Phase Equilibrium for the Esterification Reaction of Acetic Acid + Butan-1-ol at 101.3 kPa

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In this work, the thermodynamic behavior of catalytic esterification reaction equilibrium and vapor–liquid equilibria (VLE) for the quaternary reactive system acetic acid + butan-1-ol + butyl acetate + water and constituent binary systems acetic acid + butyl acetate, butan-1-ol + butyl acetate, and butan-1-ol + water have been determined at 101.3 kPa, and liquid–liquid equilibria (LLE) of the binary system butan-1-ol + water have also been determined. The esterification reaction rate of the acetic acid and butan-1-ol mixture is very slow. So, in this study, *p*-toluenesulfonic acid was selected as the catalyst to accelerate the chemical reaction. The measured VLE data were correlated by the NRTL and UNIQUAC activity coefficient models with allowance for association of acetic acid in the vapor phase.

Introduction

In the last years, reactive distillation has received increasing attention which can be attributed to the lower capital and operating cost than those of conventional processes. Moreover, the combination of certain types of reactions and separation in a process unit brings important advantages such as overcoming azeotropes and increasing reaction yield. The esterification reaction of butyl acetate is an example of such a reaction. Even though there have been investigations regarding this process,[1–3] there are no published vapor–liquid equilibrium (VLE) data of the quaternary reactive system at the same conditions.

In the present work, the VLE of the esterification reaction of acetic acid and butan-1-ol was studied. Experimental data of isobaric VLE of the quaternary acetic acid (1) + butan-1-ol (2) + butyl acetate (3) + water (4) system and of some of the nonreactive constituent binary systems were carried out at 101.3 kPa.

There is plenty of bibliographic information about the nonreactive binary systems. On one hand, some of these previous papers have been going for 50 years, and on the other hand, some papers have isotherm VLE data or have no experimental data. Therefore, once all the bibliographic information was analyzed, it was decided to determine and include in this work the experimental VLE data of the binary systems acetic acid (1) + butyl acetate (3) and butan-1-ol (2) + butyl acetate (3) together with a comparative study of these systems with the previous published works.[4–13] Since the butan-1-ol (2) + water (4) system exhibits a limited miscibility in the liquid phase, the VLE together with a few LLE (liquid–liquid equilibrium) data have been measured; also, a comparison with the literature[14–25] has been made. The binary system acetic acid (1) + water (4) was not experimentally determined as there have been many studies on this mixture.

Experimental Section

Chemicals. Butan-1-ol ($w = 99.8$ %, HPLC grade) and butyl acetate ($w > 99.0$ %, for analysis) were supplied by Aldrich Ltd. and dried over molecular sieves (Union Carbide, type 4 Å, 0.0016 m pellets). Acetic acid ($w = 99.8$ %, for analysis) was supplied by Acros Organics, and water was bidistillated. The reagents were used without further purification after GLC chromatography failed to show any significant impurities. The water content, determined using a Karl Fischer volumetric automatic titrator (Metrohm, 701 KF Titrino), was small in all chemicals ($w < 0.05$ %). The refractive indexes of the pure components were measured at 298.15 K using an Abbe refractometer Atago 3T, and the densities were measured at 298.15 K using an Anton Paar DMA 58 densimeter. Temperature was controlled to ± 0.01 K with a thermostatted bath. The uncertainties in refractive index and density measurements are ± 0.0002 and ± 0.01 $\text{kg} \cdot \text{m}^{-3}$, respectively. The experimental values of these properties and the boiling points are given in Table 1 together with those given in the literature. Appropriate precautions were taken when handling the reagents to avoid hydration.

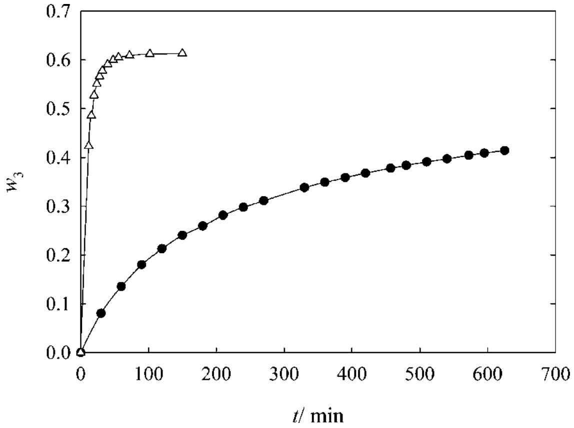

Figure 1. Variation of butyl acetate mass fraction (w_3) with the reaction time in the esterification of acetic acid with butan-1-ol at 101.3 kPa: ●, without catalyst; Δ, with $w = 1.5$ % of *p*-toluenesulfonic acid as catalyst.

