Ebulliometric Determination of Vapor−Liquid Equilibria for Methanol + Ethanol + Dimethyl Carbonate

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Boiling point data for the ternary system methanol + ethanol + dimethyl carbonate and its constituent binary systems were measured from 40.00 to 93.32 kPa using a modified Swietoslawski-type ebulliometer. Experimental data for the binary systems were correlated using the Wilson equation to determine vapor−liquid equilibria (VLE). The Wilson equation was also applied to the ternary system to predict VLE with parameters from the binary mixtures. Comparison between predicted and experimental boiling points for the ternary system showed that the Wilson equation provided useful estimates. The valley line, which was found in this system, was estimated using the Wilson binary parameters.

Introduction

Dimethyl carbonate (DMC) is a useful solvent, used as a starting material in the synthesis of polycarbonates and as a reactant in the production of a number of chemical products. Therefore, DMC is often present in a mixture with other components. However, available data on the properties of mixtures containing DMC are not completely satisfactory. The present work forms part of a program involved in the study of the thermodynamic behavior of mixtures containing DMC.

In this study, we determined vapor−liquid equilibria (VLE) of such mixtures. For this purpose, an ebulliometric method, which is frequently useful for multicomponent systems, was adopted. Boiling point data were measured for the ternary system methanol + ethanol + DMC and for the three constituent binary systems methanol + ethanol, ethanol + DMC, and methanol + DMC at 40.00, 53.33, 66.66, 79.99, and 93.32 kPa (300, 400, 500, 600, and 700 mmHg) using a modified Swietoslawski-type ebulliometer. VLE data for the methanol + ethanol + DMC system are not available in the literature.[1] Binary azeotropic data were also determined from boiling point data of the constituent binary systems methanol + DMC and ethanol + DMC.

Experimental binary boiling points were correlated using the Wilson equation.[2] Then, prediction for the ternary system was attempted by the Wilson equation using parameters from the binary mixture. Valleys were observed from the behavior of the predicted tie lines at all pressures. A valley is defined as the curve that divides patterns of vapor−liquid tie lines.[3,4] Put another way, the valley is also the boundary distillation line. In this paper, the valley of the methanol + ethanol + DMC system was estimated using the Wilson binary parameters at appropriate pressures.

Experimental Section

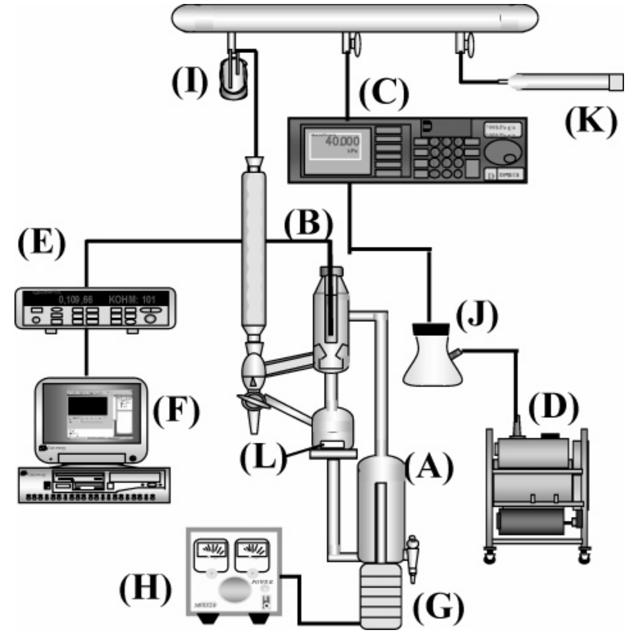

Figure 1. Schematic diagram of the experimental apparatus: A, ebulliometer; B, thermometer; C, pressure controller (DPI515); D, vacuum pump; E, data logger; F, computer; G, stick heater; H, voltage controller; I, vapor trap; J, oil trap; K, silica gel; L, stirrer chip.

Table 1. Normal Boiling Points (T_b) and Densities (ρ) of the Components

component	T_b/K exptl	T_b/K lit.	ρ (298.15 K)/kg·m^{-3} exptl	ρ (298.15 K)/kg·m^{-3} lit.
methanol	337.65	337.696[a]	786.67	786.37[a]
ethanol	351.44	351.443[a]	785.23	784.93[a]
dimethyl carbonate	363.39	363.60[b]	1063.38	1063.28[b]

[a] Ref 5. [b] Ref 6.

