Vapor-Liquid Equilibrium for the Binary Systems Ethyl Acetate-Acetic Acid and Ethyl Propionate-Propionic Acid

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Vapor-liquid equilibrium (VLE) data have been measured for mixtures of ethyl acetate with acetic acid at 338 and 346 K and for mixtures of ethyl propionate with propionic acid at 358 and 368 K. The measurements were carried out in a recirculation still similar to that of Dvorak and Boublik. The data have been consistency tested by means of a maximum-likelihood procedure providing at the same time the relevant UNIQUAC parameters. Vapor pressures of the pure substances have been measured, and the data have been correlated with the Antoine equation.

Introduction

The UNIFAC group-contribution method (*1*) is used to predict liquid-phase activity coefficients in nonelectrolyte mixtures at low to moderate pressures and at temperatures between 300 and 425 K. In order to use the method, one needs parameters for the energetic interactions between the groups. Extensive lists of such parameters have been published (*2*).

These parameters are based on experimental vapor-liquid equilibrium (VLE) data, and the reliability of the UNIFAC predictions is therefore dependent on the accuracy and broadness of the experimental VLE data base. For the estimation of the interaction between an acid group (COOH) and an ester group (CCOO), the available data are scarce (3-8). Only data for mixtures with acetic acid are available and not all of the data are thermodynamically consistent.

In order to establish a more reliable VLE data base for the COOH/CCOO interaction, VLE data have been measured for mixtures of organic acids and esters.

Experimental Section

Apparatus and Procedure. The VLE data were measured in an all-glass Dvorak-Boublik still (*9*), which provides for circulation of both the vapor and liquid phases. The equilibrium temperature was measured with a platinum resistance thermometer via a Müller bridge, SYSTEM TEKNIK AB, S1118 with an accuracy of ±0.01 °C. The pressure was measured to within 0.1 mmHg with a mercury-filled U-tube manometer (inner diameter 20 mm).

The samples drawn from the vapor and liquid phases at equilibrium were analyzed by gas-liquid chromatography (GLC) with a Hewlett-Packard 5840 A gas chromatograph. A TC detector was used and the 2-mm inner diameter glass columns (length 1.65 m) were packed with Porapaq Q, 50/80 mesh. The average accuracy of the measured vapor and liquid concentrations is ±0.5%.

Materials. Table I shows the materials used. No further purification was employed except for ethyl propionate from which impurities were removed by contact for some hours with molecular sieve pellets having 3-Å pores.

Table I. Pure Components

component	supplier
acetic acid	BDH (Aristar)
propionic acid	BASF
ethyl acetate	Merck AG (für die Chromatographie)
ethyl propionate	Fluka AG (puriss)

Analyses by GLC showed that all the components had a purity greater than 99.8%.

Vapor Pressure Measurements of the Pure Substances. The Dvorak-Boublik still was used for the measurement of the vapor pressures of the pure substances. The experimental data obtained are given in Table II together with the estimated constants of the Antoine equation.

$$\log P_i^0(\text{mmHg}) = A_i - B_i/(t(^\circ\text{C}) + C_i)$$

The deviations between experimental vapor pressures and vapor pressures calculated by means of the Antoine equation with the given constants are also shown in Table II.

VLE Measurements and Data Reduction for Ester/Acid Mixtures. Vapor-liquid equilibrium measurements were performed for binary mixtures of ethyl acetate and acetic acid at 338 and 346 K and for binary mixtures of ethyl propionate and propionic acid at 358 and 368 K. The experimental results are shown in Tables III-VI.

The equilibrium equation which has been used for the data reduction is

$$P y_i \phi_i = x_i \gamma_i P_i^0 \phi_i^0 \qquad i = 1, 2$$

where P is the total pressure; P_i^0 is the vapor pressure of component i at the equilibrium temperature T; y_i and x_i are the vapor and liquid mole fractions; ϕ_i is the fugacity coefficient of component i in the vapor phase at the equilibrium conditions while ϕ_i^0 is the fugacity coefficient of pure component i at the vapor pressure corresponding to the equilibrium temperature; γ_i is the liquid-phase activity coefficient.

The dimerization of organic acids and other deviations from ideality in the vapor phase have been taken into account as described by Fredenslund et al. (*1*).

The experimental data have been reduced by means of a maximum-likelihood procedure (*10*) using the UNIQUAC model (*11*) to describe the liquid-phase activity coefficients. The root mean squared deviations (rmsd) between experimental and calculated values of P, T, x, and y are shown in Tables III-VI together with the estimated UNIQUAC parameters.

