VLE and LLE Data Set for the System Cyclohexane + Cyclohexene + Water + Cyclohexanol + Formic Acid + Formic Acid Cyclohexyl Ester

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The six-component system cyclohexene + water + cyclohexanol + cyclohexane + formic acid + formic acid cyclohexyl ester is currently being studied with the aim of carrying out the reaction of cyclohexene and water to cyclohexanol in a reactive distillation (RD) column. Because the direct reaction path of cyclohexene hydration is strongly limited by slow reaction rates with the known catalysts, an intermediate ester-formation step with formic acid was included in the studies. The challenge that this six-component system poses for a reactive separator such as an RD column lies in the liquid−liquid phase splitting behavior. This adds a third effect besides reaction and distillation. Cyclohexane is included in these studies to represent any inert C_6 components present under industrial conditions. To be able to design an RD column, 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 chemical intermediate in nylon production. As was discussed in a previous paper,[1] its current production route has many drawbacks such as low selectivity even at low conversions, high energy consumption, and explosion risks. As was argued there, integrating reaction and separation and using the hydration reaction of cyclohexene to form cyclohexanol in a reactive distillation process could potentially solve all of these problems. This step would presumably lead to a significant reduction in both investment and operational costs.

Unluckily, however, the reaction needs a very strong acidic catalyst to reach sufficient reaction rates for a technical process. Preliminary experiments with different catalysts have shown that the catalysts are either very fine particles of less than 1 μm diameter, which are very hard to immobilize in a column without deactivation, or they are in the millimeter range but do not show sufficient activity for economic column operation. So far no catalyst that is both active enough and easy to integrate into a column is available.

This lack of a technically feasible catalyst was the reason to carry out the reaction with the help of an intermediate step. This step is the reaction of cyclohexene with formic acid to produce formic acid cyclohexyl ester (FCE), which is then split in a reverse esterification reaction under the addition of water to cyclohexanol and formic acid. The net reaction is still the hydration of cyclohexene to cyclohexanol; formic acid can be seen as a reactive entrainer that takes part in the reaction but is recycled. The reaction rates in this two-step reaction scheme are significantly higher, allowing the use of a conventional acidic ion-exchange resin as a catalyst for both steps.

For the design of a suitable coupled-column system for cyclohexanol synthesis and purification, a consistent description of the vapor− and liquid−liquid equilibria is of high importance. In our previous paper,[1] VLE and LLE data for the original four-component mixture was presented as well as NRTL parameters that describe both phenomena well. This four-component system is now expanded to six components, incorporating FCE and formic acid as additional components.

An interesting aspect of this system is the paucity of available data for FCE in the literature. This forced us to measure many parameters that are usually available. Specifically, it was not possible to find an Antoine parameter set or any solubility or VLE data for FCE. For formic acid, however, reliable VLE data was available for the binary mixture with water.[2−4] Data on the other binary pairs could not be found, however.

For this reason, VLE measurements were performed for the binary pairs cyclohexene + FCE, cyclohexanol + FCE, and cyclohexane + FCE. Because of the good literature data for formic acid + water, no further VLE measurements of this binary pair were made. Because water has a mixing gap with FCE and formic acid has mixing gaps with cyclohexene and cyclohexane, the following ternary LLE measurements were performed: cyclohexanol + water + FCE, cyclohexene + FCE + formic acid, water + FCE + formic acid, cyclohexanol + water + formic acid, and cyclohexane + FCE + formic acid.

The results of these measurements and a suggested set of NRTL[7] parameters to describe the six-component system are being presented here.

Experimental Section

Materials. To measure both LLE and VLE data, synthesis-quality (>99%) cyclohexene, cyclohexanol, cyclohex-

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

x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.015	0.047	0.0004	0.9989	0.326	0.189	0.0037	0.9959	0.393	0.250	0.0044	0.9952	0.475	0.316	0.0049	0.9948
0.085	0.056	0.0016	0.9980	0.345	0.209	0.0039	0.9957	0.411	0.258	0.0042	0.9954	0.493	0.333	0.0050	0.9947
0.150	0.080	0.0023	0.9972	0.369	0.228	0.0041	0.9956	0.416	0.283	0.0044	0.9952	0.497	0.372	0.0055	0.9943
0.208	0.118	0.0028	0.9967	0.379	0.236	0.0042	0.9954	0.428	0.301	0.0046	0.9951	0.541	0.414	0.0058	0.9941
0.257	0.146	0.0032	0.9963	0.389	0.237	0.0042	0.9954	0.453	0.305	0.0047	0.9949	0.568	0.432	0.0063	0.9937
0.295	0.166	0.0035	0.9961												