Apparatus and Procedure. The equilibrium vessel used in the measurements (Labodest VLE 602/D) was an all-glass

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Table 1. Density d, Refractive Index n_D, and Normal Boiling Point T_b of Pure Components

	d (298.15 K)/kg·m^{-3}		n_D (298.15 K)		T_b (101.3 kPa)/K	
component	exptl	lit[a]	exptl	lit[a]	exptl	lit[b]
acetic acid (1)	1043.90	1043.90	1.3696	1.3698	390.91	391.05
butan-1-ol (2)	805.60	805.77	1.3960	1.3971	390.46	390.33
butyl acetate (3)	876.02	876.40	1.3916	1.3918	399.05	399.15
water (4)	997.00	997.04	1.3332	1.3325	373.15	373.15

[a] Ref 26. [b] Ref 27.

Table 2. Experimental Vapor Pressures (P_i^o) for Acetic Acid (1) and Butyl Acetate (3)

acetic acid		butyl acetate	
T/K	P/kPa	T/K	P/kPa
328.56	9.98	334.36	9.99
330.65	10.97	336.53	10.98
332.65	11.98	338.56	11.99
336.23	13.97	342.20	13.97
339.41	15.97	345.47	15.99
342.25	17.98	348.37	17.97
344.81	19.98	351.02	19.98
347.19	21.98	353.45	21.97
349.40	23.98	355.72	23.97
352.43	26.97	357.84	25.98
355.18	29.96	359.79	27.92
357.72	32.98	362.58	30.98
360.09	35.94	365.10	33.92
362.26	38.96	367.50	36.96
365.00	42.93	369.74	39.97
366.30	44.95	373.18	44.92
369.30	49.94	376.31	49.90
372.09	54.93	379.18	54.92
374.63	59.83	381.89	59.93
377.03	64.87	384.40	64.95
379.25	69.84	386.74	69.92
381.39	74.82	388.96	74.95
383.35	79.71	391.05	79.91
385.23	84.52	393.02	84.83
387.10	89.81	394.94	89.87
388.77	94.52	396.72	94.73
390.91	101.30	399.05	101.30

dynamic recirculating still equipped with a Cottrell circulation pump, manufactured by Fischer Labor and Verfahrenstechnik (Germany). The apparatus is capable of handling pressures from (0.25 to 400) kPa and temperatures up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Hart Scientific thermometer (model 1502A) and a Pt 100 probe (Hart Scientific, model 5622) calibrated at the ENAC-Spanish Instituto Nacional de Técnica Aeroespacial. The uncertainty is estimated to be ± 0.01 K. The temperature probe was checked against the ice and steam points of distilled water. A Fisher M101 pressure control system was used to measure and control the pressure and the heating power. The measured pressure in the still was (101.3 ± 0.1) kPa. The manometer was calibrated using the vapor pressure of ultrapure water.

In each experiment, the pressure was fixed, and the heating and stirring system of the liquid mixture was turned on. The still was operated at constant pressure until equilibrium was reached. Equilibrium conditions for VLE binary systems were assumed when constant temperature and pressure were obtained for 30 min or longer. For the study of the reactive quaternary VLE system, it was necessary to reach not only physical equilibrium but also chemical equilibrium. Therefore, once chemical and phase equilibria were reached (constant temperature and pressure), 90 min approximately, samples of liquid and condensed vapor were analyzed.

The samples of the liquid were removed with special syringes that allowed withdrawal of small samples. Vapor samples were injected directly into the GC through a VW type, 6-port valve from Valco Instruments Co. The connecting tube wall was superheated with a resistance tape controlled by a potentiometer so that the vapor was not saturated and condensation was avoided.

To determine the LLE data of the butan-1-ol (2) + water (4) system, mixtures were prepared by mass, with weighing accurate to ± 0.0001 g, in Pyrex tubes of 1.6 cm o.d. The cloud point curves of the binary mixture were determined visually. The samples in the sealed and stirred Pyrex tubes were placed in a thermostat bath. A constant temperature (± 0.1 K) was maintained by circulating water through the outer jacket of the bath. Then, water was added slowly from a syringe, and stirring was applied almost continuously until the cloud point was observed. The mass of water added to reach the cloud point of the system was determined from mass differences using an analytical balance (Metter Toledo AG245). This process was repeated as many times as necessary to obtain all the experimental points.

Analysis. The composition of the sampled liquid and condensed vapor phase was determined using a CE Instruments GC 8000 Top gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 30 m, 0.454 mm i.d, capillary

Table 3. Vapor Pressure Parameters

compound	eq[a]	A_i	B_i	C_i	D_i	E_i	ref
acetic acid (1)	1	14.935	3501.76	51.624			this work[b]
	1	14.831	3424.04	55.640			[c]
	3	53.270	−6304.50	−4.298	$8.886 \cdot 10^{-18}$	6	[d]
	1	15.155	3628.18	46.716			[e]
butan-1-ol (2)	1	15.822	3499.92	78.11			[f]
butyl acetate (3)	1	15.766	4216.17	20.741			this work[b]
	2	6.151	1368.05	69.220			[g]
	3	71.340	−7285.80	−6.946	$9.989 \cdot 10^{-18}$	6	[d]
water (4)	3	73.649	−7258.20	−7.304	$4.165 \cdot 10^{-6}$	2	[d]

