Ternary Liquid−Liquid(−Liquid) Equilibria of Aniline + Cyclohexylamine + Water, Aniline + Cyclohexylamine + Octane, Aniline + Water + Toluene, and Aniline + Water + Octane

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Four ternary liquid−liquid(−liquid) equilibria in the systems aniline + cyclohexylamine (CHA) + water, aniline + CHA + octane, aniline + water + octane, and aniline + water + toluene under atmospheric pressure at (298.15 and 333.15) K are reported. The measurements were carried out by turbidity titration, gas−liquid chromatography analyses, Karl Fischer, and potentiometric titration. Predictions of the NRTL and UNIQUAC Gibbs energy models are shown based only on binary parameters of simultaneous fitting of available vapor−liquid equilibria and liquid−liquid equilibria data. In this context $P-x$ data were measured for the system aniline + octane at 383.15 K.

Introduction

Liquid−liquid equilibria (LLE) are essential for designing and realizing extraction plants. The shape of the binodal, the slope of the tie lines, and therewith the compositions of the coexisting phases have to be well-known to realize technical extraction processes. Such data are also useful for theoretical studies. The measurements of this work were compared to predictions of the widely used activity coefficient models NRTL[1] and UNIQUAC.[2] Aniline is a key compound in the aromatic chemistry. Several chemical reaction products such as diisocyanate, pigments, drugs, and pesticides are made of it. Cyclohexylamine is also a reaction product of aniline, and it is used, for example, as a corrosion inhibitor.

Experimental Section

Materials. The components octane purity 99+ %, toluene purity p.a., aniline purity p.a., and cyclohexylamine purity p.a. were purchased from Acros Organics, Belgium. The purities were judged by comparing experimental values of refractive index and density with values reported in the literature; the values are shown in Table 1. Additionally, the purities were verified by gas−liquid chromatography (GLC). The mass fractions of the substances were octane (99.9 %), toluene (99.8 %), aniline (99.5 %), and cyclohexylamine (99.9 %). Deionized and distilled water was used.

Methods. The binodals were determined by turbidity titration. This method has already been used to give reliable results on LLE in ternary systems of phenol or cresols[5] and in systems with cyclohexylamine.[6] The experimental setup consists of a tempered glass vessel with magnetic stirrer. An ultrasonic generator (UW 2070, BANDELIN Electronic, Berlin) of low power is employed for a better dispensation of the added component. The measurement happened as follows. In the vessel, a binary homogeneous mixture is prepared by weighing with an accuracy of ± 0.5 mg. The third component is added in small amounts by an automatic buret (808 Titrando, Deutsche

Table 1. Comparison of the Experimental Refractive Index, n_D, and Density, ρ, of Pure Liquids with Literature Values[3]

substance	T/K	n_D exptl	n_D lit	ρ/g·cm⁻³ exptl	ρ/g·cm⁻³ lit
octane	298.15	1.3946	1.3944	0.69849	0.6986
toluene	293.15	1.4960	1.4961	0.86678	0.8668
aniline	293.15	1.5862	1.5863	1.02172	1.0217
cylclohexylamine	288.15	1.4624	1.4625		
	303.15			0.85820	0.85777[4]
water	293.15	1.3336	1.3336	0.99816	0.9982

Metrohm, Filderstadt) with a precision of 0.02 mL. The occurrence of a second liquid phase creates an intensive turbidity that can be registered by a photometer (type 662, Deutsche Metrohm, Filderstadt). Therewith, the turbidity (LLE) can easily be detected by the transmission data that are logged by a PC. The equilibrium compositions of the liquid phases in ternary systems are determined with an average precision of ± 0.003 mol/mol. A more detailed description of the measurement procedure is given in ref 6. The tie lines and the liquid−liquid−liquid equilibria (LLLE) were determined by the analytic method. The components were equilibrated in a glass vessel with sample points at different heights. Through these, samples of each phase can be taken without the piercing of other phases. The mixture was stirred for 4 h, in doing so the temperature was kept constant within a range of ± 0.1 K. Afterward, the phases were allowed to separate for at least 24 h before the samples were taken. The composition of each phase was analyzed by GLC for organic compounds or by potentiometric titration for cyclohexylamine (716 DMS Titrino, Deutsche Metrohm, Filderstadt) and by Karl Fischer titration (787 KF Titrino, Deutsche Metrohm, Filderstadt) for water. A Hewlett-Packard 6890 gas chromatograph with flame ionization detector and HP Ultra 2 (cross-linked 5 % Ph Me silicone) column was used. The compositional analysis was based on the internal calibration standard method. The precision of the GLC analytic for the organic components is ± 0.005 mol/mol and for the potentiometric titration is 0.5 mass % of the measured value. The accuracy of the Karl Fischer titration is 1 mass % of the measured value.

