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Vapor−Liquid Equilibria of Binary Mixtures 2-Butanol + Butyl Acetate, Hexane + Butyl Acetate, and Cyclohexane + 2-Butanol at 101.3 kPa

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Vapor−liquid equiliibria were measured at 101.3 kPa for three binary mixtures of 2-butanol + butyl acetate, hexane + butyl acetate, and cyclohexane + 2-butanol. The isobaric $T-x-y$ data were reported, including an azeotropic point for the binary mixture of cyclohexane + 2-butanol. Calculations of the nonideality of the vapor phase were made with the second virial coefficients determined by the Tsonopoulos correlation equation. Various activity coefficient models were used to correlate the experimental data. Satisfactory results were obtained, and optimally fitted binary parameters are presented.

Introduction

Vapor−liquid equilibria (VLE) are important in chemical process design and development. VLE data have been measured in our laboratory for binary and ternary mixtures (Chen et al., 1996; Cheng et al., 1997). The VLE data of three binary mixtures of 2-butanol + butyl acetate, hexane + butyl acetate, and cyclohexane + 2-butanol were measured at 101.3 kPa in this study. An all-glass recirculating still was employed, and the equilibrium temperatures and compositions of the coexisting vapor and liquid phases were measured. Various thermodynamic consistency tests were examined on these systems. The experimental data were then correlated by various activity coefficient models.

Experimental Section

Chemicals. All the chemicals were high-purity grade purchased from Merck Co. All chemicals were used without further purification. No detectable impurities were found on the gas chromatography (GC) analyses. The purities of all chemicals were better than 99.6 mass %. The pure compound properties were measured, and comparisons with literature data are shown in Table 1. The refractive indices of the pure compounds were measured at (293.15 ± 0.1) K by an Abbe refractometer, Atago 3T, with an accuracy of ±0.0001. The densities of pure chemicals were measured at (293.15 ± 0.01) K using the Anton Paar DMA 60/602 density meter with an accuracy of $\pm 1.0 \times 10^{-5}$ g·cm^{-3}.

Apparatus and Procedures. The apparatus used was an all-glass recirculating still described by Paul (1976). This equipment has a side-heating unit, which ensures complete mixing of the liquid mixtures. This design also prevented liquid drop entrainment and partial condensation of the vapor phase. A digital quartz thermometer (DMT-610, Tokyo Electrical, Japan), with an accuracy of ±0.01 K, was used to measure the equilibrium temperatures. The pressure in the still was measured by a mercury barometer. The barometer pressure changes slightly, which can be observed through a tube with dibutyl phthalate. The pressure of the system was controlled according to the method of Othmer et al. (1960). The accuracy of the pressure control was within ±0.05%. The experimental temperatures were taken at this constant pressure of 101.3 kPa.

Table 1. Comparison of the Measured Normal Boiling Temperatures, Refractive Indices, and Densities of Pure Fluids in This Work with Literature Data

	T_b/K		n^D(293.15 K)		ρ(293.15 K)/ g cm^{-3}		
component	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]	GC purity (mass %)
2-butanol	372.66	372.70	1.3969	1.3971	0.8060	0.8063	>99.6
butyl acetate	399.10	399.15	1.3939	1.3942	0.8812	0.8825	>99.6
hexane	341.95	341.88	1.3746	1.3749	0.6594	0.6593	>99.6
cyclohexane	353.93	353.89	1.4263	1.4362	0.7784	0.7785	>99.6

[a] TRC Data Base (1993).

In each experiment, the liquid mixture was heated in the recirculating still at a fixed pressure of 101.3 kPa. Equilibrium was usually reached after 1 h, where the temperatures of the liquid and vapor phases were constant and their difference was within ±0.02 K. Samples of the equilibrium phases were then taken at small volumes and were analyzed in a gas chromatograph.

