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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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Table I. Physical Properties of Materials Used

material	normal bp, K		density at 298.15 K, g/cm^3		refract. index at 298.15 K	
	exptl	lit. (*4*)	exptl	lit. (*4*)	exptl	lit. (*4*)
methanol	337.69	337.65	0.7870	0.7865	1.3267	1.3265
ethanol	351.45	351.42	0.7855	0.7850	1.3595	1.3596
silicon tetramethoxide	393.27		1.0210		1.3672	
silicon tetraethoxide	437.67		0.9290		1.3815	

Table II. Experimental Vapor Pressures of Silicon Tetramethoxide and Silicon Tetraethoxide

temp, K	vapor press., mmHg	temp, K	vapor press., mmHg
	Silicon Tetramethoxide		
393.27	760.07	379.60	500.23
392.38	740.02	378.35	479.94
391.49	720.11	376.96	460.09
390.42	700.06	376.20	450.00
389.53	680.00	375.56	440.03
388.57	659.99	374.14	420.04
387.55	639.98	372.72	399.98
386.49	619.94	371.09	380.43
385.45	599.95	369.43	360.15
384.25	580.06	367.84	340.06
383.13	559.81	366.02	320.02
381.97	540.14	364.14	300.10
380.77	520.05		
	Silicon Tetraethoxide		
437.73	761.18	421.85	499.61
436.69	740.99	420.42	479.65
435.66	720.86	418.91	459.92
434.46	700.58	417.98	450.00
433.38	680.06	417.40	439.89
432.28	660.18	415.83	420.26
431.16	640.21	413.85	399.68
429.72	619.25	412.04	379.60
428.63	598.80	410.30	359.40
427.52	580.68	408.35	339.02
426.19	558.98	406.50	319.70
424.94	539.79	404.24	299.77
423.58	519.67		

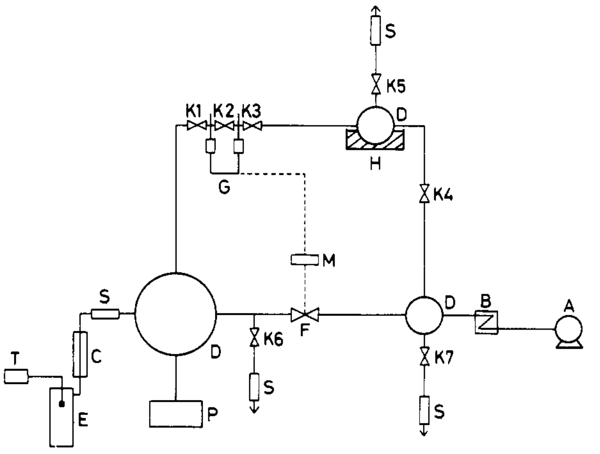

Figure 1. Experimental apparatus for measuring isobaric boiling points: (A) vacuum pump; (B) trap; (C) condenser; (D) reservoir; (E) ebulliometer; (F) solenoid valve; (G) manostat; (H) thermostat; (K) cock; (M) relay; (P) pressure gauge; (S) silica gel; (T) thermometer.

Table III. Antoine Constants for Silicon Tetramethoxide and Silicon Tetraethoxide

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

substance	*A*	*B*	*C*	$\lvert\Delta P/P\rvert_{av}$
silicon tetramethoxide	7.22669	1489.930	-50.469	0.0012
silicon tetraethoxide	7.30981	1774.343	-37.118	0.0023

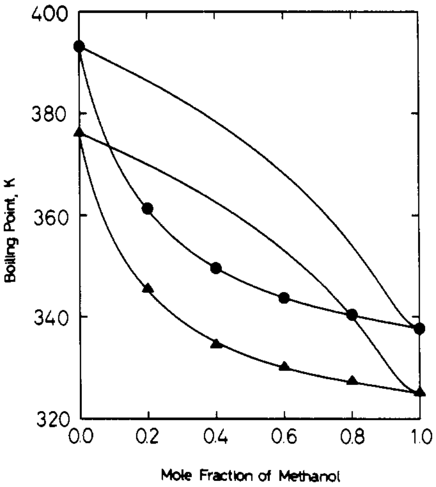

Figure 2. Experimental boiling point curves for methanol–silicon tetramethoxide: (●) 760 mmHg; (▲) 450 mmHg; (—) Wilson equation.

