J. Chem. Eng. Data **2004,** *49,* 1675−1681

VLE and LLE Data for the System Cyclohexane + Cyclohexene + Water + Cyclohexanol

Frank Steyer[†] **and Kai Sundmacher**[*,†,‡]

Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstrasse 1,
39106 Magdeburg, Germany, and Process Systems Engineering, Otto-von-Guericke-University Magdeburg,
Universitätsplatz 1, 39106 Magdeburg, Germany

The ternary system cyclohexene + water + cyclohexanol is currently being studied with the aim of carrying out the reaction of cyclohexene and water to cyclohexanol in a reactive distillation column. The challenge this system poses for such a reactive separator lies in the liquid−liquid phase splitting behavior, which adds a third effect in addition to reaction and distillation. Cyclohexane is added as a fourth component into these studies, representing any C_6 inerts. To be able to describe the activities of all four components, measurements were conducted of the liquid−liquid and vapor−liquid equilibria, and appropriate NRTL parameters matching both vapor−liquid and liquid−liquid phase splitting behavior were identified.

Introduction

Cyclohexanol is an important intermediate in nylon production and is being produced on a very large scale. The production process mainly being used today oxidizes cyclohexane with air. This process has drawbacks in being dangerous because explosive air/cyclohexane mixtures are necessarily formed during the process. Also, it produces large amounts of side products even at low conversions and requires large amounts of hydrogen for the production of cyclohexane from benzene.[1]

Asahi Chemical in Japan has pioneered a new route to cyclohexanol via hydration of cyclohexene.[2] This reaction is carried out in a slurry reactor with large amounts of extremely fine-grained solid zeolite catalysts of the HZSM5 type. The slurry is then separated after the reactor, water and catalyst are recycled, and the organic phase containing most of the product is distilled.

Because the equilibrium conversion to cyclohexanol is fairly low, this leads to large recycle streams from the top of the distillation column to the slurry reactor. This problem is exacerbated by the fact that the cyclohexene feed also contains cyclohexane and benzene as side products of the hydrogenation step that also have to be recycled because they have almost identical boiling points and cannot be separated easily by distillation.

Because cyclohexanol has a much higher boiling point, it is easily separated, making the reactor/separator an ideal device for the reactive separation of cyclohexene from the mixture with cyclohexane and cyclohexanol.

Ideally though, one would wish to have a countercurrent reaction/separation device that would allow the recycles to be internalized and that would lead to an ideal use of the heat of reaction. This is why an effort is currently under way to design a reactive distillation column to carry out this reaction. The cyclohexene + cyclohexane + benzene mixture would enter the column toward the bottom, and water would enter toward the top. The reactants would then be contacted in a countercurrent manner, and pure cyclohexane + benzene mixtures without cyclohexene would leave the column at the top.

To be able to simulate such a reactive distillation system, a complete set of thermodynamic data and a reaction kinetic model valid for the whole range of conditions within such a column is necessary. On the phase equilibrium side, initial simulations using UNIFAC have led to a qualitatively correct description of the phase behavior, but this effort has fallen short of being adequate for quantitative predictions. Some data on VLE and LLE and the azeotropes exist[3−11] but are far from being complete. In particular, we were not able to find a sufficiently large and reliable set of data to fit parameters for an activity coefficient model such as NRTL for the binary pairs cyclohexene + water, cyclohexane + water, and cyclohexene + cyclohexanol.

Because both cyclohexene and cyclohexane have very low solubilities in water, in the part-per-million range, VLE data are also especially hard to measure directly. To correctly describe the complete VLLE behavior—especially the mixing gap—measurements in ternary systems have to be performed.

As an additional challenge, the measurements of both LLE and VLE should be described with one set of NRTL parameters because one component can have only one activity at a given set of conditions. Because of the many parameter sets describing each individual phenomenon equally well, of which only a few will describe both phenomena, this is also a challenging curve fitting problem.

The results of our measurements and a suggested set of NRTL parameters to describe this system are presented here.

Materials

To ensure that the NRTL parameters fitted to the data correctly describe both VLE and LLE, measurements of these two types of equilibria were made. For both cases, cyclohexene, cyclohexane, and cyclohexanol were acquired from VWR in synthesis quality (>99%). Cyclohexene was distilled twice to remove the stabilizer. Cyclohexanol and

---

[*] To whom correspondence should be addressed. Phone: +49-391-6110-350. Fax: +49-391-6110-353. E-mail: sundmacher@mpi-magdeburg.mpg.de.
[†] Max Planck Institute for Dynamics of Complex Technical Systems.
[‡] Otto-von-Guericke-University Magdeburg.