A Shimadzu GC, type 8A, equipped with a thermal conductivity detector, was used to determine the equilibrium compositions. The GC column was made of a 3 m length stainless steel tube with 3 mm diameter and was packed with Porapak Q. The GC response peaks were integrated by using a Shimadzu C-R3A integrator. The temperature of the injection port of the GC was maintained at 503.15 K. The oven temperature of the GC was at 483.15 K. Helium gas with a purity of 99.9% was used as the carrrier gas at a flow rate of 30 cm^3/min. The GC was calibrated using mixtures of known compositions for each binary system. The relationship between peak area and composition was determined for each binary mixture. In the VLE experiments, more than three analyses were made for each liquid and vapor composition, respectively. With these repeated procedures, the accuracy of the equilibrium composition measurements was within ±0.001 mole fraction.

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Table 2. Experimental VLE Data for 2-Butanol (1) + Butyl Acetate (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
372.66	1.0000	1.0000	1.0000	
372.87	0.9757	0.9869	1.0003	1.2202
373.22	0.9504	0.9733	1.0005	1.2023
373.87	0.9041	0.9480	1.0015	1.1842
374.22	0.8808	0.9348	1.0016	1.1782
375.12	0.8195	0.8996	1.0046	1.1608
375.93	0.7634	0.8653	1.0095	1.1545
376.64	0.7218	0.8400	1.0119	1.1379
377.27	0.6730	0.8099	1.0249	1.1250
378.76	0.5906	0.7549	1.0363	1.1006
379.66	0.5439	0.7234	1.0473	1.0818
380.42	0.5062	0.6935	1.0531	1.0797
381.89	0.4404	0.6387	1.0637	1.0703
383.52	0.3694	0.5794	1.0936	1.0490
384.43	0.3246	0.5386	1.1250	1.0436
385.41	0.2941	0.5059	1.1321	1.0371
385.98	0.2741	0.4850	1.1447	1.0325
386.60	0.2505	0.4597	1.1655	1.0293
387.86	0.2153	0.4142	1.1767	1.0259
388.91	0.1850	0.3806	1.2202	1.0119
390.37	0.1477	0.3245	1.2494	1.0104
391.67	0.1205	0.2788	1.2680	1.0064
392.68	0.0979	0.2396	1.3044	1.0049
393.84	0.0781	0.1985	1.3110	1.0026
396.41	0.0347	0.0999	1.3851	1.0010
399.10	0.0000	0.0000		1.0000

Table 3. Experimental VLE Data for Hexane (1) + Butyl Acetate (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
341.95	1.0000	1.0000	1.0000	
342.12	0.9675	0.9923	1.0003	1.7095
342.69	0.9475	0.9876	1.0005	1.6629
345.14	0.8580	0.9665	1.0102	1.4867
346.19	0.8198	0.9574	1.0177	1.4353
348.28	0.7453	0.9386	1.0370	1.3425
349.78	0.6944	0.9249	1.0537	1.2874
351.35	0.6441	0.9103	1.0729	1.2395
352.55	0.6016	0.8990	1.0990	1.1886
354.48	0.5525	0.8800	1.1144	1.1654
356.19	0.5076	0.8624	1.1379	1.1365
358.14	0.4606	0.8402	1.1632	1.1181
359.99	0.4198	0.8184	1.1874	1.1160
363.70	0.3484	0.7729	1.2347	1.0696
365.69	0.3149	0.7462	1.2580	1.0579
366.50	0.3020	0.7347	1.2672	1.0544
369.97	0.2518	0.6831	1.3043	1.0398
372.34	0.2213	0.6429	1.3243	1.0374
396.14	0.1779	0.5776	1.3618	1.0230
380.32	0.1363	0.4947	1.3938	1.0164
384.30	0.1015	0.4040	1.4104	1.0163
390.87	0.0520	0.2440	1.4656	1.0027
395.68	0.0205	0.1060	1.4819	1.0002
397.78	0.0073	0.0399	1.5113	1.0001
399.10	0.0000	0.0000		1.0000