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Table 2. Binodal Curve, Tie Line Data, and Binary Data, This Work, for Aniline (1) + CHA (2) + Water (3) at (298.15 and 333.15) K and Atmospheric Pressure

	298.15 K			333.15 K		
	x_1	x_2	x_3	x_1	x_2	x_3
	0.735	0.019	0.246	0.003	0.022	0.975
	0.697	0.038	0.265	0.003	0.029	0.968
	0.661	0.053	0.286	0.004	0.038	0.958
	0.609	0.073	0.318	0.005	0.047	0.948
	0.577	0.084	0.339	0.006	0.058	0.936
	0.534	0.098	0.368	0.008	0.068	0.924
	0.490	0.110	0.401	0.010	0.077	0.913
	0.449	0.121	0.431	0.012	0.086	0.902
	0.405	0.130	0.465	0.015	0.094	0.891
	0.376	0.131	0.493	0.018	0.101	0.881
	0.341	0.141	0.518	0.024	0.112	0.864
	0.299	0.148	0.553	0.029	0.118	0.853
	0.253	0.152	0.595	0.033	0.124	0.843
	0.228	0.159	0.613	0.040	0.131	0.829
	0.190	0.158	0.652	0.054	0.141	0.805
	0.137	0.150	0.713	0.071	0.149	0.780
	0.121	0.147	0.732	0.096	0.167	0.737
	0.102	0.143	0.755	0.115	0.175	0.710
	0.088	0.138	0.774	0.140	0.183	0.677
	0.077	0.133	0.790	0.176	0.191	0.633
	0.062	0.125	0.813	0.200	0.191	0.609
	0.042	0.111	0.847	0.234	0.190	0.576
	0.035	0.100	0.865	0.276	0.187	0.537
	0.022	0.080	0.898	0.307	0.182	0.511
	0.011	0.053	0.936	0.340	0.172	0.488
	0.004	0.023	0.973	0.377	0.167	0.456
	0.007	0.000	0.993	0.417	0.158	0.425
	0.775	0.000	0.225	0.458	0.142	0.400
				0.489	0.129	0.382
				0.522	0.114	0.364
				0.536	0.111	0.353
				0.560	0.101	0.339
				0.597	0.088	0.315
				0.632	0.073	0.295
				0.671	0.053	0.276
				0.008	0.000	0.992
				0.715	0.000	0.285
Tie Lines						
a	0.320	0.132	0.548	0.092	0.170	0.738
b	0.006	0.003	0.991	0.000	0.004	0.996
a	0.233	0.150	0.617	0.118	0.170	0.712
b	0.006	0.003	0.990	0.000	0.005	0.995
a	0.122	0.149	0.729	0.218	0.184	0.598
b	0.006	0.006	0.988	0.005	0.004	0.992
a				0.165	0.193	0.642
b				0.003	0.005	0.991

[a] Top phase. [b] Bottom phase.

Table 3. Binodal Curve and Tie Line Data, This Work, for Aniline (1) + CHA (2) + Octane (3) at (298.15 and 333.15) K and Atmospheric Pressure[a]

	298.15 K			333.15 K		
	x_1	x_2	x_3	x_1	x_2	x_3
	0.096	0.008	0.896	0.303	0.010	0.687
	0.106	0.018	0.875	0.330	0.019	0.651
	0.121	0.033	0.847	0.367	0.026	0.607
	0.138	0.047	0.815	0.419	0.035	0.547
	0.158	0.065	0.777	0.477	0.040	0.483
	0.200	0.090	0.710	0.500	0.042	0.458
	0.241	0.108	0.651	0.537	0.042	0.421
	0.298	0.126	0.577	0.585	0.045	0.370
	0.384	0.143	0.473	0.602	0.044	0.354
	0.452	0.153	0.394	0.613	0.045	0.342
	0.564	0.160	0.276	0.623	0.043	0.334
	0.661	0.152	0.187	0.647	0.043	0.310
	0.742	0.128	0.129	0.676	0.042	0.282
	0.837	0.082	0.082	0.738	0.035	0.226
	0.922	0.026	0.052	0.809	0.021	0.171
	0.955	0.000	0.045	0.865	0.000	0.135
	0.086	0.000	0.914	0.275	0.000	0.725
Tie Lines						
b	0.167	0.051	0.782	0.330	0.019	0.651
c	0.815	0.080	0.105	0.746	0.031	0.223
b	0.106	0.014	0.880	0.302	0.007	0.691
c	0.894	0.030	0.076	0.867	0.007	0.126
b	0.229	0.088	0.683			
c	0.661	0.152	0.187			

[a] Binary data: aniline + octane from ref 7. [b] Top phase. [c] Bottom phase.

