Korean J. Chem. Eng., **21**(3), 699-702 (2004)

SHORT COMMUNICATION

Vapor-Liquid Equilibria for (Methyl Tertiary Butyl Ether+Methanol+Octane) and (Methyl Tertiary Butyl Ether+Methanol+*i*-Octane) Systems at Atmospheric Pressure

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(*Received 12 December 2003 • accepted 10 March 2004*)

Abstract−Isobaric vapor-liquid equilibria (VLE) of two ternary systems (methyl tertiary butyl ether+methanol+octane and methyl tertiary butyl ether+methanol+*i*-octane) were measured at atmospheric pressure by using a modified Othmer-type circulation apparatus. The VLE data of these ternary systems can be predicted by Wilson equation with the parameters determined by VLE data of constituent binary systems.

Key words: Vapor-Liquid Equilibria, Atmospheric Pressure, Methyl Tertiary Butyl Ether, Methanol, Octane, *i*-Octane

INTRODUCTION

Ethers and alcohols used as gasoline additives have received much attention as octane number enhancing and environmental protection agents. Methyl tertiary butyl ether (MTBE) seems to be one of promising ethers. The vapor-liquid equilibria (VLE) of these mixtures such as MTBE+alcohol+alkane are needed to understand the phase behavior in producing and blending operations. Therefore, in a previous study [Watanabe et al., 2003], VLE of four binary systems containing MTBE (MTBE+methanol, MTBE+heptane, MTBE +octane, and MTBE+*i*-octane) and a ternary system (MTBE+methanol+heptane) at atmospheric pressure were reported. And, it is noted that VLE of these binary systems can be correlated by Wilson equation [Wilson, 1964] and VLE of the ternary system can be predicted by using the parameters determined with binary VLE data.

In this study, as a continuation, VLE of two ternary systems (MTBE +methanol+octane and MTBE+methanol+*i*-octane) were measured at atmospheric pressure and the ternary VLE data obtained were predicted by Wilson equation with the parameters determined by VLE data of each binary system.

EXPERIMENTAL

1. Materials

MTBE was supplied by Tokyo Kasei Kogyo and methanol, octane and *i*-octane were supplied by Wako Pure Chemical Industries. They were special grade reagents and were used without further purification because no impurities were detected by the gas chromatographic analysis. Their purities are estimated to be more than 99%, 99.8%, 98%, and 99% for MTBE, methanol, octane and *i*-octane, respectively.

2. Apparatus and Procedure

A detailed description is given in the previous paper [Watanabe et al., 2003]. An all-glass Othmer-type apparatus was used and the samples of both vapor and liquid phases were analyzed with a gas chromatograph equipped with a flame ionization detector (FID) and an integrator. The temperatures were measured with copper- or iron-constantan thermocouples. The uncertainties are estimated to be within ±0.1 K in temperature and ±0.001 in mole fractions.

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RESULTS AND DISCUSSION

1. Fundamental Equation

VLE relation at low pressure can be expressed by the following equation when no significant interaction such as association occurs in vapor phase.

$$\pi y_i = \gamma_i x_i p_i^0 \quad (1)$$

where π is the total pressure (π=101.3 kPa), γ_i is the liquid phase activity coefficient, x_i and y_i are liquid and vapor phase mole fractions, respectively. Further, p_i^0 is the vapor pressure of pure component and can be calculated by using Antoine equation of which constants are presented in Table 1.

2. VLE Data

VLE data of two ternary systems (MTBE+methanol+octane and MTBE+methanol+*i*-octane) are presented in Tables 2 and 3 and illustrated in Figs. 1 and 2. The activity coefficients of each component are evaluated by Eq. (1) and are shown in Tables 2 and 3. Azeotropic points of constituent binary systems are summarized in Table 4. As shown in the table, azeotropic points present for MTBE +methanol and methanol+alkane (heptane, octane, *i*-octane) binary systems though there is no azeotropic point for MTBE+alkane bi-

Table 1. Boiling points and Antoine constants[a]

Component	Boiling point [K]	Constants			Ref.
		A	B	C	
MTBE	328.3	6.038757	1149.261	−43.150	b
Methanol	337.7	7.025886	1474.078	−44.020	b
Heptane	371.6	6.020230	1263.909	−56.718	c
Octane	398.9	6.043940	1351.938	−64.030	d
i-Octane	372.4	5.936790	1257.840	−53.415	e

[a]$\log(p^0/\text{kPa}) = A - B/[(T/K)+C]$. [b]Arce et al. [1996]. [c]Wisniak et al. [1997]. [d]Hiaki et al. [1999]. [e]Loras et al. [1999].