Table 2. Selected Liquid−Liquid Equilibrium Data for the Ternary System Cyclohexene (1) + FCE (2) + Formic Acid (3) at Room Temperature (T = 295 K)

x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.367	0.186	0.155	0.141	0.703	0.136	0.040	0.059
0.405	0.179	0.123	0.125	0.773	0.117	0.034	0.046
0.518	0.185	0.094	0.108	0.845	0.083	0.023	0.029
0.521	0.171	0.079	0.098	0.848	0.076	0.021	0.026
0.616	0.157	0.056	0.078	0.917	0.040	0.015	0.013
0.620	0.171	0.063	0.086	0.9907	0.0005	0.0086	0.0001
0.698	0.146	0.045	0.064				

ane, and formic acid were acquired from VWR. Cyclohexene was distilled twice to remove stabilizing compounds. The other chemicals were used as delivered. As in previous experiments, water used was taken from a deionizer (Millipore Milli-Q type gradient).

FCE had to be synthesized in-house because no supplier could be found for it. It was synthesized by reacting cyclohexene with a slight excess of formic acid using roughly 5 vol % Amberlyst 15 from Rohm & Haas as a heterogeneous catalyst. After having reacted this mixture for 4 h in a stirred reactor at 60 °C and for another 2 h at 80 °C, it was then separated from the catalyst and washed multiple times with deionized water to extract the remaining formic acid. During the reaction, the second liquid phase initially present had disappeared. The remaining golden-colored organic phase was then distilled three times under reduced pressure. The first vacuum distillation was to remove most of the unreacted cyclohexene. It was carried out in a rotary evaporator at 50 °C water bath temperature at 90 mbar pressure until no significant distillate stream could be observed.

The second distillation was to remove a small amount of high-boiling residue with a brownish/greenish color. To do this, almost the complete mixture was evaporated at 90 °C bath temperature and 20 mbar. The distillation was stopped when only a few milliliters were left containing mainly FCE and traces of the brown, high-boiling side product. Its nature is not known because it was not possible to identify it via GC-MSD because its boiling point was too high.

A final, third distillation at 65 °C and 20 mbar under a high reflux ratio was then used to purify the FCE to >98% purity (GC-MSD, peak area percentage). The main impurities remaining in the FCE are cyclohexene and cyclohexanol, the latter of which has almost the same boiling point and with which FCE has an azeotrope—essentially making it impossible to remove by distillation.

In general, composition 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 with a GC/MSD behind a 60 m × 250 μm × 0.1 μm DB5ms column (Hewlett-Packard 6890 or Agilent 6890N, respectively). The calibration of these GCs was done using calibration samples that were prepared gravimetrically using a Mettler Toledo type AT261 DeltaRange scale. The uncertainity associated with the composition of these calibration samples can be estimated to be <0.01 mass %. The reproducibility of the GC measurements was evaluated by repetitive measurements of the same sample using the calibrated GC. The standard deviation measured was below 0.05 mol %.

The quality of the calibration was checked by measuring samples of known composition. The remaining deviations between the GC measurements and the composition of the gravimetrically composed samples have a standard deviation of 0.31 mol %. The overall uncertainity with respect to the compositions measured via GC can be assumed to be ±0.6% (with 95% confidence). The samples were generally at room temperature (295 ± 2 K) when analyzed.

Liquid−Liquid Equilibrium Measurements. The general approach to measuring LLE data was the same as in our previous paper.[1] The results of these measurements can be found in Tables 1 to 5. The only exception to this operating procedure was for the measurement of LLE data of cyclohexanol + water + formic acid. Because of the fact that in this system a significant reaction rate was detected even at room temperature when formic acid is present, the procedure had to be changed slightly for this system.

