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Isobaric Vapor Liquid Equilibrium (VLE) Data of the Systems *n*-Butanol + Butyric Acid and *n*-Butanol + Acetic Acid

Laura A. L. Muñoz and M. Alvina Krähenbühl*

Departamento Processos Químicos—Faculdade de Engenharia Química—UNICAMP, Caixa Postal 6066,
CEP 13083-970, Campinas, SP, Brazil

Vapor liquid equilibria (VLE) of the binary systems *n*-butanol + butyric acid and *n*-butanol + acetic acid were determined at two pressures, 26.65 and 53.33 kPa. The equipment used was a flow ebulliometer, which is ideal for reactive systems. The quality of the measured $P-T-x-y$ data was verified by applying the thermodynamic consistency test of Van Ness and Fredenslund. The binary interaction parameters for the determination of the liquid-phase activity coefficients, represented by the models Wilson, UNIQUAC, and NRTL, were adjusted by using the maximum likelihood method. The nonideality of the vapor phase was considered by using a chemical theory with the correlation of Hayden and O'Connell for the calculation of the second virial coefficient and the prediction of the chemical equilibrium dimerization constant.

Introduction

This paper reports the experimental vapor liquid equilibrium (VLE) data for the binary systems *n*-butanol + butyric acid and *n*-butanol + acetic acid at two pressures, 26.65 and 53.33 kPa.

The quality of the measured data was verified by the Van Ness method with the modification proposed by Fredenslund et al.[1] The data of vapor liquid equilibria are correlated by fitting the binary interaction parameters of the models for the liquid-phase activity coefficients, by means of the maximum likelihood method, according to the procedure proposed by Stragevich.[2]

Experimental Section

Materials. All materials were supplied by Merck. The purities of the chemicals were greater than 99%, as indicated in Table 1, and were used directly without further purification. All the liquids were subjected to gas chromatography (GC) analysis, and no extra peaks appeared.

Apparatus and Procedure. The VLE measurements were carried out with a flow ebulliometer developed by Vilím et al.[4] and Hála et al.,[5] as shown in Figure 1, connected in series to the pressure controller. The temperatures in the separation camera were read with a precision thermometer calibrated by Ever Ready Thermometer Co. All the equilibrium compositions were determined by GC by means of equipment supplied from "Instrumentos Científicos C. G. Ltda.", model CG-35, equipped with a thermal conductivity detector. The GC column was carbowax with a 1.5 m length stainless steel tube and 3.175 mm diameter. Even more than three analyses were made for both liquid and vapor phase. The accuracy of temperature measurements was estimated to be ±0.05 K. The accuracy of pressure control was within ±0.133 kPa. The accuracy of the equilibrium composition measurements was within ±0.006 mole fraction.

Results and Discussion

VLE had been measured at 26.65 and 53.33 kPa for *n*-butanol + butyric acid and *n*-butanol + acetic acid. The results are shown in Tables 2 and 3. The activity coefficient γ of pure liquid i in a nonideal mixture at temperature T and pressure P was calculated according to

$$\gamma_i = \frac{y_i P}{x_i P_i^{\text{sat}}} \frac{\hat{\phi}_i^{\text{V}}}{\phi_i^{\text{sat}}} \exp\left[-\frac{V_i^{\text{L}}(P - P_i^{\text{sat}})}{RT}\right] \qquad (1)$$

Table 1. Normal Boiling Temperature and Purity of the Chemicals

	n-butanol	butyric acid	acetic acid
purity/% (GC)	min 99.5	>99	min 99.8
T_B^{lit}/K[a]	390.9	437.2	391.1
T_B^{exp}/K	390.8	437.5	390.9

[a] Reid et al.[3]