10.1021/je049902w CCC: $27.50

Table 1. Selected Liquid−Liquid Equilibrium Data for the Ternary System Cyclohexene (1) + Cyclohexanol (2) + Water (3) at T = 295 K

x'_1	x'_2	x''_1	x''_2
0	0.546	0	0.00629
0.051	0.566	0.000030	0.00598
0.097	0.564	0.000015	0.00533
0.151	0.549	0.000058	0.00435
0.186	0.532	0.000019	0.00493
0.221	0.533	0.000042	0.00573
0.267	0.506	0.000024	0.00457
0.290	0.490	0.000014	0.00451
0.316	0.486	0.000062	0.00425
0.364	0.463	0.000058	0.00410
0.398	0.441	0.000058	0.00398
0.445	0.414	0.000063	0.00383
0.511	0.376	0.000053	0.00441
0.561	0.343	0.000059	0.00328
0.614	0.311	0.000048	0.00416
0.675	0.270	0.000084	0.00385
0.705	0.242	0.000061	0.00331
0.760	0.204	0.000052	0.00346
0.816	0.160	0.000058	0.00345
0.834	0.147	0.000076	0.00323
0.9155	0.0764	0.000066	0.00153
0.9987	0	0.000078	0

Table 2. Selected Liquid−Liquid Equilibrium Data for the Ternary System Cyclohexanol (1) + Cyclohexane (2) + Water (3) at T = 295 K

x'_1	x'_2	x''_1	x''_2
0.546	0.000	0.00629	0.000000
0.583	0.032	0.00598	0.000002
0.559	0.062	0.00552	0.000004
0.555	0.094	0.00535	0.000004
0.562	0.123	0.00526	0.000006
0.546	0.151	0.00523	0.000004
0.548	0.178	0.00516	0.000004
0.500	0.248	0.00473	0.000006
0.494	0.280	0.00474	0.000004
0.487	0.313	0.00456	0.000006
0.453	0.385	0.00458	0.000010
0.413	0.439	0.00455	0.000010
0.389	0.477	0.00454	0.000009
0.360	0.527	0.00440	0.000008
0.329	0.571	0.00439	0.000012
0.290	0.635	0.00416	0.000010
0.255	0.690	0.00382	0.000010
0.197	0.769	0.00384	0.000010
0.136	0.844	0.00354	0.000010
0.070	0.922	0.00280	0.000015
0.000	0.99963	0.00000	0.000012

cyclohexane were used as delivered. Water was taken from a deionizer (Type Millipore Milli-Q Gradient). Concentration analysis was performed by gas chromatography either using an FID/TCD combination as detectors behind a 30 m × 250 μm × 0.25 μm Innowax column or using a GC/MSD behind a 60 m × 250 μm × 0.1 μm DB5ms column (Hewlett-Packard 6890 or Agilent 6890N, respectively).

The GCs were calibrated using calibration samples prepared gravimetrically using a Mettler Toledo type AT261 DeltaRange scale. The uncertainity associated with the calibration sample composition can be estimated to be less than 0.01 mass %. The reproducibility of the GC measurements was established by repetitive measurements of the same sample using the calibrated GC. The standard deviation was evaluated to be below 0.05 mol %. The quality of the calibration was evaluated by measuring samples of known composition. The deviations between the composition of the gravimetrically composed samples and the GC measurements indicated a standard deviation of 0.31 mol %. The overall uncertainity of the gas chromatographic composition analysis can be assumed to be ±0.6% (with 95% confidence). The samples were at room temperature (295 K) when analyzed.

Liquid−Liquid Equilibrium Measurements

To perform the measurements of the liquid−liquid mixing gap, a mixture of either cyclohexene with water or cyclohexane with water was made with similar volumes of both substances. The mixtures were stirred vigorously with an ultra-turrax (Type T25 basic from IKA Werke) at 13000 rpm to ensure small droplet size and large droplet surface area. A sample of the resulting liquid−liquid dispersion was then separated by a centrifuge (Type Sigma 3K30) at 10000*g* for 2 min, which always resulted in a good separation. Samples were then taken from both phases and immediately analyzed via gas chromatography.

To cover the whole range of organic phase compositions, cyclohexanol was then added stepwise to the mixtures, which were then analyzed as described above. When the cyclohexanol mole fraction in the organic phase had reached roughly 50%, the series was ended and restarted with a water + cyclohexanol mixture to which cyclohexene or cyclohexane were added stepwise. Tables 1 and 2 report the data measured for these two ternary mixtures that were later used in parameter fitting.

The measured binary solubility data for cyclohexanol + water and cyclohexane + water were complemented with binary literature data,[10,11] which show comparable solubilities under the conditions at which the data were measured here.