[a] Vapor pressure equations: (1) $\ln P°/\text{kPa} = A - B/(T/\text{K} - C)$; (2) $\log P°/\text{kPa} = A - B/(T/\text{K} - C)$; (3) $\ln P°/\text{Pa} = A + B/(T/\text{K}) + C \ln T/\text{K} + D(T/\text{K})^E$. [b] Antoine's parameters were calculated from the experimental data in Table 2. [c] Taken from Vercher et al.[32] [d] Parameters taken from Daubert and Danner.[27] [e] Parameters taken form TRC.[31] [f] Parameters taken from Dejoz et al.[30] [g] Parameters taken from Riddick.[33]

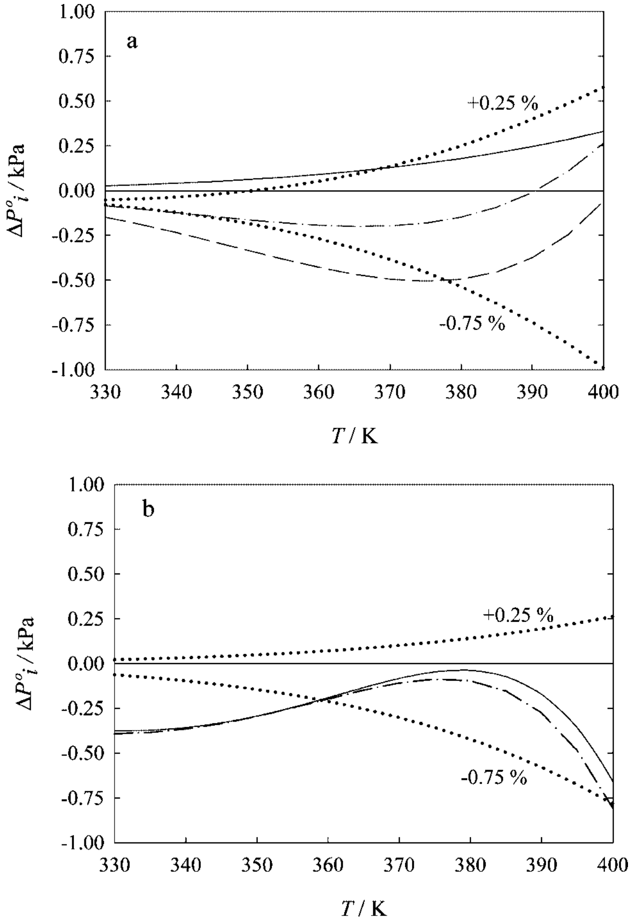

Figure 2. Differences $\Delta P_i^\circ = P_i^\circ - P_{i,\mathrm{lit}}^\circ$ obtained for vapor pressure using the parameters given in Table 3. (a) Acetic acid: —, ref 27; -----, ref 31; -•-•-, ref 32. (b) Butyl acetate: —, ref 27; -•-•-, ref 33.

Table 4. Experimental Vapor–Liquid Equilibrium Data for the Binary System Acetic Acid (1) + Butyl Acetate (3) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_3
399.05	0.000	0.000		1.000
398.42	0.059	0.076	1.866	1.009
397.92	0.113	0.146	1.662	1.020
397.46	0.167	0.208	1.507	1.037
396.80	0.222	0.273	1.408	1.062
396.41	0.275	0.336	1.340	1.077
396.04	0.328	0.396	1.281	1.094
395.48	0.390	0.462	1.226	1.123
394.98	0.443	0.515	1.184	1.154
394.62	0.498	0.568	1.145	1.183
394.16	0.557	0.622	1.112	1.221
393.72	0.607	0.670	1.093	1.252
393.21	0.660	0.716	1.073	1.299
392.57	0.710	0.759	1.060	1.355
392.23	0.756	0.800	1.048	1.390
392.00	0.801	0.837	1.035	1.432
391.68	0.848	0.876	1.024	1.483
391.37	0.895	0.914	1.016	1.546
391.18	0.936	0.947	1.008	1.617
391.01	0.972	0.976	1.003	1.727
390.91	1.000	1.000	1.000	

Table 5. Experimental Vapor–Liquid Equilibrium Data for the Binary System Butan-1-ol (2) + Butyl Acetate (3) at 101.3 kPa

