

# Isothermal Vapor–Liquid Equilibria of 2-Methoxy-2-methylbutane (TAME) + *n*-Alcohol (C<sub>1</sub>–C<sub>4</sub>) Mixtures at 323.15 and 333.15 K

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Ether mixtures containing oxygen in their body such as 2-methoxy-2-methylbutane (*tert*-amyl methyl ether; TAME) and 2-methoxy-2-methylpropane (methyl *tert*-butyl ether; MTBE) are used as octane boosters for lead-free or low-leaded gasoline because of their octane-enhancing and pollution-reducing capabilities. In this work, isothermal vapor–liquid equilibrium was measured by headspace gas chromatography, one of the static methods, for TAME + *n*-alcohol (C<sub>1</sub>–C<sub>4</sub>) binary mixtures at 323.15 and 333.15 K. The binaries showed positive deviations from Raoult's law and have minimum boiling azeotropes, except for TAME + 1-butanol. Results were correlated with  $G^E$  model equations and also compared with the values predicted by modified UNIFAC (Dortmund).

## Introduction

Vapor–liquid equilibria (VLE) are commonly measured with a recirculating still, in which usually the compositions of both the liquid and vapor phases are analyzed, while in headspace gas chromatography (HSGC), only the vapor phase is analyzed. The HSGC method was developed with the following operational features: (1) rapid analysis of samples, (2) ability to work at low sample concentrations, and (3) minimum perturbation of the equilibrium by the sampling process (Hussam and Carr, 1985). In the work of others (Weidlich and Gmehling, 1985), the true equilibrium composition of the liquid phase was calculated by an iterative method with  $G^E$  model parameters. In this work, the equilibrium liquid composition was calculated from the initial composition, peak area of the vapor phase, and thermodynamic relations.

Ether mixtures help complete combustion with the contained oxygen in their bodies. Therefore, 2-methoxy-2-methylbutane (*tert*-amyl methyl ether; TAME; C<sub>2</sub>H<sub>5</sub>C(CH<sub>3</sub>)<sub>2</sub>OCH<sub>3</sub>) and 2-methoxy-2-methylpropane (methyl *tert*-butyl ether; MTBE) are used as octane boosters for lead-free or low-leaded gasoline because of their octane-enhancing and pollution-reducing capabilities. They are less polar than alcohols and also decrease the volatility of gasoline more than alcohols.

In this work, isothermal VLE for the systems of TAME + *n*-alcohol (C<sub>1</sub>–C<sub>4</sub>) at 323.15 and 333.15 K were measured by using HSGC. We cannot find the published data on TAME + ethanol, + 1-propanol, and + 1-butanol, while TAME + methanol data exist in some papers (Marcela and Danuta, 1990). The experimental VLE data were correlated with conventional  $G^E$  models and compared with the predicted values by modified UNIFAC (Dortmund) (Weidlich and Gmehling, 1987; Gmehling et al., 1993).

## Theory

The fugacity of any solute must be equal in the equilibrium vapor and liquid phases. So at the low-pressure equilibrium state, for the vapor–liquid equilibrium state we have

$$y_i \phi_i P = \gamma_i x_i f_i^0 \quad (1)$$

According to Kolb's experiments (Kolb, 1976), the chromatographic peak area  $A_i$  for component  $i$  in the headspace

analysis is proportional to its partial vapor pressure  $P_i$ , as expressed in eqs 2 and 3.

$$A_i = C_1 P_i \quad (2)$$

$$A_i^0 = C_1 P_i^0 \quad (3)$$

where superscript "0" indicates the reference state and  $C_1$  is the calibration factor. At the low pressures, up to a few bar, we can assume that the fugacity  $f_i$  of a species is equal to its partial pressure  $P_i$ , ignoring the real gas behavior. Therefore, activity  $f_i/f_i^0$  is equal to  $P_i/P_i^0$  and the activity coefficient of component  $i$ ,  $\gamma_i$ , can be expressed as follows.