Table 4. Binodal Curve, This Work, for Aniline (1) + Toluene (2) + Water (3) at (298.15 and 333.15) K and Atmospheric Pressure[a]

298.15 K			333.15 K		
x_1	x_2	x_3	x_1	x_2	x_3
0.433	0.520	0.047	0.457	0.460	0.083
0.539	0.392	0.069	0.490	0.412	0.098
0.600	0.314	0.086	0.524	0.364	0.112
0.637	0.259	0.104	0.555	0.319	0.126
0.661	0.223	0.116	0.576	0.294	0.130
0.680	0.191	0.129	0.610	0.243	0.147
0.698	0.163	0.139	0.693	0.064	0.243
0.711	0.141	0.148	0.008	0.000	0.992
0.723	0.120	0.157	0.715	0.000	0.285
0.732	0.103	0.165	0.000	1.6E−4	0.999
0.737	0.095	0.168	0.000	0.993	0.007
0.007	0.000	0.993			
0.775	0.000	0.225			
0.000	1.2E−4	0.999			
0.000	0.997	0.003			

[a] Binary data: aniline + water, this work; toluene + water, ref 8.

Results and Discussion

Liquid−liquid−(liquid) equilibria of four ternary systems at (298.15 and 333.15) K under atmospheric pressure were determined. The experimental values are reported in Tables 2 to 5. The system aniline + CHA + water shown in Figures 1 and 2 has a type 1 miscibility gap. The two-phase region becomes slightly larger with increasing temperature. Amines + water systems are known for lower critical solution temperatures (LCST) (e.g., the systems triethylamine + water, dipropylamine + water, and butylethylamine + water are reported in the literature,[10] which all have a LCST). This is caused by weak-bonded clusters from amines with water that break down with increasing temperature; this behavior seems to be the same in the considered system. Both experimental determined binodals are presented in Figure 2 to point out the small temperature dependence. The slope of the tie lines in this system increases with increasing water and CHA concentration. The plait point is strongly asymmetric at high water concentrations close to the border of the CHA + water system. Koperska and Cieslak[11]

measured the binodal curve at 293.15 K in this system. The comparison to the binodal at 298.15 K of this work shows good agreement. Since the temperature dependence is small in this system, this is an indicator of the accuracy of the data of this work.

The miscibility gap of aniline + CHA + octane has also type 1 character. Conversely to aniline + CHA + water, the two-phase region becomes smaller with increasing temperature as presented in Figures 3 and 4. The slope of the tie lines is small so that the plait point is almost symmetrically located at the binodal.

The experimental binodal curves of the system aniline + toluene + water are shown in Figures 5 and 6. The two-phase region becomes smaller with increasing temperature. However, the temperature dependence is small; therefore, both binodal curves are shown in Figure 6. Smith and Drexel[12] also presented LLE data at 298.15 K in this system. There are only small differences between these data and those presented here, but

Table 5. Binodal Curve Data for Aniline (1) + Octane (2) + Water (3), This Work, at (298.15 and 333.15) K and Atmospheric Pressure[a]

298.15 K			333.15 K		
x_1	x_2	x_3	x_1	x_2	x_3
0.781	0.024	0.195	0.855	0.113	0.033
0.822	0.028	0.150	0.833	0.093	0.074
0.876	0.033	0.091	0.803	0.076	0.121
0.887	0.034	0.079	0.777	0.066	0.157
0.945	0.042	0.014	0.753	0.054	0.193
0.000	0.007	0.993	0.008	0.000	0.992
0.000	0.782	0.218	0.735	0.000	0.265
0.045	0.955	0.000	0.865	0.135	0.000
0.914	0.086	0.000	0.275	0.725	0.000
0.000	0.000	1.000	0.000	0.000	1.000
0.999	0.000	0.001	0.000	0.998	0.002

