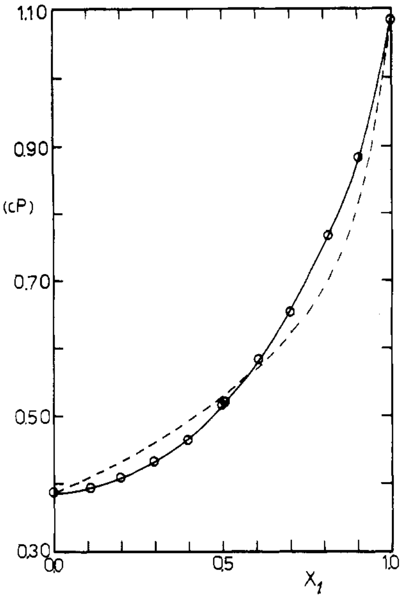

Figure 3. Dynamic viscosities of the ethanol (1)–*n*-heptane (2) mixture. (O) Experimental; (---) calculated by one-parameter GCS method; (—) calculated by the two-parameter GCS method.

between experimental and calculated viscosities of the corresponding binaries.

Seeking an improvement of the performance of the GCS method for the highly nonideal systems (such as the mixtures of ethanol), we considered ψ_{ij} composition dependent according to a van Laar type mixing rule or

$$\psi_{ij} = 1 - \frac{K_{ij}K_{ji}}{x_i'K_{ij} + x_j'K_{ji}} \qquad (15)$$

where

$$x_i' = \frac{x_i}{x_i + x_j} \qquad (16)$$

In general $K_{ij} \neq K_{ji}$. When $K_{ij} = K_{ji}$, ψ_{ij} is, as originally (*1*), independent of composition. The van Laar mixing rule, eq 15, has been chosen from among a number of other types of mixing rules as giving the most satisfactory results. Values of the binary parameters for the ethanol mixtures are reported in Table VI along with the corresponding new average absolute deviations. As observed in Table VI and shown in Figures 1–3, the improvement is significant for the binaries. When these parameters are used in the ternary system benzene–ethanol–*n*-heptane, there is a considerable improvement as shown in Table VII although still the performance of the method for this system is less satisfactory than for the system acetone–isooctane–toluene.

In conclusion, the GCS method of Teja and Rice is a useful tool for estimating the viscosities of multicomponent liquid mixtures. In mixtures containing associated components, however, the method may significantly be improved by using more general mixing rules for the pseudobinary critical parameters such as the van Laar type mixing rule of this work. The introduction of the second binary adjustable parameter is certainly an empirical one. Association effects can be taken into account in a more fundamental way (*7*). Incorporation of thermodynamic association models in models for the viscosity of liquid mixtures is in progress in our laboratory.

Acknowledgment

We are grateful to T. Evangelou and to N. Mamagakis for their collaboration.

Registry No. Benzene, 71-43-2; *n*-heptane, 142-82-5; ethanol, 64-17-5.

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Vapor–Liquid Equilibrium Determination with a Flow-Type Ebulliometer for Six Binary Systems Made of Alcohol and Amine

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Boiling points for the six binary systems made of alcohol (methanol, ethanol, and 2-propanol) and amine (ethylenediamine and dipropylamine) were measured with a flow-type ebulliometer at atmospheric pressure, and their vapor–liquid equilibrium relations were determined by using the Wilson equation.

Introduction

Vapor–liquid equilibria are required for engineering use such as in the design and operation of distillation equipment. Vapor–liquid equilibrium relations can be determined from boiling point curves which are easily obtained rather than the conventional equilibrium measurements. Many researchers proposed some ebulliometers. However, in the general batch-type ebulliometers, it is necessary to correct the difference between the liquid composition at steady state and the feed composition.

