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Phase Equlibria for Hexyl Acetate Reactive Distillation

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The esterification of acetic acid and 1-hexanol to produce hexyl acetate and water is a test system for modeling and simulation as well as design and scale-up of reactive distillation. The present work provides a complete, high-quality phase equilibrium database for that task. The available literature data were critically surveyed, and existing gaps were closed by experimental work. Vapor−liquid equilibria were studied in isobaric and isothermal experiments for the binary systems acetic acid + 1-hexanol, acetic acid + hexyl acetate, and 1-hexanol + hexyl acetate at pressures between (30 and 90) kPa, corresponding to temperatures between (355 and 440) K. Liquid−liquid equilibria were studied in the systems water + 1-hexanol, water + hexyl acetate, water + acetic acid + 1-hexanol, and water + acetic acid + hexyl acetate at temperatures between (280 and 355) K. On the basis of that data, two parameter sets for the NRTL model were determined, one for the description of vapor−liquid and one for liquid−liquid equilibria. Vapor−liquid and liquid−liquid equilibrium experiments in the quaternary system water + acetic acid + 1-hexanol + hexyl acetate were carried out and used for testing the models. The new database allows the reliable process simulation of hexyl acetate reactive distillation.

Introduction

Reactive distillation can offer advantages as compared to the classical reactor−separator concept but at the expense of increased system complexity[1]. The heterogeneously catalyzed reaction of 1-hexanol (3) with acetic acid (2) to form hexyl acetate (4) and water (1) as a byproduct was chosen as a test system to study modeling, simulation, design, and scale-up of reactive distillation in the frame of the European Community project INTINT.[2,3] For producing hexyl acetate, strong acid catalysts, such as mineral acids or acid ion-exchange resins, are used in order to obtain sufficiently high conversion rates. Autocatalysis of the hexyl acetate formation by acetic acid is very slow even at elevated temperatures. Thus, in the absence of a catalyst, the hexyl acetate system can be regarded as non-reactive.

Reliable information on phase equilibria and reaction kinetics is prerequisite for developing sound models of reactive distillation processes. Obviously, vapor−liquid equilibria (VLE) are of prime importance for reactive distillation. In the system studied here, also information on liquid−liquid equilibria (LLE) is needed, as several of the binary subsystems show large miscibility gaps. As a consequence, reactive distillation columns for the production of hexyl acetate give heteroazeotropic mixtures as top products so that a decanter below the condenser is used to separate the two liquid phases, of which the aqueous one is withdrawn and the organic one is used as reflux[3].

For thermodynamic modeling of the strong liquid-phase nonideality in the studied system the NRTL model[4] is used here. The dimerization of acetic acid in the gas phase is taken into account. Accurate modeling of both VLE and LLE can in many cases not be achieved with a single parameter set for common Gibbs excess energy models (for a more detailed discussion, see, e.g., Grob[5]). Consequently, two different sets of NRTL parameters were determined in the present work, one for the description of VLE and another for LLE. This poses no problem for the application in modeling the reactive distillation process, as the occurrence of the liquid phase split is limited to the decanter, whereas inside the column there is generally only one liquid phase.

Table 1 gives an overview of the VLE and LLE data situation for all binary subsystems of the studied quaternary system (upper-right side triangle). In the lower-left side triangle of Table 1, the sources that were finally used for the determination of the binary NRTL model parameters are shown (more details are given below). As can be seen in Table 1, VLE data for the system water + acetic acid is plentiful; consequently, no extra measurements were made on this system in this work. In the system water + 1-hexanol LLE is important. Although LLE data are available in the literature for that system, it was necessary to perform our own measurements due to big deviations between the measurements of the different sources. The literature LLE data[9] for the system water + hexyl acetate were confirmed by a few measurements of our own. The few literature data[10] on VLE in the system acetic acid + 1-hexanol are not sufficient because of their measurement at temperatures far below those present in reactive distillation, and for the systems acetic acid + hexyl acetate and 1-hexanol + hexyl acetate no literature VLE data are available at all. Consequently, VLE measurements were carried out for these three binary systems in the present work. Finally, since only the binary subsystems water + 1-hexanol and water + hexyl acetate exhibit a liquid−liquid phase split region, additional LLE measurements were made in the ternary subsystems containing acetic acid, for which the acid-free binary subsystem shows a miscibility gap: namely, water + acetic acid + 1-hexanol and water + acetic acid + hexyl acetate.

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Table 1. Overview of the Number of Available Literature Data Sets on Phase Equilibria in the Binary Subsystems of the Studied Quaternary System[a] and Sources Used for Determination of the Binary NRTL Parameters[b]

	water	acetic acid	1-hexanol	hexyl acetate
water		129 VLE, 9 γ_i^∞[c] this work: - - -	7 VLE, 19 LLE, 5 γ_i^∞,[c] 15 AZE[d] this work: LLE	1 AZE, 2 LLE this work: LLE
acetic acid	VLE: rec. data[7] LLE[e]: fit to ternary LLE data from this work		3 VLE this work: VLE	none in the literature this work: VLE
1-hexanol	VLE & LLE: fit to binary LLE data from this work + literature[8]	VLE: fit to binary VLE data from this work LLE[e]: fit to ternary LLE data from this work		none in the literature this work: VLE
hexyl acetate	VLE & LLE: fit to binary LLE data from this work + literature[9]	VLE: fit to binary VLE data from this work LLE[e]: fit to ternary LLE data from this work	VLE & LLE[e]: fit to binary VLE data from this work	

[a] Upper right-side triangle; source: Dortmund Data Bank (DDB).[6] [b] Lower left-side triangle. There are two sets of NRTL parameters: one for VLE and one for LLE. [c] Activity coefficient data at infinite dilution. [d] Azeotropic data. [e] No miscibility gap in binary system.

