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Vapor–Liquid Equilibrium Measurements for Binary Systems of Acetic Acid with Ethyl Acetate and Vinyl Acetate by the Dew–Bubble Point Temperature Method

Masahiro Kato

Department of Industrial Chemistry, Faculty of Engineering, Nihon University, Koriyama, Fukushima 963, Japan

Vapor–liquid equilibrium relations were measured for the binary systems ethyl acetate–acetic acid and vinyl acetate–acetic acid at 740 mmHg pressure by the dew–bubble point temperature method. The dew–bubble point temperature apparatus previously proposed by the authors was modified to reduce the time required for the experiment. To keep the flow rate constant, the construction of the feeder was further modified to maintain the liquid level constant in it. Vapor–liquid equilibrium relationships were obtained for the binary systems by combining the dew point temperature curve and the bubble point one. Large differences are shown among the previous experimental data in the literature for the systems of the present study. The composition analysis seems troublesome for these systems containing acetic acid in the conventional experimental methods. The present experimental method does not require any analytical instrument for the vapor–liquid equilibrium measurements. For the correlation of the experimental data, the Wilson equation was successfully applied, accounting for the association effect of acetic acid in vapor phase.

Introduction

Vapor–liquid equilibrium relations are required for practical use, such as in the design and operation of distillation equipment. In the conventional experimental methods of vapor–liquid equilibria, analytical instruments are required. For measurements of isobaric dew points, a unique vapor-mixing-type apparatus was proposed by Kojima et al. (*1*). For measurement of isobaric bubble points, many researchers (*2–4*) have proposed some ebulliometers. However, in the general batch-type ebulliometer, it is necessary to correct for the difference between the liquid composition at steady state and the feed composition. Kojima et al. (*5*) determined vapor–liquid equilibria of two-liquid-phase systems, combining the dew and bubble points separately measured.

The authors previously proposed two types of apparatus for measuring isobaric dew and bubble points. One is the vapor-mixing type (*6*), and the other is flow type (*7*). In the present work, the flow-type apparatus was further modified. Large differences in the data from the literature are observed for vapor–liquid equilibria of binary systems made of acetic acid and acetate (*8–12*). Vapor–liquid equilibrium relations were measured for the binary systems ethyl acetate–acetic acid and vinyl acetate–acetic acid at 740 mmHg pressure by the dew–bubble point temperature method.

Table I. Physical Properties of Materials Used

material	density at 25 °C, g/cm^3 exptl	density at 25 °C, g/cm^3 lit.	normal bp, °C exptl	normal bp, °C lit.
acetic acid	1.0437	1.04365 (*13*)	117.94	117.72 (*13*)
ethyl acetate	0.8943	0.8946 (*13*)	77.10	77.15 (*13*)
vinyl acetate	0.9255	0.9321^a (*10*)	72.86	72.6 (*10*)

^{a} At 20 °C.

Experimental Section

The authors (*7*) previously proposed the flow-type apparatus for measuring isobaric dew and bubble points. In the present modification, the dew point still and the bubble point still are reversed in order to reduce the time required for the experiment. The construction of the feeder is further modified to keep the constant flow rate. The modified experimental apparatus is schematically shown in Figure 1. The apparatus is entirely made of borosilicate glass. Its main parts are a bubble point still, B, a dew point still, D, three overflow tubes, O, and a feeder, F. The internal construction of both stills is almost similar to that of the small ebulliometer (*4*, *7*). An electric cartridge heater is inserted into each boiling flask, and a little glass dust is put on the wall of the heat-transfer surface to stabilize the boiling condition. In each still, the boiling vapor–liquid mixture rises through a Cottrell tube and flashes to a thermometer well. The amount of liquid contained in each still is about 15 cm^3; both stills are kept adiabatic with evacuated jackets and tapes. As shown in Figure 1, feeder F is modifid to keep the liquid level constant in it. The experimental temperatures were measured with the Hewlett-Packard 2804A quartz thermometers, calibrated by the triple point of water in a reference cell. The reliability of the thermometers used seems ±0.01 °C. The atmospheric pressures were indirectly measured by the bubble points of water in a separate ebulliometer.

Special grade reagents were supplied by the Wako Chemicals Co., Ltd. Ethyl acetate was purified with distillation. Acetic acid and vinyl acetate were used without further purification.