In this case, the samples were always prepared from the pure components directly prior to the measurements. They were composed at the lowest temperature possible without cyclohexanol freezing. After adjusting the desired composition gravimetrically, the two-phase mixtures were agitated quickly using an ultrasound tip (Bandelin electronic type UW2070). This lead to a fine dispersion that was then quickly separated again using the same centrifuge as in the other experiments. The samples of the two phases were then analyzed at room temperature as fast as the GC permitted. The concentration of FCE was monitored to detect the undesired reaction. The extent of the reaction under these conditions was not significant for the LLE measurements. (FCE mole fractions were typically below 0.1 % for the organic phase and less for the aqueous phase.) During a second run, the same procedures were used, but the samples were prepared consecutively and stored after

Table 3. Selected Liquid−Liquid Equilibrium Data for the Ternary System Water (1) + FCE (2) + Formic Acid (3) at Room Temperature (T = 295 K)

x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.047	0.953	0.9996	0.0004	0.152	0.775	0.8614	0.0019	0.222	0.628	0.7682	0.0051	0.274	0.495	0.699	0.010
0.066	0.927	0.9718	0.0006	0.153	0.771	0.8553	0.0020	0.222	0.574	0.7074	0.0068	0.285	0.427	0.638	0.014
0.083	0.907	0.9703	0.0006	0.161	0.743	0.8300	0.0028	0.236	0.577	0.7406	0.0067	0.289	0.461	0.686	0.012
0.106	0.876	0.9304	0.0009	0.188	0.689	0.7982	0.0038	0.252	0.555	0.7288	0.0079	0.295	0.419	0.673	0.014
0.113	0.867	0.9332	0.0009	0.199	0.665	0.7884	0.0046	0.256	0.526	0.7130	0.0092	0.331	0.317	0.593	0.023
0.120	0.837	0.8977	0.0013	0.202	0.630	0.7392	0.0054	0.257	0.499	0.6745	0.0092	0.389	0.233	0.555	0.039
0.131	0.829	0.8937	0.0015	0.217	0.624	0.7574	0.0057								

Table 4. Selected Liquid−Liquid Equilibrium Data for the Ternary System Cyclohexanol (1) + Water (2) + Formic Acid (3) at T = 278 K

x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.161	0.622	0.032	0.770	0.444	0.463	0.0090	0.9345
0.209	0.584	0.023	0.799	0.469	0.463	0.0083	0.9568
0.221	0.571	0.024	0.796	0.475	0.453	0.0081	0.9576
0.274	0.532	0.018	0.823	0.501	0.463	0.0075	0.9739
0.318	0.526	0.012	0.877	0.523	0.447	0.0078	0.9780
0.344	0.512	0.0108	0.8953	0.5590	0.4349	0.0073	0.9910
0.347	0.506	0.0115	0.8783	0.5626	0.4347	0.0074	0.9925
0.386	0.496	0.0097	0.9198	0.5763	0.4232	0.0072	0.9926
0.428	0.485	0.0085	0.9455				

the phases had been separated until the GC was able to analyze them. The resulting (higher) amounts of FCE were assumed to have been produced after phase separation and were accounted for accordingly.

Vapor−Liquid Equilibrium Measurements. For all measurements, the same procedures were used as in the previous paper.[1] The exact approach and the devices used are described there in detail.

Vapor−liquid equilibrium measurements were performed between cyclohexene + FCE, cyclohexanol + FCE, and cyclohexane + FCE. Even though the binary mixtures of cyclohexanol + formic acid and FCE + formic acid are fully miscible, no vapor−liquid equilibrium data was measured because they react at a substantial rate at the temperatures needed for the VLE measurements. (Cyclohexanol and FCE both have high boiling temperatures even at reduced pressure.) The measurements were performed at ambient pressure. Tables 6 to 8 show the measurement results that were used in the data fitting procedure. Our measured data was complemented by literature data for the binary system water + formic acid, for which several sources of good data exist.[2−4] The high quality and amount of literature data available for this binary pair was the reason not to measure this binary pair again.

Results and Discussion

Antoine Coefficient Determination. Because the existing literature data on FCE varied quite significantly with respect to the P, T relationship, we made our own measurements using the same approach as described in our previous paper.[1] Also, a refit of the Antoine parameters was done for formic acid. For this, literature data[5,6] was used. The FCE P, T data can be found in Table 9; the resulting Antoine parameters of all six substances are given in Table 10. Over the temperature and pressure ranges given in the Table, the calculated pressures for FCE can be assumed to lie within an interval of ±3.8 mbar of the real value (with 95% confidence). Unluckily, the literature does not give measurement accuracies for the published P, T values for formic acid. The 95% confidence interval between the literature values and the computed values can be computed as ±3.3 mbar.