T/K	x_2	y_2	γ_2	γ_3
399.05	0.000	0.000		1.000
397.48	0.058	0.103	1.404	0.994
396.08	0.116	0.191	1.363	0.994
395.02	0.166	0.256	1.323	0.999
393.98	0.220	0.321	1.296	1.004
393.07	0.275	0.379	1.262	1.014
392.34	0.325	0.425	1.227	1.031
391.78	0.380	0.473	1.190	1.046
391.23	0.430	0.517	1.171	1.060
390.72	0.485	0.559	1.142	1.087
390.44	0.541	0.601	1.112	1.113
390.17	0.596	0.640	1.084	1.151
389.93	0.651	0.681	1.065	1.189
389.74	0.708	0.723	1.046	1.242
389.54	0.756	0.759	1.036	1.301
389.55	0.802	0.797	1.024	1.351
389.56	0.847	0.836	1.017	1.413
389.68	0.891	0.878	1.011	1.471
389.83	0.933	0.921	1.007	1.544
390.13	0.970	0.963	1.003	1.602
390.46	1.000	1.000	1.000	

Table 6. Experimental Vapor–Liquid Equilibrium Data for the Binary System Butan-1-ol (2) + Water (4) at 101.3 kPa

T/K	x_2	y_2	γ_2	γ_4
373.15	0.000	0.000		1.000
369.71	0.005	0.120	54.704	0.972
368.88	0.006	0.148	52.785	0.982
367.53	0.009	0.191	49.199	0.989
365.65	0.558	0.248	1.137	1.270
365.87	0.592	0.253	1.082	2.136
366.66	0.630	0.271	1.051	2.287
368.20	0.687	0.304	1.017	2.410
369.92	0.735	0.342	0.998	2.602
370.97	0.760	0.366	0.997	2.774
373.10	0.803	0.416	0.989	2.867
375.61	0.845	0.480	0.980	3.035
378.17	0.881	0.550	0.976	3.211
381.37	0.918	0.645	0.974	3.371
385.20	0.955	0.773	0.973	3.555
389.44	0.989	0.933	0.972	3.759
390.46	1.000	1.000	1.000	

column (DB-MTBE, J & Scientific) for the nonaqueous mixture. The GC response peaks were analyzed with Chrom-Card for Windows. Column, injector, and detector temperatures were (393, 473, and 493) K, respectively, for all nonaqueous systems. The compositions of the aqueous mixture were analyzed with a TCD detector. The column used was a 80/100 Porapak Q 3 m × $3.17 \cdot 10^{-3}$ m. The optimum operation conditions were: injection temperature, 473 K; oven temperature, 393 K; detector temperature, 453 K; and detector current, 220 mA.

Very good peak separation was achieved under these conditions, and calibration analyses were carried out to convert the peak area ratio to the mass composition of the sample. At least two analyses were made of each liquid and vapor composition. The uncertainty in the mole fraction was usually ± 0.002.

Thermodynamics of VLE with Chemical Reaction

Phase Equilibrium. The activity coefficients, γ_i, for the quaternary and binary systems were calculated from the following equation:[28]

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^\circ} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^\circ)}{RT} + \frac{P}{2RT}\sum_{j=1}^{n}\sum_{k=1}^{n} y_i y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \quad (2)$$

where T is the absolute temperature; P is the total pressure, V_i^{L} is the molar liquid volume of component i; P_i° is the saturation pressure; and B_{ii} and B_{jj} are the virial coefficients. Because carboxylic acids are always present in an associated form, like

Table 7. Binary Parameters $\tau_{ij} = A_{ij} + B_{ij}/(T/\mathrm{K})$ of the NRTL and UNIQUAC Models for the Binary Systems Acetic Acid (1) + Butyl Acetate (3), Butan-1-ol (2) + Butyl Acetate (3), and Butan-1-ol (2) + Water (4)

model	system $i + j$	A_{ij}	A_{ji}	B_{ij} K	B_{ji} K	α_{ij}	bubble point AADT[a]	bubble point AADy[b]
NRTL	1 + 3	12.072	33.000	−4510.20	−3635.65	0.3	0.16	0.0075
	2 + 3	−2.532	0.960	1304.28	−479.47	0.3	0.09	0.0018
	2 + 4	6.168	43.150	−2255.13	−14393.85	0.3	0.26	0.0069
UNIQUAC[c]	1 + 3	7.923	−13.401	−5300.00	9063.40		0.17	0.0049
	2 + 3	0.552	−0.273	−272.41	113.40		0.09	0.0018
	2 + 4	−75.057	6.203	4456.45	148.42		0.33	0.0117

[a] Average absolute deviation in temperature. [b] Average absolute deviation in vapor-phase composition. [c] Volume and surface parameters from ref 38.