Apparatus and Procedures. A modified Swietoslawski-type ebulliometer was used to measure boiling points. The schematic diagram of the experimental apparatus is shown in Figure 1. The apparatus was composed of an ebulliometer, a pressure controlling circuit, and a computer to analyze data. Equilibrium temperatures were measured with a calibrated platinum resistance thermometer. Reading accuracy of the thermometer was estimated to be ± 0.01 K. Pressure in the apparatus was established by the pressure controller DPI515 supplied by Druck Co., with an accuracy of ± 0.03 kPa.

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Table 2. Experimental Boiling Points, Liquid Phase, Mole Fraction (x_1), and Temperature (T) for the Three Binary Systems

	T/K						T/K				
x_1	40.00/kPa	53.33/kPa	66.66/kPa	79.99/kPa	93.32/kPa	x_1	40.00/kPa	53.33/kPa	66.66/kPa	79.99/kPa	93.32/kPa
Methanol (1) + Ethanol (2)											
0.000	329.70	336.11	341.28	345.65	349.45	0.559	321.17	327.65	332.88	337.29	341.12
0.051	328.84	335.26	340.44	344.82	348.63	0.607	320.54	327.00	332.23	336.64	340.48
0.099	328.03	334.45	339.65	344.04	347.85	0.655	319.92	326.38	331.61	336.01	339.85
0.152	327.19	333.63	338.83	343.21	347.04	0.702	319.33	325.79	331.02	335.42	339.25
0.200	326.39	332.83	338.05	342.44	346.26	0.751	318.72	325.17	330.40	334.80	338.63
0.245	325.72	332.19	337.39	341.79	345.62	0.815	317.94	324.39	329.61	334.00	337.83
0.294	324.96	331.44	336.65	341.06	344.87	0.851	317.51	323.96	329.17	333.57	337.39
0.350	324.14	330.59	335.82	340.22	344.06	0.900	316.94	323.38	328.59	332.99	336.81
0.397	323.44	329.91	335.12	339.53	343.37	0.948	316.40	322.84	328.04	332.44	336.25
0.447	322.71	329.19	334.41	338.82	342.66	1.000	315.87	322.25	327.45	331.84	335.66
0.503	321.94	328.41	333.63	338.03	341.86						
Ethanol (1) + Dimethyl Carbonate (2)											
0.000	336.68	344.38	350.66	356.01	360.68	0.549	325.01	331.86	337.39	342.09	346.18
0.057	332.79	340.41	346.62	351.91	356.51	0.599	324.96	331.77	337.27	341.95	345.99
0.104	330.42	337.90	343.99	349.22	353.77	0.650	324.98	331.75	337.24	341.87	345.90
0.152	328.96	336.32	342.36	347.44	351.95	0.700	325.05	331.79	337.25	341.86	345.88
0.204	327.70	334.95	340.87	345.89	350.29	0.752	325.24	331.96	337.40	341.98	345.98
0.255	326.88	334.05	339.87	344.84	349.17	0.813	325.59	332.28	337.70	342.27	346.25
0.303	326.28	333.34	339.07	343.96	348.25	0.845	325.89	332.57	337.97	342.52	346.48
0.357	325.79	332.80	338.50	343.32	347.55	0.898	326.61	333.23	338.59	343.11	347.04
0.405	325.42	332.34	337.97	342.74	346.89	0.946	327.71	334.29	339.61	344.05	347.94
0.458	325.25	332.14	337.75	342.48	346.62	1.000	329.70	336.11	341.28	345.65	349.45
0.503	325.08	331.95	337.51	342.22	346.34						
Methanol (1) + Dimethyl Carbonate (2)											
0.000	336.68	344.38	350.66	356.01	360.68	0.696	314.64	321.23	326.56	331.08	335.01
0.106	325.27	332.74	338.83	344.06	348.58	0.748	314.50	321.06	326.38	330.87	334.77
0.203	320.51	327.65	333.53	338.56	342.90	0.797	314.42	320.95	326.25	330.73	334.63
0.300	318.06	325.02	330.69	335.52	339.72	0.845	314.41	320.94	326.22	330.68	334.56
0.397	316.62	323.44	328.98	333.69	337.80	0.899	314.56	321.06	326.33	330.77	334.64
0.495	315.70	322.42	327.87	332.49	336.51	0.948	314.92	321.40	326.63	331.06	334.90
0.592	315.08	321.73	327.11	331.66	335.63	1.000	315.74	322.17	327.37	331.75	335.56
0.655	314.81	321.42	326.78	331.31	335.25						

For our measurements, a mixture (ca. 160 cm^3) with known constituents was charged into the ebulliometer. The ebulliometer was connected to the vacuum line, and the system pressure was set to the desired pressure by using the pressure controller. At this stage, the mixture was brought to the boil. Attainment of steady state was confirmed by varying the temperature within ± 0.01 K per minute. For the same mixture, boiling point measurements were performed at progressively higher system pressures. The amount of vapor hold-up was estimated from counting droplets of condensed vapor after withdrawing the heater from the boiler of the ebulliometer. For this work, the ratio of the amount of vapor hold-up to that of the initially charged liquid was found to be less than 2.0×10^{-4}. Therefore, the effect of the vapor hold-up was negligible.