[a] Binary data: aniline + water, this work; octane + water, ref 9; aniline + octane, ref 7.
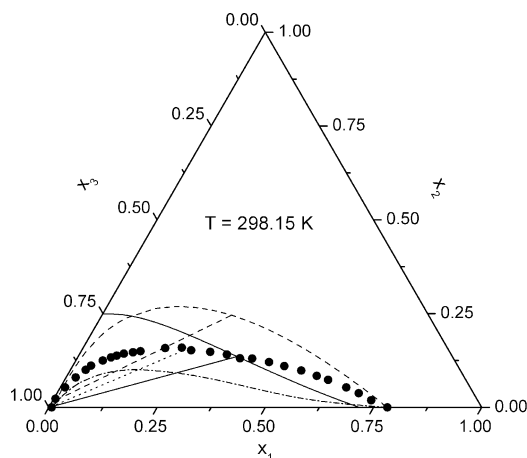
Figure 1. Binodal curve and tie lines in the system aniline (1) + CHA (2) + water (3) at 298.15 K. ● and doted line, experimental results, this work. Predictions: solid line, NRTL-1; dashed−dotted line, NRTL-2; dashed line, UNIQUAC.
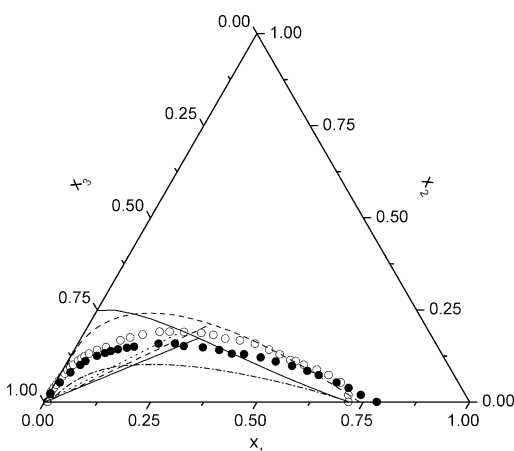
Figure 2. Binodal curve and tie lines in the system aniline (1) + CHA (2) + water (3).●, experimental results at 298.15 K, this work; ○ and doted line, experimental results at 333.15 K, this work. Predictions at 333.15 K: solid line, NRTL-1; dashed−dotted line, NRTL-2; dashed line, UNIQUAC.

the binodals subtend each other. In the region of high toluene concentration, the data of Smith and Drexel give a lower water concentration in the organic phase than the data of this work. Conversely, at high aniline concentrations, our data give a lower water concentration in the organic phase than those of Smith and Drexel.

The type 3 system aniline + octane + water illustrated in Figures 7 and 8 is characterized by a large three-phase region
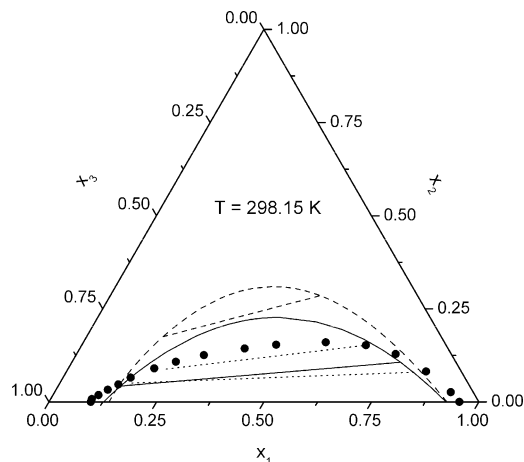

Figure 3. Binodal curve and tie lines in the system aniline (1) + CHA (2) + octane (3) at 298.15 K. ● and dotted line, experimental results, this work. Predictions: solid line, NRTL; dashed line, UNIQUAC.
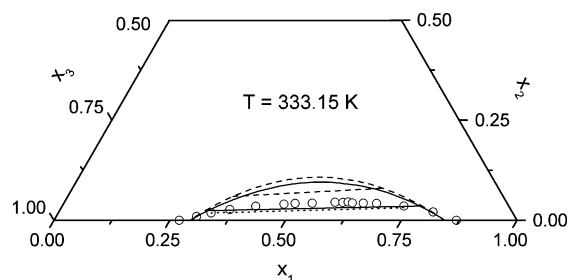