Table 2. Experimental VLE data for MTBE(1)+methanol(2)+ octane(3) at atmospheric pressure

T [K]	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	T [K]	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
334.1	0.077	0.735	0.138	0.779	1.491	1.224	4.063	344.5	0.436	0.009	0.794	0.095	1.099	8.631	1.211
332.8	0.100	0.768	0.180	0.755	1.542	1.197	4.854	332.0	0.443	0.150	0.504	0.443	1.005	3.711	1.339
332.6	0.111	0.597	0.161	0.760	1.254	1.561	2.691	329.5	0.449	0.208	0.510	0.449	1.087	3.010	1.359
332.3	0.131	0.681	0.248	0.680	1.658	1.241	3.848	335.1	0.455	0.048	0.633	0.309	1.115	7.129	1.045
331.3	0.133	0.782	0.268	0.682	1.820	1.129	6.199	329.9	0.459	0.242	0.477	0.483	0.983	2.733	1.506
333.8	0.138	0.428	0.175	0.745	1.058	2.034	1.729	328.5	0.459	0.277	0.538	0.426	1.158	2.232	1.637
331.3	0.142	0.703	0.269	0.675	1.712	1.242	3.806	336.3	0.466	0.060	0.620	0.313	1.029	5.543	1.191
333.0	0.145	0.647	0.259	0.677	1.528	1.263	3.002	332.9	0.477	0.106	0.564	0.380	1.017	4.354	1.309
334.6	0.151	0.401	0.183	0.743	0.983	2.099	1.510	328.5	0.482	0.384	0.528	0.448	1.083	1.692	2.174
332.7	0.165	0.621	0.240	0.695	1.258	1.367	3.018	342.2	0.487	0.006	0.845	0.070	1.123	10.108	1.118
332.7	0.182	0.563	0.237	0.702	1.124	1.523	2.390	325.5	0.488	0.457	0.552	0.436	1.235	1.572	3.112
328.6	0.186	0.713	0.341	0.617	1.809	1.252	4.962	342.4	0.490	0.010	0.813	0.101	1.067	8.174	1.135
338.9	0.191	0.091	0.253	0.637	0.944	6.656	1.169	328.1	0.498	0.260	0.547	0.423	1.101	2.402	1.523
333.7	0.201	0.138	0.271	0.639	1.132	5.430	1.292	325.0	0.516	0.438	0.574	0.420	1.234	1.618	1.784
329.9	0.210	0.651	0.340	0.613	1.531	1.290	3.787	340.5	0.519	0.015	0.812	0.108	1.064	6.678	1.220
335.7	0.242	0.154	0.290	0.624	0.944	4.390	1.241	328.7	0.526	0.197	0.588	0.377	1.100	2.763	1.486
328.2	0.256	0.668	0.408	0.564	1.588	1.243	4.554	332.9	0.533	0.109	0.584	0.368	0.941	4.084	1.331
328.6	0.263	0.605	0.371	0.589	1.391	1.408	3.597	332.6	0.545	0.086	0.651	0.303	1.035	4.303	1.260
332.0	0.271	0.373	0.321	0.619	1.046	2.084	1.735	328.3	0.549	0.231	0.611	0.359	1.107	2.273	1.650
332.9	0.272	0.302	0.330	0.605	1.040	2.430	1.510	326.6	0.554	0.409	0.604	0.388	1.146	1.496	2.819
333.4	0.279	0.224	0.338	0.592	1.024	3.142	1.355	338.2	0.559	0.017	0.817	0.113	1.066	6.489	1.308
327.1	0.295	0.636	0.419	0.559	1.472	1.356	4.028	331.2	0.561	0.133	0.639	0.321	1.033	3.140	1.366
334.3	0.301	0.055	0.456	0.434	1.248	9.100	1.575	328.7	0.596	0.152	0.648	0.322	1.067	3.044	1.437
326.5	0.308	0.622	0.451	0.532	1.547	1.353	3.141	328.5	0.599	0.199	0.622	0.350	1.026	2.555	1.693
330.8	0.309	0.439	0.379	0.571	1.126	1.716	2.126	334.2	0.613	0.023	0.825	0.118	1.109	5.955	1.461
332.8	0.311	0.273	0.349	0.586	0.967	2.607	1.552	327.3	0.616	0.197	0.654	0.325	1.091	2.528	1.432
333.9	0.324	0.236	0.370	0.565	0.949	2.782	1.392	326.0	0.632	0.330	0.639	0.354	1.087	1.735	2.209
334.6	0.327	0.111	0.402	0.519	1.001	5.277	1.283	326.9	0.640	0.254	0.646	0.338	1.052	2.069	1.871
329.1	0.332	0.350	0.395	0.551	1.153	2.229	1.983	326.6	0.652	0.173	0.672	0.308	1.084	2.809	1.514
329.9	0.337	0.322	0.370	0.577	1.037	2.456	1.753	333.2	0.664	0.027	0.842	0.114	1.079	5.091	1.362
326.5	0.363	0.565	0.479	0.501	1.395	1.402	3.549	325.5	0.676	0.298	0.661	0.335	1.066	1.855	2.519
332.4	0.373	0.153	0.431	0.500	1.010	4.040	1.455	333.0	0.697	0.032	0.838	0.115	1.031	4.332	1.698
329.7	0.391	0.328	0.453	0.502	1.103	2.117	1.811	328.7	0.700	0.161	0.691	0.291	0.970	2.611	1.525
328.7	0.412	0.314	0.510	0.449	1.215	2.062	1.775	327.2	0.712	0.200	0.693	0.295	1.005	2.265	1.639
326.5	0.433	0.500	0.498	0.487	1.212	1.542	3.020	326.8	0.794	0.102	0.785	0.197	1.034	3.013	2.318
334.3	0.434	0.088	0.535	0.400	1.013	5.185	1.259	328.0	0.952	0.023	0.943	0.054	0.995	3.535	1.414