Model Formulation. As in the previous paper, the NRTL model[7] was used to model the activity coefficients. Expanding the corresponding parameter set from 4 to 6 components requires an additional 27 parameters because 9 new binary pairs are now part of the set. The optimization was performed using the same objective functions and approach as used previously.

The vapor−liquid equilibrium was again formulated without Poynting correction and with fugacity coefficients equal to unity, which seems reasonable at the low pressures used. The dimerization of the formic acid was taken into account assuming reaction equilibrium between the monomer and dimer, the dimer being the reaction product.

Table 5. Selected Liquid−Liquid Equilibrium Data for the Ternary System Cyclohexane (1) + FCE (2) + Formic Acid (3) at Room Temperature (T = 295 K)

x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.374	0.228	0.179	0.201	0.662	0.200	0.048	0.126	0.812	0.119	0.024	0.073	0.913	0.070	0.0096	0.0326
0.506	0.220	0.114	0.176	0.702	0.168	0.045	0.113	0.818	0.130	0.020	0.068	0.952	0.034	0.0078	0.0158
0.539	0.234	0.085	0.168	0.714	0.178	0.034	0.105	0.861	0.094	0.016	0.053	0.959	0.036	0.0061	0.0157
0.586	0.206	0.082	0.153	0.763	0.144	0.033	0.093	0.865	0.101	0.014	0.050	0.989	0	0.0053	0
0.595	0.217	0.061	0.145	0.764	0.156	0.027	0.088	0.902	0.065	0.0109	0.0344	0.997	0	0.0046	0
0.650	0.187	0.061	0.134												

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

x_1	y_1	P/mbar	T/K	x_1	y_1	P/mbar	T/K	x_1	y_1	P/mbar	T/K	x_1	y_1	P/mbar	T/K
0.9917	0.9990	1013	356.4	0.745	0.968	1011	365.8	0.411	0.866	1014	382.4	0.165	0.673	996	404.2
0.952	0.9933	1025	358.7	0.659	0.956	1010	370.0	0.373	0.861	1018	386.5	0.133	0.604	996	409.1
0.900	0.988	1012	359.9	0.595	0.939	1021	372.1	0.299	0.816	998	390.6	0.119	0.546	1009	414.8
0.877	0.986	1026	360.6	0.577	0.936	1013	374.8	0.264	0.793	998	394.3	0.048	0.296	1009	425.1
0.839	0.979	1012	362.3	0.526	0.926	1021	374.7	0.225	0.765	1018	396.7	0.002	0.011	1010	434.9
0.815	0.978	1026	362.8												

Table 7. Vapor−Liquid Equilibrium Data for the Binary System Cyclohexanol (1) + FCE (2)

x_1	y_1	P/mbar	T/K	x_1	y_1	P/mbar	T/K	x_1	y_1	P/mbar	T/K	x_1	y_1	P/mbar	T/K
0.927	0.904	995	431.6	0.717	0.706	1022	431.1	0.508	0.531	1025	430.4	0.264	0.323	1025	431.4
0.878	0.846	995	430.8	0.681	0.675	1023	430.8	0.451	0.485	1023	430.4	0.212	0.270	1025	432.1
0.838	0.794	994	431.2	0.658	0.639	994	429.9	0.395	0.434	1011	430.3	0.152	0.198	1025	432.9
0.804	0.774	1018	431.2	0.602	0.603	1007	430.1	0.356	0.388	1024	431.6	0.110	0.159	1008	432.8
0.754	0.735	1018	430.9	0.553	0.569	1021	430.4	0.306	0.350	1025	432.0				