Vapor−Liquid Equilibrium Measurements

The measurements for vapor−liquid equilibrium at different compositions were performed in a glass recirculation still (type VLE 602, Fischer Process Technology GmbH, Bonn, Germany). This instrument allows the equilibrium concentrations in both the liquid and vapor phases to be determined and the temperature (up to 523 K) and pressure (from 250 Pa to 400 kPa) to be measured. The samples of the vapor phase are usually drawn after the vapor phase has been condensed. It is also possible to draw vapor samples directly from the gaseous phase, which is intended to give representative composition samples if two liquid phases are present in the distillate. This is convenient in the case of cyclohexanol + water where the organic phase can hold a substantial amount of water. The temperature was measured at the phase boundary with at Pt100 temperature sensor with a resolution of 0.1 K. The pressure was measured using a calibrated WIKA CPH6200 pressure sensor with a range from 0 to 160 kPa. The measurement uncertainity of the sensor is given as ±0.2% FS (±320 Pa).

The very low mutual solubilities of cyclohexene and cyclohexane with water pose a problem, however, because the liquid phase also shows phase splitting even at very low concentrations of the minority compound, which leads to an unrepresentative ratio of organic to aqueous phase in the reboiler. This is the reason that no direct measurements of the cyclohexene + water and cyclohexane + water vapor−liquid equilibria were performed.

Vapor−liquid equilibrium measurements were performed for the binary pairs cyclohexene + cyclohexanol, cyclohexene + cyclohexane, cyclohexanol + water, and cyclohexanol + cyclohexane. The measurements were performed at ambient pressure. Tables 3−6 report the measurement results that were used in the data fitting procedure.

Table 3. Selected Vapor−Liquid Equilibrium Data for the Binary System Cyclohexene (1) + Cyclohexanol (2)

x_1	y_1	P (mbar)	T (K)
0.026	0.285	1005	427.4
0.062	0.534	1005	418.1
0.088	0.606	1005	411.1
0.114	0.677	1005	403.6
0.146	0.745	1014	403.3
0.191	0.808	1023	392.3
0.221	0.861	1004	388.4
0.251	0.878	1004	385.5
0.277	0.895	1004	383.7
0.291	0.901	1003	381.1
0.329	0.928	1011	380.5
0.366	0.936	1005	375.9
0.388	0.941	1005	375.0
0.413	0.947	1005	373.8
0.447	0.953	1006	370.6
0.469	0.955	1006	372.3
0.503	0.959	1006	372.1
0.520	0.961	1006	368.1
0.557	0.965	1007	367.5
0.583	0.967	1004	365.3
0.624	0.970	1004	364.3
0.676	0.973	1009	364.6
0.707	0.976	1009	362.6
0.752	0.979	1010	362.2
0.828	0.983	1004	359.3
0.881	0.986	989	358.6
0.912	0.989	1004	357.8
0.964	0.9938	1011	357.9
0.99983	0.999962	1012	356.8

Table 4. Vapor−Liquid Equilibrium Data for the Binary System Cyclohexene (1) + Cyclohexane (2)

x_1	y_1	P (mbar)	T (K)
0.9973	0.9970	1011	356.1
0.877	0.867	1011	355.7
0.790	0.775	1011	355.5
0.704	0.693	1012	355.3
0.637	0.622	1011	355.1
0.602	0.593	1006	354.8
0.565	0.548	1010	355.0
0.545	0.531	1005	354.8
0.520	0.505	1010	354.8
0.483	0.469	1004	354.5
0.466	0.452	1009	354.7
0.421	0.408	1003	354.4
0.398	0.383	1009	354.6
0.344	0.338	1002	354.1
0.285	0.276	991	353.6
0.186	0.181	991	353.5
0.099	0.096	990	354.5
0.0010	0.0011	989	353.4

Again, the measured data were complemented by literature data for the binary systems cyclohexanol + water[5−7] and cyclohexene + cyclohexane.[3,4] The literature data on cyclohexanol + water spanned a wider range of conditions than our measurements and also showed less scatter close to the mixing gap. In general, the literature data agreed well with our own measurement results whenever measurement conditions were comparable.

