2066 *J. Chem. Eng. Data* **2008,** *53,* 2066–2071

Isobaric Vapor−Liquid Equilibria for Tetrahydropyran and Alcohol Systems

Shigemichi Uno,[†] Hiroyuki Matsuda,[†] Kiyofumi Kurihara,[†] Katsumi Tochigi,*,[†] Yoshimori Miyano,[‡] Satoru Kato,[§] and Hiroshi Yasuda[||]

Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University, 1-8 Surugadai, Kanda, Chiyoda-ku, Tokyo, 101-8308, Japan, Department of Chemistry and Bioscience, Kurashiki University of Science and the Arts, 2640 Nishinoura, Tsurajimacho, Kurashiki, Okayama, 712-8505, Japan, Department of Applied Chemistry, Tokyo Metropolitan University, 1-1 minami-osawa, Hachioji, Tokyo, 192-0397, Japan, and Corporate R&D Center, Showa Denko K.K, 5-1 Ougimachi, Kawasaki-ku, Kawasaki, Kanagawa, 210-0867, Japan

---

The vapor−liquid equilibria (VLE) data of systems including tetrahydropyran (THP) are very important for the design of manufacture processes. However, these data are scarce in the literature. The boiling points of eight binary systems containing THP at six pressures from (40.00 to 98.66) kPa were measured using a hold-up compensable ebulliometer. The systems consisting of THP + 2-butanol, THP + 2-methyl-1-propanol, and THP + 1-butanol are nonazeotropic, while those of THP + methanol, THP + ethanol, and THP + 2-propanol are azeotropic. The nonexistence of azeotropic points for THP + 1-propanol and THP + 2-methyl-2-propanol systems depends on the pressures. The measured boiling points were satisfactorily correlated using the NRTL equation. The average deviations between the experimental and calculated boiling points were 0.09 K for THP + methanol, 0.06 K for THP + ethanol, 0.04 K for THP + 2-propanol, 0.06 K for THP + 1-propanol, 0.04 K for THP + 2-methyl-2-propanol, 0.05 K for THP + 2-butanol, 0.04 K for THP + 2-methyl-1-propanol, and 0.08 K for THP + 1-butanol systems. The ASOG group pair parameters for the OH and pyran groups were also determined.

Introduction

Cyclic ethers like 1,4-dioxane and tetrahydrofuran are widely used as a solvent in reactive processes and separation processes in industrial chemical plants. Tetrahydropyran (THP) which is one of the cyclic ethers is less used industrially in comparison with 1,4-dioxane and tetrahydrofuran. The reason is that the technology to produce THP on a large scale has not yet been established. Recently, Showa Denko K.K. has established a new mass-production method for THP which is produced from hydrogen, acetaldehyde, alcohol, and acrolein.[1] In this reaction, the alcohol is necessary to ensure a nonazeotropic system in order that THP and alcohol can be separated by distillation. However, there have been few reports of vapor−liquid equilibria data on THP + alcohol systems.

In this work, the boiling points of eight binary systems (THP + methanol, THP + ethanol, THP + 2-propanol, THP + 1-propanol, THP + 2-methyl-2-propanol, THP + 2-butanol, THP + 2-methyl-1-propanol, and THP + 1-butanol) at six pressures from (40.00 to 98.66) kPa were measured using a hold-up compensable ebulliometer.[2−4] The measured boiling points were satisfactorily correlated using the NRTL equation.[5] In addition, the ASOG group pair parameters[2,6] for the OH and pyran groups were determined.

Experimental Section

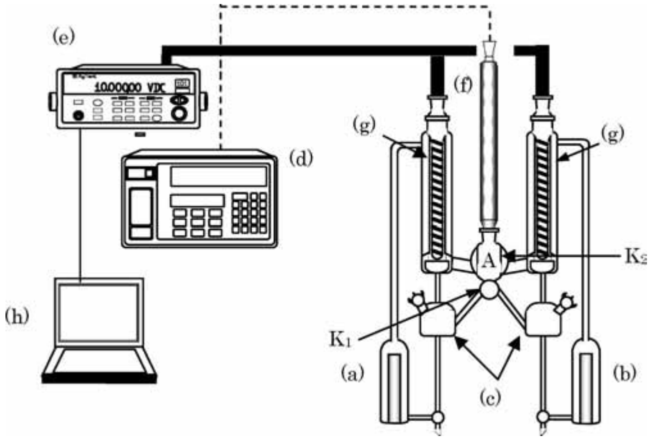

Figure 1. Schematic diagram of the experimental apparatus: a,b, ebulliometer; c, mixing trap; d, pressure controller (DPI510); e, data logger; f, condenser; g, thermometer; h, personal computer; A, vapor hold-up collector; K$_1$,K$_2$, trident tap.