Materials. All chemicals were supplied from Wako Pure Chem. Ind. Ltd, Japan. Special grade methanol and ethanol were dried with molecular sieves 3A, and first grade DMC was dried with molecular sieves 4A. The purities of the materials were checked by gas chromatography and were found to be better than 99.9 mol %. Purity was further confirmed by measuring densities and normal boiling points, which agreed well with values from the literature, as shown in Table 1.

Results and Discussion

Binary Systems. Table 2 and Figures 2 to 4 present experimental boiling point data from 40.00 to 93.32 kPa for the three constituent binary systems of methanol + ethanol, ethanol + DMC, and methanol + DMC. The two binary systems methanol + DMC and ethanol + DMC formed minimum

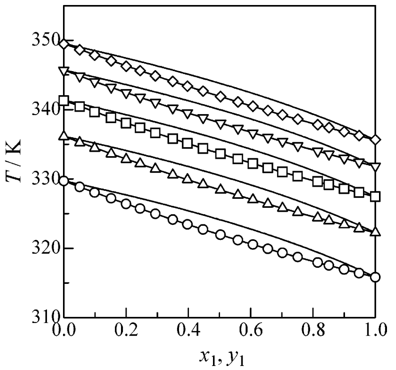

Figure 2. Temperature−composition relationship for the methanol (1) + ethanol (2) system: ○, 40.00 kPa; △, 53.33 kPa; □, 66.66 kPa; ▽, 79.99 kPa; ◇, 93.32 kPa; −, Wilson equation.

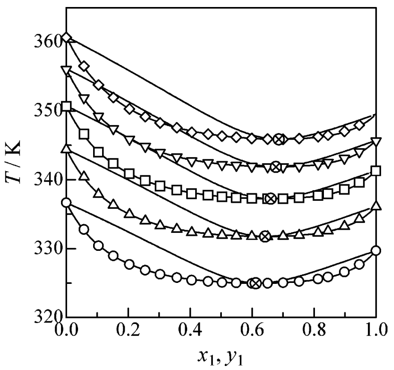

Figure 3. Temperature−composition relationship for the ethanol (1) + DMC (2) system: ○, 40.00 kPa; △, 53.33 kPa; □, 66.66 kPa; ▽, 79.99 kPa; ◇, 93.32 kPa; ⊗, azeotropic point; −, Wilson equation.

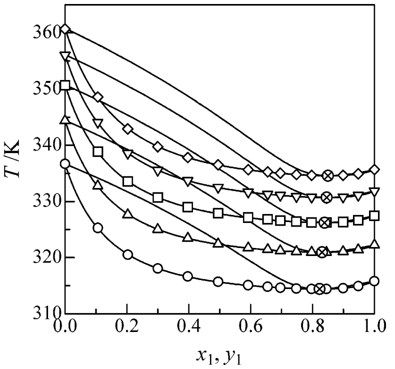

Figure 4. Temperature−composition relationship for the methanol (1) + DMC (2) system: ○, 40.00 kPa; △, 53.33 kPa; □, 66.66 kPa; ▽, 79.99 kPa; ◇, 93.32 kPa; ⊗, azeotropic point; —, Wilson equation.

Table 3. Azeotropic Temperature T_{az} and Composition x_{1az} in Mole Fraction for Ethanol + Dimethyl Carbonate and Methanol + Dimethyl Carbonate Systems with the Literature Values