Figure 4. Binodal curve and tie lines in the system aniline (1) + CHA (2) + octane (3) at 333.15 K. ○ and dotted line, experimental results, this work. Predictions: solid line, NRTL; dashed line, UNIQUAC.
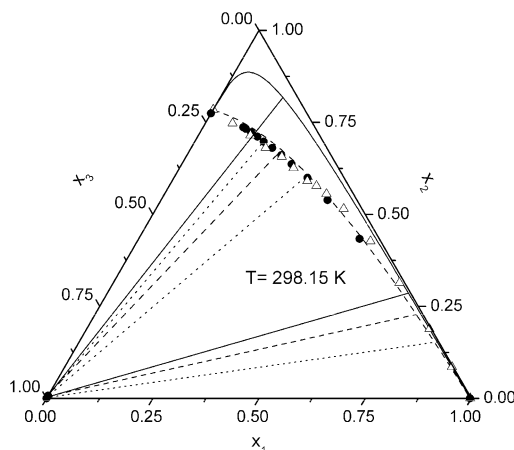

Figure 5. Binodal curve and tie lines in the system toluene (1) + aniline (2) + water (3) at 298.15 K. ●, this work; △, binodal curve and dotted lines, Smith and Drexel.[7] Predictions: solid line, NRTL; dashed line, UNIQUAC.

and three different two-phase regions. All binary border systems have miscibility gaps. Figure 9 shows the temperature dependence of the LLLE from (298.15 to 363.15) K, which becomes smaller with increasing temperature; the data are given in Table 6. The water-rich phase is almost unaffected by the temperature changes. However, the aniline content of the octane-rich phase increases rapidly, and the aniline content of the aniline-rich phase decreases with increasing temperature. Between 298.15 K and 313.15 K a phase inversion occurs because of the different temperature dependence of the density of aniline and water. At 298.15 K, the water-rich phase is the middle phase, and from 313.15 K up to 363.15 K the water-rich phase is the bottom phase. The octane-rich phase is each time the top phase.
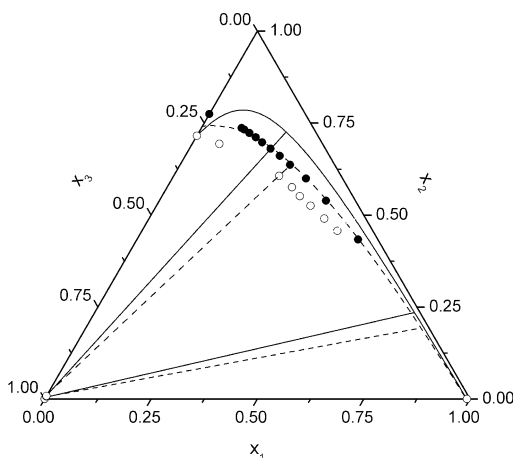
Figure 6. Binodal curve and tie lines in the system toluene (1) + aniline (2) + water (3). ○, binodal curve at 333.15 K, this work; ●, binodal curve at 298.15 K, this work. Predictions at 333.15 K: solid line, NRTL; dashed line, UNIQUAC.
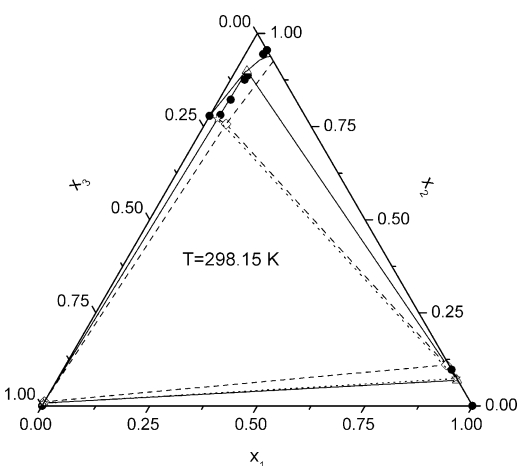

Figure 7. LL(L)E in the system octane (1) + aniline (2) + water (3) at 298.15 K. ●, binodal curve, this work; doted line with ☆, experimental LLLE results, this work. Predictions: solid line with △, NRTL; dashed line with ◇, UNIQUAC.