Apparatus. The schematic diagram of the experimental apparatus is shown in Figure 1. The ebulliometer in this work is composed of an ebulliometer (a) for trapping the vapor hold-up and a separate ebulliometer (b) for measuring the boiling points of a vapor−liquid mixture.[2−4] The capacity of each boiling flask is about 60 mL. A condenser is shared by both ebulliometers. A feature of the ebulliometer, whose benefits are given in a previous paper,[3] is that the compensation of the vapor-phase hold-up is achieved by moving the trapped condensate of the hold-up in ebulliometer (a) to ebulliometer (b). Equilibrium temperatures were measured with a calibrated platinum resistance thermometer connected to a personal computer via a digital multimeter (34970A, Agilent Technologies, Inc.). The uncertainty in temperature was estimated to be ± 0.01 K. The pressure in the apparatus was controlled using a Controller

---

* Corresponding author. Tel.: +81-3-3259-0814. Fax: +81-3-3293-7572. E-mail: tochigi@chem.cst.nihon-u.ac.jp.
[†] Nihon University.
[‡] Kurashiki University of Science and the Arts.
[§] Tokyo Metropolitan University.
[||] Showa Denko K.K.

10.1021/je800145h CCC: $40.75

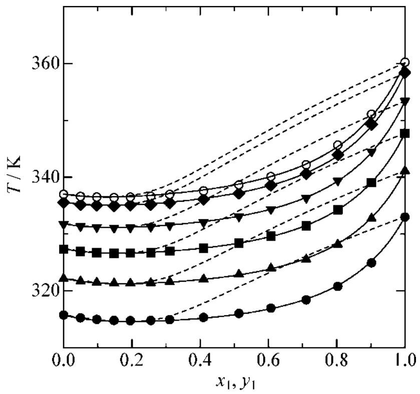

Figure 2. Isobaric vapor−liquid equilibria for the tetrahydropyran (1) + methanol (2) system: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ○, 98.66 kPa; —, $(T-x)$, - - -, $(T-y)$, NRTL equation.

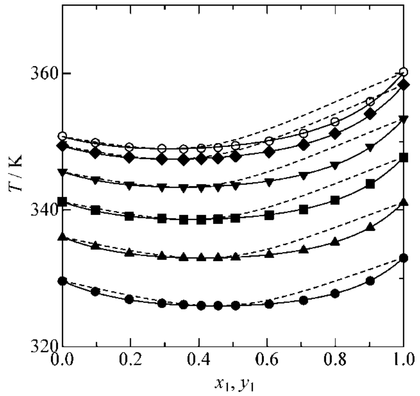

Figure 3. Isobaric vapor−liquid equilibria for the tetrahydropyran (1) + ethanol (2) system: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ○, 98.66 kPa; —, $(T-x)$, - - -, $(T-y)$, NRTL equation.

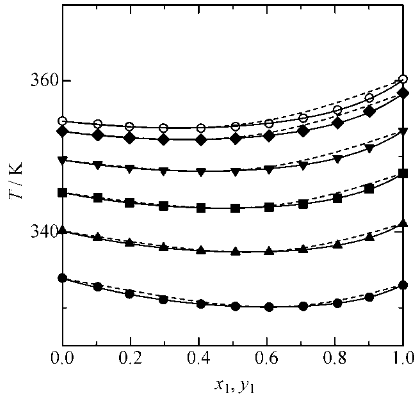

Figure 4. Isobaric vapor−liquid equilibria for the tetrahydropyran (1) + 2-propanol (2) system: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ○, 98.66 kPa; —, $(T-x)$, - - -, $(T-y)$, NRTL equation.

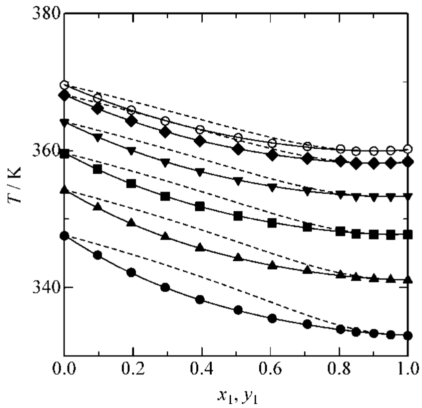

Figure 5. Isobaric vapor−liquid equilibria for the tetrahydropyran (1) + 1-propanol (2) system: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ○, 98.66 kPa; —, $(T-x)$, - - -, $(T-y)$, NRTL equation.

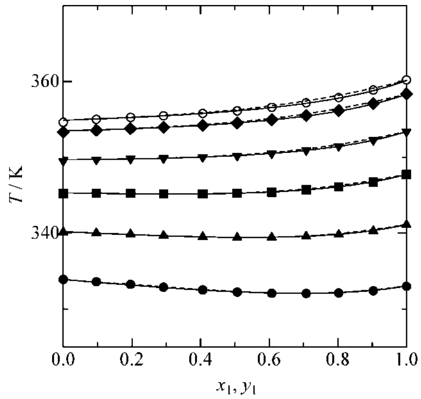

Figure 6. Isobaric vapor−liquid equilibria for the tetrahydropyran (1) + 2-methyl-2-propanol (1) system: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ○, 98.66 kPa; —, $(T-x)$, - - -, $(T-y)$, NRTL equation.