P/kPa	T_{az}/K	x_{1az}	ref
Ethanol (1) + Dimethyl Carbonate (2)			
40.00	324.97	0.612	this work
53.33	331.76	0.642	this work
66.66	337.24	0.660	this work
79.99	341.86	0.677	this work
93.32	345.88	0.686	this work
101.32	346.65	0.6154	7
101.3	348.46	0.7055	8
Methanol (1) + Dimethyl Carbonate (2)			
40.00	314.41	0.823	this work
53.33	320.94	0.831	this work
66.66	326.22	0.839	this work
79.99	330.69	0.846	this work
93.32	334.57	0.850	this work
101.32	335.85	0.8677	7
101.3	336.90	0.8503	8
102.73	337.35	0.8500	9

boiling azeotropes. Azeotropic points were determined from experimental data near azeotropic points using the following equations:

$$T = a_0 + a_1x_1 + a_2x_1^2 + a_3x_1^3 + a_4x_1^4 \tag{1}$$

$$\left(\frac{\partial T}{\partial x_1}\right) = a_1 + 2a_2x_{1az} + 3a_3x_{1az}^2 + 4a_4x_{1az}^3 = 0 \tag{2}$$

where the subscript az indicates the azeotrope. The parameters a_0−a_4 of eq 1 were determined by the least-squares method. Azeotropic composition and temperature for the binary systems ethanol + DMC and methanol + DMC are shown in Table 3.

For the ethanol + DMC and methanol + DMC systems, there are four and three isobaric VLE data sets available in the literature, respectively.[1] However, these data were measured from 95.8 to 101.3 kPa. On the other hand, the methanol + ethanol system has been quoted in 12 literature data sets at isobaric conditions from 100.898 to 506.625 kPa.[1] Thus, isobaric VLE data for these three binary systems did not cover pressures from 40.00 to 93.32 kPa, which were investigated in the present paper. Azeotropic composition and temperature for the binary systems ethanol + DMC and methanol + DMC are also shown in Table 3 and compared with those reported in the literature[7−9] in Figures 5 and 6. As these figures indicate, the behavior of azeotropic point agree with those of literature values, which were reported by Rodríguez et al.[8] for the ethanol + DMC system and by Rodríguez et al.[8] and Yunhai et al.[9] for the methanol + DMC system, respectively.

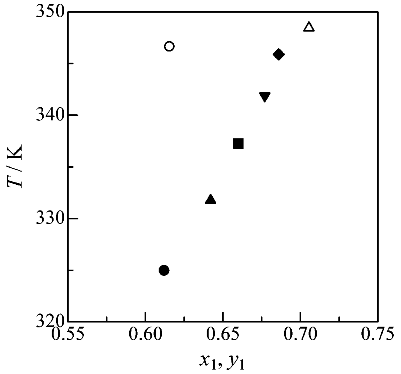

Figure 5. Azeotropic temperature T_{az} and composition x_{1az} in mole fraction on the basis of the experimental boiling point data with the literatures for the ethanol (1) + DMC (2) system. This work: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ◆, 93.32 kPa. Literature: ○, ref 7 (101.32 kPa); △, ref 8 (101.3 kPa).

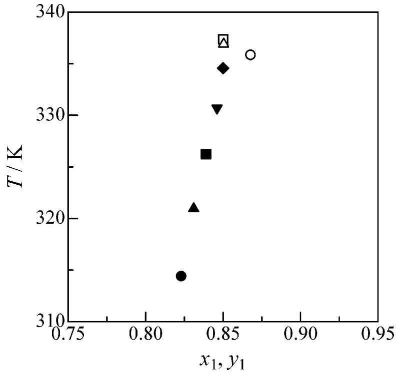

Figure 6. Azeotropic temperature T_{az} and composition x_{1az} in mole fraction on the basis of the experimental boiling point data with the literatures for the methanol (1) + DMC (2) system. This work: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ◆, 93.32 kPa. Literature: ○, ref 7 (101.32 kPa); △, ref 8 (101.3 kPa); △, ref 9 (102.73 kPa).

Ternary System. Boiling points for the ternary system methanol + ethanol + DMC were measured at 108 points of liquid composition at each pressure. Experimental results are listed in Table 4.

Data Reduction and Prediction

In this work, experimental boiling point data were correlated using the Wilson equation.[2] For this purpose, the following equation was used as the criterion of the VLE:

$$\gamma_i = \frac{Py_i}{x_iP_i^s} \tag{3}$$

Equation 3 is applicable to low-pressure equilibrium systems with an assumed ideal vapor phase. The symbols x_i and y_i are the equilibrium mole fractions of component i in the liquid and vapor phases, respectively. γ_i is the liquid-phase activity coefficient of component i, P is the total pressure, and P_i^s is the saturated vapor pressure of pure component i. Saturated vapor pressures for alcohols were calculated with the equation using the coefficients given in ref 10:

$$\log P_i^s = A + \frac{B}{T} + C\log T + DT + ET^2 \tag{4}$$

For DMC, the following equation was used:

$$\log P_i^s = A + \frac{B}{T} + C\log T + DT^E \tag{5}$$

Table 4. Experimental Boiling Points, Liquid Phase, Mole Fraction (x_i), Temperature (T) for Methanol (1) + Ethanol (2) + Dimethyl Carbonate (3) System