Figure 8. LL(L)E in the system octane (1) + aniline (2) + water (3) at 333.15 K. ○, binodal curve, this work; doted line with ☆, experimental LLLE results, this work. Predictions: solid line with △, NRTL; dashed line with ◇, UNIQUAC.
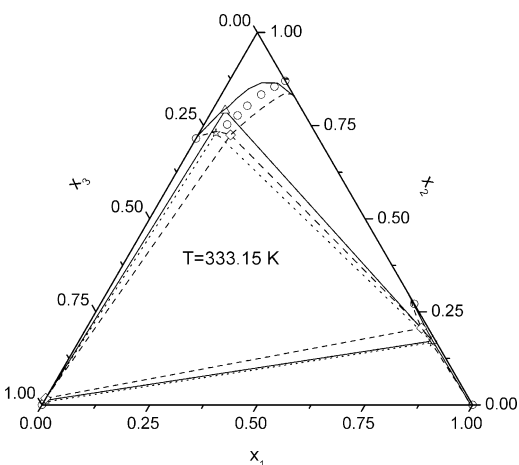
Predictions were made in these four ternary systems with the models NRTL and UNIQUAC. The binary parameters for the models were fitted simultaneously to VLE and, if available, LLE data. We tried to use all existing phase equilibrium data from literature for these binary systems. For the system aniline +
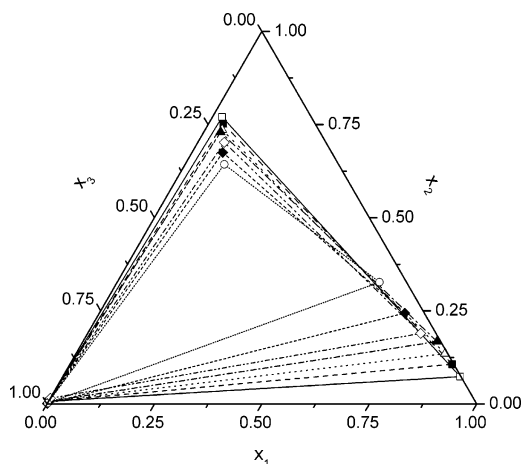

Figure 9. LLLE temperature dependence in the system octane (1) + aniline (2) + water (3), this work. □, 298.15 K; ■, 313.15 K; △, 323.15 K; ▲, 333.15 K; ◇, 343.15 K; ◆, 353.15 K; ○, 363.15 K.

Table 6. LLLE Aniline (1) + Octane (2) + Water (3) at (298.15, 313.15, 323.15, 333.15, 343.15, 353.15, and 363.15) K

	top phase			middle phase			bottom phase		
T/K	x_1	x_2	x_3	x_1	x_2	x_3	x_1	x_2	x_3
298.15	0.073	0.925	0.002	0.007	0.000	0.993	0.770	0.023	0.207
313.15	0.107	0.890	0.003	0.753	0.034	0.214	0.007	2E−5	0.993
323.15	0.135	0.859	0.006	0.736	0.040	0.224	0.007	1.6E−5	0.993
333.15	0.167	0.824	0.009	0.730	0.039	0.231	0.007	0.000	0.993
343.15	0.189	0.775	0.036	0.702	0.062	0.236	0.016	1.7E−4	0.984
353.15	0.244	0.711	0.045	0.675	0.072	0.253	0.002	1.6E−4	0.998
363.15	0.327	0.611	0.063	0.643	0.091	0.266	0.002	1.6E−4	0.998

octane only one LLE data set of Arlt and Onken[7] exists. Since for all systems vapor−liquid equilibria (VLE) data were used and no P−x−y or T−x−y data of aniline + octane are available in the literature, vapor pressure data were measured at 383.15 K with the equipment described in ref 13. The dynamic method was used to measure the octane + aniline system. In the circulation still the vapor is condensed in the cooler and because of the miscibility gap two liquid phases appear. The aniline-rich phase had stronger adhesion forces to the glass than the octane-rich phase; therefore, no useable sample (with proper amounts of both liquid phases at the sampling point) of condensed vapor was available. This is the reason no vapor phase is reported. The quality of the modeling for aniline + octane with NRTL and UNIQUAC is nearly the same. The experimental VLE data are presented in Table 7 and Figure 10. Recently, we have published simultaneous fitted parameters[13] for CHA + water, CHA + octane, and CHA + aniline. In ref 6, parameters for toluene + water and octane + water are presented. These are used in this work. Several VLE and LLE data sets for aniline + water can be found in the literature.[14−22] The data that were used in the simultaneous fitting are presented in Table 8. Here is described why some of the data are not used. The data of Speakman[15] and Dallos et al.[21] have been neglected because they presented only data at the water-rich site. Furthermore, one of the two data sets of Griswold et al.[16] (the isobaric one) is not consistent as well as the data of Kolyuchkina et al.[19] Both data sets are not included in the fitting. Additionally, LLE data of the liquid−liquid data collection of Sørensen and Arlt[10] and Sazonov et al.[22] were used. For the system aniline + toluene,[23−29] the data of Billes and Varsanyi[26] and Hollo et al.[27] were omitted, these are not thermodynamically consistent. The data of Lee et al.[28] and Desphande and Pandya[29] were also not used. Since no vapor phase is reported, no consistence test can be performed, and the deviations of the simultaneous fitting increase strongly if these data are included. The obtained parameters for the NRTL and UNIQUAC models
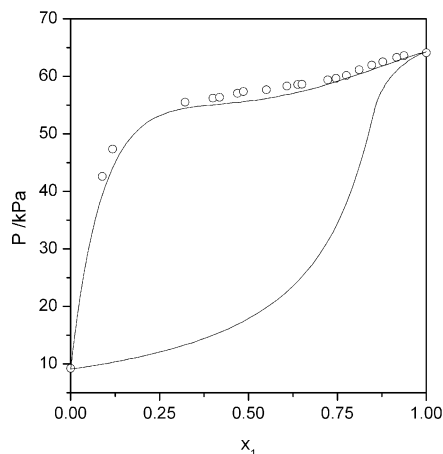
Figure 10. $P-x$ data for octane (1) + aniline (2): ○, experimental data, this work; lines: simultaneous fitting of these experimental VLE data and LLE data of Arlt and Onken[7] with UNIQUAC.