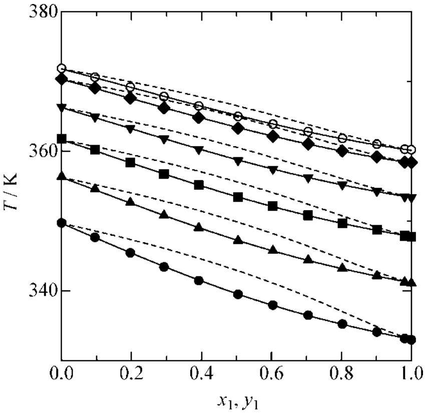

Figure 7. Isobaric vapor−liquid equilibria for the tetrahydropyran (1) + 2-butanol (2) system: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ○, 98.66 kPa; —, $(T-x)$, - - -, $(T-y)$, NRTL equation.

DPI510 (Druck Co.). The uncertainty in pressure was estimated to be ± 0.01 kPa.

Procedure. Using the ebulliometer, the boiling point of the charged mixtures was measured by the following steps:

Step 1. A calculated amount of binary mixture of known composition was charged into each ebulliometer. The charged composition was weighed in a digital balance (AX-504, Mettler-Toledo, Inc.) with an uncertainty of ± 0.1 mg. The system pressure was set to the desired pressure by using the pressure controller. At the time of measurement, the trident taps K_1 and K_2 were switched to ebulliometer (a). At first, the mixture in the ebulliometer (a) was brought to the boiling point. After reaching a steady state, the trident taps K_1 and K_2 were closed, and simultaneously, heating was stopped. Then, all the vapor-phase hold-up was trapped above the trident tap K_1.

Step 2. After switching the trident taps K_1 and K_2 to the ebulliometer (b), the trapped condensate above the trident tap K_1 was moved to the ebulliometer (b). Then, the mixture in the ebulliometer (b) was brought to the boiling point. The vapor

Table 1. Experimental Boiling Points for Tetrahydropyran (1) + Alcohol (2) Systems