Antoine Coefficient Determination

To describe the temperature dependence of the pure-component vapor pressures, the Antoine equation was used

$$\log_{10}(P/\text{bar}) = A_i - \frac{B_i}{T/\text{K} + C_i} \qquad (1)$$

Table 5. Selected Vapor−Liquid Equilibrium Data for the Binary System Cyclohexanol (1) + Water (2)

x_1	y_1	P (mbar)	T (K)
0.697	0.113	1001	381.0
0.778	0.120	1009	383.1
0.814	0.133	1001	385.9
0.834	0.140	999	385.5
0.854	0.160	1003	389.7
0.880	0.213	1004	398.3
0.896	0.237	1010	396.3
0.923	0.334	1010	404.0
0.942	0.382	1011	411.2
0.967	0.509	1009	419.8
0.972	0.559	1008	422.1
0.989	0.786	1024	429.2
0.992	0.826	1010	423.9

Table 6. Selected Vapor−Liquid Equilibrium Data for the Binary System Cyclohexanol (1) + Cyclohexane (2)

x_1	y_1	P (mbar)	T (K)
0.9990	0.981	1014	433.2
0.998	0.982	1014	433.1
0.990	0.885	1014	430.2
0.971	0.691	1011	423.8
0.908	0.361	1012	407.0
0.804	0.159	1012	390.3
0.770	0.117	1006	382.0
0.669	0.082	1006	380.7
0.606	0.050	1004	370.2
0.531	0.038	1016	367.8
0.503	0.040	1006	363.4
0.498	0.033	1006	362.0
0.416	0.035	1006	358.7
0.399	0.035	1004	360.3
0.302	0.020	1005	356.3
0.262	0.020	1005	355.9
0.242	0.018	1007	358.7
0.172	0.015	1007	356.8
0.122	0.015	1005	355.1
0.098	0.012	1005	355.7
0.064	0.015	1005	354.7
0.014	0.0040	1004	354.2

In this equation, P is the pressure; T is the temperature; and A_i, B_i, and C_i are substance-specific parameters for which some literature data exist. Because literature data for the Antoine parameters are frequently fitted to measurements that were initially not intended for this purpose, some additional measurements were performed in the VLE device described above.

To fit the parameters to the experimental data, a simple sum of least-squares minimization was performed with the help of a global optimization algorithm.[12] The accuracy of the fit was very good, always giving a standard deviation between measured and calculated pressures at a given temperature in the range of (0.33 to 1.03) mbar. The measurement data for the four substances considered are reported in Tables 7−10. The fitted Antoine parameters can be found in Table 11.

The calculated values sometimes differ significantly from some of the data reported in the literature. This is especially true for cyclohexanol, where deviations between the pressure values calculated using the literature parameters[13] and the pressure values calculated with the above coefficients (within the temperature range defined in the literature) are partly above 30 mbar.

The values for water, on the other hand, are known very precisely, and the literature data[13] agree with the data reported here to within the 95% confidence intervals.

Table 7. Measured vs Calculated Vapor Pressures of Cyclohexene

T (K)	P (mbar)	P_{calc} (mbar)	ΔP (mbar)
310.15	198.0	197.2	0.8
320.35	297.0	297.5	−0.5
328.05	397.0	397.7	−0.7
334.20	496.0	495.8	0.2
339.55	596.0	596.1	−0.1
344.25	697.0	696.8	0.2
348.45	798.0	797.8	0.2
352.20	898.0	897.3	0.7
356.35	1018.0	1018.6	−0.6

Table 8. Measured vs Calculated Vapor Pressures of Cyclohexanol

T (K)	P (mbar)	P_{calc} (mbar)	ΔP (mbar)
322.25	5.0	5.3	−0.3
330.95	10.0	9.8	0.2
341.70	20.0	19.6	0.4
353.80	39.5	39.4	0.1
367.25	79.0	79.1	−0.1
382.40	158.5	158.7	−0.2
399.50	317.5	317.8	−0.3
419.05	637.5	637.0	0.5
433.30	1000.5	1000.7	−0.2

Table 9. Measured vs Calculated Vapor Pressures of Water

T (K)	P (mbar)	P_{calc} (mbar)	ΔP (mbar)
306.30	49.0	48.7	0.3
319.25	98.5	98.7	−0.2
333.35	198.5	197.7	0.8
342.40	297.5	297.9	−0.4
349.10	397.0	397.1	−0.1
354.60	496.5	498.1	−1.6
359.10	596.5	595.9	0.6
363.15	698.0	697.1	0.9
366.75	798.5	798.8	−0.3
369.90	899.0	897.5	1.5
372.90	999.5	1000.8	−1.3

Table 10. Measured vs Calculated Vapor Pressures of Cyclohexane

T (K)	P (mbar)	P_{calc} (mbar)	ΔP (mbar)
308.15	198.0	197.0	1.0
318.30	297.0	297.6	−0.6
325.95	397.0	397.9	−0.9
332.10	497.0	496.7	0.3
337.45	597.0	597.8	−0.8
342.05	698.0	697.2	0.8
346.25	799.0	798.9	0.1
350.00	900.5	899.3	1.2
354.05	1017.5	1018.5	−1.0

Because the literature data on water can be assumed to be very precise, this shows that the measurement technique used here allows for accurate measurement of the temperature/pressure relationship.

