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Indirect Determination of Vapor–Liquid Equilibria by a Small Ebulliometer. Tetrahydrofuran–Alcohol Binary Systems

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For the four binary systems of tetrahydrofuran and alcohol (methyl, ethyl, isopropyl, and *n*-propyl), boiling points were measured with a small ebulliometer at atmospheric pressure, and vapor–liquid equilibrium relations were indirectly determined by using the Wilson equation. Values of the Wilson parameters were calculated to minimize the sum of squares of deviations in the boiling points for all data points.

Vapor–liquid equilibrium relations are required for practical use such as in the design and operation of distillation equipment. It is possible to determine vapor–liquid equilibrium relationships indirectly from boiling-point curves which can be easily and reliably measured, rather than those from the conventional equilibrium measurements (*2*).

In the present investigation, boiling points were measured with a small ebulliometer at atmospheric pressure for the four binary systems of tetrahydrofuran (THF) and alcohol (methyl, ethyl, isopropyl, and *n*-propyl), and vapor–liquid equilibrium relations were determined from the experimental boiling-point data by using the Wilson equation (*10*).

Experimental Section

The experimental apparatus for the measurement of boiling points is shown in Figure 1. The cross sections are shown at the right-hand side of the still. In the small ebulliometer, the required amount is ~15 cm^3 per boiling-point measurement. It is constructed entirely of borosilicate glass. An electric cartridge heater is inserted into the boiling flask, and a little glass dust is put on the wall of the heat-transfer surface to stabilize the boiling condition. In the still, the boiling vapor–liquid mixture rises through a Cottrell tube and flushes to a thermometer well. Asbestos tapes cover the entire apparatus except the condenser. The boiling points were measured with a mercury thermometer calibrated to ±0.1 °C in accordance with the standard platinum resistance thermometer. The atmospheric pressures were measured with the Fortin barometer. The solution of desired composition was prepared within 1 min in a 30-cm^3 Erlenmeyer flask with a stopper by mixing each pure substance, which was weighed by use of syringes and an automatic balance. To minimize the change of composition, the prepared solution was immediately used for the experiment. The accuracy of the composition seems to be within ±0.0005 mole fraction. The time required for the boiling-point measurement was ~5 min after the solution came to a boil. Special grade reagents supplied by the Koso Chemical Co., Ltd., were used without further purification. The physical properties of the reagents used are listed in Table I.

Results

The raw data of boiling points t^* and the experimental atmospheric pressures π^* are presented in Table II. The experimental raw data of boiling points were then corrected to 760 mmHg pressure by using eq 1, where m indicates the coefficient

$$t = t^* + m(760 - \pi^*) \qquad (1)$$

(dt/dP) which is evaluated in the form of eq 2. The values of

$$m = m_1x_1 + m_2x_2 \qquad (2)$$

m_1 and m_2 were obtained from eq 3, derived from the Antoine

$$m_i = \left(\frac{\mathrm{d}t}{\mathrm{d}P_i}\right) = \frac{(t_i + C_i)^2}{(2.303)(760B_i)} \qquad (3)$$

$$t_i = \frac{B_i}{A_i - \log{(760)}} - C_i \qquad (4)$$

equation. A, B, and C are Antoine constants as shown in Table III. In the present work, the maximum, arithmetic mean, and minimum values for the correction were +0.9, +0.6, and +0.3 °C, respectively. The boiling points corrected to 760 mmHg pressure are given in Table II and shown in Figure 2.

The vapor–liquid equilibrium relations were calculated from the experimental boiling-point data corrected to 760 mmHg pressure. The expressions proposed by Wilson (*10*) for representing the activity coefficients, γ_1 and γ_2, were employed in the present investigation (eq 5 and 6). Assuming that the

$$\ln \gamma_1 = -\ln{(x_1 + \Lambda_{12}x_2)} + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \qquad (5)$$

$$\ln \gamma_2 = -\ln{(x_2 + \Lambda_{21}x_1)} + x_1\left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{\Lambda_{12}x_2 + x_1}\right) \qquad (6)$$

vapor is an ideal gas and that the volumetric effect of liquid is negligible on the evaluation of the activity coefficient in the liquid phase gives eq 7, where x, Λ, π, and P, respectively, denote

$$\pi = \gamma_1P_1x_1 + \gamma_2P_2x_2 \qquad (7)$$

the liquid composition, the Wilson parameter, the total pressure, and the vapor pressure. Table III shows the Antoine constants used for the evaluations of vapor pressures in the present investigation.

Simultaneous solution of eq 5–7 would provide the required information of vapor–liquid equilibria. Values of the Wilson parameters Λ_{12} and Λ_{21} were determined to minimize the sum of squares of deviations in the boiling points for all data points by using a digital computer (*6*). Table IV shows the Wilson parameters obtained in the present investigation. The average

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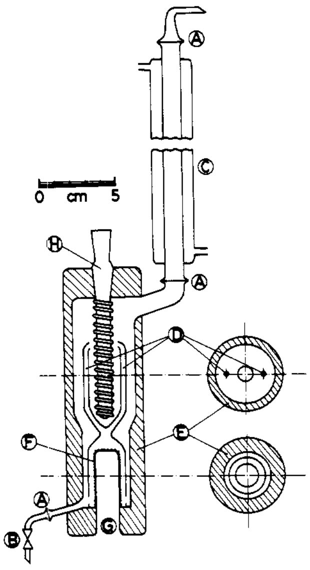

Figure 1. Experimental apparatus: (A) ball joint; (B) cock; (C) condenser; (D) cottrell tube; (E) evacuated jacket; (F) glass dust; (G) heater tube; (H) thermometer well.