	T/K					
	P/kPa					
x_1	40.00	53.33	66.66	79.99	93.32	98.66
Tetrahydropyran (1) + Methanol (2)						
0.0000	315.75	322.15	327.34	331.73	335.57	336.98
0.0495	315.24	321.70	326.92	331.34	335.19	336.60
0.0972	314.96	321.46	326.73	331.19	335.06	336.49
0.1478	314.80	321.33	326.61	331.08	334.97	336.40
0.1956	314.74	321.31	326.63	331.13	335.05	336.48
0.2554	314.78	321.40	326.74	331.25	335.18	336.63
0.3108	314.93	321.59	326.98	331.53	335.50	336.96
0.4101	315.31	322.03	327.47	332.08	336.10	337.57
0.5136	316.02	322.87	328.40	333.08	337.16	338.66
0.6073	316.94	323.93	329.58	334.36	338.56	340.10
0.7108	318.40	325.53	331.46	336.34	340.62	342.18
0.8032	320.77	328.16	334.24	339.39	343.94	345.63
0.9022	324.93	332.76	339.05	344.48	349.28	351.07
1.0000	332.98	341.09	347.72	353.38	358.37	360.22
Tetrahydropyran (1) + Ethanol (2)						
0.0000	329.62	335.99	341.20	345.60	349.42	350.82
0.0966	328.07	334.67	340.00	344.50	348.41	349.86
0.1959	326.93	333.66	339.10	343.71	347.71	349.20
0.2915	326.35	333.21	338.75	343.43	347.50	349.00
0.3551	326.16	333.04	338.60	343.30	347.40	348.91
0.4069	326.02	332.97	338.60	343.36	347.51	349.04
0.4562	326.01	332.99	338.64	343.43	347.61	349.14
0.5074	326.02	333.08	338.80	343.65	347.87	349.43
0.6061	326.24	333.43	339.25	344.19	348.51	350.10
0.7069	326.78	334.12	340.08	345.14	349.57	351.21
0.7990	327.78	335.28	341.42	346.64	351.22	352.92
0.9022	329.63	337.45	343.84	349.29	354.09	355.87
1.0000	332.98	341.09	347.72	353.38	358.37	360.22
Tetrahydropyran (1) +2-Propanol (2)						
0.0000	333.94	340.18	345.25	349.55	353.30	354.67
0.1037	332.77	339.26	344.52	348.97	352.84	354.27
0.1968	331.83	338.51	343.91	348.48	352.46	353.92
0.2966	331.08	337.93	343.47	348.15	352.24	353.74
0.4067	330.51	337.52	343.19	348.00	352.19	353.73
0.5080	330.20	337.35	343.15	348.07	352.36	353.94
0.6065	330.10	337.40	343.32	348.34	352.73	354.34
0.7066	330.20	337.66	343.72	348.88	353.38	355.05
0.8075	330.60	338.24	344.47	349.78	354.42	356.13
0.9012	331.42	339.27	345.68	351.16	355.95	357.72
1.0000	332.98	341.09	347.72	353.38	358.37	360.22
Tetrahydropyran (1) + 1-Propanol (2)						
0.0000	347.55	354.18	359.56	364.11	368.08	369.55
0.0969	344.74	351.67	357.28	362.02	366.14	367.64
0.1946	342.20	349.38	355.19	360.08	364.34	365.90
0.2936	340.01	347.37	353.32	358.34	362.70	364.31
0.3945	338.24	345.76	351.84	356.96	361.41	363.05
0.5058	336.72	344.29	350.45	355.66	360.20	361.86
0.6059	335.48	343.16	349.42	354.73	359.35	361.04
0.7076	334.65	342.45	348.79	354.17	358.86	360.58
0.8042	333.91	341.79	348.22	353.68	358.46	360.22
0.8491	333.52	341.42	347.84	353.33	358.12	359.90
0.9011	333.29	341.25	347.75	353.28	358.13	359.92
0.9500	333.09	341.13	347.69	353.28	358.19	359.99
1.0000	332.98	341.09	347.72	353.38	358.37	360.22
Tetrahydropyran (1) + Methyl-2-propanol (2)						
0.0000	333.90	340.13	345.21	349.53	353.32	354.61
0.0965	333.59	340.02	345.24	349.68	353.57	355.00
0.1961	333.25	339.86	345.24	349.80	353.79	355.26
0.2923	332.86	339.67	345.19	349.87	353.96	355.47
0.4064	332.51	339.51	345.20	350.02	354.23	355.79
0.5070	332.23	339.41	345.24	350.20	354.53	356.12
0.6074	332.07	339.43	345.42	350.50	354.95	356.59
0.7079	332.04	339.57	345.71	350.93	355.50	357.18
0.8028	332.10	339.80	346.10	351.46	356.16	357.88
0.9035	332.39	340.28	346.74	352.26	357.10	358.88
1.0000	332.98	341.09	347.72	353.38	358.37	360.22
Tetrahydropyran (1) + 2-Butanol (2)						
0.0000	349.73	356.36	361.77	366.36	370.38	371.86
0.0955	347.67	354.58	360.19	364.94	369.09	370.62
0.1964	345.44	352.62	358.41	363.32	367.60	369.18
0.2928	343.42	350.79	356.77	361.82	366.22	367.83
0.3920	341.46	349.02	355.14	360.31	364.83	366.49
0.5045	339.50	347.18	353.41	358.69	363.29	364.99
0.6042	337.94	345.75	352.09	357.46	362.16	363.90
0.7050	336.50	344.38	350.82	356.28	361.05	362.81
0.8030	335.25	343.20	349.69	355.22	360.06	361.84
0.9015	334.09	342.14	348.70	354.31	359.21	361.02
0.9811	333.15	341.24	347.86	353.50	358.46	360.28
1.0000	332.98	341.09	347.72	353.38	358.37	360.22
Tetrahydropyran (1) + 2-Methyl-1-propanol (2)						
0.0000	357.45	364.17	369.67	374.35	378.45	379.96
0.0973	354.26	361.38	367.15	372.03	376.29	377.86
0.1968	350.92	358.40	364.41	369.50	373.91	375.53
0.2956	347.80	355.47	361.69	366.94	371.49	373.17
0.3939	345.03	352.90	359.27	364.63	369.28	371.01
0.4941	342.40	350.39	356.84	362.30	367.06	368.82
0.6054	339.93	347.96	354.50	360.03	364.86	366.63
0.7033	337.94	346.00	352.58	358.18	363.05	364.85
0.8010	336.22	344.30	350.89	356.50	361.40	363.21
0.9029	334.49	342.57	349.18	354.83	359.76	361.58
1.0000	332.98	341.09	347.72	353.38	358.37	360.22
Tetrahydropyran (1) + 1-Butanol (2)						
0.0000	366.76	373.74	379.43	384.26	388.49	390.04
0.0977	361.61	369.07	375.09	380.16	384.60	386.24
0.1952	356.24	364.14	370.58	375.96	380.62	382.31
0.2912	351.94	360.08	366.67	372.17	376.93	378.71
0.3910	347.88	356.20	362.88	368.52	373.39	375.22
0.4936	344.44	352.72	359.47	365.17	370.16	371.99
0.6079	341.35	349.64	356.35	362.06	367.03	368.86
0.7049	339.04	347.23	354.00	359.68	364.66	366.48
0.8050	336.80	344.99	351.66	357.35	362.33	364.17
0.9028	334.94	343.07	349.73	355.41	360.39	362.23
0.9708	333.50	341.61	348.25	353.91	358.88	360.71
1.0000	332.98	341.09	347.72	353.38	358.37	360.22

hold-ups in Step 1 and Step 2 were equal. When no temperature fluctuation was observed, the boiling point of the mixture was obtained. After reaching an equilibrium state, the boiling point measurement was performed at a progressively higher system pressure.