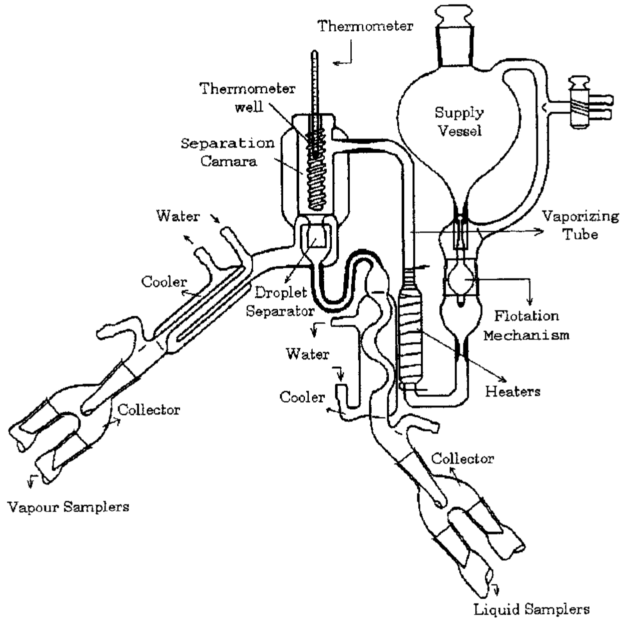

Figure 1. Flow ebulliometer still.

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* Corresponding author. E-mail: mak@feq.unicamp.br.

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Table 2. Experimental Data for the System *n*-Butanol + Butyric Acid

$P = 26.65$ kPa			$P = 53.33$ kPa		
T/K	x_1	y_1	T/K	x_1	y_1
397.63	0.0000	0.0000	416.62	0.0000	0.0000
396.05	0.0160	0.0584	413.65	0.0483	0.1448
394.85	0.0472	0.1609	411.35	0.0908	0.2546
393.55	0.0736	0.2108	407.95	0.1605	0.4038
391.55	0.1069	0.3017	397.85	0.3751	0.7209
389.75	0.1526	0.3898	395.35	0.4488	0.7954
387.25	0.1991	0.4933	392.55	0.5059	0.8592
385.75	0.2314	0.5408	389.75	0.5820	0.9203
383.05	0.2927	0.6411	385.25	0.7094	0.9704
375.45	0.4609	0.8401	383.95	0.7440	0.9816
372.25	0.5476	0.8877	383.05	0.7701	0.9908
369.75	0.6315	0.9409	373.70	1.0000	1.0000
367.95	0.7061	0.9606			
364.05	0.8108	0.9818			
361.45	0.9072	0.9959			
357.55	1.0000	1.0000			

Table 3. Experimental Data for the System *n*-Butanol + Acetic Acid

$P = 26.65$ kPa			$P = 53.33$ kPa		
T/K	x_1	y_1	T/K	x_1	y_1
352.61	0.0000	0.0000	371.15	0.0000	0.0000
353.45	0.0825	0.0435	371.85	0.0528	0.0358
354.55	0.1460	0.0845	372.95	0.1118	0.0738
355.75	0.2135	0.1266	373.45	0.1538	0.0991
356.95	0.2832	0.1872	374.05	0.1901	0.1287
357.65	0.3363	0.2271	374.75	0.2368	0.1675
358.15	0.3675	0.2681	375.25	0.2835	0.1965
358.55	0.4001	0.3074	376.25	0.3667	0.2941
358.75	0.4206	0.3370	377.05	0.4806	0.3822
359.15	0.4555	0.3761	377.45	0.5693	0.5202
359.95	0.5643	0.5017	377.55	0.6122	0.6086
360.25	0.6055	0.5779	377.55	0.6295	0.6283
360.35	0.6741	0.6647	377.55	0.7053	0.7062
360.35	0.7304	0.7424	377.45	0.7265	0.7547
360.15	0.7639	0.7909	376.95	0.8218	0.8977
359.75	0.8451	0.8849	376.35	0.8809	0.9507
359.35	0.8827	0.9371	375.75	0.9202	0.9767
358.65	0.9416	0.9767	374.65	0.9753	0.9992
357.55	1.0000	1.0000	373.75	1.0000	1.0000