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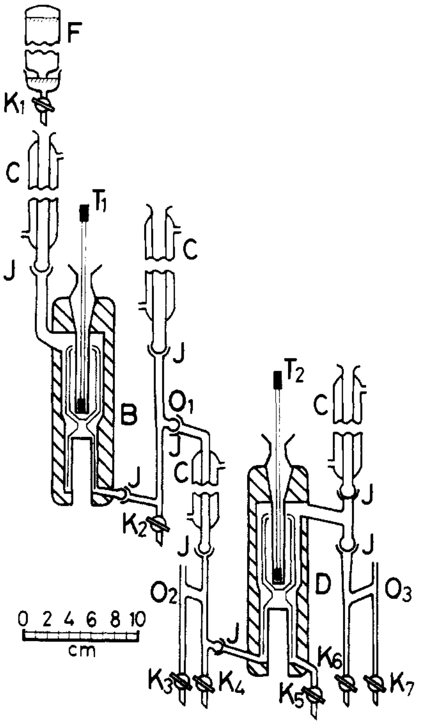

Figure 1. Experimental apparatus for the dew-bubble point temperature method: (B) bubble point still; (C) condenser; (D) dew point still; (F) feeder; (J) ball joint; (K) cock; (O) overflow tube; (T) thermometer.

Table II. Experimental Dew and Bubble Point Data at 740 mmHg Pressure

	ethyl acetate–acetic acid		vinyl acetate–acetic acid	
acetate mol fracn	dew point, °C	bubble point, °C	dew point, °C	bubble point, °C
0.000		117.07		117.07
0.050	115.93	113.36	115.45	109.88
0.100	114.27	109.73	113.46	104.19
0.200	110.93	103.30	109.50	95.96
0.300	107.60	97.88	105.36	90.16
0.400	104.20	93.33	101.20	85.80
0.500	100.71	89.37	97.02	82.84
0.600	97.14	86.50	92.66	80.02
0.700	93.30	83.64	88.05	77.72
0.800	89.04	81.07	83.22	75.65
0.900	84.13	78.59	78.16	73.79
0.950	81.02	77.39	75.48	72.93
1.000		76.30		72.06

The physical properties of materials used are listed in Table I.

The experimental procedure is almost the same with that described in the previous work (*7*). At the start of experiments, cocks K_3 and K_7 are opened, and cocks K_2, K_4, K_5, and K_6 are closed. A prepared solution of given composition is charged from feeder F continuously and the flow rate is controlled with cock K_1. The liquid from the bubble point still B partially overflows through the branched tube O_2. The solution of desired composition was prepared in a 200-cm^3 Erlenmeyer flask with a stopper by mixing each pure substance, which was accurately weighed within ±1 mg by use of an automatic balance. After attaining steady state, the liquid composition in the bubble point still B and the vapor composition in the dew point still D must agree with the feed composition. The temperatures obtained in the stills, B and D, respectively, should therefore equal the bubble point and the dew point at the feed composition.

Results

With the modified apparatus shown in Figure 1, the dew and bubble points were measured for the binary systems of acetic

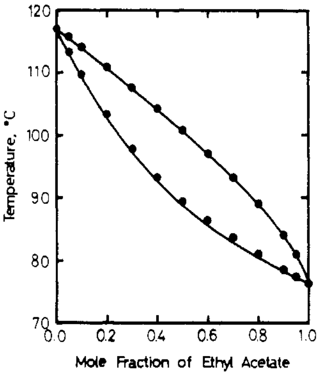

Figure 2. Experimental dew-bubble points for the ethyl acetate–acetic acid system at 740 mmHg pressure: (●) experimental; (—) Wilson equation.

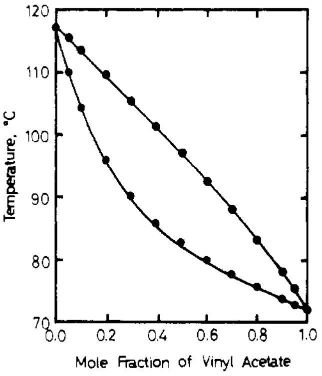

Figure 3. Experimental dew-bubble points for the vinyl acetate–acetic acid system at 740 mmHg pressure: (●) experimental; (—) Wilson equation.

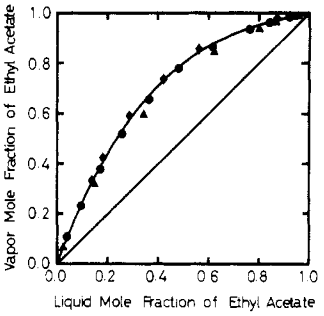

Figure 4. Vapor–liquid equilibria for ethyl acetate–acetic acid at 740 mmHg pressure: (●) this work; (—) Wilson equation; (▲) Bushmakin–Lutugina (*8*), 760 mmHg; (◆) Garner–Ellis–Pearce (*9*), 760 mmHg.