		T/K							T/K				
x_1	x_2	40.00/kPa	53.33/kPa	66.66/kPa	79.99/kPa	93.32/kPa	x_1	x_2	40.00/kPa	53.33/kPa	66.66/kPa	79.99/kPa	93.32/kPa
0.052	0.853	325.97	332.62	337.97	342.50	346.45	0.500	0.350	318.71	325.31	330.64	335.15	339.07
0.050	0.665	324.31	331.05	336.49	341.08	345.09	0.500	0.300	318.18	324.79	330.13	334.64	338.58
0.050	0.641	324.25	331.01	336.46	341.08	345.10	0.500	0.250	317.73	324.36	329.72	334.24	338.19
0.050	0.617	324.20	330.95	336.40	341.00	344.99	0.500	0.200	317.34	323.98	329.35	333.87	337.82
0.050	0.594	324.16	330.92	336.39	340.98	344.99	0.500	0.150	316.95	323.60	328.99	333.54	337.48
0.050	0.570	324.11	330.88	336.35	340.96	344.97	0.500	0.100	316.59	323.25	328.66	333.23	337.20
0.103	0.852	326.38	332.94	338.25	342.74	346.63	0.500	0.050	316.23	322.90	328.29	332.85	336.83
0.102	0.808	325.28	331.90	337.25	341.79	345.77	0.501	0.025	315.98	322.68	328.11	332.71	336.72
0.100	0.720	324.13	330.81	336.22	340.78	344.74	0.600	0.380	319.96	326.46	331.70	336.15	339.99
0.101	0.629	323.51	330.22	335.64	340.22	344.21	0.599	0.361	319.39	325.91	331.19	335.64	339.50
0.100	0.540	323.21	329.93	335.36	339.92	343.92	0.600	0.320	318.49	325.05	330.34	334.81	338.70
0.100	0.450	323.06	329.83	335.28	339.87	343.86	0.600	0.280	317.85	324.41	329.71	334.20	338.10
0.100	0.360	323.07	329.90	335.43	340.08	344.05	0.600	0.240	317.33	323.92	329.25	333.74	337.66
0.099	0.270	323.15	330.01	335.47	340.15	344.21	0.600	0.200	316.89	323.49	328.82	333.32	337.24
0.100	0.180	323.46	330.39	335.98	340.68	344.81	0.601	0.160	316.52	323.12	328.45	332.97	336.89
0.101	0.090	324.16	331.25	337.08	342.05	346.41	0.600	0.120	316.16	322.78	328.13	332.65	336.58
0.104	0.045	324.64	332.04	338.10	343.22	347.66	0.600	0.080	315.83	322.45	327.80	332.34	336.28
0.149	0.766	324.66	331.26	336.60	341.13	345.06	0.600	0.040	315.50	322.12	327.49	332.03	336.00
0.198	0.762	325.07	331.64	336.95	341.41	345.30	0.600	0.020	315.32	321.94	327.31	331.85	335.82
0.197	0.723	324.01	330.62	335.94	340.45	344.37	0.700	0.285	318.84	325.32	330.55	334.98	338.84
0.200	0.640	322.80	329.46	334.84	339.38	343.33	0.697	0.273	318.42	324.92	330.18	334.62	338.38
0.197	0.562	322.15	328.81	334.21	338.75	342.72	0.700	0.240	317.67	324.18	329.45	333.90	337.78
0.199	0.481	321.70	328.38	333.78	338.33	342.31	0.700	0.210	317.10	323.64	328.92	333.39	337.27
0.200	0.400	321.29	327.97	333.40	337.98	341.96	0.700	0.180	316.64	323.19	328.48	332.95	336.84
0.197	0.321	321.13	327.90	333.39	338.01	342.06	0.700	0.150	316.24	322.79	328.09	332.58	336.47
0.200	0.240	320.86	327.60	333.06	337.63	341.63	0.700	0.120	315.89	322.45	327.76	332.24	336.15