Table IV. Experimental Boiling Points for Four Binary Systems at 760 and 450 mmHg[a]

liquid mole fracn of alcohol	bp, K							
	I		II		III		IV	
	760 mmHg	450 mmHg	760 mmHg	450 mmHg	760 mmHg	450 mmHg	760 mmHg	450 mmHg
0.000	393.27	376.20	437.67	417.98	393.27	376.20	437.67	417.98
0.200	361.35	345.58	366.32	352.01	371.29	355.24	382.95	367.07
0.400	349.66	334.62	352.37	337.65	361.87	347.06	369.32	353.48
0.600	343.75	330.18	344.93	331.19	356.81	343.06	360.45	346.27
0.800	340.46	327.40	341.22	328.11	353.76	340.61	355.60	342.42
1.000	337.69	325.15	337.69	325.15	351.48	338.90	351.48	338.90

[a] Systems: I, methanol–silicon tetramethoxide; II, methanol–silicon tetraethoxide; III, ethanol–silicon tetramethoxide; IV, ethanol–silicon tetraethoxide.

Table V. Wilson Parameters Obtained for Four Binary Systems

system		760 mmHg			450 mmHg		
compd 1	compd 2	Λ_{12}	Λ_{21}	$\lvert\Delta T\rvert_{av}$, K	Λ_{12}	Λ_{21}	$\lvert\Delta T\rvert_{av}$, K
methanol	silicon tetramethoxide	1.2921	0.2305	0.08	1.1763	0.2249	0.23
methanol	silicon tetraethoxide	1.1364	0.2484	0.16	1.3112	0.1589	0.21
ethanol	silicon tetramethoxide	1.2692	0.3076	0.06	1.0674	0.3404	0.09
ethanol	silicon tetraethoxide	1.0664	0.5187	0.30	1.3660	0.2735	0.13

Table VI. Calculated Vapor-Liquid Equilibrium Compositions for Four Binary Systems at 760 and 450 mmHg[a]

liquid mole fracn of alcohol	vapor mole fracn of alcohol							
	I		II		III		IV	
	760 mmHg	450 mmHg	760 mmHg	450 mmHg	760 mmHg	450 mmHg	760 mmHg	450 mmHg
0.100	0.535	0.562	0.820	0.826	0.411	0.432	0.706	0.716
0.200	0.712	0.731	0.911	0.915	0.594	0.608	0.838	0.847
0.300	0.799	0.812	0.943	0.947	0.699	0.705	0.893	0.901
0.400	0.851	0.859	0.960	0.963	0.768	0.768	0.924	0.930
0.500	0.886	0.890	0.970	0.973	0.818	0.813	0.944	0.948
0.600	0.911	0.913	0.977	0.979	0.857	0.849	0.958	0.961
0.700	0.931	0.931	0.982	0.984	0.889	0.880	0.970	0.971
0.800	0.949	0.947	0.987	0.988	0.920	0.911	0.980	0.980
0.900	0.969	0.967	0.992	0.992	0.953	0.947	0.990	0.988

[a] Systems: I, methanol-silicon tetramethoxide; II, methanol-silicon tetraethoxide; III, ethanol-silicon tetramethoxide; IV, ethanol-silicon tetraethoxide.

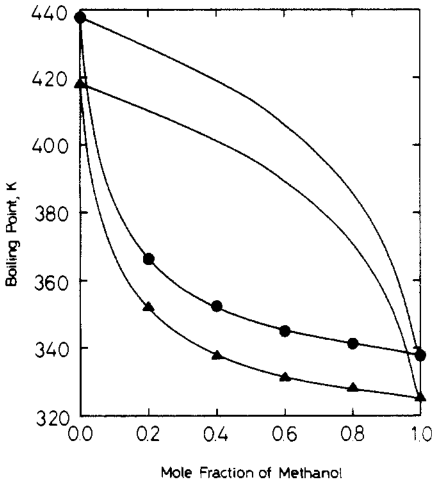

Figure 3. Experimental boiling point curves for methanol-silicon tetraethoxide: (●) 760 mmHg; (▲) 450 mmHg; (—) Wilson equation.

