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Vapor−Liquid Equilibria for the Quaternary System Ethanol + Acetone + Benzene + Hexane

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Isobaric vapor−liquid equilibria at 101.33 kPa and isothermal vapor−liquid equilibria at 308.15 K, 318.15 K, and 328.15 K for the quaternary system ethanol + acetone + benzene + hexane were measured using an inclined ebulliometer with a pumplike stirrer. The results were well correlated by the extended UNIQUAC equation with temperature-dependence binary parameters.

Introduction

Isobaric vapor−liquid equilibria (VLE) at 101.33 kPa and isothermal VLE at 308.15 K, 318.15 K, and 328.15 K for the quaternary system ethanol + acetone + benzene + hexane are reported. The measured results are compared with those calculated from the UNIQUAC equation with only temperature-dependence binary parameters, obtained from the literature binary VLE for the following six constituent mixtures: ethanol + acetone; ethanol + benzene; ethanol + hexane; acetone + benzene; acetone + hexane; benzene + hexane.

Experimental Section

All chemicals (analytical reagent grade) were supplied by Hangzhou Chemical Reagent Plant and were further purified by fractionation. The final physical properties of materials used are listed in Table 1.

The boiling temperatures at 101.33 kPa and the vapor pressures at the temperatures 308.15 K, 318.15 K, and 328.15 K were determined by using an inclined ebulliometer with a pumplike stirrer as described previously (Li et al., 1995). The equilibrium temperatures were measured by a standard platinum resistance thermometer connected with a digital multimeter (Keithley 195A) with final accuracy of ±0.01 K. The pressure was indirectly measured from the boiling points of pure water in a separate ebulliometer. The accuracy of pressures were estimated as ±0.04 kPa. The solution of desired composition was prepared in an approximately 65-cm^3 inclined ebulliometer by mixing each pure substance, which was accurately weighed within ±1 mg by use of an automatic balance. The compositions were accurate to better than ±0.0005. The operating procedures have been described elsewhere (Zhou et al., 1990).

Results and Correlations

Table 2 shows the experimental results for the quaternary system. The experimental quaternary VLE results were analyzed using the UNIQUAC equation with only temperature-dependence parameters obtained from the literature binary VLE data.

At equilibrium

$$p y_i \phi_i = x_i f_i^{0L} \gamma_i \exp(\nu_i^L p/RT) \qquad (1)$$

Table 1. Physical Properties of Materials

	refractive index at 293.15 K		boiling points/K	
materials	observed	reported	observed	reported
ethanol	1.3611	1.36143[a]	351.30	351.435[e]
acetone	1.3588	1.35868[b]	329.34	329.23[f]
benzene	1.5010	1.50111[c]	353.26	353.206[g]
hexane	1.3751	1.37486[d]	341.95	341.869[h]

[a] TRC fa-5000. [b] TRC a-5800. [c] TRC fa-3200. [d] TRC fa-1010. [e] TRC k-5000. [f] TRC k-5800. [g] TRC k-2976. [h] TRC k-1440.

Table 2. Experimental Vapor−Liquid Equilibrium at 101.33 kPa and at Three Temperatures for the Quaternary System Ethanol (1) + Acetone (2) + Benzene (3) + Hexane (4)

			T/K	p/kPa		
x_1	x_2	x_3	101.33 kPa	308.15 K	318.15 K	328.15 K
0.3320	0.2648	0.2213	330.40	43.83	64.85	93.59
0.3029	0.3596	0.2023	330.04	44.71	65.92	94.84
0.3000	0.5188	0.1088	329.78	44.99	66.63	95.75
0.1024	0.7143	0.1052	328.04	48.90	71.54	101.70
0.4655	0.3708	0.0892	331.17	42.65	63.11	91.09
0.6034	0.2399	0.0918	333.61	38.26	57.21	83.32
0.1049	0.5023	0.3117	330.97	43.53	64.11	91.95
0.2947	0.3407	0.2875	332.62	40.32	59.84	86.58
0.4797	0.1840	0.2682	334.85	36.19	54.40	79.75
0.1149	0.3211	0.4845	334.23	38.41	56.95	82.16
0.3068	0.1458	0.4776	336.23	34.13	51.60	75.75
0.1131	0.1417	0.6619	337.48	33.58	50.27	73.09
0.0999	0.3328	0.3403	330.38	44.60	65.63	93.90
0.1109	0.1433	0.4898	333.83	39.08	57.68	83.29
0.1006	0.5345	0.1121	326.04	52.58	76.68	108.89
0.1259	0.1534	0.1231	328.35	47.55	70.05	100.62
0.0983	0.3810	0.1109	326.01	52.48	76.59	109.06
0.1129	0.1547	0.2963	330.76	43.66	64.39	92.56
0.1134	0.3149	0.1131	326.31	51.80	75.69	108.01
0.0965	0.1483	0.3300	331.19	43.04	63.51	91.21
0.1018	0.2405	0.3500	330.44	44.24	65.24	93.60
0.1082	0.0872	0.5338	335.09	36.94	54.98	79.63

where ν_i^L are the pure liquid molar volumes calculated form the modified Rackett equation (Spencer and Danner, 1972), R is the gas constant, and ϕ_i are the fugacity coefficients calculated from the volume explicit virial equation truncated after the second term

$$\ln \phi_i = (2\sum_j y_j B_{ij} - \sum_k \sum_j y_k y_j B_{kj}) p/RT \qquad (2)$$

where B_{ij} are the second virial coefficients estimated from the generalized method of Hayden and O'Connell (1975). f_i^{0L} were calculated from the method of Prausnitz et al. (1980). The liquid-phase activity coefficients γ_i were calculated from the UNIQUAC equation (Anderson and Prausnitz, 1978). The parameters of the UNIQUAC equa-