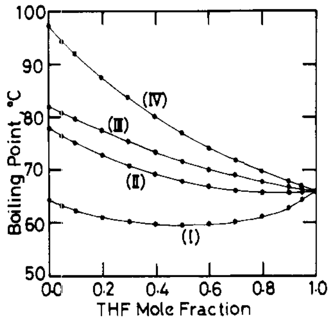

Figure 2. Experimental boiling-point curves at 760 mmHg pressure: (I) THF–methanol; (II) THF–ethanol; (III) THF–2-propanol; (IV) THF–1-propanol.

Table I. Physical Properties of Materials Used

	normal boiling point, °C		density at 25 °C, g/cm^3	
material	obtained	reported	obtained	reported
tetrahydrofuran	65.8	65.75(7)	0.8822	0.8820(7)
methanol	64.4	64.501(9)	0.7866	0.78653(9)
ethanol	78.0	78.27(9)	0.7854	0.78511(9)
2-propanol	81.8	82.29(9)	0.7806	0.78083(9)
1-propanol	97.4	97.19(9)	0.8000	0.79985(9)

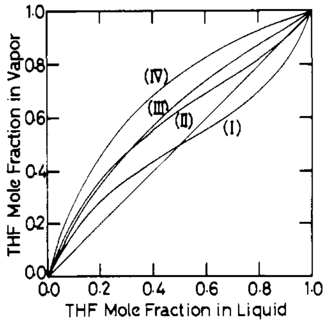

Figure 3. Vapor–liquid equilibria at 760 mmHg pressure: (I) THF–methanol; (II) THF–ethanol; (III) THF–2-propanol; (IV) THF–1-propanol.

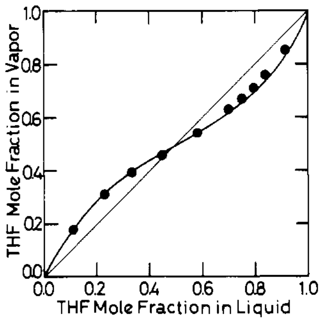

Figure 4. Vapor–liquid equilibria for THF–methanol system: (—) ours, 760 mmHg; (●) Papousek-Pago (*5*), 600 mmHg.

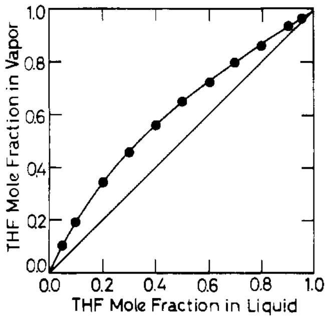

Figure 5. Vapor–liquid equilibria for THF–2-propanol system at 760 mmHg pressure: (—) ours; (●) Shnitko et al. (*8*).

deviations of the boiling points were 0.04, 0.05, 0.06, and 0.09 °C, respectively, for the binary systems of THF–methanol,

Table II. Experimental Boiling-Point Data[a]

	system I			system II			system III			system IV		
x_1	t^* [b]	π^* [c]	t [d]	t^* [b]	π^* [c]	t [d]	t^* [b]	π^* [c]	t [d]	t^* [b]	π^* [c]	t [d]
0.00	63.9	744.7	64.4	77.5	745.3	78.0	81.1	743.2	81.8	96.9	746.1	97.4
0.05	62.7	743.9	63.2	76.1	746.6	76.6	80.3	743.4	80.8	94.0	750.9	94.3
0.10	61.7	742.4	62.3	74.7	745.8	75.2	79.2	743.2	79.7	91.8	750.5	92.1
0.20	60.4	742.1	61.0	72.3	745.4	72.8	76.9	743.9	77.5	87.6	750.6	87.9
0.30	59.6	742.7	60.2	70.4	745.3	70.9	74.8	744.1	75.4	83.5	749.5	83.9
0.40	59.0	741.9	59.7	68.8	745.2	69.3	72.9	738.9	73.4	79.8	749.1	80.2
0.50	58.9	741.5	59.6	67.5	745.3	68.0	70.9	738.6	71.6	76.7	749.1	77.1
0.60	59.0	740.9	59.7	66.5	745.4	67.1	69.4	738.8	70.2	74.0	748.5	74.4
0.70	59.5	740.6	60.3	65.8	745.9	66.3	68.2	738.3	69.0	71.6	749.2	72.0
0.80	60.4	740.3	61.1	65.3	745.8	65.9	66.9	738.2	67.8	69.4	749.2	69.8
0.90	62.1	740.2	62.8	65.2	746.0	65.8	65.9	738.2	66.8	67.4	749.5	67.8
0.95	63.3	739.6	64.1	65.2	746.0	65.8	65.4	738.3	66.3	66.4	749.4	66.8
1.00	65.2	743.9	65.8	65.3	746.6	65.8	64.9	738.3	65.8	65.3	745.8	65.8

[a] System I: THF(1)–methanol(2). System II: THF(1)–ethanol(2). System III: THF(1)–2-propanol(2). System IV: THF(1)–1-propanol(2). [b] t^* = raw data of boiling points, °C. [c] π^* = experimental atmospheric pressure, mmHg. [d] t = boiling points corrected to 760 mmHg pressure, °C.