Experimental Section

Chemicals. Acetic acid (p.a. grade), 1-hexanol (synthesis grade), and hexyl acetate (synthesis grade) were purchased from Merck. Acetic acid was used without further purification, whereas 1-hexanol and hexyl acetate were further purified in a batch distillation to remove light boiling impurities. The final mass fraction purities of acetic acid, 1-hexanol, and hexyl acetate were determined by gas chromatography to be 0.998 g/g, 0.989 g/g, and 0.992 g/g, respectively. Furthermore, bi-distilled water was used.

Analysis. Analysis was carried out by gas chromatography using a Hewlett-Packard HP6890 equipped with an auto sampler. A capillary column (HP-INNOWax, HP 19091N-213; length 30 m, nominal diameter 320 μm, nominal film thickness 5 μm) was used together with a split injector (250 °C, 51.3 kPa excess pressure, split ratio 100:1) and a thermal conductivity detector (210 °C). The carrier gas was helium. The temperature program was as follows: 60 °C for 2 min, heating to 150 °C at 40 °C/min, 150 °C for 3 min, heating to 180 °C at 40 °C/min, 180 °C for 2 min. 1,4-Dioxane was used as internal standard. Thirty-three test mixtures covering the entire concentration range relevant for the measurements of this work yield an average relative deviation between analysis and weighed test mixture compositions of 0.7 mol % for 1-hexanol, 1.1 mol % for hexyl acetate, 2.9 mol % for acetic acid, and 2.1 mol % for water. Water concentrations of less than 0.005 g/g were analyzed using Karl Fischer titration (Metrohm 701 KF Titrino). The average relative deviation of water mass fractions obtained with this method is 1.0 mass %. In addition to the test mixtures, 100 % tests (i.e., summation of mass fractions of all components, which have been independently determined by the internal standard method) confirm the high quality of the analysis with results between 1.00 and 1.02 g/g.

Vapor–Liquid Equilibrium Measurements. The vapor–liquid equilibrium measurements were made in a circulation still of the Gillespie type.[11] The apparatus used in the present work is an improved version of that described by Rafflenbeul and Hartmann.[12] A detailed description of the apparatus and its operation has been given by Hasse.[13] Temperature was measured with a resistance thermometer Pt100, calibrated with a remaining uncertainty of ±0.005 K. The overall uncertainty in the temperature measurement is larger and estimated to be below 0.1 K. The pressure was measured with a pressure transducer (Baratron, MKS Instruments) calibrated with a remaining uncertainty of 0.12 %. The overall uncertainty in the pressure measurement is estimated to be below 0.2 %.

Before sampling, pressure, and temperature data acquisition, for each measurement, the apparatus was allowed to equilibrate for at least 30 min. Temperature fluctuations of the isobaric measurements have a standard deviation of 0.03 K during that time. For analysis, 1 mL samples from the liquid and the condensed vapor phase were withdrawn through silicone septas. Most of the measurements were carried out as isobaric series. For one isothermal series of measurements the pressure was adjusted in each experiment to yield the desired temperature.

Liquid–Liquid Equilibrium Measurements. Liquid–liquid equilibrium experiments were made in a liquid-thermostated double-jacket glass batch vessel with a volume of 300 mL. Temperature was measured using a resistance thermometer Pt100, calibrated with a remaining uncertainty of ±0.005 K.

The experimental procedure started with intense stirring of the sample for at least 15 min to allow equilibration, followed by a settling period. Samples were taken about 10 min after complete phase separation. During the whole process the temperature was constant to ±0.05 K, which is also the estimated uncertainty in the temperature measurement. For analysis, 1 mL samples of both phases were withdrawn through permanently installed sampling ports, taking care for sufficient purging.

For quality purposes, the material balances were evaluated for all quaternary experiments. This was made using the overall feed composition together with the phase equilibrium compositions. The split ratio can then be determined independently from the results for each component. The deviation of these results from their mean value is 2.8 % in average.

Results

Pure Component Vapor Pressures. Pure component boiling temperature measurements were carried out for all four pure components of the studied mixtures at pressures between (25 and 90) kPa. The results for water and acetic acid indicate that the pressure and temperature measurements from this work exhibit an uncertainty within the limits given above. At given temperature, the measured vapor pressure deviates in average by 0.1 % (water) and 0.15 % (acetic acid) from the correlations given in the Dortmund Data Bank.[6] The vapor pressure measurements for 1-hexanol and hexyl acetate were necessary due to the insufficient literature data situation. The available cor-

Table 2. Experimental Data on Pure Component Boiling Temperatures for 1-Hexanol (3) and Hexyl Acetate (4)

p/kPa	T_3/K	T_4/K	p/kPa	T_3/K	T_4/K
25.0	391.07	397.97	60.0	414.44	425.57
30.0	395.62	403.36	65.0	416.75	428.26
35.0	399.65	408.02	70.0	418.98	430.93
40.0	403.15	412.14	75.0	421.05	433.38
45.0	406.36	416.02	80.0	423.01	435.68
50.0	409.25	419.47	85.0	424.87	437.92
55.0	411.92	422.59	90.0	426.69	439.98