Materials. Special grade methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol were supplied by Wako Pure Chemical Industries, Ltd. All chemicals were stored over molecular sieves to reduce the water content. The purities of materials were checked by gas chromatography and were found to be better than 99.9 mol % for methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-1-propanol and better than 99 mol % for 2-butanol and 2-methyl-2-propanol. THP was supplied by Showa Denko K.K and found to be better than 99.6 mol %. The experimental density and boiling point of THP are $8.79 \cdot 10^2$ $kg \cdot m^{-3}$ (298.15 K) and 361.23 K, respectively, and they agreed with values ($8.772 \cdot 10^2$ $kg \cdot m^{-3}$ (298.15 K) and 361 K) from the literature.[7,8]

Experimental Results

The boiling points of eight binary systems (THP + methanol, THP + ethanol, THP + 2-propanol, THP + 1-propanol, THP + 2-methyl-2-propanol, THP + 2-butanol, THP + 2-methyl-1-propanol, and THP + 1-butanol) were measured in the range of (40.00 to 98.66) kPa. The experimental boiling point data are listed in Table 1 and are graphically shown in Figures 2 to 9. The systems consisting of THP + 2-butanol, THP + 2-methyl-1-propanol, and THP + 1-butanol are nonazeotropic,

Table 2. Determined Parameters and Deviations between Experimental and Calculated Boiling Points for Eight Binary Systems Using the NRTL Equation

parameter	tetrahydropyran (1) + methanol (2)	tetrahydropyran (1) + ethanol (2)	tetrahydropyran (1) + 2-propanol (2)
a_{12}/J·mol^{-1}	$-8.5719\cdot10^{-1}$	$3.3456\cdot10^{3}$	$4.2175\cdot10^{3}$
b_{12}/J·mol^{-1}·K^{-1}	$-1.8476\cdot10^{-2}$	$3.1820\cdot10^{-4}$	$1.8819\cdot10^{-1}$
c_{12}/J·mol^{-1}·K^{-2}	$1.4481\cdot10^{-4}$	$-1.8033\cdot10^{-2}$	$-9.8253\cdot10^{-3}$
a_{21}/J·mol^{-1}	$5.8959\cdot10^{3}$	$9.1460\cdot10^{2}$	8.3661
b_{21}/J·mol^{-1}·K^{-1}	-7.9446	$1.2562\cdot10^{-1}$	-2.2168
c_{21}/J·mol^{-1}·K^{-2}	$-1.5961\cdot10^{-3}$	$1.9013\cdot10^{-3}$	$-4.8739\cdot10^{-3}$
α_{12}	0.22	0.41	0.21
Dev^{a}/K	0.09	0.06	0.04
$g_{12} - g_{22}$/J·mol^{-1}	$2.7757\cdot10^{2}$	$8.7132\cdot10^{2}$	$1.9397\cdot10^{3}$
$g_{21} - g_{11}$/J·mol^{-1}	$2.9150\cdot10^{3}$	$1.5045\cdot10^{3}$	$-3.3197\cdot10^{2}$
α_{12}	0.31	0.30	0.35
Dev^{a}/K	0.09	0.13	0.14

parameter	tetrahydropyran (1) + 1-propanol (2)	tetrahydropyran (1) + 2-methyl-2-propanol (2)	tetrahydropyran (1) + 2-butanol (2)
a_{12}/J·mol^{-1}	$3.5351\cdot10^{3}$	$3.5690\cdot10^{3}$	$1.2677\cdot10^{4}$
b_{12}/J·mol^{-1}·K^{-1}	$9.5695\cdot10^{-3}$	$1.3757\cdot10^{-1}$	$-2.7827\cdot10^{1}$
c_{12}/J·mol^{-1}·K^{-2}	$-6.1266\cdot10^{-3}$	$-2.3301\cdot10^{-3}$	$1.1791\cdot10^{-2}$
a_{21}/J·mol^{-1}	-6.9654	$4.6638\cdot10^{1}$	$-3.2295\cdot10^{3}$
b_{21}/J·mol^{-1}·K^{-1}	$-5.2186\cdot10^{-2}$	-6.6269	$1.7594\cdot10^{-2}$
c_{21}/J·mol^{-1}·K^{-2}	$-8.6351\cdot10^{-3}$	$9.6653\cdot10^{-4}$	$2.3469\cdot10^{-3}$
α_{12}	0.24	0.27	0.20
Dev^{a}/K	0.06	0.04	0.05
$g_{12} - g_{22}$/J·mol^{-1}	$3.2314\cdot10^{3}$	$2.1370\cdot10^{3}$	$3.1054\cdot10^{3}$
$g_{21} - g_{11}$/J·mol^{-1}	$-1.4667\cdot10^{3}$	$-1.2045\cdot10^{3}$	$-1.8718\cdot10^{3}$
α_{12}	0.21	0.42	0.36
Dev^{a}/K	0.13	0.11	0.15