$$\gamma_i = \frac{P_i}{x_i P_i^0} \quad (4)$$

$$\gamma_i = \frac{A_i}{x_i A_i^0} \quad (5)$$

Therefore, the ratio of the activity coefficients of a binary system is

$$\frac{\gamma_1}{\gamma_2} = \frac{x_2 A_1 A_2^0}{x_1 A_2 A_1^0} \quad (6)$$

On the basis of the Gibbs–Duhem equation, Redlich and Kister (1948) introduced eq 7 for isothermal vapor–liquid equilibria.

$$\int_0^1 \ln \left( \frac{\gamma_1}{\gamma_2} \right) dx_1 = 0 \quad (7)$$

Equation 7 is used as a thermodynamic consistency test in the isothermal case. In order to be the correct VLE data, the experimental data should satisfy eq 7. Therefore, substituting eq 6 into eq 7, the ratio of reference peak area ( $A_i^0$ ) will be obtained from

$$\int_0^1 \ln \left( \frac{x_2 A_1}{x_1 A_2} \right) dx_1 = \ln \left( \frac{A_1^0}{A_2^0} \right) \quad (8)$$

The left term of eq 8 can be integrated with a polynomial

**Table 1. Purities, Measured Densities,  $\rho/g\text{ cm}^{-3}$ , at 298.15 K, and Antoine Constants of Pure Components**

components	GC analysis (mass %)	density, $\rho/g\text{ cm}^{-3}$		Antoine constant <sup>e</sup>		
		present study	lit. value	A	B	C
TAME	99.9	0.7704 <sup>a</sup>	0.7703 <sup>b</sup>	5.976 31	1208.390	217.907
methanol	99.8	0.7864	0.786 37 <sup>c</sup>	7.205 87	1581.271	239.184
ethanol	99.9	0.7850	0.785 00 <sup>c</sup>	7.237 10	1592.864	226.184
1-propanol	99.8	0.7995	0.799 60 <sup>c</sup>	7.503 85	1788.080	227.438
1-butanol	99.8	0.8055	0.805 80 <sup>d</sup>	6.962 90	1558.190	196.881

<sup>a</sup> At 293.15 K values. <sup>b</sup> Calculated value at 293.15 K. <sup>c</sup> Data from Riddick et al. (1986). <sup>d</sup> Data from Venkataramana et al. (1995). <sup>e</sup> Data from Gmehling et al. (1977).