Table 3. Parameters A_i, B_i, and C_i for Pure Component Vapor Pressure Antoine Equation

Antoine equation: $\ln(p_i/\mathrm{Pa}) = A_i + (B_i/(C_i + T/\mathrm{K}))$			
	A_i	B_i	C_i
water[a]	23.2212	−3833.95	−45.3734
acetic acid[a]	22.1352	−3684.44	−43.8141
1-hexanol[b]	21.2074	−3015.87	−118.9169
hexyl acetate[b]	20.9987	−3421.82	−83.2500

[a] Dortmund Data Bank.[6] [b] Fitted to the data from Table 2.

Table 4. Isobaric Vapor−Liquid Equilibria in the System Acetic Acid (2) + 1-Hexanol (3)

$p = 30$ kPa			$p = 60$ kPa			$p = 90$ kPa		
T/K	x_2	y_2	T/K	x_2	y_2	T/K	x_2	y_2
395.25	0.0225	0.0365	413.99	0.0281	0.0420	426.39	0.0263	0.0380
394.90	0.0438	0.0720	413.67	0.0472	0.0724	425.99	0.0461	0.0701
393.87	0.0907	0.1627	412.86	0.0833	0.1369	425.01	0.0874	0.1442
392.70	0.1340	0.2510	411.80	0.1245	0.2133	424.12	0.1244	0.2067
391.48	0.1698	0.3309	410.74	0.1625	0.2889	422.99	0.1612	0.2738
390.21	0.2083	0.4150	410.50	0.1709	0.3015	390.01	0.9356	0.9863
381.89	0.4087	0.7363	403.56	0.3555	0.6213	389.36	0.9503	0.9895
373.64	0.5698	0.8843	396.78	0.4968	0.7888	388.63	0.9683	0.9933
366.58	0.7208	0.9477	390.30	0.6341	0.8897	388.19	0.9785	0.9954
358.68	0.9146	0.9884	384.60	0.7607	0.9445	387.88	0.9858	0.9969
358.57	0.9173	0.9886	377.69	0.9289	0.9871	387.54	0.9933	0.9984
357.21	0.9530	0.9936	377.58	0.9310	0.9875			
356.62	0.9681	0.9956	376.85	0.9484	0.9908			
356.32	0.9756	0.9967	376.14	0.9667	0.9940			
356.01	0.9835	0.9976	375.74	0.9767	0.9957			
355.71	0.9907	0.9986	375.43	0.9841	0.9970			
			375.10	0.9919	0.9983			

relations or measurements for 1-hexanol[6,14−16] scatter by more than 1 % in terms of pressure in the temperature range of interest. For hexyl acetate, the only primary data found in the literature[17] covers only the temperature range from (278 to 308) K (pressure range (0.05 to 0.4) kPa). In addition, the correlations found in the literature[6,14] deviate significantly without giving details about primary data sources. The experimental results from the present work for 1-hexanol and hexyl acetate are listed in Table 2. They were used to fit Antoine equation parameters. The resulting correlation deviates by less than 0.1 % in average from the data shown in Table 2. For water and acetic acid, Antoine parameters from Dortmund Data Bank[6] were used. The full set of Antoine parameters is given in Table 3 together with the correlation equation.

Vapor−Liquid Equilibria. Isobaric vapor−liquid equilibrium measurements were carried out at (30, 60, and 90) kPa. The results for the three binary systems studied in this work are presented in Table 4 (acetic acid + 1-hexanol), Table 5 (acetic acid + hexyl acetate), and Table 6 (1-hexanol + hexyl acetate). Additionally, one isothermal data set was taken for 1-hexanol + hexyl acetate at 140 °C. The results are given in Table 7. It should be noted that the mole fractions of water and hexyl acetate formed by autocatalyzed reaction in the course of the acetic acid + 1-hexanol experiments were typically below 0.001 mol/mol of hexyl acetate in the liquid phase and 0.015 mol/mol of water in the vapor phase. These amounts were neglected.

Table 5. Isobaric Vapor−Liquid Equilibria in the System Acetic Acid (2) + Hexyl Acetate (4)

$p = 30$ kPa			$p = 60$ kPa			$p = 90$ kPa		
T/K	x_2	y_2	T/K	x_2	y_2	T/K	x_2	y_2
398.51	0.0584	0.2090	423.17	0.0241	0.0783	439.12	0.0081	0.0286
393.50	0.1204	0.3971	421.92	0.0381	0.1293	435.96	0.0330	0.1286
389.57	0.1834	0.5321	420.61	0.0523	0.1751	432.25	0.0699	0.2448
384.42	0.2786	0.6658	417.30	0.0902	0.2846	428.24	0.1278	0.3672
380.08	0.3515	0.7593	414.73	0.1197	0.3629	427.46	0.1329	0.3861
376.67	0.4135	0.8124	412.55	0.1426	0.4323	423.42	0.1841	0.5005
371.93	0.5273	0.8775	407.49	0.2240	0.5746	423.38	0.1883	0.4976
368.24	0.6217	0.9160	406.44	0.2382	0.6073	417.66	0.2755	0.6337
364.23	0.7347	0.9489	402.45	0.3292	0.6903	413.19	0.3609	0.7188
361.83	0.8058	0.9616	398.53	0.3892	0.7632	408.19	0.4651	0.7964
359.78	0.8656	0.9769	394.94	0.4754	0.8155	406.85	0.4959	0.8206
357.47	0.9409	0.9892	392.61	0.5124	0.8431	402.56	0.5997	0.8760
			389.84	0.5852	0.8806	397.95	0.7045	0.9200
			385.99	0.6803	0.9175	395.34	0.7728	0.9399
			382.30	0.7807	0.9476	393.29	0.8294	0.9576
			380.11	0.8455	0.9666	390.05	0.9249	0.9805
			377.19	0.9326	0.9850			