In order to further illustrate the data reduction, Table III gives values of the fugacity coefficient ratios ϕ_i/ϕ_i^0 and of the calculated activity coefficients γ_i for ethyl acetate (*1*)-acetic acid (2) at 338 K. Figure 1 shows deviations between experimental and calculated values of the pressure P and vapor mole fraction y_1 as a function of the liquid mole fraction x_1. The

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Table II. Experimental Vapor Pressures, Antoine Constants (A, B, C), and Root Mean Squared Deviations (rmsd)

	acetic acid		propionic acid		ethyl acetate		ethyl propionate	
	t/°C	P/mmHg	t/°C	P/mmHg	t/°C	P/mmHg	t/°C	P/mmHg
	57.54	81.02	80.91	79.00	34.83	149.14	48.94	119.61
	62.43	100.71	95.64	149.73	37.72	169.72	54.65	152.98
	68.18	128.80	102.75	199.47	40.62	192.64	61.77	205.30
	70.75	143.25	108.45	248.61	46.10	242.59	66.85	250.94
	73.82	162.32	113.17	296.73	47.48	257.05	71.61	300.73
	78.89	198.63	118.01	353.69	50.80	293.78	75.55	347.99
	82.30	226.43	121.46	399.75	52.40	313.03	79.11	395.48
	85.15	252.07	124.91	450.51	55.07	347.24	82.43	444.34
	90.03	301.56	127.89	498.58	55.38	351.51	85.76	498.71
	93.74	344.38	130.74	548.60	58.66	398.07	88.61	548.85
	97.68	395.10	133.10	592.81	61.64	444.54	91.10	595.94
	101.12	444.17	135.37	638.07	64.70	496.77	93.56	645.44
	104.70	500.51	137.49	683.12	67.41	547.12	96.30	705.16
	107.52	549.07			69.79	594.72	97.55	733.30
	109.90	592.67			72.21	645.97		
	113.81	670.11			74.34	694.26		
A	7.30500		7.61681		6.98455		7.14068	
B	1481.961		1652.129		1179.242		1335.788	
C	217.078		207.974		210.292		214.889	
rmsd/mmHg	0.09		0.05		0.09		0.12	

Table III. Experimental VLE Data for Ethyl Acetate (1)-Acetic Acid (2) at 338 K[a]

T/K	P/mmHg	x_1	y_1	ϕ_1/ϕ_1^0	ϕ_2/ϕ_2^0	γ_1	γ_2
338.26	144.72	0.0750	0.2205	1.519	0.920	1.182	0.999
338.23	159.76	0.1093	0.3112	1.435	0.902	1.195	0.997
338.30	173.60	0.1389	0.3762	1.381	0.890	1.204	0.996
338.30	204.20	0.2105	0.5185	1.276	0.890	1.217	0.994
338.33	237.96	0.2894	0.6425	1.198	0.916	1.221	0.993
338.22	267.29	0.3599	0.7284	1.149	0.956	1.216	0.995
338.24	303.97	0.4498	0.7991	1.113	1.011	1.199	1.005
338.24	346.84	0.5617	0.8818	1.074	1.169	1.162	1.037
338.31	369.82	0.6161	0.9066	1.064	1.246	1.138	1.069
338.31	401.67	0.7091	0.9458	1.047	1.474	1.095	1.156
338.16	412.42	0.7446	0.9552	1.044	1.558	1.077	1.209
rmsd of UNIQUAC Maximum-Likelihood Fitting							
0.06	0.14	0.0060	0.0069				

[a] Parameters: $r_1 = 3.4786$, $q_1 = 3.1160$, $a_{12} = 474.6$, $r_2 = 2.2024$, $q_2 = 2.0720$, $a_{21} = -229.4$.

Table IV. Experimental VLE Data for Ethyl Acetate (1)-Acetic Acid (2) at 346 K[a]

T/K	P/mmHg	x_1	y_1
346.12	194.56	0.0676	0.2018
346.16	211.56	0.0975	0.2814
346.13	231.51	0.1349	0.3645
346.34	266.75	0.1935	0.5015
346.20	312.44	0.2776	0.6375
346.09	353.40	0.3529	0.7223
346.23	401.76	0.4393	0.8069
346.10	455.47	0.5523	0.8687
346.19	472.31	0.5755	0.8897
346.10	530.18	0.6956	0.9377
346.10	547.43	0.7411	0.9522
rmsd of UNIQUAC Maximum-Likelihood Fitting			
0.08	0.15	0.0103	0.0105

[a] Parameter: $r_1 = 3.4786$, $q_1 = 3.1160$, $a_{12} = 547.4$, $r_2 = 2.2024$, $q_2 = 2.0720$, $a_{21} = -252.8$.

Table V. Experimental VLE Data for Ethyl Propionate (1)-Propionic Acid (2) at 358 K[a]

T/K	P/mmHg	x_1	y_1
358.06	134.28	0.0874	0.2991
358.05	154.40	0.1338	0.4151
358.10	173.07	0.1732	0.4979
358.23	199.90	0.2286	0.5997
358.19	242.60	0.3265	0.7219
358.14	278.67	0.4151	0.8043
358.18	323.13	0.5281	0.8751
358.25	358.11	0.6219	0.9159
358.07	403.43	0.7583	0.9591
358.19	435.86	0.8494	0.9776
rmsd of UNIQUAC Maximum-Likelihood Fitting			
0.12	0.24	0.0077	0.0060

[a] Parameters: $r_1 = 4.1530$, $q_1 = 3.6560$, $a_{12} = 468.8$, $r_2 = 2.8768$, $q_2 = 2.6120$, $a_{21} = -240.8$.