Table 8. Selected Vapor−Liquid Equilibrium Data for the Binary System Cyclohexane (1) + FCE (2)

x_1	y_1	P/mbar	T/K	x_1	y_1	P/mbar	T/K	x_1	y_1	P/mbar	T/K	x_1	y_1	P/mbar	T/K
0.013	0.124	1008	428.6	0.240	0.790	1015	391.6	0.562	0.935	1020	367.8	0.799	0.975	1001	360.6
0.040	0.322	1008	420.7	0.282	0.830	998	384.8	0.608	0.945	1000	366.8	0.872	0.984	996	356.8
0.068	0.428	1008	414.7	0.336	0.867	1000	382.4	0.653	0.956	996	366.0	0.905	0.988	1019	356.8
0.107	0.575	999	409.5	0.413	0.900	1014	375.7	0.691	0.963	1000	362.3	0.949	0.990	1020	355.5
0.150	0.639	1008	403.1	0.466	0.914	996	376.2	0.754	0.973	997	361.9	0.9989	0.99998	1001	353.3
0.204	0.739	999	394.9												

Table 9. Measured and Calculated Vapor Pressures of FCE and Their Differences at Several Temperatures

FCE			
T/K	*P*/mbar	P_{calc}/mbar	ΔP/mbar
307.35	6.0	6.1	−0.1
316.55	10.0	10.5	−0.5
328.65	20.0	20.2	−0.2
342.50	40.0	40.0	0.0
358.05	80.0	79.4	0.6
375.65	159.0	158.6	0.4
395.55	318.0	316.9	1.1
418.50	638.0	638.0	0.0
434.95	998.0	997.8	0.2

Table 10. Antoine Coefficients, Valid Temperature Range Δ*T*, and Standard Deviations between Measurements and Calculations for the Six Components[a]

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
FCE	4.09578	1489.03	−71.4825	305−435	0.3437
formic acid	4.57631	1608.22	−21.8974	265−385	1.6700

[a] Antoine coefficients for formic acid were fitted to literature data.[5,6] Parameters for cyclohexene, cyclohexanol, water, and cyclohexane were taken from our previous publication.[1] The Antoine equation used was $\log_{10}(P) = A - B/(T + C)$ for *P* in bars and *T* in K.

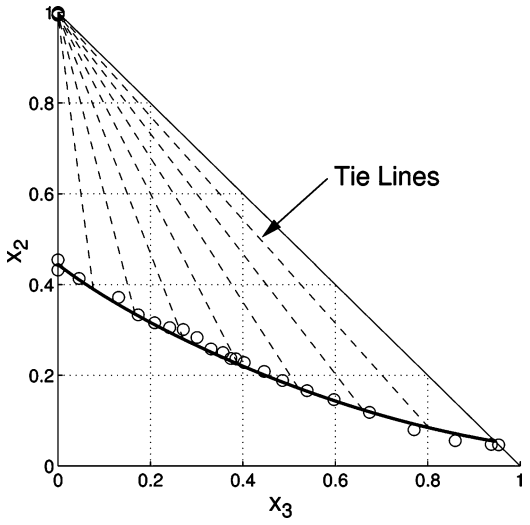

Figure 1. Comparison of the complete set of measurement data (circles) with the computed values (lines) using the NRTL parameter set of Table 11 for cyclohexanol (1) + water (2) + FCE (3) at ambient temperature (295 K) and pressure.

The equilibrium constant was computed via

$$K_{eq} = k e^{-\Delta G_R/RT} = \frac{P_{dimer}}{P^2_{monomer}} \quad (1)$$

In this equation, K_{eq} is the equilibrium constant, *k* is a constant factor, ΔG_R is the Gibbs enthalpy of reaction, *R* is the universal gas constant, *T* is the temperature in Kelvin, and the *P*s are the partial pressures in bar of the monomer and dimer, respectively. The parameters needed for this computation were fitted using data from the literature.[8] The value obtained for *k* was 2.4726×10^{-9} /bar; the value for ΔG_R was -6.3766×10^4 J/mol. The saturation pressure computed via the Antoine equation is for the sum of the vapor pressures of the dimer and monomer.