Over the temperature and pressure ranges given in the tables, all calculated pressures can be assumed to lie within an interval of ±3.8 mbar of the real value (with 95% confidence).

Model Formulation

To approximate the activity coefficients γ_i, the NRTL model[14] was chosen because it is capable of describing both vapor−liquid and liquid−liquid equilibria. It has three parameters that have to be identified per binary pair, denoted as a_{ij}, g_{ij}, and g_{ji}. These parameters were identified using the different kinds of measurement data as follows:

Table 11. Antoine Coefficients, Valid Temperature Range ΔT, and Standard Deviations between Measurements and Calculations for the Four Given Components

substance	A	B	C	ΔT (K)	σ (mbar)
cyclohexene	3.98075	1206.02	−52.7753	310−360	0.6374
cyclohexanol	4.06566	1258.75	−123.673	320−435	0.3293
water	5.00749	1605.78	−52.2025	300−375	1.0270
cyclohexane	3.96959	1191.56	−53.2741	305−355	0.9905

In the case of the vapor−liquid equilibrium data at low pressures, the vapor−liquid equilibrium condition can be written as

$$x_i \gamma_i P_i^{\mathrm{sat}} = y_i P \tag{2}$$

In this equation, x_i and y_i denote the liquid and vapor mole fractions, respectively, which can both be measured. The γ_i are the activity coefficients, which are calculated using the NRTL equation; P is the overall pressure, which is also measured; and P_i^{sat} can be calculated from the measured temperature using the Antoine equation.

This equation leads to the following objective function, δ_{VLE}, to be minimized

$$8\delta_{\mathrm{VLE}} = \sum_{n=1}^{\mathrm{NVLE}} \frac{2}{{\sigma_{\mathrm{P}}}^2}\Big[P_n^{\mathrm{m}} - \sum_{i=1}^{\mathrm{NC}} x_{i,n}^{\mathrm{m}}\, \gamma_{i,n}^{\mathrm{c}}\, P_{i,n}^{\mathrm{sat}}(T_n^{\mathrm{m}})\Big]^2 + \sum_{n=1}^{\mathrm{NVLE}} \sum_{i=1}^{\mathrm{NC}} \left[\frac{1}{{\sigma_{x,\mathrm{VLE}}}^2}\left(x_{i,n}^{\mathrm{m}} - \frac{y_{i,n}^{\mathrm{m}} P_n^{\mathrm{m}}}{\gamma_{i,n}^{\mathrm{c}} P_{i,n}^{\mathrm{sat}}(T_n^{\mathrm{m}})}\right)^2 + \frac{1}{{\sigma_y}^2}\left(y_{i,n}^{\mathrm{m}} - \frac{x_{i,n}^{\mathrm{m}}\, \gamma_{i,n}^{\mathrm{c}}\, P_{i,n}^{\mathrm{sat}}(T_n^{\mathrm{m}})}{P_n^{\mathrm{m}}}\right)^2 + \frac{1}{{\sigma_\gamma}^2}\left(\gamma_{i,n}^{\mathrm{c}} - \frac{y_{i,n}^{\mathrm{m}}\, P_n^{\mathrm{m}}}{x_{i,n}^{\mathrm{m}}\, P_{i,n}^{\mathrm{sat}}(T_n^{\mathrm{m}})}\right)^2\right] \tag{3}$$

In this equation, superscripts m and c denote measured and calculated values, respectively. NC and NVLE are the number of components and the number of VLE measurement points, respectively.

The first term on the right-hand side is the sum of the squared deviations between the measured and calculated overall pressures for each measurement point. The second term is the difference between the measured and calculated liquid-phase mole fractions. The third term is the difference between the measured and calculated vapor mole fractions, and the fourth term is the difference between the measured and calculated activity coefficients. All of the deviations are weighted with their corresponding variances σ^2. The associated standard deviations were estimated to be 45 mbar, 0.044, 0.04, and 0.20, respectively. These values were calculated by averaging over very many measurement data and show the *relative* accuracies of the different measurement types. They cannot, however, be seen as the direct standard deviations between the correlation and the measurement values because these differed significantly between different binary systems, as will be shown later.