**Table 2. Isothermal Vapor–Liquid Equilibrium Data of TAME + *n*-Alcohol (C<sub>1</sub>–C<sub>4</sub>) at 323.15 K**

<i>P</i> (calc)/kPa	<i>x</i> <sub>1</sub>	<i>y</i> <sub>1</sub>	$\gamma_1$	$\gamma_2$	<i>P</i> (calc)/kPa	<i>x</i> <sub>1</sub>	<i>y</i> <sub>1</sub>	$\gamma_1$	$\gamma_2$	<i>P</i> (calc)/kPa	<i>x</i> <sub>1</sub>	<i>y</i> <sub>1</sub>	$\gamma_1$	$\gamma_2$
Methanol (1) + TAME (2)														
32.19	0.0151	0.1015	3.8997	1.0007	52.71	0.2483	0.5414	2.0692	1.0961	59.98	0.6999	0.7281	1.1232	1.8518
34.39	0.0286	0.1694	3.6663	1.0019	54.71	0.3066	0.5743	1.8449	1.1451	60.10	0.7499	0.7531	1.0864	2.0220
37.02	0.0461	0.2409	3.4835	1.0039	56.04	0.3469	0.5967	1.7354	1.1798	60.02	0.8003	0.7836	1.0577	2.2170
38.63	0.0571	0.2802	3.4102	1.0050	56.05	0.3995	0.5967	1.5072	1.2831	59.67	0.8527	0.8213	1.0342	2.4679
40.39	0.0725	0.3199	3.2088	1.0093	57.33	0.4485	0.6260	1.4405	1.3253	59.04	0.8999	0.8619	1.0175	2.7771
42.05	0.0871	0.3550	3.0863	1.0127	58.50	0.5000	0.6534	1.3764	1.3822	58.78	0.9147	0.8750	1.0118	2.9329
45.12	0.1213	0.4142	2.7740	1.0253	58.61	0.5517	0.6568	1.2561	1.5294	57.94	0.9454	0.9113	1.0050	3.2087
47.88	0.1547	0.4628	2.5780	1.0373	59.39	0.6074	0.6885	1.2117	1.6062	57.43	0.9603	0.9317	1.0026	3.3622
50.51	0.2003	0.5060	2.2970	1.0636	59.70	0.6511	0.7047	1.1632	1.7221	54.26	0.9752	0.9547	1.0011	3.5333
Ethanol (1) + TAME (2)														
31.38	0.0287	0.0892	3.3070	1.0025	38.08	0.2996	0.3879	1.6698	1.1340	37.40	0.7504	0.6184	1.0437	1.9485
32.20	0.0438	0.1240	3.0839	1.0050	38.43	0.3489	0.4165	1.5538	1.1737	36.06	0.8034	0.6834	1.0387	1.9782
32.87	0.0582	0.1522	2.9087	1.0081	38.64	0.4054	0.4417	1.4258	1.2364	35.09	0.8489	0.7309	1.0232	2.1283
33.63	0.0746	0.1839	2.8079	1.0106	38.73	0.4585	0.4662	1.3336	1.3009	33.67	0.9003	0.7978	1.0105	2.3259
34.23	0.0899	0.2082	2.6841	1.0148	38.70	0.5069	0.4882	1.2626	1.3687	33.24	0.9150	0.8179	1.0061	2.4276
34.86	0.1124	0.2343	2.4617	1.0247	38.59	0.5500	0.5158	1.2257	1.4148	32.04	0.9461	0.8738	1.0021	2.5567
35.97	0.1494	0.2814	2.2945	1.0354	38.38	0.6044	0.5467	1.1758	1.4986	31.41	0.9603	0.9047	1.0018	2.5713
36.86	0.1993	0.3216	2.0152	1.0643	38.16	0.6491	0.5660	1.1270	1.6085	30.75	0.9754	0.9378	1.0009	2.6518
37.64	0.2486	0.3611	1.8519	1.0904	37.61	0.7003	0.6071	1.1041	1.6800	30.04	0.9904	0.9740	1.0001	2.7695
TAME (1) + Propanol (2)														
12.28	0.0152	0.0789	2.1678	1.0001	23.06	0.3504	0.6430	1.4417	1.1038	28.81	0.8010	0.8584	1.0519	1.7853
12.97	0.0289	0.1401	2.1434	1.0004	24.44	0.3987	0.6873	1.4353	1.1069	29.09	0.8496	0.8828	1.0298	1.9736
14.36	0.0595	0.2458	2.0217	1.0031	24.96	0.4492	0.7039	1.3326	1.1690	29.31	0.9002	0.9139	1.0139	2.2024
15.00	0.0743	0.2883	1.9834	1.0045	26.24	0.5013	0.7440	1.3268	1.1734	29.36	0.9163	0.9246	1.0093	2.3035
16.13	0.1002	0.3557	1.9508	1.0061	26.61	0.5481	0.7554	1.2498	1.2544	29.40	0.9307	0.9360	1.0072	2.3615
17.89	0.1497	0.4454	1.8135	1.0167	27.06	0.5998	0.7718	1.1864	1.3445	29.42	0.9460	0.9480	1.0044	2.4668
19.55	0.1999	0.5170	1.7226	1.0278	27.59	0.6485	0.7925	1.1487	1.4186	29.42	0.9621	0.9617	1.0019	2.5945
20.93	0.2485	0.5701	1.6360	1.0431	28.02	0.7008	0.8119	1.1060	1.5348	29.42	0.9742	0.9732	1.0011	2.6591
22.33	0.2992	0.6183	1.5718	1.0593	28.42	0.7500	0.8335	1.0762	1.6493	29.39	0.9877	0.9866	1.0003	2.7807
TAME (1) + 1-Butanol (2)														
6.00	0.0299	0.2730	1.8665	1.0005	16.23	0.2992	0.7951	1.4695	1.0559	25.51	0.7501	0.9325	1.0803	1.5330
6.73	0.0450	0.3616	1.8406	1.0009	17.70	0.3499	0.8229	1.4184	1.0734	26.06	0.7989	0.9405	1.0452	1.7158
7.48	0.0600	0.4350	1.8476	1.0006	18.80	0.3991	0.8412	1.3500	1.1058	26.94	0.8489	0.9540	1.0314	1.8229
8.18	0.0752	0.4912	1.8206	1.0017	20.08	0.4502	0.8609	1.3085	1.1312	27.78	0.8991	0.9673	1.0182	2.0011
8.81	0.0904	0.5344	1.7749	1.0041	21.27	0.4995	0.8773	1.2726	1.1602	28.01	0.9145	0.9713	1.0134	2.0936
9.26	0.1006	0.5614	1.7613	1.0049	22.19	0.5492	0.8895	1.2245	1.2108	28.30	0.9305	0.9764	1.0118	2.1346
11.25	0.1494	0.6563	1.6839	1.0116	22.98	0.5998	0.8998	1.1743	1.2809	28.48	0.9433	0.9797	1.0076	2.2708
12.88	0.2006	0.7135	1.5606	1.0275	23.89	0.6492	0.9116	1.1429	1.3396	28.72	0.9590	0.9845	1.0042	2.4219
15.39	0.2501	0.7778	1.6302	1.0147	24.79	0.7003	0.9232	1.1134	1.4144	29.17	0.9886	0.9951	1.0004	2.7980