The fugacity coefficients of the vapor phase were calculated by means of the chemical theory with the correlation of Hayden and O'Connell[6] for the calculation of the second virial coefficient and the prediction of the chemical equilibrium dimerization constant. The vapor pressures of the pure components were expressed by the Antoine equation in the form

$$\log P_i^{\mathrm{sat}}(\mathrm{mmHg}) = A_i - \frac{B_i}{t\,(^\circ\mathrm{C}) + C_i} \qquad (2)$$

The experimental vapor pressure measured in this work are given in Table 4, and the Antoine constants of the chemicals were obtained by fitting these experimental data. In Table 10 are given all the parameters of the pure properties used in this investigation.

A test was done to have an idea of ester formation. The method of the area percentage in the chromatographic analysis was used. In such a method it is not required to specify data of the pure components involved in the system; the area of the chromatogram is just taken into consideration. In Tables 5 and 6 the results are shown and it is verified that there was a small amount of ester formed in both systems. In general it was less than 0.05% in the liquid and vapor phases for the both pressures. The amount of ester formed is not significant, and it can be ignored in the calculations.

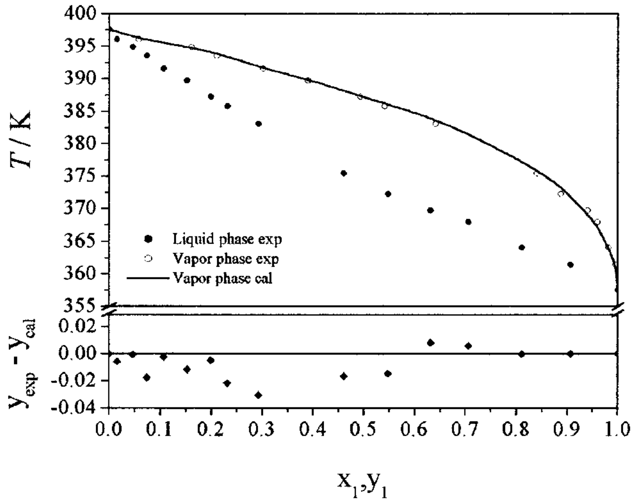

Figure 2. Thermodynamic consistency test for *n*-butanol + butyric acid at 26.65 kPa.

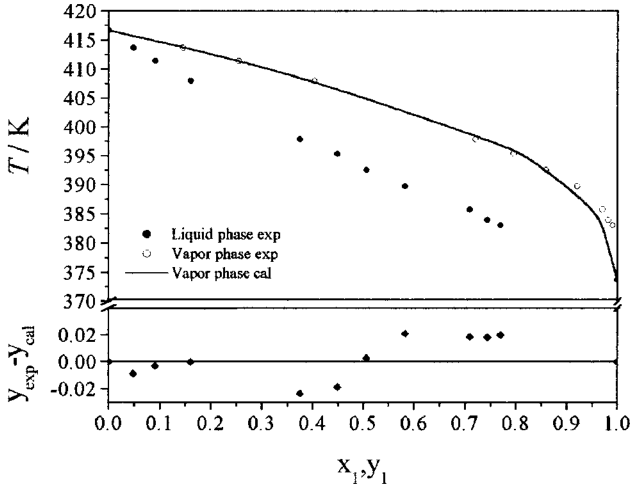

Figure 3. Thermodynamic consistency test for *n*-butanol + butyric acid at 53.33 kPa.