nary systems. The present work indicates that the ternary azeotropic point cannot be observed though the constituent two binary systems possess the azeotropic points.

3. Prediction

Based on Eq. (1), x-y relation can be predicted by using activity coefficients. To date, the following Wilson equation is recognized to be one of useful equations.

$$\ln\gamma_i = -\ln\left(\sum_j x_j\Lambda_{ij}\right) + 1 - \sum_k \frac{x_k\Lambda_{ki}}{\sum_j x_j\Lambda_{kj}} \quad (2)$$

where Λ_{ij} and Λ_{ji} are the parameters adjusted by using VLE data of the binary (i+j) system. Therefore, one can predict VLE of a multicomponent system by using VLE data of constituent binary systems.

The Wilson parameters are shown in Table 5. These parameters were determined by using VLE data of binary systems. Table 5 contains the binary systems of which parameters are shown in the previous paper [Watanabe et al., 2003]. Their values in Table 5 are slightly different from the previous values because they are re-adjusted in this work to give more precise fit.

VLE relation of a ternary system can be predicted by Eqs. (1) and (2) with the binary parameters given in Table 5. The prediction performance is summarized in Table 6. The previous ternary system (MTBE+methanol+heptane) is included in the table for comparison. Graphical illustrations are shown in Figs. 1 and 2. As shown in Table 6 and Figs. 1 and 2, it is noted that VLE of the present ternary systems can be predicted by Wilson equation.

CONCLUSION

Table 3. Experimental VLE data for MTBE(1)+methanol(2)+*i*-octane(3) at atmospheric pressure