Table VI. Experimental VLE Data for Ethyl Propionate (1)-Propionic Acid (2) at 368 K[a]

T/K	P/mmHg	x_1	y_1
368.08	191.95	0.0788	0.2566
368.04	213.72	0.1139	0.3506
368.06	250.34	0.1737	0.4816
368.12	281.00	0.2201	0.5719
368.07	338.41	0.3194	0.7066
368.06	386.60	0.4058	0.7867
368.14	447.53	0.5163	0.8570
368.05	480.44	0.5845	0.8926
368.07	489.26	0.5976	0.8982
368.05	573.05	0.7735	0.9572
rmsd of UNIQUAC Maximum-Likelihood Fitting			
0.10	0.15	0.0084	0.0073

[a] Parameters: $r_1 = 4.1530$, $q_1 = 3.6560$, $a_{12} = 499.5$, $r_2 = 2.8768$, $q_2 = 2.6120$, $a_{21} = -253.9$.

Table VII. Comparison between Different Models for the Fitting of Experimental VLE Data for Ethyl Propionate (1)-Propionic Acid (2) at 368 K[a]

	rmsd			
model	T/K	P/mmHg	x_1	y_1
UNIQUAC	0.05	0.09	0.0081	0.0091
2-parameter Margules	0.07	0.14	0.0078	0.0092
3-parameter Margules	0.06	0.11	0.0080	0.0091
4-parameter Margules	0.06	0.14	0.0064	0.0093

[a] Procedure from Prausnitz et al. (1980).

other systems give results similar to those presented in Table III and Figure 1.

In order to test whether the UNIQUAC model is suitable for the systems considered in this paper, we have also reduced the experimental data by means of UNIQUAC and two-, three-, and four-parameter Margules equations and a maximum-likelihood procedure as described by Prausnitz et al. (*12*). The results

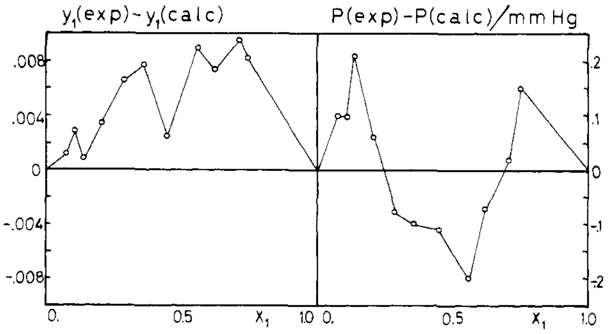

Figure 1. Deviations between experimental and calculated values of y_1 and P for ethyl acetate (1)–acetic acid (2) at 338 K.

with the UNIQUAC model were almost identical with the results with the Margules equations. An example is shown in Table VII for the system ethyl proprionate (1)–propionic acid (2) at 368 K. The slight differences between the root mean squared deviations for UNIQUAC in Tables VI and VII are due to small differences in the programs by Kemény et al. (*10*) and Prausnitz et al. (*12*).

Conclusion

The mean deviations between the experimental and calculated values of P, T, x, and y are comparable to the experimental uncertainties. All four data sets may therefore be considered to be thermodynamically consistent and the data sets may be included in the data base of reliable VLE data for UNIFAC parameter estimations.

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Glossary

a_{12}, a_{21}	UNIQUAC parameters in Kelvin
A, B, C	constants in the Antoine equation
P	pressure in mmHg
P_i^0	vapor pressure in mmHg of component i
q_i	surface area parameter of component i
r_i	volume parameter of component i
t	temperature °C
T	temperature in Kelvin
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
ϕ_i	fugacity coefficient of component i in mixture
ϕ_i^0	fugacity coefficient of pure component i
γ_i	activity coefficient

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Phase Equilibria in the H_2/C_2H_6 System at Temperatures from 92.5 to 280.1 K and Pressures to 560 MPa

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Experimental data for liquid–vapor phase compositions of H_2/C_2H_6 are reported for 19 temperatures in the range 92.5–280.1 K and pressures up to 560 MPa. The data have been obtained by using a vapor-recirculating apparatus. The entire region of liquid–vapor coexistence has been explored for the first time. The mixture critical line and the pressure–temperature trace of the three-phase line solid–liquid–vapor have been located. These lines intersect at 138 K and 725 MPa to form an upper critical end point. Results obtained up to 52 MPa have been compared to published data.

Introduction

The study of the phase behavior of H_2/C_2H_6 presented in this paper continues in the research work on H_2/X systems reported in previous papers (*1–5*); these studies are designed to provide accurate data for design purposes and to explore patterns of phase behavior in H_2/X systems at high pressures. H_2 and ethane are both important components in industrial processes. The separation of H_2 from gases like ethane and other lower hydrocarbons requires the knowledge of the phase diagram of the binary mixtures. Optimal conditions for separation processes are often found at higher pressures. systematic and accurate data covering wide ranges of temperature and pressures are also important for testing theoretical methods of phase equilibrium prediction.

Data available in the literature for H_2/C_2H_6 are limited to 52 MPa (*6*, *7*) and cover only a small portion of the entire liquid-

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