Table 4. Experimental Vapor Pressures for the Pure Components

acetic acid		*n*-butanol		butyric acid	
P/kPa	T/K	P/kPa	T/K	P/kPa	T/K
20.00	345.15	26.66	357.50	20.82	391.50
25.72	351.45	27.73	358.20	23.31	394.30
26.67	352.35	30.00	360.10	26.13	397.50
28.04	353.65	34.16	363.10	28.89	399.80
30.00	355.35	39.97	366.80	32.06	402.60
37.08	361.05	40.47	367.00	37.49	407.10
50.00	369.45	50.00	372.20	42.06	409.90
53.84	371.55	53.45	373.90	47.62	413.10
60.00	374.75	60.00	376.80	50.00	415.20
70.00	379.35	66.63	379.50	54.26	417.50
74.65	381.35	80.00	384.40	58.13	419.30
79.99	383.55	86.81	386.60	60.00	420.50
		95.00	389.10	63.85	422.00
				66.66	423.30
				70.00	425.20
				75.00	427.30
				79.99	428.90

All the binary systems were tested for their thermodynamic consistency by means of the Van Ness method modified by Fredenslund et al.[1] The mean deviation between experimental and calculated y values should be lower than 1×10^{-2}. In this method, the heat of mixing is neglected.

Table 5. Chromatographic Analyses in Percent Area for the System *n*-Butanol + Butyric Acid

$P = 26.65$ kPa						$P = 53.33$ kPa					
liquid phase			vapor phase			liquid phase			vapor phase		
n-butanol	butyric acid	*n*-butyl butyrate	*n*-butanol	butyric acid	*n*-butyl butyrate	*n*-butanol	butyric acid	*n*-butyl butyrate	*n*-butanol	butyric acid	*n*-butyl butyrate
0.00	100.00	0.00	0.00	100.00	0.00	0.00	100.00	0.00	0.00	100.00	0.00
1.55	98.40	0.05	5.68	94.19	0.13	6.16	93.80	0.04	18.00	82.00	0.00
4.59	95.38	0.03	15.68	84.30	0.02	11.45	88.52	0.03	30.68	69.31	0.02
7.16	92.82	0.02	20.61	79.38	0.01	15.64	84.31	0.05	39.69	60.28	0.03
10.42	89.55	0.03	29.57	70.42	0.01	36.98	63.00	0.02	71.63	28.36	0.01
14.89	85.07	0.03	38.31	61.68	0.01	44.17	55.81	0.02	79.06	20.92	0.02
19.29	80.69	0.02	48.62	51.37	0.00	49.88	50.12	0.00	85.58	14.42	0.00
22.63	77.35	0.02	53.37	46.62	0.01	59.54	40.46	0.00	91.82	8.18	0.00
28.68	71.31	0.01	60.71	39.28	0.02	70.35	29.65	0.00	96.96	3.04	0.00
45.53	54.46	0.01	83.69	16.29	0.02	73.84	26.14	0.01	98.10	1.89	0.01
54.05	45.93	0.02	76.01	23.93	0.07	76.51	26.14	0.00	99.06	0.94	0.00
62.48	37.50	0.02	93.91	6.06	0.03	100.00	0.00	0.00	100.00	0.00	0.00
70.02	29.98	0.00	95.92	4.05	0.03						
80.62	19.35	0.03	99.98	0.00	0.02						
90.46	9.52	0.01	99.99	0.00	0.01						
100.00	0.00	0.00	100.00	0.00	0.00						

Table 6. Chromatographic Analyses in Percent Area for the System *n*-Butanol + Acetic Acid

