca,j}$$

where R is the universal gas constant.

Pitzer – Debye – Hückel contribution

$$\frac{G^{E,\mathrm{PDH}}}{RT} = -\left(\sum_n x_n \right) \frac{4 A_x I_x}{\rho} \ln\left(1 + \rho \sqrt{I_x} \right)$$

$$I_x = \frac{1}{2} \sum x_i z_i^2$$

$$A_x = \frac{1}{3} \sqrt{\frac{1{,}000}{M_s}} \sqrt{2\pi N_A d} \left(\frac{e^2}{\epsilon k T} \right)^{3/2}$$

where ρ is the closest approach parameter ($\rho = 14.9$), z_i is the charge number, M_s is the solvent molecular weight, N_A is Avagadro”snumber, d is the solution density, ϵ is the solution dielectric constant, and e is the elementary charge.

Born contribution

$$\frac{G^{E,\mathrm{Born}}}{RT} = \frac{e^2}{2kT} \left(\frac{1}{\epsilon} - \frac{1}{\epsilon_w} \right) \sum_i \frac{x_i z_i^2}{r_i}$$

where r_j is the Born radius and ϵ_w is the dielectric constant of water.

Brønsted – Guggenheim contribution

$$\frac{G^{E,\mathrm{BG}}}{RT} = \frac{1{,}000}{\sum_k x_k M_k} \frac{\sum_j \sum_{k>j} \beta_{jk}^{ca} x_j x_k}{T} x_a x_c$$

Details about the modeling are given by Van Bochove et al. (2000).

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