Table 6. Isobaric Vapor−Liquid Equilibria in the System 1-Hexanol (3) + Hexyl Acetate (4)

$p = 30$ kPa			$p = 60$ kPa			$p = 90$ kPa		
T/K	x_3	y_3	T/K	x_3	y_3	T/K	x_3	y_3
402.87	0.0263	0.0396	425.05	0.0210	0.0327	439.63	0.0160	0.0246
402.43	0.0490	0.0732	424.73	0.0365	0.0560	439.27	0.0315	0.0480
401.69	0.0902	0.1318	424.08	0.0664	0.1005	438.70	0.0554	0.0843
401.07	0.1268	0.1815	423.14	0.1101	0.1646	438.01	0.0853	0.1287
400.30	0.1721	0.2398	422.34	0.1513	0.2209	437.16	0.1212	0.1797
399.38	0.2369	0.3186	420.83	0.2359	0.3236	436.31	0.1634	0.2329
399.31	0.2384	0.3179	419.75	0.2983	0.3897	435.34	0.2131	0.2965
398.07	0.3523	0.4353	419.69	0.3052	0.3991	435.10	0.2254	0.3092
396.99	0.4852	0.5543	418.96	0.3657	0.4537	434.44	0.2657	0.3561
396.33	0.5959	0.6437	418.43	0.4018	0.4891	433.63	0.3062	0.4024
396.01	0.6434	0.6828	418.41	0.4034	0.4933	432.18	0.3970	0.4964
395.68	0.7371	0.7587	417.38	0.4927	0.5687	432.01	0.3998	0.4948
395.66	0.7783	0.7928	417.09	0.5234	0.6006	431.46	0.4365	0.5350
395.54	0.8168	0.8248	416.39	0.5819	0.6549	430.85	0.4798	0.5722
395.53	0.8574	0.8603	416.06	0.6269	0.6876	429.89	0.5557	0.6393
395.54	0.8782	0.8795	415.48	0.7221	0.7659	429.67	0.5746	0.6568
395.63	0.8871	0.8876	415.10	0.7839	0.8131	428.96	0.6494	0.7180
395.56	0.9091	0.9082	414.69	0.8608	0.8779	428.54	0.7008	0.7581
395.51	0.9319	0.9302	414.87	0.8825	0.8967	428.49	0.7158	0.7670
395.59	0.9563	0.9545	414.56	0.8966	0.9083	428.19	0.7384	0.7874
395.66	0.9811	0.9800	414.48	0.9245	0.9320	427.71	0.7898	0.8282
395.70	0.9906	0.9899	414.45	0.9438	0.9489	427.38	0.8405	0.8685
			414.42	0.9603	0.9637	427.38	0.8796	0.9005
			414.33	0.9727	0.9749	427.17	0.8851	0.9041
						427.05	0.9150	0.9285
						426.90	0.9450	0.9533
						426.77	0.9766	0.9800

Table 7. Isothermal Vapor−Liquid Equilibria in the System 1-Hexanol (3) + Hexyl Acetate (4)

$T = 413.15$ K					
p/kPa	x_3	y_3	p/kPa	x_3	y_3
41.89	0.0254	0.0406	51.19	0.4139	0.5054
42.22	0.0368	0.0580	54.71	0.6003	0.6646
43.08	0.0655	0.1013	57.23	0.9125	0.9211
43.90	0.0913	0.1397	57.40	0.9343	0.9401
44.70	0.1175	0.1754	57.45	0.9566	0.9601
47.25	0.2188	0.3022	57.32	0.9797	0.9812
49.67	0.3225	0.4160	57.18	0.9894	0.9901

Throughout the present paper, x_i and y_i denote the liquid and vapor phase mole fraction of component i, respectively. Activity coefficients are not given explicitly—they can be directly calculated from the given information. Details are given by Schmitt.[18]

VLE measurements in the quaternary system water + acetic acid + 1-hexanol + hexyl acetate were made at 32.5 kPa in order to allow model validation. The compositions were chosen according to the concentrations present in the

Table 8. Vapor–Liquid Equilibria in the System Water (1) + Acetic Acid (2) + 1-Hexanol (3) + Hexyl Acetate (4) at 32.5 kPa

T/K	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
382.12	0.0235	0.2496	0.4942	0.2327	0.2572	0.3947	0.2292	0.1189
395.23	0.0039	0.1002	0.4376	0.4584	0.0221	0.2154	0.4090	0.3535
383.83	0.0186	0.2449	0.4732	0.2633	0.2025	0.4201	0.2372	0.1401
394.48	0.0039	0.1243	0.3344	0.5374	0.0180	0.2928	0.3020	0.3872
362.40	0.0636	0.3979	0.3094	0.2291	0.3859	0.4697	0.0745	0.0699
397.70	0.0040	0.0253	0.5194	0.4513	0.0253	0.0483	0.5487	0.3777
356.77	0.1368	0.4676	0.2869	0.1087	0.5435	0.3904	0.0411	0.0250
393.75	0.0031	0.1311	0.3648	0.5010	0.0299	0.2968	0.3168	0.3565