The authors (*1*, *2*) previously proposed the apparatus for measuring isobaric dew and bubble points. In the present study, a flow-type ebulliometer was newly constructed. Boiling points were measured with the flow-type ebulliometer for the six binary systems made of alcohol (methanol, ethanol, and 2-propanol) and amine (ethylenediamine and dipropylamine), and

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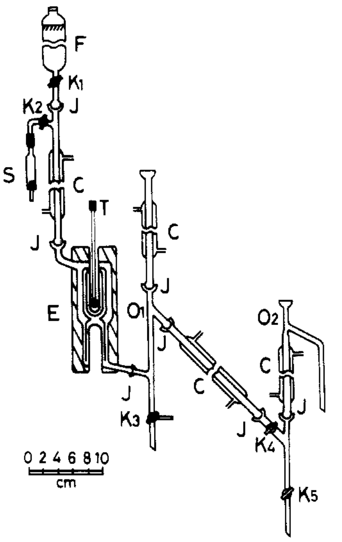

Figure 1. Flow-type ebulliometer: (C) condenser; (E) ebulliometer; (F) feeder; (J) ball joint; (K) cock; (O) overflow tube; (S) silica gel tube; (T) quartz thermometer.

Table I. Physical Properties of Materials Used

material	normal bp, K exptl	normal bp, K lit.	density at 293.15 K, g/cm^3 exptl	density at 293.15 K, g/cm^3 lit.
methanol	337.69	337.68 (*4*)	0.7919	0.7915 (*4*)
ethanol	351.49	351.50 (*4*)	0.7894	0.7894 (*4*)
2-propanol	355.42	355.41 (*4*)	0.7840	0.7851 (*5*)
ethylenediamine	390.29	390.41 (*5*)	0.8984	0.8977 (*6*)
dipropylamine	382.56	382.55 (*8*)	0.7362	0.7387 (*7*)

their vapor-liquid equilibria were determined by using the Wilson equation. Vapor-liquid equilibrium data for those systems are not available in literature.

Experimental Section

The experimental apparatus for the measurement of boiling points is schematically shown in Figure 1. The apparatus is entirely constructed of borosilicate glass. The main parts are an ebulliometer E, feeder F, thermometer T, silica-gel tube S, four condensers C, two overflow tubes O, and five cocks K. The liquid volume in the ebulliometer E is about 25 cm^3. 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.

At the start of experiments, the solution of desired composition was prepared about 100 cm^3 at exact intervals of 0.100 mole fraction in a flask with a stopper by mixing each pure substance which was precisely weighed by use of syringes and an automatic balance, similar to the previous works (*2*, *3*). The reliability of the composition was within ±0.001 mole fraction. Cocks K_2 and K_4 were opened, and cocks K_3 and K_5 were closed. The prepared solution was continuously charged to the ebulliometer through cock K_1 and boiled. The vapor-liquid mixture flashed to the thermometer well in the ebulliometer. The liquid overflowed through the overflow tubes O_1 and O_2. After attainment of steady state, the boiling point was measured with the thermometer T. A Hewlett-Packard 2804A quartz thermometer calibrated by the triple point of water in a reference cell was used for the present experiment. The reliability of the thermometer seems to be ±0.01 K. The steady state was confirmed with the constancy of the boiling point temperature of ±0.01 K. The atmospheric pressures were measured by a Fortin barometer with an accuracy of ±0.01 kPa.

Special grade reagents of alcohols and amines were supplied by Koso Chemical Co. Ltd. and Wako Pure Chemical Industry Co. Ltd., respectively. The reagents were further purified by distillation with a packed column. The physical properties of the materials used are listed in Table I.

Table II. Experimental Boiling Points for Six Binary Systems at 98.66 kPa[a]

mole fracn of alcohol	bp, K I	II	III	IV	V	VI
0.000	389.42	389.42	389.42	381.68	381.68	381.68
0.100	386.46	387.13	386.64	369.91	373.59	374.07
0.200	383.00	384.56	383.85	362.83	368.46	369.77
0.300	378.91	381.39	380.84	357.97	364.85	366.86
0.400	374.60	377.76	377.52	354.29	362.16	364.46
0.500	368.82	373.71	373.99	351.00	359.81	362.40
0.600	362.46	369.22	370.35	348.02	357.91	360.67
0.700	355.39	364.17	366.32	345.15	356.03	359.06
0.800	347.97	359.33	362.03	342.31	354.34	357.57
0.900	341.47	354.41	358.02	339.57	352.58	356.17
1.000	337.02	350.81	354.75	337.02	350.81	354.75

[a] Systems: I, methanol-ethylenediamine; II, ethanol-ethylenediamine; III, 2-propanol-ethylenediamine; IV, methanol-dipropylamine; V, ethanol-dipropylamine; VI, 2-propanol-dipropylamine.