parameter	tetrahydropyran (1) + 2-methyl-1-propanol (2)	tetrahydropyran (1) + 1-butanol (2)
a_{12}/J·mol^{-1}	$1.0542\cdot10^{4}$	$1.1334\cdot10^{4}$
b_{12}/J·mol^{-1}·K^{-1}	$-2.2216\cdot10^{1}$	$-2.3415\cdot10^{1}$
c_{12}/J·mol^{-1}·K^{-2}	$4.1908\cdot10^{-3}$	$3.6928\cdot10^{-3}$
a_{21}/J·mol^{-1}	$-2.2517\cdot10^{3}$	$-2.5472\cdot10^{3}$
b_{21}/J·mol^{-1}·K^{-1}	$1.8358\cdot10^{-1}$	$-6.3481\cdot10^{-2}$
c_{21}/J·mol^{-1}·K^{-2}	$1.7328\cdot10^{-3}$	$3.5927\cdot10^{-3}$
α_{12}	0.33	0.25
Dev^{a}/K	0.04	0.08
$g_{12} - g_{22}$/J·mol^{-1}	$3.2769\cdot10^{3}$	$2.9534\cdot10^{3}$
$g_{21} - g_{11}$/J·mol^{-1}	$-1.9331\cdot10^{3}$	$-1.5772\cdot10^{3}$
α_{12}	0.39	0.44
Dev^{a}/K	0.17	0.22

[a] Dev $= 1/N\sum_{k=1}^{N} |T_{\mathrm{exptl}} - T_{\mathrm{calcd}}|_k$; N = the number of the data points.

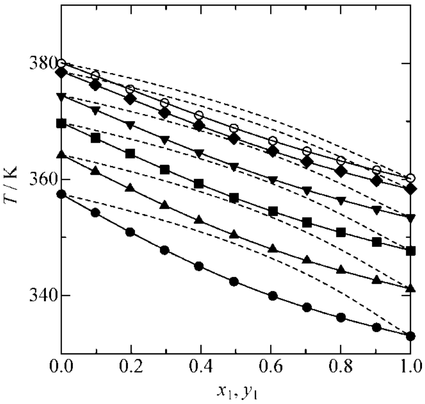

Figure 8. Isobaric vapor−liquid equilibria for the tetrahydropyran (1) + 2-methyl-1-propanol (2) system: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ○, 98.66 kPa; —, (T−x), - - -, (T−y), NRTL equation.

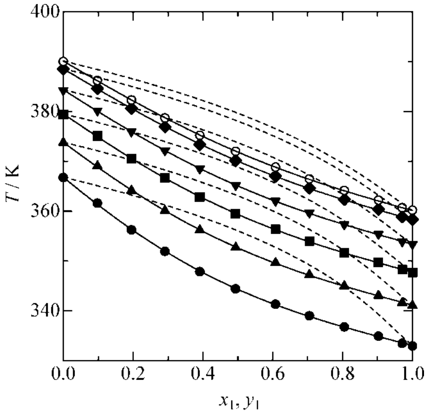

Figure 9. Isobaric vapor−liquid equilibria for the tetrahydropyran (1) + 1-butanol (2) system: ●, 40.00 kPa; ▲, 53.33 kPa; ■, 66.66 kPa; ▼, 79.99 kPa; ♦, 93.32 kPa; ○, 98.66 kPa; —, (T−x), - - -, (T−y), NRTL equation.

while those of THP + methanol, THP + ethanol, and THP + 2-propanol are azeotropic. For THP + 1-propanol and THP + 2-methyl-2-propanol systems, the nonexistence or existence of azeotropic points depends on the pressures. THP + 1-propanol is nonazeotropic in the range of (40.00 to 53.33) kPa and azeotropic in the range of (66.66 to 98.66) kPa. The THP + 2-methyl-2-propanol binary system is azeotropic in the range of (40.00 to 66.66) kPa and nonazeotropic in the range of (79.99 to 98.66) kPa.

Data Reduction

In this work, the experimental boiling point data were correlated with the NRTL equation.[5] In the correlation, the liquid phase activity coefficient was calculated using the following expression.

$$\gamma_i = \frac{Py_i}{P_i^\circ x_i} \tag{1}$$

In this work, the saturated vapor pressures of the pure components i, P_i°, were calculated using the Antoine equation. The Antoine constants for THP and other compounds were obtained from our previous paper[9] and from the literature,[7] respectively. The binary interaction parameters of the NRTL equation, $g_{ij} - g_{jj}$, were expressed by the following polynomial expression of temperature

$$g_{ij} - g_{jj} = a_{ij} + b_{ij}T/\mathrm{K} + c_{ij}(T/\mathrm{K})^2 \tag{2}$$

The fitting parameters a_{ij}, b_{ij}, and c_{ij} for eq 2 and the nonrandomness parameter α_{12} were estimated so that the following objective function was minimized by the Marquardt method[10]

$$F_{\mathrm{obj}} = \sum_{k=1}^{N} (T_{\mathrm{exptl}} - T_{\mathrm{calcd}})_k^2 \tag{3}$$