Table 9. Liquid–Liquid Equilibria in the System Water (1) + 1-Hexanol (3)[a]

T/K	x'_3	x''_1	T/K	x'_3	x''_1
283.38	0.0013	0.2941	313.26	0.0010	0.3208
293.35	0.0011	0.3016	333.02	0.0011	0.3424
298.36	0.0011	0.3039	353.15	0.0012	0.3769

[a] (′) and (″) refer to the heavy (aqueous) and light (organic) phases, respectively.

Table 10. Liquid–Liquid Equilibria in the System Water (1) + Hexyl Acetate (4)[a]

T/K	x'_4	x''_1
283.15	0.0001	0.0313
298.14	nd[b]	0.0555
318.14	nd[b]	0.0548

[a] (′) and (″) refer to the heavy (aqueous) and light (organic) phases, respectively. [b] nd, not detected.

Table 11. Liquid–Liquid Equilibria in the System Water (1) + Acetic Acid (2) + 1-Hexanol (3)[a]

T/K	x'_1	x'_2	x''_1	x''_2
283.32	0.9761	0.0224	0.3426	0.0678
	0.9516	0.0466	0.3591	0.1256
	0.9274	0.0703	0.3919	0.1686
	0.8781	0.1174	0.4667	0.2260
	0.8405	0.1488	0.5534	0.2430
	0.8141	0.1694	0.5919	0.2428
	0.7379	0.2060	no phase split	
298.20	0.9483	0.0498	0.3855	0.1340
	0.8914	0.1044	0.4679	0.2119
	0.8006	0.1725	0.6530	0.2223
	0.9640	0.0345	0.3588	0.1020
	0.9284	0.0692	0.4138	0.1701
	0.7245	0.2048	no phase split	
318.15	0.9800	0.0187	0.3595	0.0647
	0.9582	0.0400	0.3912	0.1171
	0.9298	0.0675	0.4392	0.1648
	0.8796	0.1135	0.5316	0.2115
	0.8878	0.1064	0.5144	0.2069
	0.8523	0.1344	0.6020	0.2159
	0.7255	0.1957	no phase split	

[a] (′) and (″) refer to the heavy (aqueous) and light (organic) phases, respectively.

reactive distillation experiments described by Schmitt et al.[3]. Table 8 shows the results. The shift of the mixture compositions due to the autocatalytic reaction in the experiments was within the experimental uncertainty and not discernible from the data.

Liquid–Liquid Equilibria. Liquid–liquid equilibrium experiments were carried out in the binary systems water + 1-hexanol and water + hexyl acetate as well as in the ternary systems water + acetic acid + 1-hexanol and water + acetic acid + hexyl acetate at enviromental pressure. The results for the binary systems are presented in Tables 9 and 10; the ternary ones are presented in Tables 11 and 12. It should be noted that in any of the potentially reactive systems the mole fraction of new components formed by the autocatalyzed reaction was always below 0.003 mol/mol and thus negligible. Entries with the remark "no phase split" refer to measurements just outside the phase split region.

Table 12. Liquid–Liquid Equilibria in the System Water (1) + Acetic Acid (2) + Hexyl Acetate (4)[a]

T/K	x'_1	x'_2	x''_1	x''_2
283.16	0.9436	0.0562	0.0732	0.0732
	0.8989	0.1005	0.1133	0.1371
	0.8473	0.1513	0.1542	0.2032
	0.7966	0.1993	0.2086	0.2646
	0.7317	0.2578	0.2835	0.3216
	0.5471	0.3502	no phase split	
298.14	0.9448	0.0550	0.0831	0.0723
	0.8914	0.1080	0.1319	0.1498
	0.8384	0.1592	0.1840	0.2202
	0.7710	0.2224	0.2402	0.2781
	0.5352	0.3474	no phase split	
318.15	0.9989	0.0011	0.0547	0.0024
	0.9446	0.0552	0.1009	0.0742
	0.8819	0.1171	0.1585	0.1601
	0.8420	0.1556	0.1882	0.2025
	0.7821	0.2112	0.2431	0.2628
	0.7174	0.2647	0.3175	0.3134
	0.5634	0.3319	no phase split	

[a] (′) and (″) refer to the heavy (aqueous) and light (organic) phases, respectively.

Table 13. Liquid–Liquid Equilibria in the System Water (1) + Acetic Acid (2) + 1-Hexanol (3) + Hexyl Acetate (4) at 25 °C[a]

x'_1	x'_2	x'_3	x'_4	x''_1	x''_2	x''_3	x''_4
0.8386	0.1540	0.0066	0.0008	0.4878	0.2638	0.1879	0.0605
0.8249	0.1656	0.0082	0.0012	0.5052	0.2690	0.1665	0.0593
0.8066	0.1805	0.0109	0.0021	0.5312	0.2723	0.1424	0.0540
0.7242	0.2437	0.0182	0.0132	0.5595	0.3018	0.0686	0.0701
0.8427	0.1503	0.0064	0.0006	0.4787	0.2620	0.2019	0.0574

[a] (′) and (″) refer to the heavy (aqueous) and light (organic) phases, respectively.