0.200	0.160	320.73	327.58	333.13	337.85	341.93	0.700	0.090	315.58	322.15	327.47	331.96	335.87
0.198	0.080	320.77	327.81	333.54	338.41	342.67	0.700	0.060	315.28	321.85	327.17	331.67	335.59
0.197	0.040	320.77	327.92	333.74	338.66	342.97	0.700	0.030	315.00	321.57	326.90	331.41	335.32
0.299	0.666	323.66	330.25	335.55	340.01	343.87	0.700	0.015	314.86	321.44	326.77	331.28	335.20
0.300	0.630	322.74	329.32	334.65	339.16	343.07	0.800	0.190	317.79	324.26	329.48	333.89	337.72
0.298	0.562	321.59	328.23	333.59	338.13	342.07	0.798	0.181	317.48	323.96	329.20	333.62	337.46
0.297	0.492	320.89	327.54	332.92	337.46	341.40	0.800	0.160	316.96	323.45	328.70	333.13	336.98
0.299	0.420	320.35	327.02	332.39	336.96	340.89	0.800	0.140	316.49	323.00	328.26	332.70	336.56
0.301	0.349	319.87	326.52	331.89	336.45	340.37	0.800	0.120	316.12	322.64	327.90	332.35	336.22
0.296	0.281	319.56	326.15	331.55	336.10	340.09	0.800	0.100	315.78	322.31	327.58	332.03	335.90
0.298	0.211	319.19	325.93	331.32	335.88	339.81	0.800	0.080	315.48	322.01	327.29	331.75	335.63
0.303	0.140	318.81	325.58	331.05	335.64	339.64	0.800	0.060	315.21	321.75	327.03	331.49	335.49
0.298	0.071	318.55	325.40	330.99	335.69	339.79	0.800	0.040	314.97	321.51	326.79	331.26	335.14
0.301	0.035	318.32	325.20	330.84	335.54	339.68	0.800	0.020	314.74	321.28	326.57	331.03	334.92
0.400	0.570	322.34	328.87	334.13	338.59	342.46	0.800	0.010	314.62	321.17	326.46	330.93	334.82
0.398	0.542	321.56	328.13	333.44	337.93	341.83	0.850	0.135	317.04	323.51	328.74	333.15	336.99
0.400	0.480	320.45	327.07	332.41	336.92	340.84	0.900	0.095	316.79	323.24	328.45	332.84	336.66
0.400	0.420	319.72	326.36	331.71	336.24	340.18	0.899	0.091	316.62	323.08	328.29	332.70	336.54
0.399	0.360	319.18	325.82	331.19	335.75	339.70	0.900	0.080	316.34	322.80	328.02	332.44	336.27
0.400	0.300	318.73	325.39	330.78	335.33	339.30	0.900	0.070	316.06	322.53	327.76	332.17	336.00
0.398	0.241	318.37	325.04	330.43	335.00	338.97	0.900	0.060	315.82	322.30	327.53	331.96	335.79
0.401	0.180	317.95	324.63	330.05	334.63	338.61	0.900	0.050	315.58	322.06	327.30	331.72	335.56
0.400	0.120	317.56	324.27	329.71	334.32	338.30	0.900	0.040	315.38	321.87	327.11	331.53	335.38
0.401	0.060	317.14	323.91	329.39	334.00	338.03	0.900	0.030	315.18	321.67	326.91	331.35	335.21
0.403	0.030	316.88	323.67	329.18	333.85	337.93	0.900	0.020	315.00	321.50	326.75	331.18	335.04
0.500	0.475	321.10	327.64	332.91	337.35	341.21	0.900	0.010	314.83	321.33	326.58	331.01	334.87
0.498	0.452	320.46	327.00	332.29	336.77	340.67	0.900	0.005	314.75	321.25	326.51	330.95	334.81
0.500	0.400	319.45	326.04	331.36	335.85	339.76	0.950	0.045	316.21	322.65	327.86	332.26	336.08