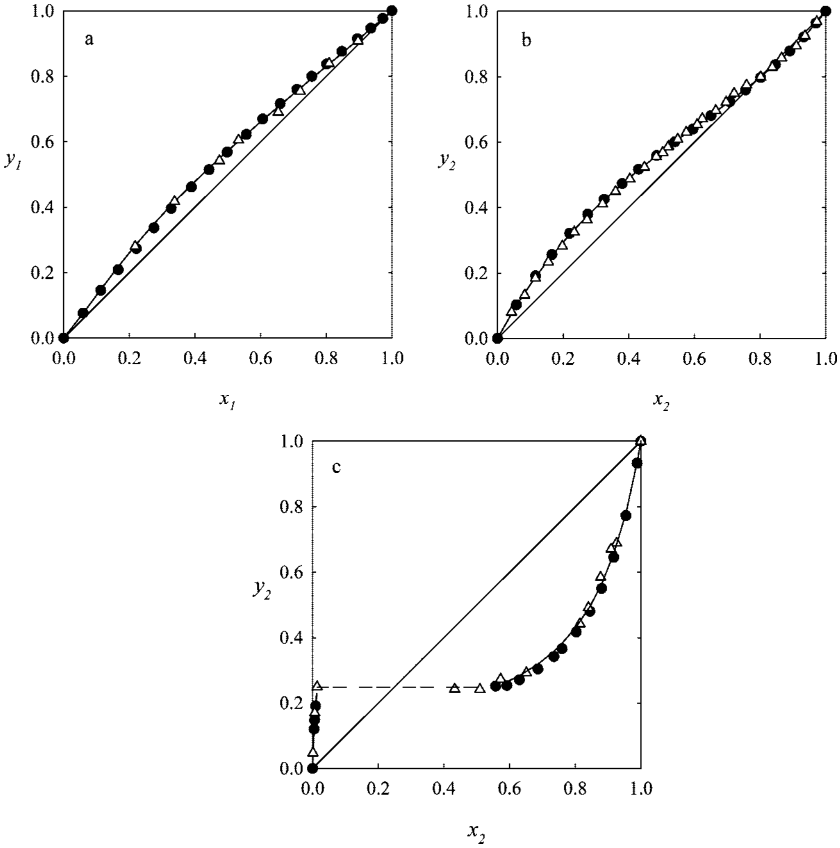

Figure 3. Binary x−y diagram at 101.3 kPa of the systems. (a) Acetic acid (1) + butyl acetate (3): ●, this work; Δ, ref 4; —, UNIQUAC model. (b) Butan-1-ol (2) + butyl acetate (3): ●, this work; Δ, ref 13; —, UNIQUAC model. (c) Butan-1-ol (2) + water (4): ●, this work; Δ, ref 21; —, NRTL model.

a dimer or trimer, in both the vapor and liquid phases even at low pressures, a significant deviation in the fugacity coefficient may exist using the ideal gas assumption. To account for the nonideal behavior, a chemical theory is commonly used to calculate the vapor fugacity coefficient. In this study, the Hayden−O′Connell model[29] was used for this purpose.

Kinetics of Chemical Reaction. A binary mixture of 0.38 mass fraction of acetic acid + 0.62 mass fraction of butan-1-ol was charged into the equilibrium still and boiled at constant pressure (101.3 kPa) for approximately 12 h. Samples of the liquid phase were collected every 30 min. It was found that the rate of esterification was very slow; only a mass fraction of 0.4 of butyl acetate was formed during the whole period (9 h). To accelerate the reaction rate, w = 1.5 % of *p*-toluenesulfonic acid (as catalyst) was added to the liquid phase. It was found that already after 90 min the mass fraction reached a constant value (61.2 %), and the temperature in the system remained constant, indicating that the state of both chemical and phase equilibrium was attained. Figure 1 shows the experimental results of butyl acetate concentrations at different periods for the cases with and without catalyst.

Results and Discussion

Pure Component Vapor Pressures. The pure component vapor pressures P_i° for butan-1-ol (2) and water (4) were taken from refs 27 and 30. For acetic acid (1) and butyl acetate (3), pure component vapor pressures were determined as a function of the temperature, using the same equipment as that for obtaining the VLE data. The pertinent results appear in Table 2.

The measured vapor pressures were correlated using the Antoine equation

$$\ln P_i/\mathrm{kPa} = A_i - \frac{B_i}{T/\mathrm{K} - C_i} \tag{3}$$

whose parameters A_i, B_i, and C_i are reported in Table 3 together with some literature values. The deviations, $\Delta P_i^\circ = P_i^\circ - P_{i,\mathrm{lit}}^\circ$ calculated by means of the Antoine equation using the constant values from Table 3 have been graphically represented in Figure 2.