T [K]	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
331.6	0.046	0.442	0.070	0.707	1.378	2.042	1.638
331.8	0.078	0.359	0.082	0.693	0.934	2.447	1.495
335.0	0.088	0.136	0.120	0.606	1.095	4.953	1.170
330.9	0.101	0.665	0.143	0.663	1.292	1.312	3.198
330.3	0.125	0.494	0.188	0.621	1.407	1.696	1.973
328.8	0.157	0.762	0.271	0.618	1.692	1.165	5.694
330.0	0.169	0.610	0.228	0.611	1.272	1.368	2.900
328.6	0.187	0.737	0.315	0.589	1.662	1.156	5.335
333.2	0.197	0.151	0.224	0.559	0.965	4.422	1.183
332.3	0.209	0.159	0.248	0.556	1.036	4.348	1.135
329.3	0.226	0.558	0.281	0.578	1.201	1.454	2.678
329.0	0.233	0.620	0.311	0.573	1.300	1.317	3.257
330.7	0.237	0.284	0.246	0.572	0.957	2.670	1.481
329.9	0.237	0.464	0.276	0.567	1.100	1.675	2.104
331.5	0.258	0.192	0.278	0.540	0.966	3.603	1.253
329.0	0.260	0.539	0.322	0.555	1.206	1.464	2.545
327.7	0.264	0.676	0.399	0.539	1.538	1.198	4.463
330.2	0.264	0.321	0.275	0.555	0.974	2.342	1.621
328.8	0.290	0.381	0.322	0.530	1.086	1.995	1.882
328.6	0.318	0.429	0.380	0.513	1.179	1.729	1.782
329.0	0.327	0.512	0.334	0.545	0.995	1.513	3.131
328.6	0.334	0.459	0.388	0.503	1.145	1.587	2.208
328.8	0.366	0.359	0.388	0.496	1.037	1.984	1.768
330.7	0.375	0.176	0.409	0.440	1.003	3.323	1.311
326.7	0.397	0.553	0.483	0.476	1.277	1.348	3.776
326.2	0.408	0.543	0.515	0.450	1.348	1.327	3.274
327.9	0.410	0.395	0.448	0.464	1.101	1.750	1.958
328.8	0.427	0.262	0.444	0.439	1.018	2.407	1.574
325.8	0.441	0.514	0.531	0.439	1.303	1.391	3.117
331.8	0.469	0.093	0.507	0.354	0.963	4.823	1.184
328.4	0.475	0.266	0.495	0.407	1.033	2.239	1.598
328.0	0.519	0.240	0.524	0.387	1.016	2.400	1.574
326.9	0.532	0.283	0.552	0.377	1.080	2.067	1.742
325.1	0.540	0.421	0.593	0.387	1.215	1.543	2.488
328.6	0.544	0.200	0.550	0.363	0.995	2.634	1.435
330.2	0.546	0.070	0.554	0.333	0.950	6.441	1.174
329.0	0.572	0.153	0.590	0.318	1.004	2.959	1.379
330.2	0.620	0.138	0.561	0.330	0.848	3.242	1.774
324.8	0.633	0.337	0.651	0.335	1.148	1.691	2.330
330.1	0.669	0.041	0.705	0.205	0.990	6.742	1.229
324.6	0.701	0.273	0.687	0.303	1.102	1.902	2.012
328.1	0.763	0.086	0.640	0.293	0.840	5.054	1.886
324.6	0.766	0.214	0.729	0.263	1.071	2.106	1.866
324.4	0.816	0.168	0.772	0.222	1.072	2.287	1.701
326.9	0.822	0.072	0.780	0.187	0.988	4.054	1.401
328.4	0.847	0.047	0.751	0.186	0.879	5.776	2.532
324.6	0.848	0.138	0.800	0.194	1.061	2.407	2.067
324.7	0.877	0.112	0.818	0.179	1.046	2.718	1.570

Isobaric VLE relations of ternary systems containing MTBE were measured at atmospheric pressure by using a modified Othmer-type circulation apparatus. The data are reported for two ternary systems: MTBE+methanol+octane and MTB+methanol+*i*-octane. For the present data, the prediction performance of Wilson equation with the parameters determined by VLE data of the constituent binary systems were discussed. The results show that the Wilson equation can be adopted to predict VLE of the present ternary systems.

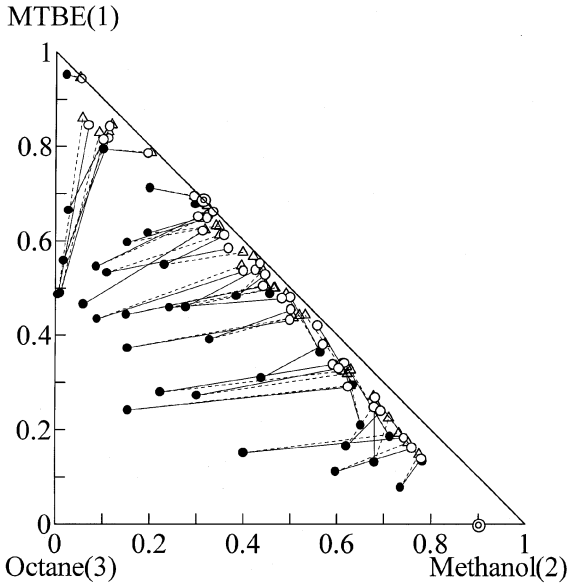

Fig. 1. Tie-lines for MTBE(1)+methanol(2)+octane(3) at atmospheric pressure: (●) experimental data of liquid phase, (○) experimental data of vapor phase, (△) predicted values of vapor phase by Wilson equation, (◎) azeotropic point.