Table 4. Experimental VLE Data for Cyclohexane (1) + 2-Butanol (2) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2
372.66	0.0000	0.0000		1.0000
368.41	0.0364	0.1615	3.0495	1.0113
366.76	0.0543	0.2213	2.9165	1.0177
362.48	0.1095	0.3751	2.7293	1.0226
358.49	0.1796	0.4950	2.4179	1.0398
356.27	0.2433	0.5706	2.2015	1.0635
353.10	0.3672	0.3589	1.8381	1.1555
352.45	0.4095	0.6802	1.7327	1.1694
351.94	0.4456	0.6855	1.6502	1.2367
351.53	0.4808	0.7097	1.5800	1.2836
350.93	0.5558	0.7341	1.4379	1.4115
350.68	0.5962	0.7457	1.3713	1.5018
350.59	0.6139	0.7507	1.3441	1.5462
350.34	0.6662	0.7669	1.2742	1.6917
350.24	0.7142	0.7794	1.2112	1.8793
350.17	0.7463	0.7893	1.1761	2.0294
350.14	0.7828	0.7998	1.1373	2.2576
350.13	0.8058	0.8073	1.1155	2.4325
350.12	0.8077	0.8088	1.1149	2.4376
350.14	0.8109	0.8099	1.1113	2.4627
350.18	0.8220	0.8137	1.1001	2.5602
350.27	0.8571	0.8275	1.0700	2.9440
350.44	0.8936	0.8449	1.0426	3.5331
350.73	0.9229	0.8637	1.0232	4.2371
351.28	0.9502	0.8911	1.0090	5.1289
353.93	1.0000	1.0000	1.0000	

Table 5. Pure Component Properties Used in This Work[a]

component	T_c/K	P_c/kPa	ω	a	b	c
2-butanol	536.0	4189.8	0.571	6.268 23	1126.887	−108.291
butyl acetate	579.2	3109.8	0.410	6.135 05	1355.816	−70.705
hexane	507.5	3009.9	0.305	6.410 60	1469.286	−7.702
cyclohexane	553.5	4009.8	0.212	6.032 45	1124.124	−44.911

[a] The critical constants and acentric factors were taken from Daubert and Danner (1989). Those for hexane were taken from TRC Data Bases (1993). The parameters in the vapor pressure equation (log P_i^{sat} (kPa) = $a_i - b_i/(T(\mathrm{K}) + c_i)$) were taken from Richard and Stanislaw (1987).

Results and Discussion

VLE had been measured at 101.3 kPa for 2-butanol + butyl acetate, hexane + butyl acetate, and cyclohexane + 2-butanol. The results are shown in Tables 2−4, respectively. The liquid-phase activity coefficients γ_i were calculated by the classical equation

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

where ϕ is the fugacity coefficient and x and y are the equilibrium mole fractions in the liquid and vapor phases, respectively. P^{sat} is the saturated vapor pressure, and V^L is the saturated liquid molar volume.

The fugacity coefficient was calculated by using the virial equation of state truncated at the second virial term. The second virial coefficient was determined from the correlation equation according to Tsonopoulos (1974). The critical constants were taken from literature (TRC Data Base, 1993; Daubert and Danner, 1989). The vapor pressures of the pure compounds were expressed by the Antoine equation

$$\log P_i^{sat}/\mathrm{kPa} = a_i - b_i/[T/\mathrm{K} + c_i] \qquad (2)$$

The constants a, b, and c in eq 2 were taken from literature (Richard and Stainslaw, 1987). Those values of various pure fluids are shown in Table 5. The liquid molar volumes were calculated by the Rackett equation (Spencer and Danner, 1972). The calculated activity coefficients for each binary mixture are also listed in Tables 2−4. All binary mixtures show positive deviations. The activity coefficients were used in thermodynamic consistency test where Herington's method (Gmehling et al., 1980), Kojima's method (Kojima et al., 1990), and Wisniak's method (Wisniak, 1993) were employed. These methods include both point tests and integral tests that have been used by various authors to examine the experimental data. The criteria of consistency for each method and the results for thermodynamic consistency tests are shown in Table 6. It is demonstrated that all three binary systems satisfy the requirements for various consistency test methods.