LLE experiments were also carried out in the quaternary system water + acetic acid + 1-hexanol + hexyl acetate, again to allow checking the quality of the model prediction. The feed compositions used in the LLE experiments represent typical decanter feed compositions observed in reactive distillation experiments[3]. Table 13 shows the results of these LLE measurements.

Modeling

The system water + acetic acid + 1-hexanol + hexyl acetate with its miscibility gap, various azeotropes, and acetic acid dimerization in the gas phase is characterized by a strongly nonideal behavior. Only a brief outline of the modeling of the thermodynamic properties of that system is presented here; for a more detailed discussion, see Schmitt.[18]

Liquid phases were modeled neglecting the pressure dependence of the chemical potential and accounting for the nonidealities using the NRTL model[4] with a temperature-dependent interaction parameter (Δg_{ij}) defined as

$$\frac{\Delta g_{ij}}{RT} = a_{ij} + \frac{b_{ij}}{T/\mathrm{K}} \tag{1}$$

The vapor phase was modeled taking the dimerization of acetic acid into account via chemical theory and neglecting all other nonidealities. For more details about chemical

Table 14. NRTL Model Parameters for the Description of VLE

component 1 component 2	water acetic acid	water 1-hexanol	water hexyl acetate	acetic acid 1-hexanol	acetic acid hexyl acetate	1-hexanol hexyl acetate
a_{12}	0.2652	−0.1522	−1.7481	0.1848	−4.3047	2.6355
a_{21}	−0.0713	−3.1777	−1.3148	−0.6778	4.2800	−3.2599
b_{12}	354.22	1945.07	3545.58	714.13	1871.70	−839.81
b_{21}	−36.720	1381.31	998.70	−192.44	−1616.74	1225.85
α	0.4158	0.3323	0.2	0.3	0.3	0.3

Table 15. NRTL Model Parameters for the Description of LLE

component 1 component 2	water acetic acid	water 1-hexanol	water hexyl acetate	acetic acid 1-hexanol	acetic acid hexyl acetate	1-hexanol hexyl acetate
a_{12}	2.1656	−0.1522	−1.7481	−2.8409	−2.9897	2.6355
a_{21}	−1.1818	−3.1777	−1.3148	0.8255	5.8822	−3.2599
b_{12}	−174.40	1945.07	3545.58	1091.75	801.34	−839.81
b_{21}	236.42	1381.31	998.70	−351.26	−1264.46	1225.85
α	0.3	0.3323	0.2	0.2	0.2	0.3

theory, see, for example, Gmehling and Onken[7] from which also the dimerization equilibrium constant for acetic acid was taken.

Determination of NRTL Model Parameters. For reasons already explained in the Introduction, two different sets of NRTL parameters were determined: one for the description of VLE and another for the description of LLE. Attempts to find solutions for a common description of both types of data did not yield results with sufficient accuracy for a proper description of the studied reactive distillation process. Similar observations were recently made for a related system by Grob.[5] The parameter sets presented below are the result of extensive studies of different variants, which cannot be discussed here. The aim of these studies was to find a practicable solution, which gives good results for the equilibria that are important in process simulation of the reactive distillation process under investigation[3].

Table 1 gives, in the lower left triangle of the matrix entries, an overview over the sources that were used for the determination of the binary NRTL parameters. The parameters for VLE calculations for water + acetic acid are adopted from Gmehling and Onken[7] (recommended values); the ones for acetic acid + 1-hexanol and acetic acid + hexyl acetate, respectively, were fitted to the binary VLE data from the present work (Tables 4 and 5). For LLE calculation, the binary parameters of these systems were fitted to LLE data in the ternary systems water + acetic acid + 1-hexanol and water + acetic acid + hexyl acetate (cf. Tables 11 and 12), since the binary systems water + acetic acid, acetic acid + 1-hexanol and acetic acid + hexyl acetate show no miscibility gap. For the remaining three binary systems, it turned out that a distinction between binary parameters for VLE and LLE calculations was not necessary. Therefore, only one parameter set is presented for each of these binary systems. For water + 1-hexanol and water + hexyl acetate, the binary parameters were determined from the LLE data of the present work (cf. Tables 9 and 10), extended with selected literature data.[8,9] For 1-hexanol + hexyl acetate, the parameters were determined from the VLE data of the present work (cf. Table 6). Note that the choice of the sources for the determination of the model parameters is related to the importance of the individual interactions for the different separation tasks in the reactive distillation column (VLE) and its decanter (LLE). For more details, see Schmitt.[18]

The parameter set for the description of VLE is presented in Table 14; that for the description of LLE is presented in Table 15. For more details on the mathematical fitting, see Schmitt.[18]

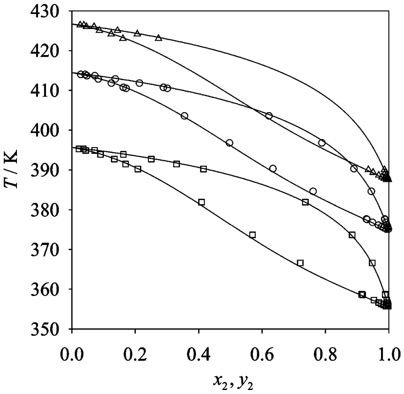

Figure 1. Vapor−liquid equilibria in the system acetic acid (2) + 1-hexanol (3): experimental data from this work (□, 30 kPa; ○, 60 kPa; △, 90 kPa) and correlation with the NRTL model (—; parameters from Table 14).