Table 3. Azeotropic Compositions Calculated Using the NRTL Parameters

P/kPa	x_1	T/K
	Tetrahydropyran (1) + Methanol (2)	
40.00	0.194	314.60
53.33	0.174	321.25
66.66	0.158	326.61
79.99	0.144	331.14
93.32	0.132	335.06
98.66	0.127	336.50
	Tetrahydropyran (1) + Ethanol (2)	
40.00	0.450	325.98
53.33	0.408	332.99
66.66	0.374	338.63
79.99	0.345	343.37
93.32	0.319	347.48
98.66	0.309	348.98
	Tetrahydropyran (1) + 2-Propanol (2)	
40.00	0.608	330.12
53.33	0.538	337.37
66.66	0.476	343.18
79.99	0.418	348.04
93.32	0.363	352.23
98.66	0.341	353.76
	Tetrahydropyran (1) + 1-Propanol (2)	
40.00, 53.33	nonazeotrope	
66.66	0.962	347.74
79.99	0.937	353.31
93.32	0.914	358.16
98.66	0.905	359.94
	Tetrahydropyran (1) + 2-Methyl-2-propanol (2)	
40.00	0.692	332.07
53.33	0.536	339.44
66.66	0.320	345.18
79.99 to 98.66	nonazeotrope	
	Tetrahydropyran (1) + 2-Butanol (2)	
40.00 to 98.66	nonazeotrope	
	Tetrahydropyran (1) + 2-Methyl-1-propanol (2)	
40.00 to 98.66	nonazeotrope	
	Tetrahydropyran (1) + 1-Butanol (2)	
40.00 to 98.66	nonazeotrope	

Table 5. Deviations between Experimental and Calculated Boiling Points for Eight Binary Systems Using the ASOG Contribution Method

system	average deviation[a]/K	maximum deviation/K
tetrahydropyran + methanol	0.27	0.62
tetrahydropyran + ethanol	0.37	0.78
tetrahydropyran + 2-propanol	0.17	0.46
tetrahydropyran + 1-propanol	0.18	0.46
tetrahydropyran + 2-methyl-2-propanol	0.73	1.43
tetrahydropyran + 2-butanol	0.53	1.26
tetrahydropyran + 2-methyl-1-propanol	0.48	1.28
tetrahydropyran + 1-butanol	0.13	0.73

[a] Average deviation $= 1/N\sum_{k=1}^{N} |T_{\mathrm{exptl}} - T_{\mathrm{calcd}}|_k$; N = the number of the data points.

The determined fitting parameters for eq 2 and the average deviations between the experimental and calculated boiling points are summarized in Table 2. The case of temperature independence of parameter $g_{ij} - g_{jj}$ was also shown additionally in Table 2. The NRTL equation gave good correlation for all eight binary mixtures examined in this work. The correlated results are graphically shown as solid lines (boiling point) and broken lines (dew point) in Figures 2 to 9. The average deviations between the experimental and calculated boiling points were (0.09, 0.06, 0.04, 0.06, 0.04, 0.05, 0.04, and 0.08) K for THP + methanol, + ethanol, + 2-propanol, + 1-propanol, + 2-methyl-2-propanol, + 2-butanol, + 2-methyl-1-propanol, and + 1-butanol, respectively.

In addition, the azeotropic points for the six systems (THP + methanol, THP + ethanol, THP + 2-propanol, THP + 1-propanol, and THP + 2-methyl-2-propanol) were determined from the NRTL equation. The azeotropic composition and temperature are shown in Table 3.

Determinations of ASOG Group Pair Parameters. The ASOG group contribution method[2,6] is given by the following equations

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{G}} \tag{4}$$

$$\ln \gamma_i^{\mathrm{C}} = 1 - \frac{\nu_i^{\mathrm{FH}}}{\sum_j \nu_j^{\mathrm{FH}} x_j} + \ln \frac{\nu_i^{\mathrm{FH}}}{\sum_j \nu_j^{\mathrm{FH}} x_j} \tag{5}$$

$$\ln \gamma_i^{\mathrm{G}} = \sum \nu_{ki} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \tag{6}$$

where $\Gamma_k^{(i)}$ is the activity coefficient in the standard state.

Table 4. ASOG Group Pair Parameters $m_{k,l}$ and $n_{k,l}$[a]

l	CH_2		ArCH		H_2O		OH		pyran	
k	m	n	m	n	m	n	m	n	m	n
CH_2	0.0^b	0.0^b	-0.7457^b	146.0^b	-0.2727^b	-277.3^b	-41.2503^b	7686.4^b	-1.2277^c	288.1^c
ArCH	0.7297^b	-176.8^b	0.0^b	0.0^b	-0.7444^b	-180.4^b	2.2682^b	-1111.5^{a}	1.2569^c	-511.3^c
H_2O	0.5045^b	-2382.3^b	0.3197^b	-694.2^b	0.0^b	0.0^b	1.4318^b	-280.2^{a}	-4.6492^c	958.5^c
OH	4.7125^b	-3060^b	-0.2115^b	-0.2^b	-5.8341^b	-3221.4^b	0.0^b	0.0^b	-0.0687^d	-660.6^d
pyran	1.0013^c	-248.1^c	-0.9633^c	406.8^c	1.0696^c	-476.0^c	-0.8366^d	-14.405^d	0.0^c	0.0^c