Table III. Smoothed Data of Vapor–Liquid Equilibria at 740 mmHg Pressure

ethyl acetate–acetic acid			vinyl acetate–acetic acid		
	acetate mole fracn			acetate mole fracn	
temp, °C	liquid	vapor	temp, °C	liquid	vapor
117.07	0.000	0.000	117.07	0.000	0.000
114.00	0.040	0.107	110.00	0.048	0.185
110.00	0.096	0.230	105.00	0.092	0.307
105.00	0.173	0.377	100.00	0.147	0.430
100.00	0.259	0.519	95.00	0.212	0.545
95.00	0.363	0.654	90.00	0.301	0.657
90.00	0.482	0.777	85.00	0.425	0.763
86.00	0.617	0.863	80.00	0.605	0.863
82.00	0.764	0.934	78.00	0.689	0.902
80.00	0.842	0.961	76.00	0.785	0.939
78.00	0.922	0.983	74.00	0.890	0.972
76.30	1.000	1.000	72.06	1.000	1.000

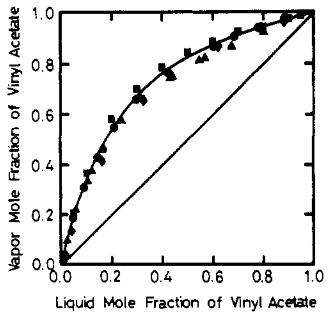

Figure 5. Vapor-liquid equilibria for vinyl acetate-acetic acid at 740 mmHg pressure: (●) this work; (—) Wilson equation; (▲) Capkova-Fried (*10*), 760 mmHg; (◆) Morrison-Shaw (*11*), 760 mmHg; (■) Pao (*12*), 760 mmHg.

Table IV. Wilson Parameters Obtained from Equilibrium Data[a]

system	Λ_{12}	Λ_{21}	$\lvert\Delta t\rvert_{av}$	$\lvert\Delta y\rvert_{av}$
ethyl acetate (1)-acetic acid (2)	1.6609	0.2491	0.38	0.008
vinyl acetate (1)-acetic acid (2)	1.1251	0.3061	0.24	0.005

[a] $\lvert\Delta t\rvert_{av}$: average absolute difference of temperature, °C. $\lvert\Delta y\rvert_{av}$: average absolute difference of vapor mole fraction.

acid with ethyl acetate and vinyl acetate at atmospheric pressures. The experimental dew and bubble points obtained are listed in Table II and shown in Figures 2 and 3. The experimental temperatures were corrected to the values at 740 mmHg pressure, using the same procedure described in the previous paper (*4*). The smoothed vapor-liquid equilibrium data obtained are listed in Table III and shown in Figures 4 and 5. Nonnegligible large differences exist among the data from the literature (*8*-*12*). The present experimental data lie between the literature data as shown in Figures 4 and 5.

The vapor-liquid equilibrium data were correlated with the Wilson equation (*14*), accounting for the dimerization effect of acetic acid in vapor phase with the procedure shown in the literature (*15*, *16*).

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \quad (1)$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) + x_1\left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{\Lambda_{12}x_2 + x_1}\right] \quad (2)$$

$$Q = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 = -x_1 \ln (x_1 + \Lambda_{12}x_2) - x_2 \ln (x_2 + \Lambda_{21}x_1) \quad (3)$$

The Wilson parameters were determined from the *Q*-function curves, as shown in Figure 6 and Table IV. For vapor pressures of pure components, Antoine equation was used (*17*). The solid lines in Figures 2 and 5 show the equilibrium curves calculated with the Wilson equation by using the parameters given in Table IV. The average absolute differences of temperature and vapor composition between the experimental data and calculated ones are shown in Table IV.

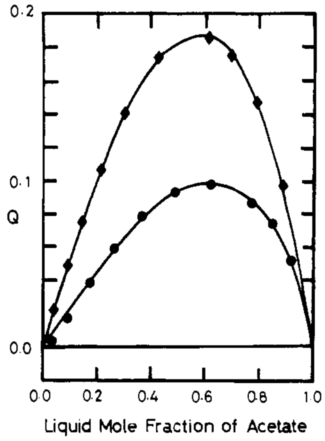

Figure 6. *Q*-function curves: (●) ethyl acetate-acetic acid; (◆) vinyl acetate-acetic acid; (—) Wilson equation.

Glossary

x	mole fraction in liquid phase
Q	*Q* function, eq 3

Greek Letters

γ	activity coefficient
Λ	Wilson parameter

Subscripts

1	acetate
2	acetic acid

Registry No. Ethyl acetate, 141-78-6; acetic acid, 64-19-7; vinyl acetate, 108-05-4.

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