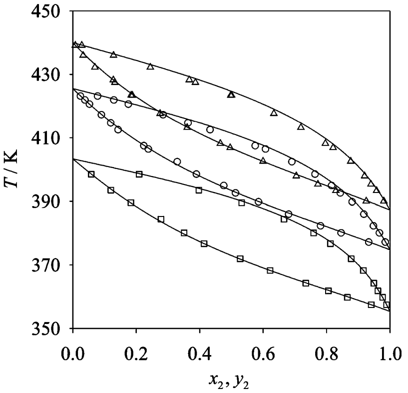

Figure 2. Vapor−liquid equilibria in the system acetic acid (2) + hexyl acetate (4): experimental data from this work (□, 30 kPa; ○, 60 kPa; △, 90 kPa) and correlation with the NRTL model (—; parameters from Table 14).

Results for Vapor−Liquid Equilibria. In Figures 1, 2, and 3 the results from the model are compared to the isobaric data taken in the present work for the systems acetic acid + 1-hexanol, acetic acid + hexyl acetate, and 1-hexanol + hexyl acetate, respectively. In all cases, good correlations of the data were obtained. The results for the isothermal data set of 1-hexanol + hexyl acetate at 140 °C are similar to those shown in Figure 3. There is no data in the literature for these three binary systems to validate the model. Figure 4 shows a comparison of literature data for VLE in the system water + 1-hexanol to the present model. Note that for this system, the NRTL parameters were fitted only to LLE data. Good agreement between the prediction and the experimental data is observed. Similar

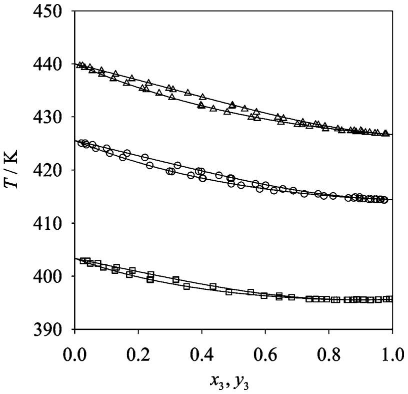

Figure 3. Vapor−liquid equilibria in the system 1-hexanol (3) + hexyl acetate (4): experimental data from this work (□, 30 kPa; ○, 60 kPa; △, 90 kPa) and correlation with the NRTL model (—; parameters from Table 14).

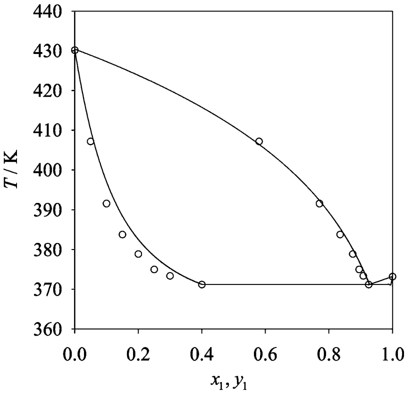

Figure 4. Vapor−liquid equilibria in the system water (1) + 1-hexanol (3) at 101.3 kPa: experimental data from Tunik et al.[19] (○) and prediction with the NRTL model (—; parameters from Table 14).

Table 16. Azeotropic Data for the Systems Water (1) + 1-Hexanol (3) and Water (1) + Hexyl Acetate (4) at 101.3 kPa[a]

	water (1) + 1-hexanol (3)		water (1) + hexyl acetate (4)	
	T/K	$x_1 = y_1$	T/K	$x_1 = y_1$
experiment[19−21]	97.7−97.8	0.921−0.939	97.4	0.926
model prediction	98.0	0.928	97.6	0.916

[a] Comparison of experimental data from literature with NRTL model predictions (parameters from Table 14).

results are obtained for azeotropic data in that system, cf. Table 16. Table 16 also contains azeotropic data for the system water + hexyl acetate. Also for that system, the NRTL parameters were fitted only to LLE data. Again, good agreement between the model predictions and the experimental data is observed.

Also the model predictions for vapor−liquid equilibria in the quaternary system water + acetic acid + 1-hexanol + hexyl acetate using the NRTL parameters given in Table 14 are good. Flash calculations at constant temperature and pressure were carried out for that system. The deviations between the experimental results from Table 8 and the simulations were always smaller than 0.025 mol/mol for the liquid-phase mole fractions and 0.05 mol/mol for the vapor phase mole fractions. The average deviation is as small as 0.009 mol/mol and 0.016 mol/mol for the liquid and vapor phase, respectively. For numerical results, see Schmitt.[18] This good agreement shows that the model is well-suited for process simulations of the studied reactive distillation.

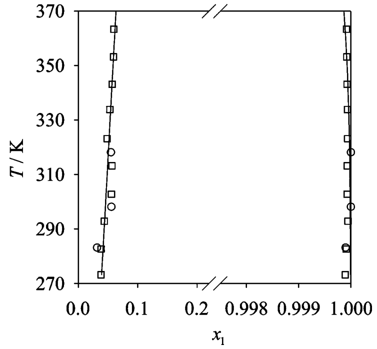

Figure 5. Liquid−liquid equilibria in the system water (1) + hexyl acetate (4): experimental data (○, this work; □, Stephenson and Stuart[9]) and correlation with the NRTL model (—; parameters from Table 15).