$P = 26.65$ kPa						$P = 53.33$ kPa					
liquid phase			vapor phase			liquid phase			vapor phase		
n-butanol	acetic acid	*n*-butyl acetate	*n*-butanol	acetic acid	*n*-butyl acetate	*n*-butanol	acetic acid	*n*-butyl acetate	*n*-butanol	acetic acid	*n*-butyl acetate
0.00	100.00	0.00	0.00	100.00	0.00	0.00	100.00	0.00	0.00	100.00	0.00
10.12	89.88	0.00	5.83	94.62	0.00	6.52	93.47	0.01	4.44	95.56	0.00
17.63	82.37	0.00	10.35	89.64	0.01	13.98	86.02	0.00	9.07	90.93	0.00
25.36	74.63	0.01	15.35	84.64	0.01	18.54	81.46	0.00	12.10	87.90	0.00
33.07	66.90	0.03	22.27	77.61	0.01	22.70	77.30	0.00	15.60	84.36	0.04
38.85	61.14	0.01	26.89	73.10	0.01	27.97	72.03	0.00	20.12	79.87	0.01
42.61	57.38	0.01	31.43	68.56	0.01	33.01	66.99	0.00	23.44	76.55	0.01
45.49	54.50	0.01	35.71	64.28	0.01	42.01	57.99	0.00	34.27	65.73	0.00
47.61	52.39	0.00	38.88	61.11	0.01	53.65	46.34	0.00	43.62	56.35	0.02
51.14	48.85	0.01	42.99	56.98	0.02	62.32	37.68	0.00	42.41	57.58	0.01
61.84	38.15	0.01	55.74	44.24	0.02	66.39	33.60	0.01	66.04	33.94	0.02
65.76	34.23	0.01	63.14	36.84	0.02	68.01	31.99	0.00	67.90	32.09	0.01
72.13	27.86	0.01	71.23	28.72	0.05	74.97	25.03	0.00	75.05	24.94	0.01
77.21	22.77	0.02	78.21	21.76	0.04	76.87	23.12	0.00	79.36	20.61	0.02
80.21	19.79	0.00	82.53	17.43	0.04	82.36	17.64	0.00	89.14	10.86	0.00
87.21	12.78	0.02	90.55	9.41	0.04	87.36	12.64	0.00	94.14	5.86	0.00
90.39	9.60	0.01	94.88	5.09	0.03	91.03	8.91	0.06	96.78	3.16	0.06
95.27	4.72	0.01	98.09	1.87	0.04	97.96	1.98	0.05	98.84	1.15	0.01
100.00	0.00	0.00	100.00	0.00	0.00	100.00	0.00	0.00	100.00	0.00	0.00

Table 7. Mean Deviations of Y from the Consistency Test

system	$\lvert\overline{\Delta y}\rvert$ $P_{26.65}$	$\lvert\overline{\Delta y}\rvert$ $P_{53.33}$
n-butanol + butyric acid	0.0101	0.0112
n-butanol + acetic acid	0.0081	0.0099

Table 7 presents the obtained mean deviations for each set. The graphic representation of the consistency results together with the experimental data for each pressure is in Figures 2−5. It can be seen that there is a good distribution between positive and negative differences of Δy, indicating no systematic errors.

The VLE experimental data of all binary systems were used to obtain the interaction parameters of three activity coefficient models: Wilson, NRTL, and UNIQUAC.[3] The fitted parameters were obtained through an algorithm based on the principle of the maximum likelihood method developed by Stragevitch.[2]

The fitted parameters together with the mean values of the absolute deviations of the equilibrium temperature (ΔT) and the mole fraction of the vapor phase (Δy) are shown in Tables 8 and 9. For the NRTL model, the parameter α_{ij} was considered to be a constant equal to 0.2. It was seen that the value of this parameter causes no significant influence on the results. The calculated results for the Wilson, UNIQUAC, and NRTL models are illustrated in Figures 6−9.

Table 8. Correlation Parameters and Absolute Mean Deviations in Boiling Temperatures and Vapor-Phase Mole Fractions for the System *n*-Butanol + Butyric Acid

model	$A_{12}{}^{a}$	$A_{21}{}^{a}$	$\lvert\overline{\Delta y}\rvert$	$\lvert\overline{\Delta T}\rvert$
	$P = 26.65$ kPa			
Wilson	−426.76	506.20	0.0137	0.62
UNIQUAC	307.95	−264.96	0.0125	0.71
NRTL	−689.15	854.56	0.0098	1.37
	$P = 53.33$ kPa			
Wilson	−503.27	700.97	0.0207	0.59
UNIQUAC	372.04	−306.93	0.0192	0.74
NRTL	990.78	−802.15	0.0170	1.38
	Global (26.65 and 53.33 kPa)			
Wilson	−440.27	504.74	0.0173	0.60
UNIQUAC	295.88	−265.43	0.0161	0.71
NRTL	−764.97	988.39	0.0138	1.41