Table 11. NRTL Parameters with Associated Standard Deviations between Different Measurement Types and Calculations for the Six Given Components[a]

binary pair	g_{12}/J/mol	g_{21}/J/mol	α_{12}	σ_y	σ_P/mbar	$\sigma_{x,LLE}$	binary pair	g_{12}/J/mol	g_{21}/J/mol	α_{12}	σ_y	σ_P/mbar	$\sigma_{x,LLE}$
cyclohexene (1) + cyclohexanol (2)	3568.41	−0.962835	0.802522	0.0279	41.5		cyclohexanol (1) + formic acid (2)	−1778.81	3290.04	0.689468			0.00893 (4)
cyclohexene (1) + water (2)	14 175.4	21 695.0	0.267206			0.00497	water (1) + cyclohexane (2)	25 048.5	17 650.0	0.258799			0.00681
cyclohexene (1) + cyclohexane (2)	42.4813	60 957.2	0.831053	0.00386	9.20		water (1) + FCE (2)	15 899.1	5877.86	0.286963			0.00458 (1)
cyclohexene (1) + FCE (2)	−2390.29	3308.21	0.215759	0.0120	29.7		water (1) + formic acid (2)	3507.57	−4043.93	0.139498			
cyclohexene (1) + formic acid (2)	7828.68	7619.60	0.342528			0.0162 (2)	cyclohexane (1) + FCE (2)	3627.17	−2134.86	0.315477	0.0154	56.6	
cyclohexanol (1) + water (2)	1336.76	10 959.4	0.359706	0.0151	131.7		cyclohexane (1) + formic acid (2)	10 153.6	9943.91	0.287689			0.0120 (5)
cyclohexanol (1) + cyclohexane (2)	19.9341	4071.64	0.993301	0.0230	91.7		FCE (1) + formic acid (2)	−415.705	3158.48	0.765244			0.0162 (3)
cyclohexanol (1) + FCE (2)	1540.33	337.622	0.313377	0.0132	8.28								

[a] The numbers in parentheses behind the $\sigma_{x,LLE}$ figures denote the Table or Figure that these values are computed for because these are actually from ternary mixtures.

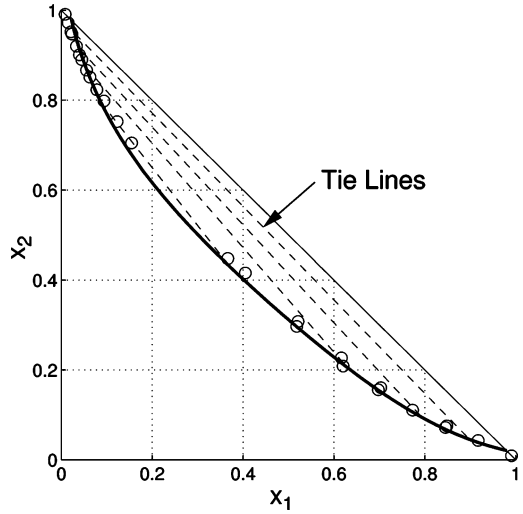

Figure 2. Comparison of the complete set of measurement data (circles) with the computed values (lines) using the NRTL parameter set of Table 11 for cyclohexene (1) + FCE (2) + formic acid (3) at ambient temperature (295 K) and pressure.

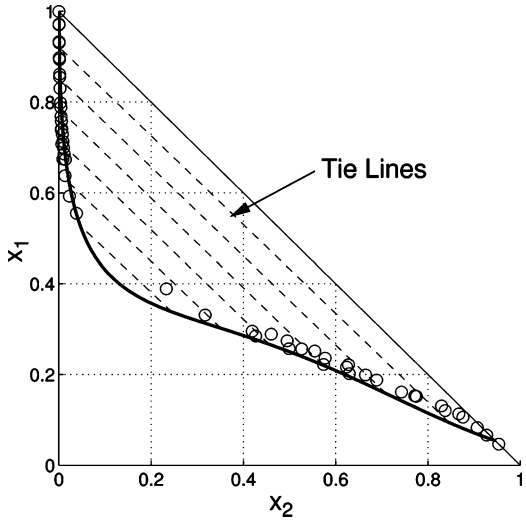

Figure 3. Comparison of the complete set of measurement data (circles) with the computed values (lines) using the NRTL parameter set of Table 11 for water (1) + FCE (2) + formic acid (3) at ambient temperature (295 K) and pressure.