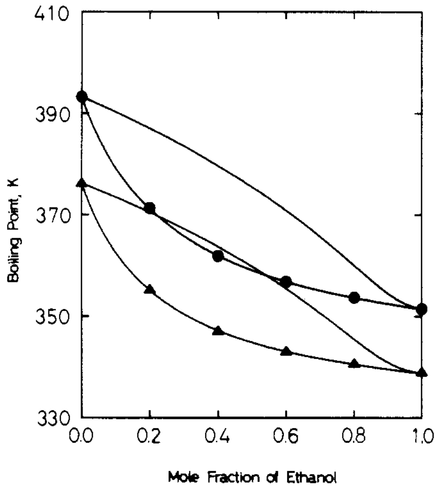

Figure 4. Experimental boiling point curves for ethanol-silicon tetramethoxide: (●) 760 mmHg; (▲) 450 mmHg; (—) Wilson equation.

Wilson parameter, and activity coefficient. For the vapor pressures of alcohols, the Antoine constants given by Boublik et al. (*6*) were used in the present study.

Assuming that vapor phase is an ideal gas, 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 calculated vapor-liquid equilibrium compositions are listed in Table VI and shown in Figures 2-5. Figure 6 shows the calculated vapor-liquid equilibrium relations of four binary alcohol-alkoxide systems at 760 mmHg pressure, using the Wilson equation.

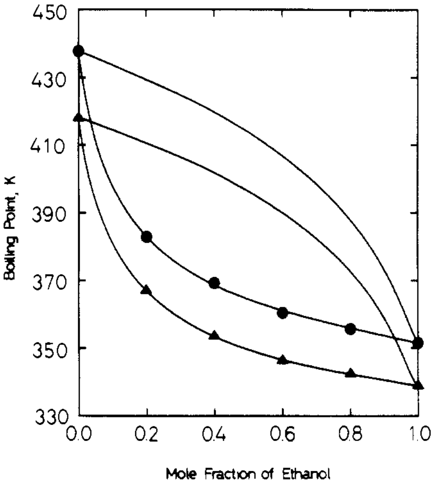

Figure 5. Experimental boiling point curves for ethanol-silicon tetraethoxide: (●) 760 mmHg; (▲) 450 mmHg; (—) Wilson equation.

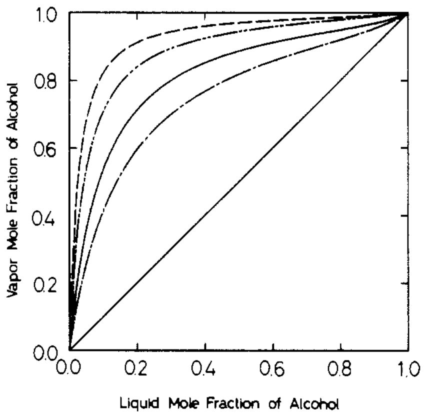

Figure 6. Calculated vapor-liquid equilibria for four binary systems at 760 mmHg: (—) methanol-silicon tetramethoxide; (- - -) methanol-silicon tetraethoxide; (- - -) ethanol-silicon tetramethoxide; (- - - -) ethanol-silicon tetraethoxide.

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Glossary

A, *B*, *C*	Antoine constants
P	pressure, mmHg
T	temperature, K
x	liquid mole fraction
γ	activity coefficient
Λ	Wilson parameter

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Subscripts

1, 2 components

Registry No. MeOH, 67-56-1; EtOH, 64-17-5; $(MeO)_4Si$, 681-84-5; $(EtO)_4Si$, 78-10-4.

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Vapor–Liquid Equilibrium of 1,3-Dioxolane Systems

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We report here the vapor–liquid equilibrium of 1,3-dioxolane and of binary mixtures of 1,3-dioxolane separately with cyclohexane at 313.15 and 333.15 K, with heptane at 313.15 and 343.15 K, with water at 318.15 and 343.15 K, with ethanol at 313.15 and 338.15 K, and with chloroform at 308.15 and 323.15 K. These data are correlated with five liquid activity coefficient models using the maximum likelihood parameter estimation method with a correlation for nonideal vapor-phase behavior.