Table 5. Constants of the Pure Components for the Vapor Pressure Equation

	component				
	A	B	C	D	E
methanol[a,b]	44.7420	−3244.7	−13.988	6.6365×10^{-3}	-1.0507×10^{-13}
ethanol[a,b]	22.9691	−2864.2	−5.0474	3.7448×10^{-11}	2.7361×10^{-7}
dimethyl carbonate[c]	51.5595	−5991.3	−11.7365	1.3402×10^{-17}	6.000

[a] $\log(P_i^s/\text{kPa}) = A + B/(T/\text{K}) + C \log(T/\text{K}) + D(T/\text{K}) + E(T/\text{K})^2$. [b] Ref 7. [c] $\log(P_i^s/\text{kPa}) = A + B/(T/\text{K}) + C \log(T/\text{K}) + D(T/\text{K})^E$.

Coefficients in eq 5 were determined from our experimental data. Coefficients in eqs 4 and 5 are listed in Table 5.

Binary Systems. Binary parameters for the Wilson equation, $\lambda_{ij} - \lambda_{ii}$, were expressed according to the following temperature-dependent function:

$$\lambda_{ij} - \lambda_{ii} = \sum_{k=0}^{2} A_{ijk} T^k \qquad (6)$$

where A_{ijk} is an adjustable parameter. The liquid molar volume for the pure component (V_i^L) in the Wilson equation was treated as the constant value, which was determined from a density at 298.15 K, as shown in Table 1.

Parameters of the Wilson equation were evaluated by the Marquardt method.[11] The following objective function (OF) was minimized during optimization of the binary Wilson parameters:

$$\text{OF} = \sum_{l=1}^{\text{NDP}} (T_{\text{calcd}} - T_{\text{exptl}})_l^2 \qquad (11)$$

Table 6. Parameters and Deviations between the Calculated and Experimental Boiling Temperatures (Δ*T*) for the Three Binary Systems Using the Wilson Equation[a]

parameter	methanol (1) + ethanol (2)		ethanol (1) + dimethyl carbonate (2)		methanol (1) + dimethyl carbonate (2)	
A_{121}/J·mol^{-1}	−5286.74		−7538.94		−13427.7	
A_{122}/J·mol^{-1}·K^{-1}	17.1000		74.2974		111.6726	
A_{123}/J·mol^{-1}·K^{-2}	0		−0.132355		−0.184471	
A_{211}/J·mol^{-1}	6654.04		−681.838		11949.4	
A_{212}/J·mol^{-1}·K^{-1}	−21.1721		15.2547		−64.2433	
A_{213}/J·mol^{-1}·K^{-2}	0		−0.0232398		0.0946385	
P/kPa	ΔT_{av}/K	ΔT_{max}/K	ΔT_{av}/K	ΔT_{max}/K	ΔT_{av}/K	ΔT_{max}/K
40.00	0.01	0.03	0.06	0.14	0.03	0.07
53.33	0.02	0.04	0.05	0.15	0.03	0.10
66.66	0.02	0.05	0.06	0.17	0.03	0.08
79.99	0.01	0.03	0.06	0.16	0.03	0.08
93.32	0.02	0.06	0.06	0.18	0.03	0.08

[a] $\Delta T = |T_{\mathrm{calcd}} - T_{\mathrm{exptl}}|$; $\Delta T_{\mathrm{av}} = \sum_{k=1}^{\mathrm{NDP}} \Delta T_k/\mathrm{NDP}$; NDP = number of data points.

Table 7. Deviations between the Calculated and Experimental Boiling Temperatures (Δ*T*) for the Methanol + Ethanol + Dimethyl Carbonate System Using the Wilson Equation[a]

	P/kPa				
	40.00	53.33	66.66	79.99	93.32
ΔT_{av}/K	0.06	0.08	0.09	0.10	0.10
ΔT_{max}/K	0.16	0.19	0.29	0.49	0.65

[a] $\Delta T = |T_{\mathrm{calcd}} - T_{\mathrm{exptl}}|$; $\Delta T_{\mathrm{av}} = \sum_{k=1}^{\mathrm{NDP}} \Delta T_k/\mathrm{NDP}$; NDP = number of data points.

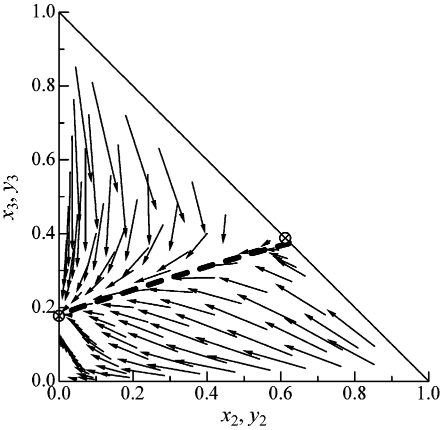

Figure 7. Vapor−liquid equilibrium tie lines for the methanol (1) + ethanol (2) + DMC (3) system at 40.00 kPa: ⊗, binary azeotropic points; →, Wilson equation.