[a] Pyran: $\nu_{ki} = 6$, $\nu_i^{\mathrm{FH}} = 6$. [b] Ref 6. [c] Ref 2. [d] This work.

$$\ln \Gamma_k = 1 - \sum_l \frac{X_l a_{l,k}}{\sum_m X_m a_{l,m}} - \ln \sum_l X_l a_{k,l} \tag{7}$$

$$X_l = \frac{\sum_j x_j \nu_{lj}}{\sum_j x_j \sum_l \nu_{lj}} \tag{8}$$

$$a_{kl} = \exp\left(m_{kl} + \frac{n_{kl}}{T}\right) \tag{9}$$

where m_{kl} and n_{kl} are ASOG group pair parameters.

The determined ASOG group pair parameters for the OH and pyran groups are listed in Table 4, and the average deviations between the experimental and calculated boiling points are listed in Table 5. The ASOG group pair parameters of pyran, CH_2, ArCH, and H_2O were obtained from the literature.[2,6]

Using these values, the vapor−liquid equilibria data containing pyrans, alkanes, aromatic hydrocarbons, water, and alcohols can be estimated.

Conclusions

In this work, the boiling points of eight binary systems at six pressures from (40.00 to 98.66) kPa were measured using a hold-up compensable ebulliometer. The systems consisting of THP + 2-butanol, THP + 2-methyl-1-propanol, and THP + 1-butanol are nonazeotropic, while those of THP + methanol, THP + ethanol, and THP + 2-propanol are azeotropic. The existence of azeotropic points for THP + 1-propanol and THP + 2-methyl-2-propanol systems depends on the pressures. The measured boiling points were satisfactorily correlated using the NRTL equation. The average deviations between the experimental and calculated boiling points were (0.09, 0.06, 0.04, 0.06, 0.04, 0.05, 0.04, and 0.08) K for THP + methanol, + ethanol, + 2-propanol, + 1-propanol, + 2-methyl-2-propanol, + 2-butanol, + 2-methyl-1-propanol, and + 1-butanol, respectively. The ASOG group pair parameters for the OH and pyran groups were also determined.

Acknowledgment

THP of this work was supplied by Showa Denko K.K.

Literature Cited

(1) Showa Denko K. K. Japanese Patent Disclosure WO2006062211, 2006.
(2) Uno, S.; Matsuda, H.; Kurihara, K.; Tochigi, K.; Miyano, Y.; Kato, S.; Yasuda, H. Measurements of vapor-liquid equilibria for binary systems including tetrahydropyran. *J. Jpn. Petrol. Inst.* **2008**, *51*, 107–113.
(3) Uno, S.; Kikkawa, S.; Matsuda, H.; Kurihara, K.; Tochigi, K.; Ochi, K. Measurement of Vapor-Liquid Equilibria for Binary Systems Using a Hold-up Compensable Ebulliometer. *J. Chem. Eng. Jpn.* **2007**, *40*, 288–294.
(4) Uno, S.; Matsuda, H.; Kurihara, K.; Tochigi, K.; Ochi, K. Determination of NRTL Parameters for Aqueous Solutions Using a Vapor Hold-up Compensable Ebulliometer. *Kagaku Kougaku Ronbunshu* **2007**, *33*, 391–395.
(5) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.
(6) Tochigi, K.; Tiegs, D.; Gmehling, J.; Kojima, K. Determination of New ASOG Parameters. *J. Chem. Eng. Jpn.* **1990**, *23*, 453–463.
(7) Poling, B. E.; Prausnitz, J. M.; O'Connell J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2000; pp A.47−A.60.
(8) Riddick, J. A.; Bunger, W.; Sakano, T. K. *Organic Solvents Physical Properties and Methods of Purification*, 4th ed.; John Wiley & Sons: New York, 1986.
(9) Miyano, Y.; Uno, S.; Tochigi, K.; Kato, S.; Yasuda, H. Henry's Law Constants and Infinite Dilution Activity Coefficients of Propane, Propene, Butane, 2-Methylpropane, 1-Butene, 2-Methylpropene *trans*-2-Butene, cis-2-Butene, 1,3-Butadiene, Dimethylether, Chloroethane, 1,1-Difluoroethane, and Hexane in Tetrahydropyran. *J. Chem. Eng. Data* **2007**, *52*, 2245–2249.
(10) Marquardt, D. W. An Algorithm for Least-Squares Estimation of Nonlinear Parameters. *Soc. Ind. Appl. Math.* **1963**, *11*, 431–441.

Received for review February 29, 2008. Accepted June 26, 2008.

JE800145H