[a] The binary adjustable parameters for various models are as follows: Wilson, $A_{ij} = (\lambda_{ij} - \lambda_{ii})$; NRTL, $A_{ij} = (g_{ij} - g_{jj})$; UNIQUAC, $A_{ij} = (u_{ij} - u_{jj})$.

It can be seen from Tables 8 and 9 that all the adjustments are equivalent. The resulting mean deviations of the

Table 9. Correlation Parameters and Absolute Mean Deviations in Boiling Temperatures and Vapor-Phase Mole Fractions for the System *n*-Butanol + Acetic Acid

model	A_{12}[a]	A_{21}[a]	$\overline{\lvert\Delta y\rvert}$	$\overline{\lvert\Delta T\rvert}$
	$P = 26.65$kPa			
Wilson	566.02	−191.96	0.0044	0.46
UNIQUAC	−234.83	397.44	0.0043	0.45
NRTL	−588.54	923.62	0.0043	0.34
	$P = 53.33$ kPa			
Wilson	733.69	−222.73	0.0090	0.65
UNIQUAC	−273.77	498.38	0.0088	0.64
NRTL	−705.70	1208.1	0.0071	0.50
	Global (26.65 and 53.33 kPa)			
Wilson	656.82	−208.80	0.0071	0.51
UNIQUAC	−254.31	446.40	0.0071	0.54
NRTL	−641.65	1044.5	0.0066	0.39

[a] The binary adjustable parameters for various models are as follows: Wilson, $A_{ij} = (\lambda_{ij} - \lambda_{ii})$; NRTL, $A_{ij} = (g_{ij} - g_{jj})$; UNIQUAC, $A_{ij} = (u_{ij} - u_{jj})$.

Table 10. Pure Component Properties Used in This Work

parameter	*n*-butanol	butyric acid	acetic acid
A_i[a]	7.32672	7.76035	9.00908
B_i[a]	1302.39	1780.62	2749.36
C_i[a]	175.114	201.590	330.948
T_c[b]/K	563.1	628.0	592.7
P_c[b]/bar	44.2	52.7	57.9
V_c[b]/cm^3·mol^{-1}	275.0	290.0	171.0
ϖ[b]	0.593	0.683	0.447
V[b]/cm^3·mol^{-1}	91.97	92.43	57.54
R_D[c]/Å	3.225	3.134	2.595
ETA[c]	2.20	4.50	4.50
R[d]	3.4543	3.5512	2.2024
q ($q = q'$)[d]	3.0520	3.1520	2.0720

[a] Adjusted with the collected experimental data: t/°C and P/mmHg. [b] Reid et al.[3] [c] Fredenslund et al.[1] [d] Gmehling et al.[7]

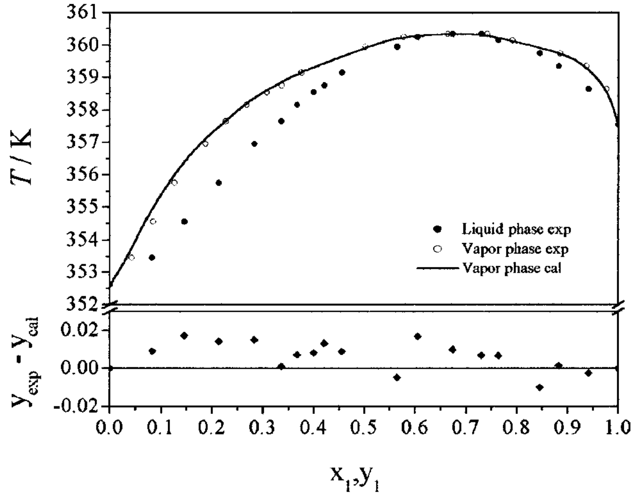

Figure 4. Thermodynamic consistency test for *n*-butanol + acetic acid at 26.65 kPa.