Because of the large number of data and parameters that were to be fitted to one another, a subset approach was introduced into the optimization. This means that for any given binary, ternary, or quarternary subsystem for which the parameters were to be fitted the appropriate data subset was generated including all data that can have an influence on the appropriate parameter set. This allowed us to reduce the computational effort in finding the parameter sets significantly and to make the task parallel to some extent. The computational effort was still considerable, and there might exist a parameter set that describes the data even better than the one presented here. As a final fine-tuning step of the 45 parameters, a maximum likelihood approach was applied to the overall data set and all parameters simultaneously that led to a slight quality increase of the fit.

Because the data of the four-component system were included in the optimization, a change in the resulting parameter set is visible. This mainly reflects the influence that the new data has on the overall optimization. For this reason, the whole parameter set consisting of 45 parameters is reported here as Table 11.

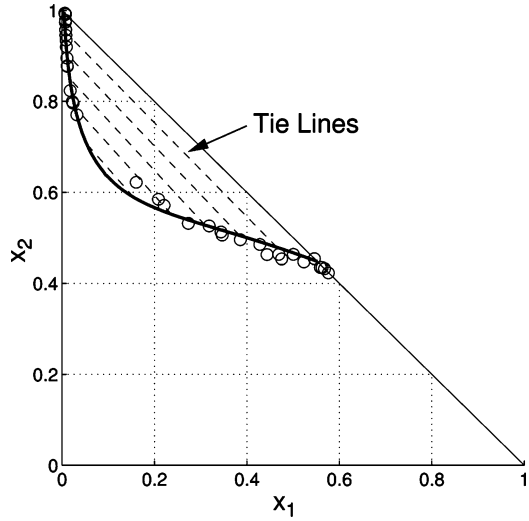

Figure 4. Comparison of the complete set of measurement data (circles) with the computed values (lines) using the NRTL parameter set of Table 11 for cyclohexanol (1) + water (2) + formic acid (3) at a temperature of 278 K and ambient pressure.

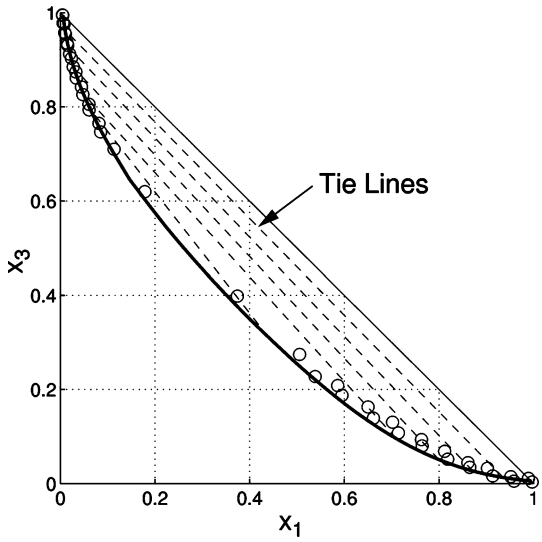

Figure 5. Comparison of the complete set of measurement data (circles) with the computed values (lines) using the NRTL parameter set of Table 11 for cyclohexane (1) + FCE (2) + formic acid (3) at ambient temperature (295 K) and pressure.

Simulated Results vs Experimental Results. The optimized parameter set of Table 11 was used to compute the binodal curves for the ternary systems that had been measured. The comparison of the measurement data and the computations using this parameter set can be found as Figures 1 to 5. The changes in the binodal curves of the cyclohexene + cyclohexanol + water and cyclohexanol + water + cyclohexane systems were so small that they were practically indistinguishable from the curves plotted in our previous paper,[1] so they are not shown again here.

Computations of the McCabe−Thiele diagrams were also performed for the measured systems. These plots compare the computations with the measurements and can be found as Figures 6 to 8. The comparison for water + formic acid was not shown because the literature data used was measured at quite different pressures and would thus give multiple curves and thus multiple figures. The fit of the computations to the literature measurements was of similar quality to that of the other binary pairs, however. Overall, the quality of the fits to the measurement data can be seen to be very good, especially when considering