The factor of 2 for the pressure deviations was introduced to compensate for the fact that the overall pressure was evaluated only once per measurement point, whereas the other measurement values are evaluated twice as NC is 2 in this case for every binary pair. The factor of 8 on the

Table 12. NRTL Parameters with Associated Standard Deviations[a] between Different Measurement Types and Calculations for the Four Given Components

binary pair	g_{12} (J/mol)	g_{21} (J/mol)	α_{12}	σ_y	σ_P (mbar)	$\sigma_{x,LLE}$
cyclohexene (1) + cyclohexanol (2)	3300.09	157.301	0.79362	0.0251	37.4	–
cyclohexene (1) + water (2)	13522.7	21495.6	0.24319	–	–	0.00640
cyclohexene (1) + cyclohexane (2)	35.3067	36469.3	0.89828	0.00392	9.26	–
cyclohexanol (1) + water (2)	−569.408	12237.7	0.26904	0.0350	85.2	–
cyclohexanol (1) + cyclohexane (2)	958.747	6334.27	0.86274	0.00655	54.5	–
water (1) + cyclohexane (2)	26171.4	17556.3	0.25118	–	–	0.00639

[a] Standard deviations given for cyclohexene + water and cyclohexane + water are between the calculated and measured ternary binodal curves with cyclohexanol.

left-hand side was introduced to compensate for the fact that every measurement point is now evaluated eight times.

The liquid−liquid equilibrium data were used to evaluate the activities of all substances present in the two liquid phases. If the parameter set describes the measurement data well, the difference between the activities in the two liquid phases should be zero, which leads to an objective function δ_{LLE}

$$3\delta_{LLE} = \sum_{n=1}^{NLLE}\sum_{i=1}^{NC}\frac{1}{\sigma_{x,LLE}^{2}}(x'^{m}_{i,n}\gamma'^{c}_{i,n} - x''^{m}_{i,n}\gamma''^{c}_{i,n})^2 \qquad (4)$$

In eq 4, the single and double primes denote the two liquid phases, and NLLE is the number of LLE measurement points. Here, the individual mole fractions were assumed to have a relative standard deviation of 0.0224. Again, an adjustment was made to compensate for the typical NC = 3 evaluations of every measurement point in the ternary systems. The correction factor was adjusted accordingly for binary LLE data.

The 18 NRTL parameters (6 binary pairs of 3 parameters each) were fitted simultaneously to the overall data set. Because there was a substantial amount of measurement data available that also showed a certain amount of scatter (especially in the case of cyclohexanol + water), a selection of data points to be included in the optimization was performed (the result of this selection is what is reported here in Tables 1−6). In cases where it was considered that the literature data were of equal or better quality than our own measurement data and where the data were measured at similar conditions, literature data[3−11] were also included in the optimization. The simultaneous fitting of all data types was considered to be necessary because parameter sets describing binary VLE measurements well will usually not be very good at describing ternary LLE measurements as well and vice versa.

Again, a global evolution strategy approach[12] was selected for the optimization. The sum of the above deviation functions (eqs 3 and 4) was used as an objective function. The resulting set of NRTL parameters is presented in Table 12 together with the standard deviations it shows with respect to different types of data measured.

It can be seen in this table that the standard deviations varied considerably with the system being studied. The magnitude of the standard deviations is in the range to be expected for the measurement techniques used, so that the fit can be considered to be satisfactory. There is a certain likelihood, however, that a parameter set exists that better describes the data. This is due to the fact that the computational demand of such an 18-dimensional global optimization is quite significant and time considerations had to be taken into account when performing the optimization. The overall fit was better than what was initially achieved when fitting only binary pairs individually.

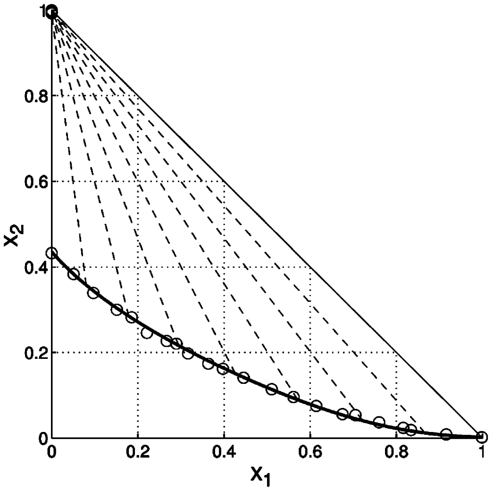

Figure 1. Comparison of the complete set of measurement data (circles) with the computed values (lines) using the NRTL parameter set of Table 12 for cyclohexene (1) + water (2) + cyclohexanol (3) at ambient pressure and temperature (295 K).

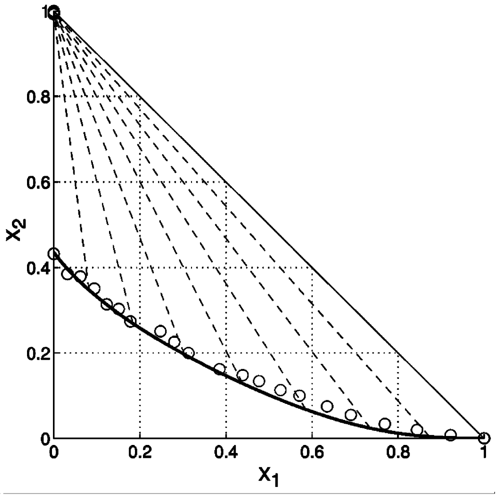

Figure 2. Comparison of the complete set of measurement data (circles) with the computed values (lines) using the NRTL parameter set of Table 12 for cyclohexane (1) + water (2) + cyclohexanol (3) at ambient temperature (295 K) and pressure.