The experimental results were then used to obtain the binary parameters in various activity coefficient models.

Table 6. Consistency Test Results of the Binary VLE Experimental Data of This Work

test	criterion of consistency (character: +)	2-butanol (1) + butyl acetate (2)	hexane (1) + butyl acetate (2)	cyclohexane (1) + 2-butanol (2)
Herington method	$D - J < 10$	−0.95 (+)	−12.40 (+)	−8.39 (+)
Kojima method				
(a) point test	$\delta < 5$	2.772 (+)	2.665 (+)	4.648 (+)
(b) area test	$A < 3$	2.973 (+)	0.469 (+)	2.702 (+)
(c) infinite dilution test	$I_1 < 30$	2.525 (+)	9.068 (+)	6.035 (+)
	$I_2 < 30$	1.813 (+)	7.351 (+)	3.250 (+)
Wisniak method	$d < 5$	3.647 (+)	1.905 (+)	1.573 (+)

Table 7. Correlation Parameters and Absolute Average Deviations in Boiling Temperature (ΔT) and Vapor-Phase Mole Fraction (Δy) for the Binary Mixtures

equations	A_{12}/ kJ mol^{-1}	A_{21}/ kJ mol^{-1}	α_{12}	Δy_1	ΔT/K
	2-Butanol (1) + Butyl Acetate (2)				
Wilson	0.078	0.110		0.005	0.32
NRTL	3.855	−2.480	0.2	0.002	0.05
UNIQUAC	0.402	0.438		0.004	0.24
	Hexane (1) + Butyl Acetate (2)				
Wilson	0.254	1.517		0.002	0.11
NRTL	0.725	0.790	0.2	0.003	0.15
UNIQUAC	0.153	0.217		0.002	0.12
	Cyclohexane (1) + 2-Butanol (2)				
Wilson	0.196	5.895		0.004	0.22
NRTL	6.125	−0.804	0.2	0.008	0.35
UNIQUAC	2.089	−0.675		0.006	0.31

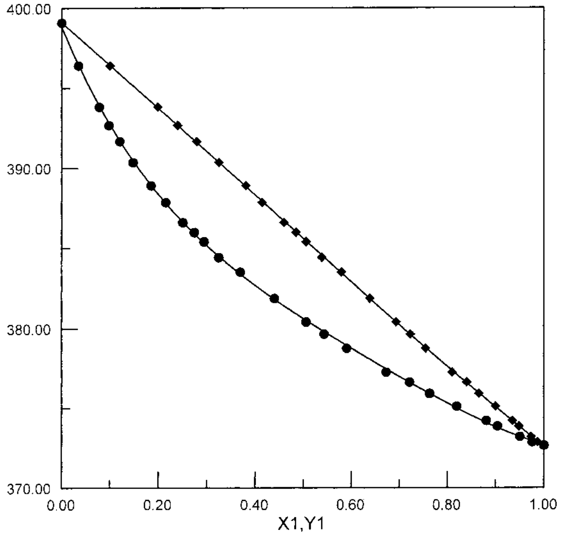

Figure 1. $T-x-y$ curve for 2-butanol (1) + butyl acetate (2) at 101.3 kPa. (—) Wilson model. Experimental data: (●) liquid phase; (◆) vapor phase.