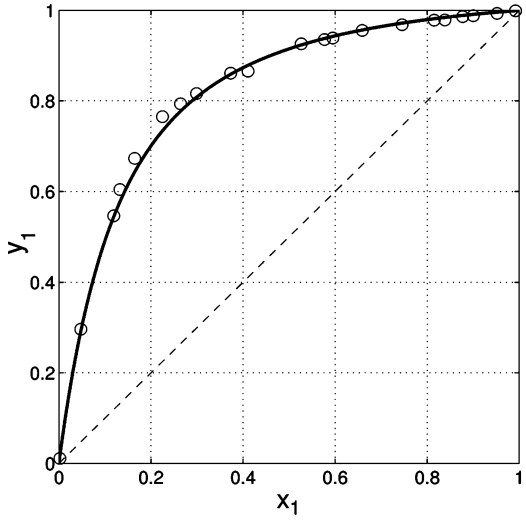

Figure 6. $x-y$ diagram of the system cyclohexene (1) + FCE (2). The circles show the complete set of measured values at ambient pressure and the curve the fitted NRTL interpolation using the parameter set of Table 11 at average pressure (1012 mbar).

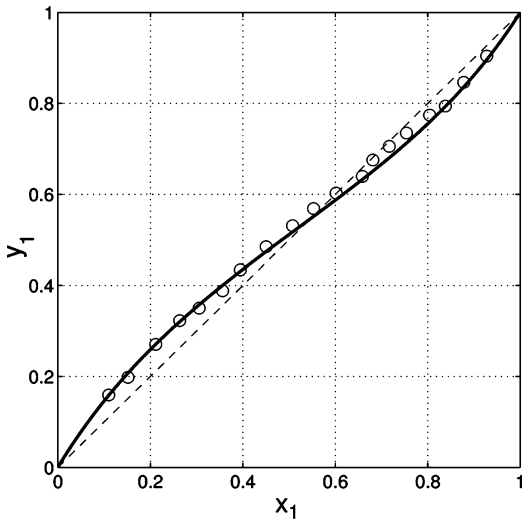

Figure 7. $x-y$ diagram of the system cyclohexanol (1) + FCE (2). The circles show the complete set of measured values at ambient pressure and the curve the fitted NRTL interpolation using the parameter set of Table 11 at average pressure (1014 mbar).

that the same parameter set is being used to describe the VLE and LLE behavior.

Conclusions

The binary vapor−liquid equilibria for cyclohexene + FCE, cyclohexanol + FCE, and cyclohexane + FCE were measured at ambient pressure. Also, liquid−liquid equilibria were measured for the ternary systems cyclohexanol + water + FCE, cyclohexene + FCE + formic acid, water + FCE + formic acid, cyclohexanol + water + formic acid, and cyclohexane + FCE + formic acid. The first of these five ternary systems shows type II phase behavior; the other four show type I phase behavior. The P, T relationship of FCE was measured. Parameters for Antoine's equation were computed for FCE and formic acid, for which the measurement data was taken from the literature. A

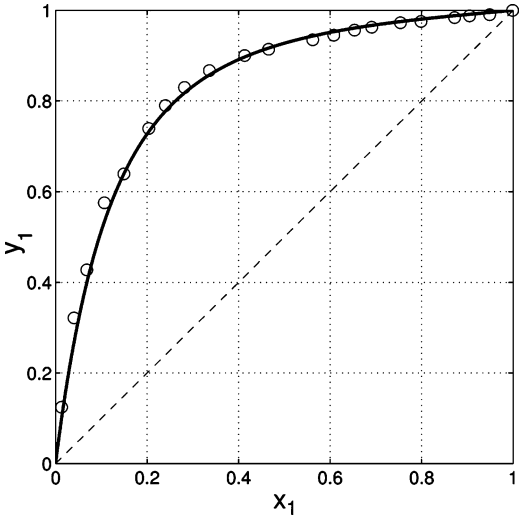

Figure 8. $x-y$ diagram of the system cyclohexane (1) + FCE (2). The circles show the complete set of measured values at ambient pressure and the curve the fitted NRTL interpolation using the parameter set of Table 11 at average pressure (1005 mbar).

set of 45 NRTL parameters was computed that describe the overall phase behavior well.

The six-component system shows six heteroazeotropes, an additional low-boiling azeotrope between cyclohexanol + FCE, and a high-boiling azeotrope between formic acid + water. Cyclohexanol as the desired product has the same boiling point as FCE and has an azeotrope with it. For this reason, a reactive separator has to be designed very carefully to yield pure cyclohexanol as a product.

Acknowledgment

We thank Mrs. E. Felsch and Mrs. B. Stein for carrying out many of the measurements.

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