variables can be attributed to experimental errors and ester formation that was neglected. However, when Figures 6−9 are analyzed, it appears that a significant displacement appears for the system *n*-butanol + acetic acid between the experimental data and the calculated curve. This is due to the smaller temperature interval (∼8 K) for this system compared to that for the other system (∼40 K).

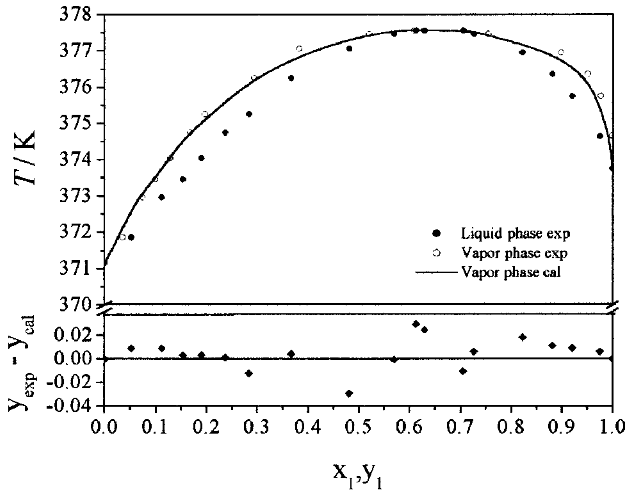

Figure 5. Thermodynamic consistency test for *n*-butanol + acetic acid at 53.33 kPa.

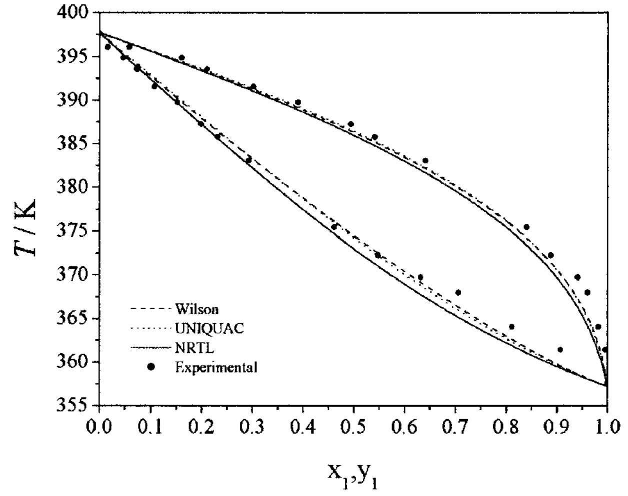

Figure 6. System *n*-butanol + butyric acid at 26.65 kPa.

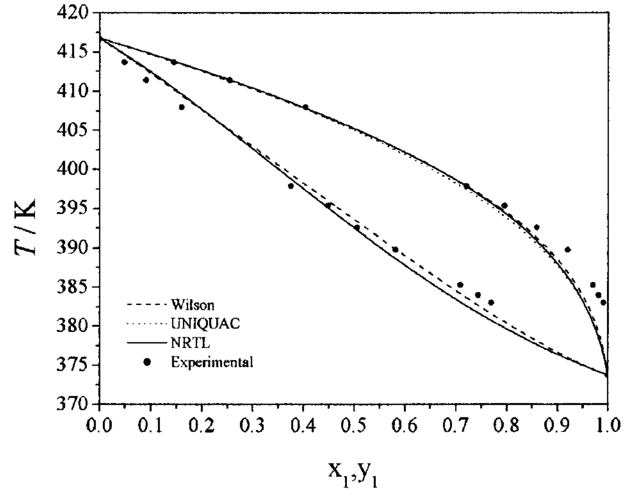

Figure 7. System *n*-butanol + butyric acid at 53.33 kPa.