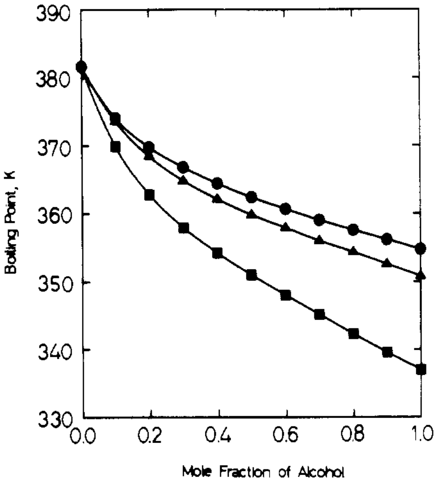

Figure 2. Experimental boiling point curves for systems containing dipropylamine at 98.66 kPa: (■) methanol-dipropylamine; (▲) ethanol-dipropylamine; (●) 2-propanol-dipropylamine.

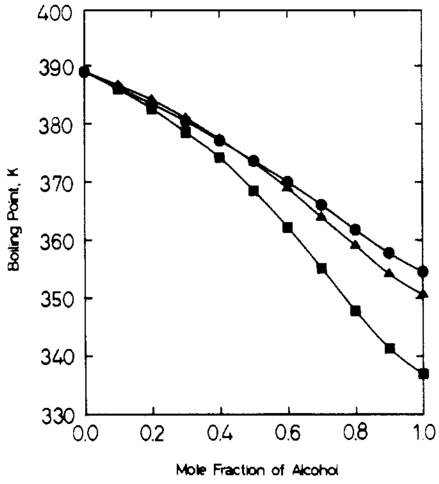

Figure 3. Experimental boiling point curves for systems containing ethylenediamine at 98.66 kPa: (■) methanol-ethylenediamine; (▲) ethanol-ethylenediamine; (●) 2-propanol-ethylenediamine.

Results

The experimental boiling points were corrected from the raw data to those at 98.66 kPa, similar to the previous work (*3*). The boiling points at 98.66 kPa are given in Table II and shown in Figures 2 and 3. The vapor-liquid equilibrium relations were

Table III. Antoine Constants of Materials Used (*10*)

$\log P[\text{kPa}] = A - B/(T[\text{K}] + C)$

material	*A*	*B*	*C*
methanol	7.196 05	1574.99	-34.29
ethanol	7.336 91	1652.05	-41.68
2-propanol	7.241 81	1580.92	-53.54
ethylenediamine	6.249 76	1350.00	-72.15
dipropylamine	6.330 39	1415.40	-55.15

Table IV. Parameters Used for Vapor-Phase Correction

material	P_c, MPa	T_c, K	v, cm^3/mol	R', Å	μ, D	η
methanol (*12*)	7.957	513.20	40.45	1.536	1.66	1.63
ethanol (*12*)	6.383	516.30	58.39	2.250	1.69	1.40
2-propanol (*12*)	4.762	508.40	76.40	2.726	1.66	1.32
ethylenediamine (*13*)	6.292	592.95	66.80	2.629[a]	1.90	0.20[b]
dipropylamine (*13*)	3.141	550.15	137.00	3.978[a]	1.04	0.20[b]

[a] Evaluated from its parachor. [b] Assumed as 0.20.