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Table 3. Binary Temperature-Dependence Parameters for the UNIQUAC Equation

binary mixture	a_{AB}/K	a_{BA}/K
ethanol (A) + acetone (B)	$4.29 - 75.75T_k - 49.23T_k^2$	$633.97 - 126.17T_k - 110.84T_k^2$
ethanol (A) + benzene (B)	$-38.95 - 41.93T_k - 42.35T_k^2$	$1642.33 - 403.04T_k - 259.94T_k^2$
ethanol (A) + hexane (B)	$46.47 - 84.95T_k - 60.20T_k^2$	$1135.37 + 1088.55T_k - 815.33T_k^2$
acetone (A) + benzene (B)	$-62.91 - 11.00T_k - 11.55T_k^2$	$175.69 - 16.90T_k - 17.05T_k^2$
acetone (A) + hexane (B)	$17.70 - 25.82T_k - 15.24T_k^2$	$286.64 - 10.83T_k - 25.38T_k^2$
benzene (A) + hexane (B)	$16.22 - 8.99T_k - 11.87T_k^2$	$92.71 - 14.72T_k - 21.50T_k^2$

Table 4. Root-Mean-Square (RMS) Deviations for Binary Mixtures

system	condition	$10^2\,\delta p/p$	δT/K	$10^3\,\delta y$	reference
ethanol + acetone	305.15 K	0.64		9.3	Gordon and Hines, 1946
	313.15 K	0.56		7.0	Chu et al., 1950
	321.15 K	0.21		6.0	Gordon and Hines, 1946
	328.15 K	1.31		21.8	Vinichenko and Susarev, 1966
	101.325 kPa		0.24	16.7	Amer et al., 1956
ethanol + benzene	298.15 K	0.15		4.8	Smith and Robinson, 1970
	313.15 K	0.72		9.4	Udovenko and Fatkulina, 1952
	318.15 K	0.50		4.7	Brown and Smith, 1954
	323.15 K	0.64		37.0	Zharov and Morachevskii, 1963
	328.15 K	0.65		5.9	Fu et al., 1995
	333.15 K	0.61		4.7	Fu et al., 1995
	23.998 kPa		0.14	7.9	Nielsen and Weber, 1959
	53.329 kPa		0.13	5.7	Nielsen and Weber, 1959
	101.325 kPa		0.15	7.6	Wang et al., 1990
ethanol + hexane	308.15 K	0.57		9.8	Kudryavtseva and Susarev, 1963
	318.15 K	0.69		15.0	Kudryavtseva and Susarev, 1963
	328.15 K	0.51		16.4	Kudryavtseva and Susarev, 1963
	333.15 K	1.17		12.6	Lindberg and Tassios, 1971
	101.325 kPa		0.18	7.7	Kudryavtseva and Susarev, 1963
acetone + benzene	298.15 K	0.59		3.8	Tasic et al., 1978
	303.15 K	0.53		10.3	Kraus and Linek, 1971
	308.15 K	3.04		16.2	Litvinov, 1940
	313.15 K	1.91		4.0	Kraus and Linek, 1971
	318.15 K	0.34		3.3	Brown and Smith, 1957
	323.15 K	0.38		5.0	Kraus and Linek, 1971
	98.392 kPa		0.18	7.4	Tallmadge and Canjar, 1954
	101.325 kPa		0.18	7.2	Free and Hutchison, 1959
acetone + hexane	293.15 K	0.86		8.4	Rall and Schaefer, 1959
	308.15 K	0.90		13.5	Kudryavtseva and Susarev, 1963
	318.15 K	0.81		6.5	Kudryavtseva and Susarev, 1963
	328.15 K	0.72		8.4	Kudryavtseva and Susarev, 1963
	101.325 kPa		0.09	6.5	Kudryavtseva and Susarev, 1963
benzene + hexane	298.15 K	0.18		1.4	Harris and Dunlop, 1970
	303.08 K	0.36			Jain et al., 1970
	312.94 K	0.31			Jain et al., 1970
	328.15 K	0.83		3.6	Yuan et al., 1963
	26.664 kPa		0.13	10.4	Michishita et al., 1971
	39.997 kPa		0.15	14.4	Michishita et al., 1971

Table 5. Quaternary Calculated Results

	$\delta T/K$	$10^2\,\delta p/p$		
	101.33 kPa	308.15 K	318.15 K	328.15K
mean deviation	0.11	0.60	0.40	0.33
RMS deviation	0.14	0.77	0.48	0.42

tion as a function of temperature are given by the following equation:

$$a_{ij} = a_{ij}^{(0)} + a_{ij}^{(1)} T_k + a_{ij}^{(2)}\, T_k^2 \qquad (3)$$

with $T_k = T/T_0$, where T_0 is an arbitrarily chosen reference temperature, in this case 315.00 K.

The optimum temperature-dependence parameters were obtained by minimizing the objective function J, using modified the Powell optimization technique (Powell, 1964). The objective function is defined as

$$J = \sum_j \left(\frac{p - p_{\mathrm{exp}}}{p_{\mathrm{exp}}} \right)_j^2 \qquad (4)$$

The optimum binary temperature-dependence parameters a_{ij} are listed in Table 3. Table 4 shows the root-mean-square deviations between experimental and the most probable calculated values of the measured variables: δp for pressure; δT for temperature; δy for vapor mole fraction. The correlation results are in very good agreement with the literature data. The deviations between the quaternary experimental results and those calculated from the binary temperature-dependence parameters from Table 3 are presented in Table 5. It shows that the UNIQUAC equation can be well used for predicting quaternary VLE data.

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