Nonreactive Binary Systems. Experimental isobaric VLE data of the binary systems acetic acid (1) + butyl acetate (3), butan-

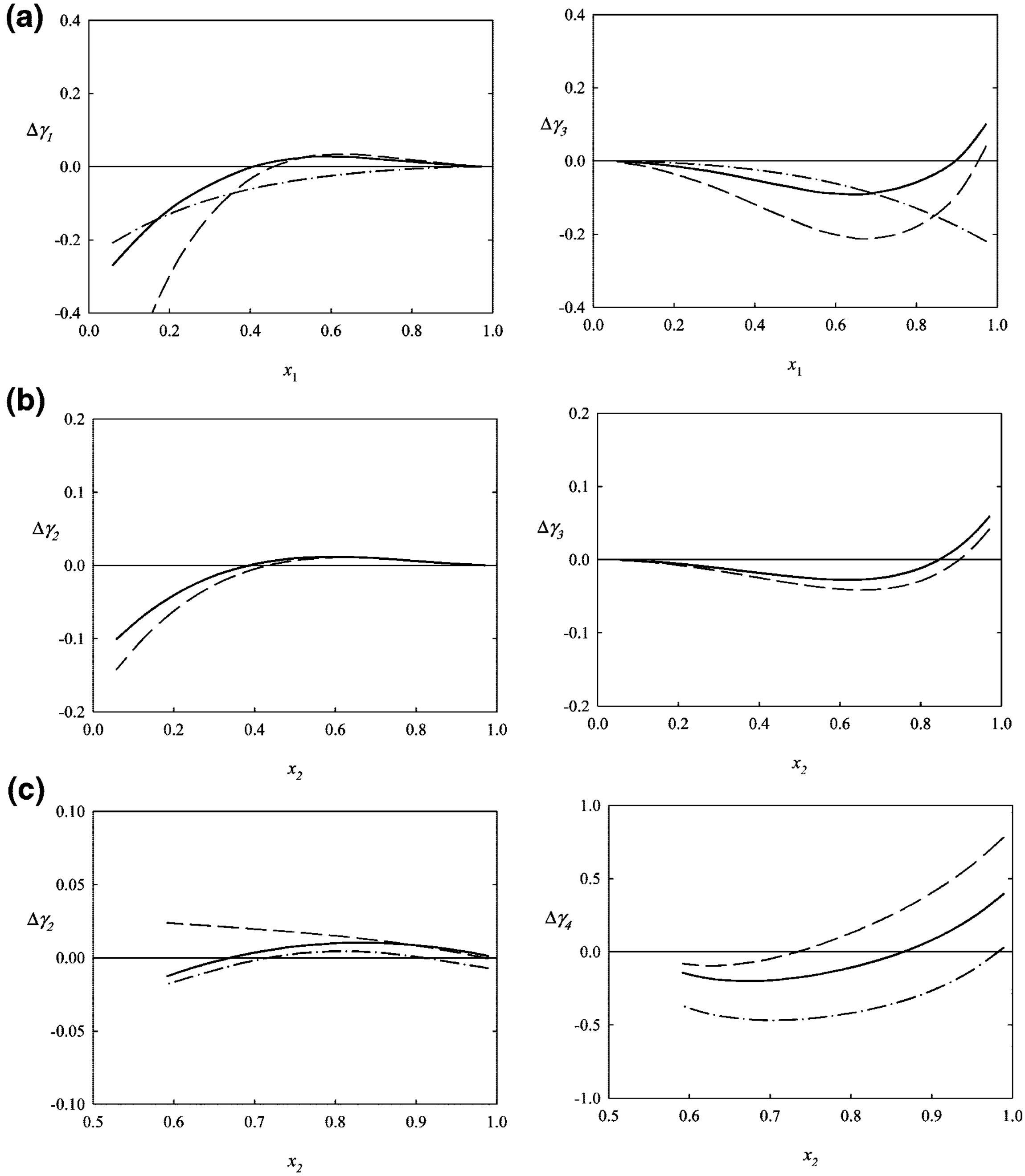

Figure 4. Deviations of activity coefficients calculated with the UNIQUAC binary parameters obtained in this work from those calculated with the UNIQUAC binary parameters corresponding to VLE data found in the literature. (a) Acetic acid (1) + butyl acetate (3): —, ref 6; ----, ref 5; -•-•-, ref 4. (b) Butan-1-ol (2) + butyl acetate (3): —, ref 11; ----, ref 12. (c) Butanol-1-ol (2) + water (4): —, ref 20; ----, ref 21; -•-•-, ref 22.

1-ol (2) + butyl acetate (3), and butyl alcohol (2) + water (4) are reported in Tables 4 to 6.

The experimental VLE data were found to be thermodynamically consistent by the Herington[34] method with a tolerance not greater than 10 %. It was found that the data were thermodynamically consistent when the association of acetic acid in the vapor phase was considered, applying the Hayden and O'Connell method,[29] but it was not the case when ideal gas assumption was applied.

Experimental data were correlated using the NRTL[35] and UNIQUAC[36] equations. The regression was carried out using the Aspen Plus v2006 chemical process simulator,[37] in which the generalized least-squares method, the maximum-likelihood principle, and the Britt−Luecke algorithm were used to minimize the average absolute relative deviation (AARD), defined as

$$\mathrm{AARD} = \sum_i^n \frac{|T_i^{\mathrm{calcd}} - T_i|/T_i}{n} + \sum_i^n \frac{|x_i^{\mathrm{calcd}} - x_i|/x_i}{n} + \sum_i^n \frac{|y_i^{\mathrm{calcd}} - y_i|/y_i}{n} \qquad (4)$$

The binary interaction parameters evaluated from the regression for these two models are shown in Table 7. Figure 3 shows a comparison between experimental and calculated data using the UNIQUAC and NRTL models.