Table V. Wilson Parameters Obtained for Six Binary Systems at 98.66 kPa

system	Λ_{12}	Λ_{21}	$\lvert\Delta T\rvert_{av}$, K
methanol (1)-ethylenediamine (2)	4.3899	0.7200	0.41
ethanol (1)-ethylenediamine (2)	2.8804	0.8999	0.39
2-propanol (1)-ethylenediamine (2)	3.0129	0.5660	0.23
methanol (1)-dipropylamine (2)	0.3830	1.7226	0.52
ethanol (1)-dipropylamine (2)	0.4400	1.4458	0.16
2-propanol (1)-dipropylamine (2)	0.3562	1.5453	0.08

determined from the experimental boiling point data by using the following Wilson equations (*9*):

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

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

where x, Λ, and γ, respectively, denote the liquid mole fraction, Wilson parameter, and activity coefficient. For the vapor pressures of pure components, the Antoine constants given by Reid et al. (*10*) were used in the present study, as shown in Table III. The vapor-phase corrections were made with Hayden and O'Connell (*11*, *12*), using the parameters shown in Table IV. The association parameter of unlike molecules was evaluated as the arithmetic mean of the constituent pure components. 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, as shown in Table V. The vapor–liquid equilibrium compositions are listed in Table VI and shown in Figures 4 and 5.

The flow-type ebulliometer presented in this study seems effective for the rapid determination of vapor–liquid equilibria and especially useful for odorous chemicals such as amines.

Table VI. Vapor–Liquid Equilibrium Compositions for Six Binary Systems at 98.66 kPa[a]

liquid mole fracn of alcohol	vapor mole fracn of alcohol					
	I	II	III	IV	V	VI
0.100	0.181	0.158	0.174	0.373	0.298	0.282
0.200	0.364	0.325	0.340	0.557	0.461	0.433
0.300	0.538	0.489	0.492	0.674	0.573	0.540
0.400	0.691	0.639	0.627	0.757	0.661	0.627
0.500	0.813	0.765	0.743	0.821	0.734	0.703
0.600	0.900	0.861	0.837	0.872	0.798	0.771
0.700	0.956	0.928	0.908	0.913	0.855	0.834
0.800	0.985	0.969	0.957	0.947	0.908	0.893
0.900	0.997	0.991	0.987	0.976	0.956	0.948

[a] Systems: I, methanol–ethylenediamine; II, ethanol–ethylenediamine; III, 2-propanol–ethylenediamine; IV, methanol–dipropylamine; V, ethanol–dipropylamine; VI, 2-propanol–dipropylamine.

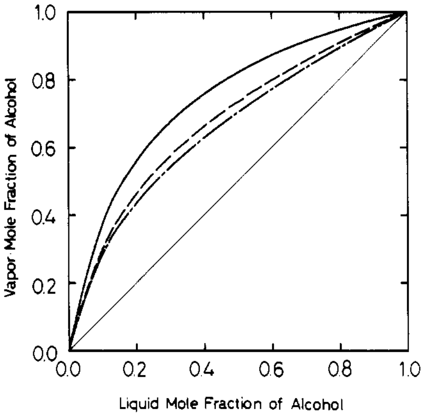

Figure 4. Calculated vapor–liquid equilibrium relations for systems containing dipropylamine at 98.66 kPa: (—) methanol–dipropylamine; (- - -) ethanol–dipropylamine; (— - —) 2-propanol–dipropylamine.

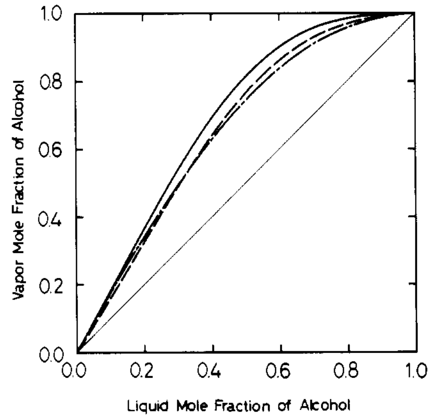

Figure 5. Calculated vapor–liquid equilibrium relations for systems containing ethylenediamine at 98.66 kPa: (—) methanol–ethylenediamine; (- - -) ethanol–ethylenediamine; (— - —) 2-propanol–ethylenediamine.