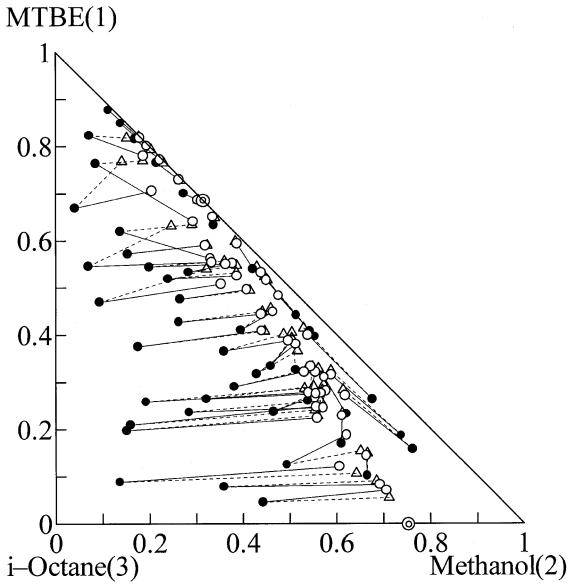

Fig. 2. Tie-lines for MTBE(1)+methanol(2)+*i*-octane(3) at atmospheric pressure: (●) experimental data of liquid phase, (○) experimental data of vapor phase, (△) predicted values of vapor phase by Wilson equation, (◎) azeotropic point.

Table 4. Azeotropic points of constituent binary systems

System	$x_{1,az}$ [a]	T_{az} [K] [b]	Ref.
MTBE(1)+methanol(2)	0.695	324.3	c
Methanol(1)+heptane(2)	0.746	331.9	d
Methanol(1)+octane(2)	0.895	336.0	d
Methanol(1)+*i*-octane(2)	0.752	332.1	d

[a]Mole fraction of the lower boiling point component at the azeotropic point.
[b]Boiling point of the azeotropic binary mixture.
[c]Watanabe et al. [2003].
[d]Budantseva et al. [1975].

Table 5. Wilson parameters and correlation performance

System	Λ_{12} [-]	Λ_{21} [-]	ΔT [K]	Δy_1 [-]	Ref.
MTBE(1)+methanol(2)	0.5004	0.4804	0.3	0.009	a
MTBE 1)+heptane(2)	0.4206	1.4908	0.9	0.012	a
MTBE(1)+octane(2)	2.0778	0.2115	1.0	0.013	a
MTBE(1)+*i*-octane(2)	0.8862	0.9287	0.4	0.006	a
Methanol(1)+heptane(2)	0.07643	0.07686	0.6	0.007	b
Methanol(1)+octane(2)	0.09749	0.05240	0.3	0.003	b
Methanol(1)+*i*-octane(2)	0.1072	0.08442	0.6	0.005	b

$\Delta T = \sum_k |T_{cal} - T_{exp}|_k$ /N, $\Delta y_1 = \sum_k |y_{1,cal} - y_{1,exp}|_k$ /N, N=number of data points.
[a]Watanabe et al. [2003].
[b]Budantseva et al. [1975].

Table 6. Prediction performance for MTBE(1)+methanol(2)+alkane(3)

System	ΔT [K]	Δy_1 [-]	Δy_2 [-]	Δy_3 [-]
MTBE(1)+methanol(2)+heptane(3)	1.1	0.018	0.020	0.008
MTBE(1)+methanol(2)+octane(3)	0.9	0.013	0.013	0.006
MTBE(1)+methanol(2)+*i*-octane(3)	0.5	0.020	0.016	0.007

$\Delta T = \sum_k |T_{cal} - T_{exp}|_k$ /N, $\Delta y_i = \sum_k |y_{i,cal} - y_{i,exp}|_k$ /N, (i=1, 2, 3), N=number of data points.

NOMENCLATURE

p_i^0 : vapor pressure of pure component i [Pa]
x_i : liquid phase mole fraction of component i [-]
y_i : vapor phase mole fraction of component i [-]

Greek Letters

γ_i : liquid phase activity coefficient of component i [-]
Λ_{12}, Λ_{21} : Wilson interaction parameters between components 1 and 2 [-]
π : total pressure (=101.3 kPa) [Pa]

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