equation such as

$$\ln\left(\frac{x_2 A_1}{x_1 A_2}\right) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \dots \quad (9)$$

The value of  $\ln(A_1^0/A_2^0)$  can be evaluated from eqs 8 and 9. Then the ratio of activity coefficients  $\gamma_1/\gamma_2$  can be evaluated from eq 6 and the individual activity coefficient can be obtained from eqs 10 and 11, respectively.

$$\ln \gamma_1 = \int_0^{x_1} \ln(\gamma_1/\gamma_2) dx_1 + x_2 \ln(\gamma_1/\gamma_2) \quad (10)$$

$$\ln \gamma_2 = \int_0^{x_1} \ln(\gamma_1/\gamma_2) dx_1 - x_1 \ln(\gamma_1/\gamma_2) \quad (11)$$

The total pressure and partial pressure are derived from Raoult's law or the simplified form of eq 1. Then, the vapor phase mole fraction for component *i*, *y<sub>i</sub>*, can be obtained from eq 12.

$$y_i = \frac{P_i}{P} = \frac{y_i P}{(y_1 P + y_2 P)} \quad (12)$$

In the HSGC method, the liquid phase is equilibrated with the vapor phase, which is vaporized from the liquid in a closed small vessel. Therefore, it must be considered that the originally given liquid composition in a vessel is not the same as the equilibrium composition because the liquid vaporized in the closed vessel until equilibrium is reached; i.e., the true liquid phase equilibrium composition must be recalculated. The SRK equation of state (eq 13) was used to recalculate the liquid phase composition (Soave, 1972).