Glossary

A, *B*, *C*	Antoine constants
P	pressure, kPa
P_c	critical pressure, MPa
R'	mean radius of gyration, Å
T	temperature, K
T_c	critical temperature, K
v	molar volume, cm^3/mol
x	liquid mole fraction
γ	activity coefficient
Λ	Wilson parameter
η	association parameter
μ	molecular dipole moment, D

Subscripts

1, 2	components

Registry No. MeOH, 67-56-1; EtOH, 64-17-5; 2-PrOH, 67-63-0; Pr_2NH, 142-84-7; ethylenediamine, 107-15-3.

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Ebulliometric Measurement of Vapor–Liquid Equilibria for Four Binary Systems: Methanol + Silicon Tetramethoxide, Methanol + Silicon Tetraethoxide, Ethanol + Silicon Tetramethoxide, and Ethanol + Silicon Tetraethoxide

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Vapor pressures of silicon tetramethoxide and silicon tetraethoxide were measured with a small ebulliometer. Boiling points for the four binary systems made of alcohol (methanol and ethanol) and alkoxide (silicon tetramethoxide and silicon tetraethoxide) were further measured at 760 and 450 mmHg pressures, and their vapor–liquid equilibrium relations were determined by using the Wilson equation.

Introduction

Vapor–liquid equilibria are required for engineering use such as in the design and operation of distillation equipment. Vapor–liquid equilibrium relations can be determined from boiling point curves which are easily obtained rather than the conventional equilibrium measurements.

The authors (*1–3*) previously proposed the apparatus for measuring isobaric boiling points. In the present study, vapor pressures of silicon tetramethoxide and silicon tetraethoxide were measured and correlated with the Antoine equation. Vapor pressures of those substances are not available in the literature. Boiling points were further measured for four binary systems made of alcohol (methanol and ethanol) and alkoxide (silicon tetramethoxide and silicon tetraethoxide) at 760 and 450 mmHg pressures, and their vapor–liquid equilibria were indirectly determined by using the Wilson equation. Vapor–liquid equilibrium data for those alcohol–alkoxide systems are not available in literature.

Experimental Section

The experimental apparatus for the measurement of boiling points is schematically shown in Figure 1. The ebulliometer E is essentially the same as the previous ones (*2*, *3*). The liquid volume in the ebulliometer E is about 25 cm^3. 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. The boiling vapor–liquid mixture flashes to the thermometer well in the ebulliometer.

At the start of experiments, the solution of desired composition was prepared by mixing each pure substance which was weighed by use of syringes and an automatic balance, similar to the previous works (*2*, *3*). The reproducibility of the composition was within 0.001 mole fraction. Cocks K_1, K_2, K_3, and K_4 were opened, and K_5, K_6, K_7, and solenoid valve F were closed. The system pressure was reduced to the desired pressure. Next, cocks K_2 and K_4 were closed, and the pressue was kept constant with the manostat G. The prepared solution was then boiled.

After attainment of steady state, the boiling point was measured with the thermometer T. The Hewlett-Packard 2804A quartz thermometer calibrated by the triple point of water in a reference cell was used for the present experiment. The reproducibility of the thermometer was ±0.01 K. The experimental pressures were controlled with a precision of ±0.03 mmHg in the present work. The pressures were measured by the Ruska 3850 quartz bourdon gauge with a precision of ±0.02 mmHg.

Special grade reagents of alcohols supplied by the Wako Pure Chemical Industry Co. Ltd. were further purified by distillation. Special grade reagents of alkoxides supplied by the High Purity Chemical Laboratory Co. Ltd. with the guarantee of 99.999% purity were used without further purification. The physical properties of the materials used are listed in Table I.

Results

The experimental vapor pressures of silicon tetramethoxide and silicon tetraethoxide are given in Table II. Those data were correlated by using the Antoine equation. The Antoine constants of those alkoxides were determined as shown in Table III.

The experimental boiling points for four binary systems at 760 and 450 mmHg pressures are given in Table IV. The vapor–liquid equilibrium relations were determined from the experimental boiling point data by using the following Wilson equations (*5*):

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

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

where x, Λ, and γ, respectively, denote the liquid mole fraction,

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