Figure 4 shows, for the three binary systems studied, the deviations between the activity coefficients calculated with the UNIQUAC parameters obtained in this work and those calculated with the UNIQUAC parameters for the VLE bibliographic data.

Table 8. Experimental Liquid–Liquid Equilibrium Data for the Binary System Butan-1-ol (2) + Water (4)

	organic phase	aqueous phase
T/K	x_2	x_2
323.15	0.4574	0.0167
333.15	0.4387	0.0162
343.15	0.4189	0.0172
353.15	0.3965	0.0181
362.45	0.3673	0.0187

In general, it can be observed that the deviations are low, and the highest deviation happens for the acetic acid (1) + butyl acetate (3) binary system, probably owing to the presence of acetic acid. In this work, the activity coefficients have been calculated applying the Hayden and O'Connell method (nonideal vapor phase), whereas the bibliographic UNIQUAC parameters had been obtained considering the ideal vapor phase. For the butan-1-ol (2) + water (4) binary system, only the alcohol-rich phase has been represented, since the water-rich phase is low and the activity coefficients calculated in this region have too much distortion; therefore, we think that the values are not representative.

Some liquid–liquid experimental data of the butan-1-ol (2) + water (4) binary system have also been obtained between (50 and 90) °C. The experimental results are given in Table 8 and Figure 5. As can be observed, the similarity of our experimental data and the previous published data is very good.

Quaternary System. VLE data for the quaternary reactive system acetic acid (1) + butan-1-ol (2) + butyl acetate (3) + water (4) are reported in Table 9.

The quaternary data were found to be thermodynamically consistent by the Wisniak and Tamir[39] modification of the McDermott−Ellis test[40] ($D < D_{\max}$ at all data points) and the Wisniak $L-W$ test[41] ($0.92 < L_i/W_i < 1.10$).

Table 9. Experimental Vapor–Liquid Equilibrium Data for the Quaternary System Acetic Acid (1) + Butan-1-ol (2) + Butyl Acetate (3) + Water (4) at 101.3 kPa

T/K	x_1	x_2	x_3	y_1	y_2	y_3
365.61	0.048	0.305	0.123	0.005	0.141	0.092
365.85	0.105	0.213	0.183	0.015	0.098	0.134
366.40	0.008	0.460	0.039	0.000	0.206	0.035
367.01	0.100	0.237	0.265	0.016	0.101	0.152
367.16	0.000	0.523	0.000	0.000	0.248	0.001
367.99	0.210	0.087	0.184	0.055	0.047	0.158
368.05	0.122	0.221	0.343	0.030	0.123	0.230
368.45	0.074	0.334	0.316	0.014	0.180	0.202
368.55	0.160	0.171	0.360	0.045	0.096	0.247
369.67	0.044	0.446	0.270	0.008	0.229	0.176
370.32	0.314	0.052	0.187	0.139	0.042	0.221
370.35	0.238	0.101	0.353	0.092	0.058	0.247
371.45	0.027	0.549	0.238	0.004	0.282	0.153
372.37	0.303	0.064	0.328	0.147	0.038	0.234
373.37	0.015	0.628	0.203	0.002	0.327	0.143
373.79	0.122	0.182	0.593	0.039	0.105	0.293
374.56	0.406	0.040	0.280	0.202	0.026	0.218
374.81	0.120	0.176	0.617	0.042	0.104	0.307
374.92	0.023	0.562	0.314	0.004	0.310	0.188
377.23	0.024	0.346	0.370	0.064	0.254	0.250
377.24	0.115	0.161	0.683	0.045	0.101	0.341
377.65	0.558	0.012	0.126	0.376	0.004	0.129
381.24	0.100	0.136	0.763	0.051	0.101	0.409
381.94	0.033	0.305	0.661	0.013	0.232	0.383
383.35	0.786	0.004	0.064	0.629	0.000	0.063
383.79	0.236	0.051	0.712	0.148	0.040	0.412
384.45	0.346	0.026	0.579	0.239	0.021	0.358
384.98	0.477	0.018	0.467	0.348	0.014	0.304
386.78	0.712	0.009	0.252	0.522	0.006	0.227
386.81	0.079	0.094	0.826	0.053	0.093	0.525
387.59	0.752	0.007	0.236	0.632	0.003	0.174

The VLE of a binary mixture is usually clearly depicted in a two-dimensional phase diagram. Unfortunately, there is no such significant phase diagram for a quaternary mixture, although Lee and Kuo[42] drew a three-dimensional diagram showing the equilibrium temperature and the experimental and calculated compositions of two constituent components of the mixture. Actually, such diagrams still do not give a clear relation of vapor and liquid in the same way a binary phase diagram does. So, the quaternary data are represented on a tetrahedral composition square in Figure 6.