Introduction

Cyclic ethers are frequently used as solvents in chemical industry because of their unique physicochemical nature. Tetrahydrofuran has a single cyclic ether group, 1,4-dioxane has two cyclic ether groups separated by two methylene groups, while 1,3-dioxolane has two cyclic ether groups separated by one methylene group. Vapor–liquid equilibrium (VLE) data have already been published for mixtures of tetrahydrofuran (*1*, *2*) and of 1,4-dioxane (*3*) with alkanes, water, and chloroform. We measured VLE of mixtures containing 1,3-dioxolane in order to obtain liquid activity coefficients for these mixtures which is of inherent interest and also of use in testing proximity effects in current group contribution activity coefficient models (which will be done elsewhere.) Five binary mixtures were measured, each at two isotherms: the VLE of 1,3-dioxolane with cyclohexane at 313.15 and 333.15 K, with heptane at 313.15 and 343.15 K, with water at 318.15 and 343.15 K, with ethanol at 313.15 and 338.15 K, and with chloroform at 308.15 and 323.15 K.

Experiments

The experimental equipment and operating procedures have been described in detail previously (*4*). The VLE measurements were done with a Stage-Muller dynamic still. The temperature was measured with a platinum resistance thermometer (Rosemount Model 162N) accurate to 0.02 K with a resolution of 0.001 K. Pressures were measured with an accuracy of 0.02 kPa by using a Wallace-Tiernan Model FA-187 precision mercury manometer. Vapor and liquid equilibrium samples were analyzed by using a Hewlett-Packard Model 5730 gas chromatograph with a Model 3390 integrator, after calibration with gravimetrically prepared samples. The compositions determined in this way are accurate to better than 0.005 in mole fraction.

Table I. Pure Component Vapor Pressure of 1,3-Dioxolane ($C_3H_6O_2$)

temp, K	press., kPa	temp, K	press., kPa
304.443	18.018	329.590	51.609
304.460	18.025	333.294	59.328
308.195	21.373	337.050	68.052
313.343	26.793	340.606	77.295
317.920	32.478	343.290	84.772
321.450	37.525	347.540	97.959
325.525	44.144		

Table II. Antoine Constants Used in This Work

$$\log P(\text{kPa}) = A - \frac{B}{T(^\circ\text{C}) + C}$$

component	*A*	*B*	*C*	temp range, °C
1,3-dioxolane	6.23182	1236.70	217.235	30–75
cyclohexane	6.15159	1301.67	233.445	20–80
heptane	5.90871	1196.68	208.230	20–100
water	7.21358	1739.35	234.100	40–49
water	7.10946	1678.948	228.970	70–79
ethanol	7.16879	1552.60	222.419	30–78
chloroform	5.96288	1106.94	218.552	30–60

In this study 1,3-dioxolane, cyclohexane, heptane, and chloroform were of Gold Label quality from Aldrich Chemical Co. and were used as received. The water used was filtered, distilled, and deionized. Ethanol is 200-proof dehydrated alcohol from U.S. Industrial Chemicals Corp. The vapor pressures of cyclohexane, heptane, chloroform, water, and ethanol agree to within 0.1 kPa with literature values (*5*). The vapor pressure of 1,3-dioxolane that we measured is slightly different from the one data set reported (*5*). However, our measured vapor pressure data for 1,3-dioxolane, listed in Table I, are not only better fit with the Antoine equation than the other measurements, but also are in better agreement with the reported normal boiling point (*6*). Consequently, we believe our measurements to be of high accuracy. The Antoine constants that we determined from our vapor pressure measurements are listed in Table II. The binary isothermal VLE data we measured are listed in Table III. These data satisfy thermodynamic consistency tests (*7*).

Results and Discussion

We correlated our measured vapor–liquid equilibrium data with five liquid activity coefficient models using the maximum likelihood parameter estimation method, with a nonideal vapor phase correction using second virial coefficients obtained from the correlation of Hayden and O'Connell (*8*). The second virial coefficients we used are listed in Table IV. The experimental

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