Simulated Results vs Experimental Results

Using the above NRTL parameter from Table 12, the binodal curves were calculated and compared with the measurement data. This comparison can be found in Figures 1 and 2.

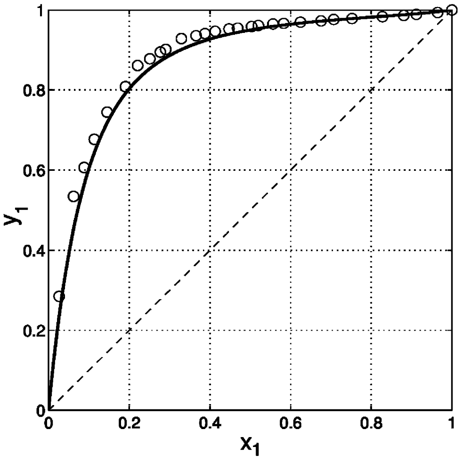

Figure 3. $x-y$ diagram of the system cyclohexene (1) + cyclohexanol (2). The circles show the complete set of measured values at ambient pressure; the curve shows the fitted NRTL interpolation at average pressure (1006 mbar).

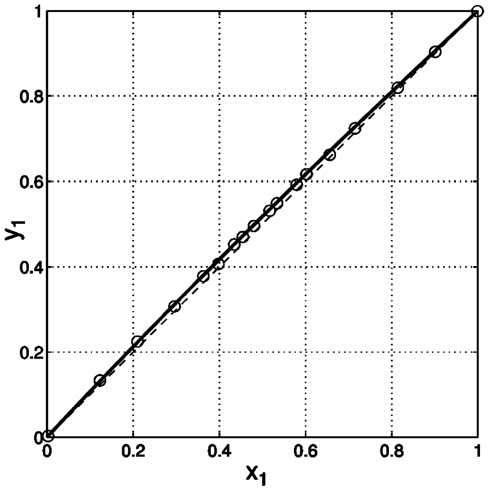

Figure 4. $x-y$ diagram of the system cyclohexane (1) + cyclohexene (2). The circles show the complete set of measured values at ambient pressure; the curve shows the fitted NRTL interpolation at average pressure (1004 mbar).

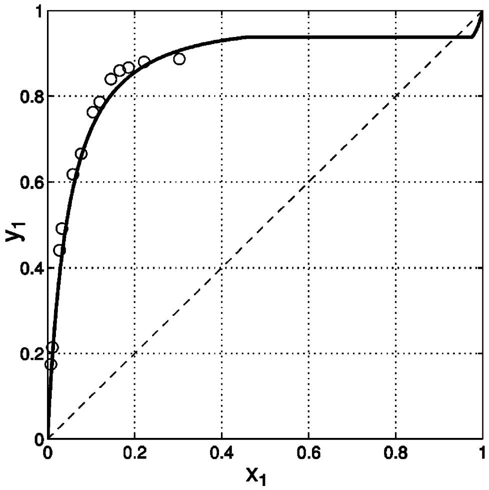

Figure 5. $x-y$ diagram of the system water (1) + cyclohexanol (2). The circles show the complete set of measured values at ambient pressure; the curve shows the fitted NRTL interpolation at average pressure (1008 mbar).

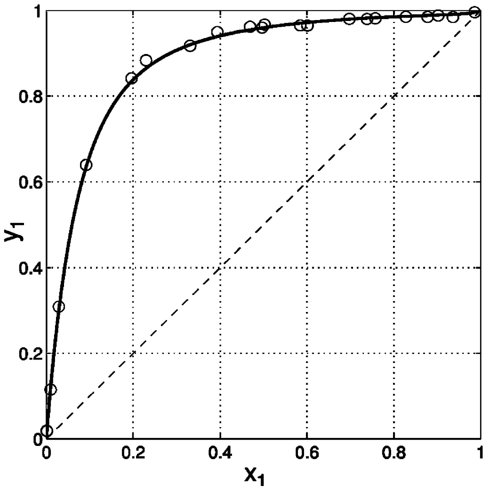

Figure 6. $x-y$ diagram of the system cyclohexane (1) + cyclohexanol (2). The circles show the complete set of measured values at ambient pressure; the curve shows the fitted NRTL interpolation at average pressure (1008 mbar).