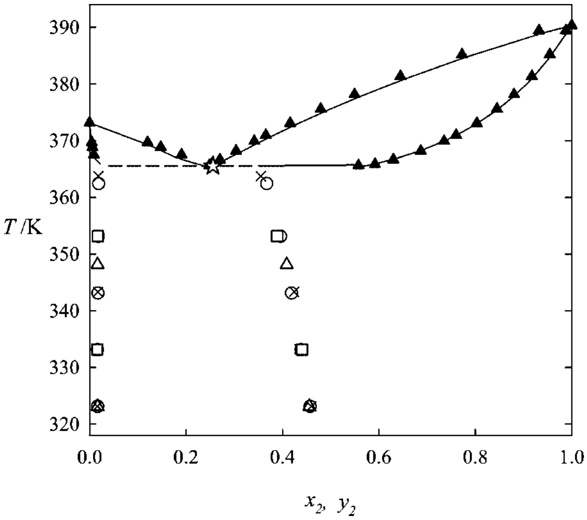

Figure 5. VLE and LLE experimental and predicted results for butan-1-ol (2) + water (4). Experimental LLE data: ○, this work; ×, ref 23; Δ, ref 24; □, ref 25. Experimental VLE data: ▲, this work; ☆, azeotrope; —, NRTL model; ---, extrapolated line.

Furthermore, the composition of the ternary azeotrope that appears in Figure 6 can be determined experimentally. An equimolar mixture of acetic acid (1) and butan-1-ol (2) is introduced into a distillation column reboiler (Fischer SPALTROHR-column HMS-500, controlled by a Fischer system D301-C with a separating power equivalent to 100 theoretical

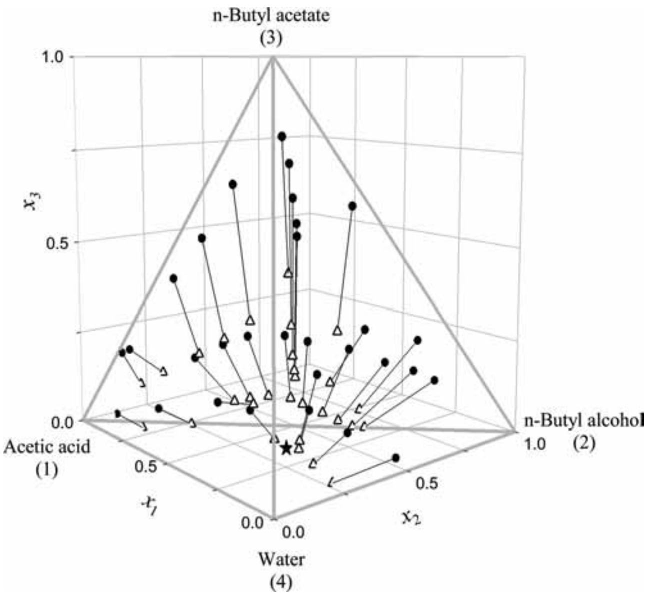

Figure 6. Experimental VLE data for the quaternary system acetic acid (1) + butan-1-ol (2) + butyl acetate (3) + water (4) at 101.3 kPa: ●, liquid phase; Δ, vapor phase; ★, ternary azeotrope butan-1-ol (2) + butyl acetate (3) + water (4).

Table 10. Ternary Azeotrope of Butan-1-ol (2) + Butyl Acetate (3) + Water (4) at 101.3 kPa

T/K	x_2	x_3	x_4	ref
363.10	0.052	0.155	0.793	this work
363.15	0.048	0.240	0.712	[a]

[a] Taken from Berg.[43]

trays). The reboiler thus serves as a reactor at the same time. Working at a high reflux ratio (>50), the minimum boiling ternary azeotrope (heterogeneous) is obtained overhead. The composition and temperature of this heteroazeotrope are shown in Table 10.

Conclusions

In this study, the thermodynamic behavior of catalytic esterification reaction equilibrium and vapor–liquid equilibria (VLE) for the quaternary reactive system acetic acid + butan-1-ol + butyl acetate + water were carried out in a glass dynamic recirculating equilibrium cell. The original reaction rate was so slow that a catalyst is needed to reach equilibrium as quickly as possible. *p*-Toluenesulfonic acid (as catalyst) was added to reduce reaction equilibrium time and had no effect on phase equilibrium.

Nonreactive VLE binary systems acetic acid + butyl acetate, butan-1-ol + butyl acetate, and butan-1-ol + water at 101.3 kPa and LLE data of the butan-1-ol + water binary system have also been determined. Moreover, nonreactive VLE and LLE data have been compared with previous reported data.

UNIQUAC and NRTL equations have been used to correlate experimental binary data. During data correlation, the association of acetic acid in the vapor phase was considered by the Hayden and O′Connell chemical reaction approach.

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