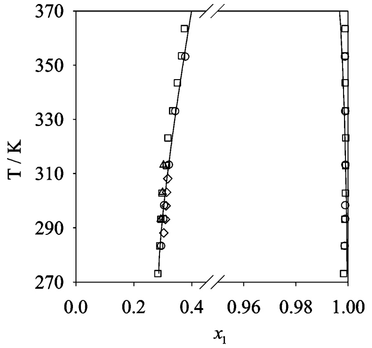

Figure 6. Liquid−liquid equilibria in the system water (1) + 1-hexanol (3): experimental (○, this work; □, Stephenson et al.[8]; △, Sazonov et al.[22]; ◇, Tokunaga et al.[23]) and correlation with the NRTL model (—; parameters from Table 15).

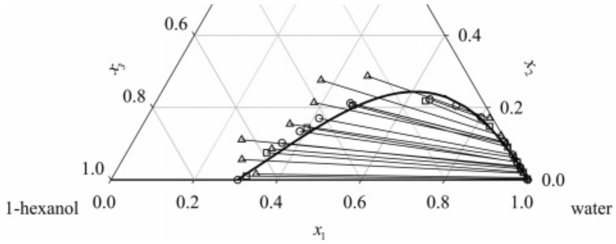

Figure 7. Liquid−liquid equilibria in the system water (1) + acetic acid (2) + 1-hexanol (3) at 25 °C: experimental data (○, this work; □, Saito et al.[24]; △, Fahim et al.[25]) and correlation with the NRTL model (—; parameters from Table 15).

Results for Liquid−Liquid Equilibria. In Figure 5, experimental LLE data from the present work and from the literature[9] for the system water + hexyl acetate is shown together with the results from their correlation with the NRTL model (parameters: cf. Table 15). The agreement between data and model is good.

The LLE experiments in the water + 1-hexanol system carried out in the present work were necessary as available literature data was inconsistent. In Figure 6, the experimental data from the present study are shown together with data sets from literature which seem to be reliable.[8,22,23] The experimental data are compared to the results from the NRTL model, which was fitted to the data from the present work, extended with data from Stephenson and Stuart.[8] Again, the agreement is good.

Figures 7 and 8 show experimental results and correlations for ternary LLE in the systems water + acetic acid + 1-hexanol and water + acetic acid + hexyl acetate. The

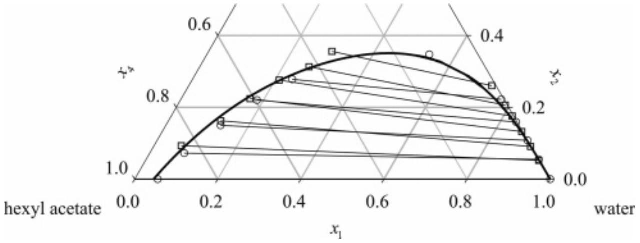

Figure 8. Liquid−liquid equilibria in the system water (1) + acetic acid (2) + hexyl acetate (4) at 25 °C: experimental data (○, this work; □, Blanco et al.[26]) and correlation with the NRTL model (—; parameters from Table 15).

model results are correlations, as the binary NRTL parameters for the three binary subsystems containing acetic acid were fitted to the ternary LLE data as described above. Besides experimental data from the present work, also results from the literature are shown. In the system water + acetic acid + 1-hexanol, cf. Figure 7, the results of Saito et al.[24] are in good agreement with the data measured in this work and were therefore included in the parameter fit whereas the strongly scattering data of Fahim et al.[25] were not used. The correlation of the data with the NRTL model is good, with only a small but systematic deviation for the composition of the organic phase. In the system water + acetic acid + hexyl acetate (cf. Figure 8), the experimental data of Blanco et al.[26] show slight but systematic deviations from the data obtained in the present work and were therefore not used for the parameter fit. The correlation of the experimental data with the NRTL model is good for this system as well.

The NRTL model predictions were checked against quaternary LLE data in the system water + acetic acid + 1-hexanol + hexyl acetate. Deviations between the isothermal liquid−liquid-phase split calculations and the experimental results from Table 13 were always smaller than 0.015 mol/mol for the aqueous phase mole fractions and 0.03 mol/mol for the organic phase mole fractions. The average deviation is as small as 0.006 mol/mol and 0.009 mol/mol for the aqueous and organic phase, respectively. Again, for numerical results, see Schmitt.[18] The good agreement proves the applicability of the model to decanter simulations in the studied reactive distillation process.

Conclusions

The production of hexyl acetate from acetic acid and 1-hexanol with the additional product water is an important test system for heterogeneously catalyzed reactive distillation. For developing models of that process, it is crucial to have a reliable experimental database and thermodynamic model of phase equilibria in systems containing water, acetic acid, 1-hexanol, and hexyl acetate. On the basis of a detailed literature study and extensive new experimental work, a comprehensive database for VLE and LLE in these systems was provided. To meet the accuracy demands of reactive distillation process simulation, two separate sets of NRTL model parameters were determined: one for the description of VLE and another one for LLE. The comparison of these models with experimental data from the present work and from literature shows that they give reliable predictions for the conditions encountered in reactive distillation.

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