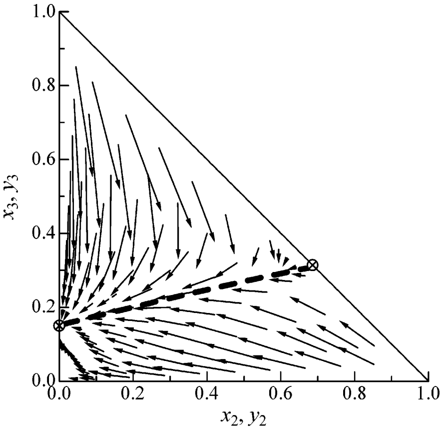

Figure 8. Vapor−liquid equilibrium tie lines for the methanol (1) + ethanol (2) + DMC (3) system at 93.32 kPa: ⊗, binary azeotropic points; →, Wilson equation.

where NDP is the number of experimental data, and T_{calcd} and T_{exptl} are the calculated and experimental boiling temperatures, respectively. The evaluated values of parameters for the Wilson equation are listed in Table 6.

The calculated results are shown in Figures 2 to 4. The symbols represent experimental data, and the solid lines are the results of data reduction carried out with the Wilson equation. In these figures, the calculated vapor coexistence curves are also shown.

Ternary System. Predicted results using the binary Wilson parameters as in Table 6 are shown in Table 7. Illustrative diagrams are shown in Figures 7 and 8. In those figures, tails of arrows represent liquid-phase mole fractions x_2 and x_3, and heads of arrows represent vapor-phase fractions y_2 and y_3. The solid lines are the predicted results using the Wilson equation. For this ternary system, valleys were observed from the behavior of predicted tie lines in both figures. The valleys connected the two binary minimum boiling points of methanol + DMC and ethanol + DMC. The valleys, which were estimated according to the methods by Naka et al.,[3,4] are shown as the heavy broken line in Figures 7 and 8. This method can be performed using an iterative calculation of boiling points with the Wilson equation from the appropriate starting point, which is the neighborhood of the azeotrope of the ethanol + DMC system.

Conclusion

VLE data were determined on the basis of experimental boiling point data for three constituent binary systems (methanol + ethanol, ethanol + DMC, and DMC + methanol) and the ternary system (methanol + ethanol + DMC) from 40.00 to 93.32 kPa. The binary ethanol + DMC and methanol + DMC systems showed a minimum boiling point azeotrope.

The Wilson equation was applied to the binary systems to correlate VLE with the ternary system for predicting its VLE behavior. For this ternary system, valley lines were also estimated using the Wilson equation.

Literature Cited

(1) Dortmund Data Bank. DDBST GmbH: Oldenburg, 2005; http://www.ddbst.de.

(2) Wilson, G. M. Vapor−liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

(3) Naka, Y.; Kobayashi, K.; Takamatsu, T. Computational methods for obtaining ridge and valley in vapor−liquid equilibrium relationship for azeotropic mixtures, *Kagaku Kogaku Ronbunshu* **1975**, *1*, 186−190.

(4) Naka, Y.; Kobayashi, K.; Ochi, H.; Takamatsu, T. The effect of valley and ridge on composition profile in an azeotropic continuous distillation column. *J. Chem. Eng. Jpn.* **1983**, *1*, 39−42.
(5) Riddick, J. A.; Bunger, W.; Sakano, T. K. *Organic Solvents Physical Properties and Methods of Purification*, 4th ed.; John Wiley & Sons: New York, 1986.
(6) Romolo, F.; Fabio, C. Vapor−liquid equilibria, excess molar enthalpies and excess molar volumes of dimethyl carbonate + 1,2-epoxybutane at 288.15, 298.15, or 313.15 K. *J. Chem. Eng. Data* **1996**, *41*, 736−740.
(7) Lecat, M. *Tables Azeotropiques*; Monograph L'Auteur: Bruxelles, 1949.
(8) Rodríguez, A.; Canosa, J.; Dominguez, A.; Tojo, J. Vapour + liquid equilibria of dimethyl carbonate with linear alcohols and estimation of interaction parameters for the UNIFAC and ASOG Method. *Fluid Phase Equilib.* **2002**, *201*, 187−201.
(9) Yunhai, S.; Honglai, L.; Kun, W.; Wende, X.; Ying, H. Measurements of isothermal vapor−liquid equilibrium of binary methanol/dimethyl carbonate system under pressure. *Fluid Phase Equilib.* **2005**, *234*, 1−10.
(10) Carl, L. Y. *Handbook of Vapor Pressure*; Gulf Publishing Co.: Houston, 1994.
(11) Marquardt, D. W. An algorithm for least-squares estimation of nonlinear parameters. *Soc. Ind. Appl. Math*. **1963**, *11*, 431−441.

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