Conclusion

According to the results of the consistency test, it can be said that the reported data are good enough to represent the systems, since they are right at the cutoff at which Fredenslund et al.[1] consider data to be consistent. Analyses of experimental data of all binary systems using the Wilson, NRTL, and UNIQUAC equations show that all

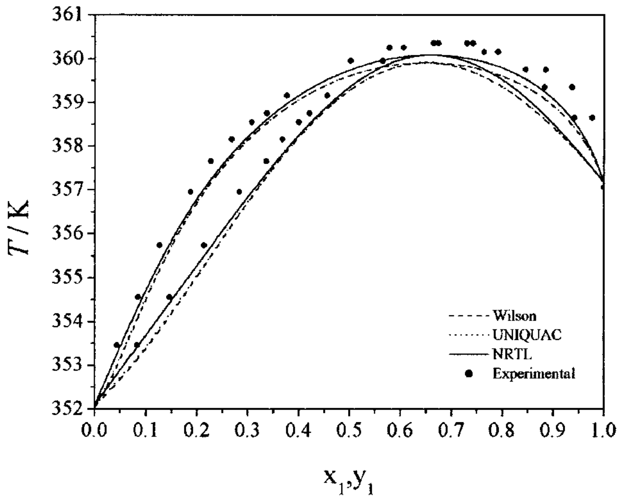

Figure 8. System *n*-butanol + acetic acid at 26.65 kPa.

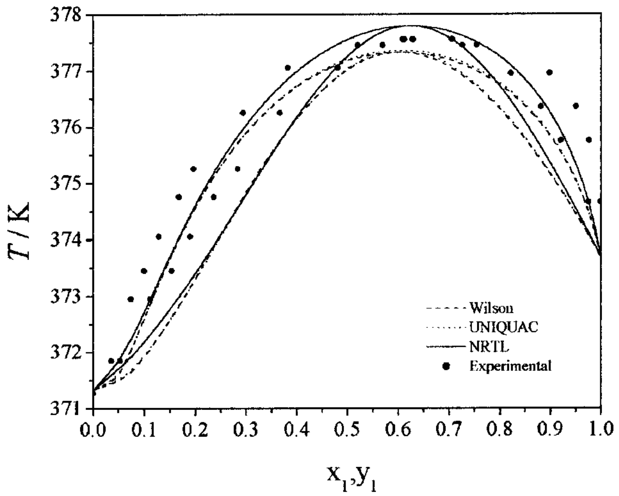

Figure 9. System *n*-butanol + acetic acid at 53.33 kPa.

three models were generally satisfactory. It can be assumed that no reaction between the compounds has taken place in the systems, since the amount of ester formed can be neglected.

Acknowledgment

The authors thank Mr. D. R. Queiroz for collaboration on the measurements.

Nomenclature

A = Antoine coefficient
B = Antoine coefficient
C = Antoine coefficient
ETA = association parameter
$g_{ij}-g_{jj}$ = NRTL binary parameters of components i and j
P = pressure
P_c = critical pressure
P^{sat} = saturated vapor pressure
q = UNIQUAC area parameter
r = UNIQUAC volumetric parameter
R = ideal gas constant
R_D = radius of gyration
V_c = critical volume
V^L = liquid molar volume
T = temperature
T_b = boiling temperature
T_c = critical temperature
$u_{ij}-u_{jj}$ = UNIQUAC binary parameters of components i and j
x = mole fraction of liquid phase
y = mole fraction of vapor phase
α_{ij} = NRTL parameter nonrandom
γ_i = activity coefficient of component i
$\lambda_{ij}-\lambda_{ii}$ = Wilson binary parameters of components i and j
ϕ^{sat} = saturated vapor-phase fugacity coefficient
ϖ = acentric factor

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