Table 7. $P-x$ Data for Octane (1) + Aniline (2)

		Octane (1) + Aniline (2) at 383.15 K			
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.000	9.21	0.486	57.35	0.776	60.15
0.089	42.59	0.550	57.65	0.811	61.13
0.118	47.33	0.608	58.29	0.847	61.96
0.322	55.52	0.639	58.58	0.878	62.52
0.400	56.20	0.651	58.60	0.917	63.27
0.419	56.35	0.723	59.39	0.938	63.60
0.469	57.05	0.746	59.66	1.000	64.09

and the deviations are summarized in Table 8. Parameters were determined for the activity coefficient models using eq 1 and the objective function Q of Renon et al.[30] (eq 2):

$$C_{ij}/R = C_{ij}^C + C_{ij}^T(T - 273.15 \text{ K}) \qquad (1)$$

where $C_{ij} = u_{ij} - u_{jj}$ for UNIQUAC and $C_{ij} = g_{ij} - g_{jj}$ for NRTL:

$$Q = \Pi_1 \sum_i \left(\frac{100}{P_{\text{exptl}}}\right)_i^2 (P_{\text{calcd}} - P_{\text{exptl}})_i^2 +$$

$$\Pi_2 \sum_i (100)_i^2 (y_{\text{calcd}} - y_{\text{exptl}})_i^2 + \Pi_3 \sum_i (100)_i^2 (x'_{\text{calcd}} - x'_{\text{exptl}})_i^2 +$$

$$\Pi_4 \sum_i (100)_i^2 (x''_{\text{calcd}} - x''_{\text{exptl}})_i^2 \quad (2)$$

where P is the pressure, y is the vapor phase mole fraction, x'

and x'' are the mole fractions of the different phases at LLE, and Π_i is a weighting factor.

Figures 1 and 2 present predictions of NRTL and UNIQUAC in the system aniline + CHA + water. UNIQUAC predicts a two-phase region at both temperatures of (298.15 and 333.15) K, which is too large. Additionally, the binodal curve is smaller than predicted at the higher temperature, conversely to the experimental result. The deviations at 298.15 K are larger than at 333.15 K. The slope of the tie lines is in good agreement with the experiment. For NRTL, two results are presented since with the parameters from ref 13 for CHA + water based only on VLE data a non-existent miscibility gap is predicted, result NRTL-1. It is known[1] that a high value of α prevents calculation of immiscibility (e.g., for symmetrical miscibility gaps the limit is α = 0.42). For asymmetrical miscibility gaps, the limit is far larger. The calculation of demixing could be inhibited with an α = 1.1 and C_{12} = 288.22 K; C_{21} = 582.80 K, result NRTL-2. However, the ternary miscibility gap is now predicted to be too small for both temperatures.

Predictions of the system aniline + CHA + octane are shown in Figures 3 and 4. For the lower temperature of 298.15 K, NRTL has an advantage over UNIQUAC. The two-phase region is calculated with smaller deviations but also not satisfactorily in comparison to the experiment. The tie lines of NRTL and UNIQUAC agree well with the experimental one. The predicted miscibility gap in this system at 333.15 K is again too large but a good result for the very flat binodal curve.