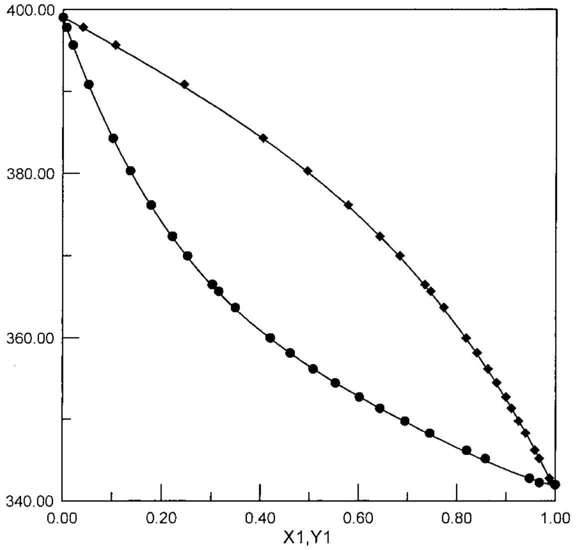

Figure 2. $T-x-y$ curve for hexane (1) + butyl acetate (2) at 101.3 kPa. (—) Wilson model. Experimental data: (●) liquid phase; (◆) vapor phase.

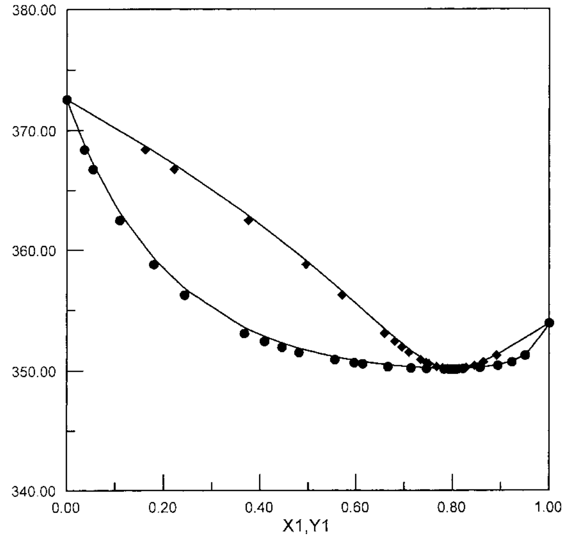

Figure 3. $T-x-y$ curve for cyclohexane (1) + 2-butanol (2) at 101.3 kPa. (—) Wilson model. Experimental data: (●) liquid phase; (◆) vapor phase.

The Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) models were used in the regressions. The expressions of the activity coefficients for each model are listed in the literature (Gmehling et al., 1979). The following objective function was minimized in the regressions:

$$Q = \sum_N \sum_i \left(\frac{\gamma_i^{\mathrm{exp}} - \gamma_i^{\mathrm{cal}}}{\gamma_i^{\mathrm{exp}}} \right)^2 \tag{3}$$

The regression results are shown in Table 7. The deviations in vapor-phase compositions and equilibrium temperatures are reasonably small, and it is indicated that all three activity coefficient models are suitable to represent the binary experimental data. The $T-x-y$ diagrams of these binary systems are shown in Figures 1−3, respectively. The binary mixture of cyclohexane (1) + 2-butanol (2) has an azeotrope. The azeotropic temperature at 101.3 kPa is 350.12 K with $x_1 = 0.809$. No azeotrope was found for the other two binary systems. To our knowledge, no isobaric VLE data at 101.3 kPa has been shown in the literature for binary mixtures of 2-butanol + butyl acetate and hexane + butyl acetate. VLE data at 101.3 kPa for the binary mixture of cyclohexane + 2-butanol have been presented by Zong et al. (1983). Our experimental data show better thermodynamic consistency as well as correlation results using various activity coefficient models. The azeotropic point for this binary mixture was not determined by Zong et al. (1983), but it has been carefully measured and reported in this study.

Conclusion

Vapor−liquid equilibria of three binary mixtures of 2-butanol + butyl acetate, hexane + butyl acetate, and cyclohexane + 2-butanol were measured at 101.3 kPa. The results of all binary mixtures satisfy the requirements for various thermodynamic consistency tests. Three activity coefficient models are employed to correlate the experimental data. The correlation of results is satisfactory, and the deviations in vapor-phase compositions and equilibrium temperatures are reasonably small.

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