Table III. Antoine Constants[a]

material	A	B	C
THF(1)	6.99515	1202.290	226.254
methanol(4)	8.00902	1541.861	236.154
ethanol(4)	8.04610	1555.547	222.830
2-propanol(1)	7.74021	1359.517	197.527
1-propanol(1)	7.74416	1437.686	198.463

[a] $\log P/\text{mmHg} = A - B/[t(°\text{C}) + C]$.

Table IV. Wilson Parameters

	system[a]			
Λ	I	II	III	IV
Λ_{12}	0.6661	1.0465	1.4248	1.5245
Λ_{21}	0.6023	0.4758	0.4275	0.4052

[a] System I: THF(1)–methanol(2). System II: THF(1)–ethanol(2). System III: THF(1)–2-propanol(2). System IV: THF(1)–1-propanol(2).

Table V. Vapor–Liquid Equilibria at 760 mmHg Pressure, Evaluated from Wilson Equation[a]

	system I		system II		system III		system IV	
x_1	y_1	t, °C	y_1	t, °C	y_1	t, °C	y_1	t, °C
0.00	0.000	64.5	0.000	78.3	0.000	82.2	0.000	97.2
0.05	0.094	63.2	0.109	76.7	0.098	81.0	0.138	94.6
0.10	0.170	62.3	0.202	75.2	0.186	79.7	0.256	92.2
0.20	0.283	60.9	0.350	72.8	0.339	77.4	0.444	87.7
0.30	0.368	60.2	0.464	70.8	0.466	75.3	0.584	83.8
0.40	0.437	59.8	0.555	69.3	0.572	73.4	0.690	80.2
0.50	0.498	59.6	0.631	68.1	0.661	71.7	0.770	77.1
0.60	0.559	59.8	0.698	67.1	0.737	70.2	0.832	74.4
0.70	0.626	60.2	0.762	66.4	0.805	68.9	0.883	72.0
0.80	0.706	61.1	0.826	65.9	0.868	67.8	0.925	69.8
0.90	0.818	62.8	0.901	65.7	0.931	66.8	0.963	67.9
0.95	0.896	64.1	0.946	65.8	0.964	66.4	0.981	66.9
1.00	1.000	66.0	1.000	66.0	1.000	66.0	1.000	66.0

[a] System I: THF(1)–methanol(2). System II: THF(1)–ethanol(2). System III: THF(1)–2-propanol(2). System IV: THF(1)–1-propanol(2).

-ethanol, -2-propanol, and -1-propanol.

The vapor–liquid equilibrium relations obtained in the present work are listed in Table V and shown in Figure 3. Figure 4 shows the equilibrium relations for the THF–methanol system, in which the previous data (*5*) are those at 600 mmHg pressure. In the THF–2-propanol system, our data agreed fairly well with the previous data (*8*) as shown in Figure 5, with the absolute arithmetic mean difference of 0.0057 mole fraction in vapor composition.

The azeotropic-point determination from only boiling-point measurement seems essentially unreliable, but the azeotropic points evaluated here from the Wilson equation for the THF–methanol and THF–ethanol systems are as follows: for the THF–methanol system, 0.496 mole fraction THF at 59.6 °C [0.497 mole fraction THF at 60.7 °C (*3*)]; for the THF–ethanol system, 0.905 mole fraction THF at 65.7 °C [0.85 mole fraction THF (*3*)]. If one makes a comparison with the previous data (*3*), the agreements of azeotropic composition are excellent for the THF–methanol system, but not so good for THF–ethanol system.

The small ebulliometer shown in the present paper seems powerful for the rapid determination of vapor–liquid equilibria and for experiments with expensive chemicals.

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Glossary

A, B, C	Antoine constants
m	differential value (dt/dP)
P	vapor pressure, mmHg
t	temperature, °C
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Greek Notation

γ	activity coefficient
Λ	Wilson parameter
π	total pressure, mmHg

Subscripts

i	component
1	tetrahydrofuran
2	alcohol

Superscript

•	raw data

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Densities of *n*-Hexane–Aromatic Hydrocarbon Mixtures

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Densities of binary mixtures of *n*-hexane with toluene, ethylbenzene, propylbenzene, and butylbenzene were measured at 298.15 and 323.15 K by using a 10-mL pycnometer and are reported in this paper.

Introduction

The purpose of this paper is to report measurements of the densities of binary mixtures of *n*-hexane with several aromatic hydrocarbons. These measurements were made as part of a

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