UNIQUAC delivers an excellent prediction of the system toluene + aniline + water at 298.15 K. NRTL predicts for both temperatures a far too large two-phase region, and the binodal curve has an obvious maximum which the experimental values do not show (see Figures 5 and 6). Similar results with the NRTL model were obtained already by Schmelzer et al.[5] in systems of 2-cresol + toluene + water or 2-cresol + octane + water.

The LLLE of the system aniline + octane + water is well-predicted at 298.15 K by UNIQUAC (Figure 7). Only the aniline content of the octane-rich phase is slightly underestimated. NRTL delivered a far too high aniline content in the aniline-rich phase. Both models reflect the LLE and LLLE behavior with only small deviations at 333.15 K (Figure 8).

Conclusions

Four ternary liquid−liquid(−liquid) equilibria under atmospheric pressure at (298.15 and 333.15) K were reported: aniline

Table 8. Fitted Parameters (Eqs 1 and 2) for NRTL and UNIQUAC, Used Data Sets for the Fitting and the Deviations in Vapor Pressure, Vapor Phase Composition and in Systems with LLE the Average Mole Fraction Deviation for the Miscibility Gap

binary systems	fitted data	model	C_{12}^C/K	C_{21}^C/K	C_{12}^T	C_{21}^T	ΔP/%[c]	Δy/%[d]	Δx/%[d]
aniline (1) + water (2)	refs 10, 14, 16−18, 20−22	NRTL (α = 0.40)	888.33	1259.43	−4.8719	0.0361	2.14	0.57	1.24
		UNIQUAC	187.22	66.00	2.7364	−1.9277	2.52	0.79	1.38
aniline (1)+ octane (2)	ref 7, this work	NRTL (α = 0.30)	626.37	511.68	0.1338	−2.3954	2.38		4.54
		UNIQUAC	17.26	252.88	−0.2092	−0.2284	2.64		4.82
aniline (1) + CHA (2)[a]		NRTL (α = 0.47)	−325.43	−19.70	5.7392	−1.8710	1.14	0.64	
		UNIQUAC	−144.97	5.46	3.4764	−1.6882	1.07	0.76	
aniline (1) + toluene (2)	ref 23−25	NRTL (α = 0.47)	193.13	307.88	0.6304	−1.4573	0.65	0.35	
		UNIQUAC	66.85	61.30	0.4435	−0.8561	0.75	0.35	
CHA (1) + water (2)[a]		NRTL (α = 0.47)	−13.11	1186.17			1.83	1.87	
		UNIQUAC	−13.51	30.03	0.8887	−0.1823	2.05	1.85	
CHA (1) + octane (2)[a]		NRTL (α = 0.47)	112.31	135.08			1.03	0.59	
		UNIQUAC	−44.05	107.52			1.13	0.67	
octane (1) + water (2)[b]		NRTL (α = 0.20)	2141.80	3260.80	−7.5243	12.5243	2.67	1.69	0.004
		UNIQUAC	1558.09	381.79	−5.8408	1.8703	2.71	1.68	0.004
toluene (1) + water (2)[b]		NRTL (α = 0.20)	1397.47	1983.05	−5.3412	6.0602	2.58	1.46	0.008
		UNIQUAC	1016.32	311.50	−3.6809	0.8284	2.74	1.49	0.007

[a] Parameter taken from ref 13. [b] Parameter taken from ref 6. [c] $P = 100/n_p\sum((|P_{\text{calcd}} - P_{\text{exptl}}|)/P_{\text{exptl}})$, where n_p is the number of data points. [d] $\Delta Z = 100/n_p\sum(|Z_{\text{calcd}} - Z_{\text{exptl}}|)$ where Z represents y or x.

+ CHA + water, aniline + CHA + octane, aniline + toluene + water, and aniline + octane + water. Predictions based only on binary parameters of simultaneous fitting of available VLE and LLE data were made with the models NRTL and UNIQUAC. The results of the predictions are not very satisfactory. Considering the strong association effects in these systems, the models cannot be expected to give better results since no term for association is included. Too large two-phase regions were obtained in all type 1 and type 2 miscibility gaps systems except the UNIQUAC results in the system aniline + toluene + water. Better results were achieved in the system aniline + octane + water. The large three-phase region is well-predicted especially with UNIQUAC; only NRTL results at 298.15 K give a too large three-phase region.

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