The parameter set was also used for calculating $x-y$ diagrams for the binary mixtures cyclohexene + cyclohexanol, cyclohexene + cyclohexane, cyclohexanol + water, and cyclohexanol + cyclohexane. These are shown in comparison to the measured values in Figures 3−6.

It should be noted here that the standard deviations for cyclohexanol + water are fairly large for the data set measured. This can also be seen in Figure 6 as a fairly strong scattering of the data. This indicates that the VLE apparatus used is not well suited for systems exhibiting liquid phase splitting. This was one of the reasons literature data were included into the overall optimization.

Conclusions

The binary vapor−liquid equilibria for cyclohexene + cyclohexanol, cyclohexene + cyclohexane, cyclohexanol + water, and cyclohexanol + cyclohexane were measured at ambient pressure. In addition, liquid−liquid equilibria were measured at ambient temperature in the two ternary systems cyclohexene + cyclohexanol + water and cyclohexanol + water + cyclohexane. Both of these ternary systems show type II phase behavior. Finally, the $P-T$ relationships for the four components were measured. Using the Antoine equation and the NRTL equation, a set of parameters was generated that describes the equilibria well. The overall system shows three low-boiling azeotropes that are associated with the mixing gaps. Cyclohexanol as a reaction product of cyclohexene and water can easily be separated as it has by far the highest boiling point and is sufficiently far from any azeotropes that it should usually be found as a pure bottom product in the distillation.

Acknowledgment

The authors thank Mrs. M. Savova, Mrs. E. Felsch, and Mrs. B. Stein for carrying out many of the measurements.

Literature Cited

(1) Steyer, F.; Qi, Z.; Sundmacher, K. Synthesis of Cyclohexanol by Three-Phase Reactive Distillation−Influence of Kinetics on Phase Equilibria. *Chem. Eng. Sci.* **2002**, *57*, 1511−1520.

(2) Ishida, H.; Fukuoka, Y.; Mitsui, O.; Kono, M. Liquid-Phase Hydration of Cyclohexene with Highly Siliceous Zeolites. *Stud. Surf. Sci. Catal.* **1994**, *83*, 473−480.

(3) Mesnage, J.; Marsan, A. A. Vapor−Liquid Equilibrium at Atmospheric Pressure. *J. Chem. Eng. Data* **1971**, *16*, 434−439.

(4) Harrison, J. M.; Berg, L. Vapor−Liquid Equilibria of Binary Hydrocarbon Systems. *Ind. Eng. Chem.* **1946**, *38*, 117−120.

(5) Tunik, S. P.; Lesteva, T. M.; Chernaya, V. I. Phase Equilibria in the Water−Alcohols−Formaldehyde Systems. I. The Liquid−

Vapor Equilibria in the Systems Water−C_6 and C_7 Alcohols. *Russ. J. Phys. Chem.* **1977**, *51*, 751.

(6) Zharikov, L. K.; Krylova, K. S.; Kopylevich, G. M.; Tikhonova, N. K.; Oparina, G. K.; Serafimov, L. A. Phase Equilibria in Systems Water−Aniline, Water−Cyclohexanol, Ethanol−Aniline, and Ethanol−Cyclohexanol. *J. Appl. Chem. USSR* **1975**, *48*, 1306−1308.

(7) Gorodetsky, J. Ya.; Olevsky, V. M. Vestnik data taken from: Gmehling, J.; Onken, U.; Arlt, W. *Vapor−Liquid Equilibrium Data Collection: Tables and Diagrams of Data of Binary and Multicomponent Mixtures up to Moderate Pressures*; DECHEMA: Frankfurt am Main, Germany, 1991; Part 1: Aqueous−Organic Systems, p 514.

(8) Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. *Azeotropic Data*; VCH: Weinheim, Germany, 1994; Part 2.

(9) *Hydrocarbons with Water and Seawater*; IUPAC−NIST Solubility Data Series; Shaw, D. G., Kertes, A. S., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 37, Part I.

(10) *Alcohols with Water*; IUPAC−NIST Solubility Data Series; Barton, A. F. M., Kertes, A. S., Eds.; Pergamon Press: Oxford, U.K., 1984; Vol. 15.

(11) *Solubilities of Inorganic and Organic Compounds*; Stephen, H., Stephen, T., Eds.; Pergamon Press: Oxford, U.K., 1963; Vol. 1, Part I.

(12) Steyer, F.; Sundmacher, K. Global Optimization Approach to Identifying Parameter Sets for Chemical Engineering Calculations. *Chem. Eng. Process.*, manuscript to be published.

(13) *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology (NIST): Gaithersburg, MD, Mar 2003.

(14) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135−144.

Received for review March 9, 2004. Accepted June 23, 2004.

JE049902W