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + bv} \quad (13)$$

where

**Table 3. Isothermal Vapor-Liquid Equilibrium Data  $P(\text{calc})/\text{kPa}$  of TAME +  $n$ -Alcohol ( $C_1$ - $C_4$ ) at 333.15 K**

$P(\text{calc})/\text{kPa}$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$P(\text{calc})/\text{kPa}$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$P(\text{calc})/\text{kPa}$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
Methanol (1) + TAME (2)														
47.11	0.0148	0.1077	4.0504	1.0009	81.71	0.2991	0.5877	1.9003	1.1283	91.75	0.7489	0.7537	1.0928	2.1116
50.90	0.0301	0.1855	3.7161	1.0027	83.74	0.3475	0.6092	1.7378	1.1772	91.66	0.8007	0.7854	1.0639	2.3154
56.79	0.0590	0.2877	3.2788	1.0085	86.64	0.3999	0.6409	1.6436	1.2168	91.19	0.8507	0.8177	1.0372	2.6117
59.79	0.0764	0.3331	3.0843	1.0129	88.13	0.4495	0.6579	1.5269	1.2854	90.16	0.8997	0.8602	1.0199	2.9475
62.15	0.0887	0.3662	3.0360	1.0144	88.69	0.5053	0.6657	1.3832	1.4063	89.75	0.9151	0.8733	1.0133	3.1429
62.99	0.0982	0.3774	2.8645	1.0205	89.98	0.5507	0.6872	1.3290	1.4701	89.16	0.9302	0.8901	1.0093	3.2940
68.53	0.1493	0.4487	2.4379	1.0422	90.80	0.5999	0.7028	1.2593	1.5825	88.43	0.9450	0.9099	1.0073	3.3942
75.62	0.1995	0.5268	2.3637	1.0492	91.13	0.6497	0.7121	1.1822	1.7576	86.72	0.9751	0.9517	1.0011	3.9469
79.13	0.2483	0.5616	2.1187	1.0832	91.56	0.7004	0.7328	1.1338	1.9165	85.51	0.9898	0.9789	1.0002	4.1642
Ethanol (1) + TAME (2)														
45.23	0.0153	0.0685	4.3027	1.0034	57.57	0.2980	0.4062	1.6716	1.1422	56.15	0.8008	0.6980	1.0423	1.9965
46.19	0.0293	0.0949	3.1907	1.0100	58.22	0.3489	0.4346	1.5447	1.1859	54.71	0.8505	0.7494	1.0265	2.1505
49.06	0.0607	0.1732	2.9797	1.0129	58.68	0.4006	0.4610	1.4384	1.2377	52.97	0.9005	0.8061	1.0096	2.4215
50.00	0.0747	0.1976	2.8145	1.0171	58.94	0.4489	0.4844	1.3548	1.2936	52.32	0.9149	0.8264	1.0062	2.5026
51.23	0.0893	0.2287	2.7941	1.0177	59.08	0.5014	0.5101	1.2801	1.3617	51.53	0.9288	0.8513	1.0055	2.5222
51.67	0.0989	0.2397	2.6663	1.0227	59.06	0.5493	0.5331	1.2208	1.4351	50.67	0.9451	0.8785	1.0029	2.6269
53.50	0.1498	0.2885	2.1951	1.0503	58.86	0.6004	0.5625	1.1746	1.5116	49.79	0.9602	0.9065	1.0008	2.7407
55.67	0.1994	0.3484	2.0718	1.0630	58.08	0.7003	0.6250	1.1038	1.7046	48.78	0.9749	0.9390	1.0003	2.7781
56.91	0.2495	0.3835	1.8636	1.0965	57.64	0.7497	0.6433	1.0534	1.9266	47.80	0.9887	0.9715	1.0000	2.8273
TAME (1) + 1-Propanol (2)														
20.49	0.0148	0.0752	2.4357	1.0001	35.51	0.3001	0.5966	1.6556	1.0639	43.13	0.7500	0.8057	1.0866	1.7425
21.71	0.0298	0.1400	2.3902	1.0005	37.03	0.3490	0.6309	1.5699	1.0915	43.43	0.7996	0.8302	1.0574	1.9132
23.69	0.0595	0.2326	2.1708	1.0049	38.26	0.3980	0.6584	1.4844	1.1286	43.64	0.8503	0.8616	1.0370	2.0975
24.42	0.0749	0.2639	2.0168	1.0101	39.30	0.4483	0.6825	1.4031	1.1760	43.67	0.8999	0.8955	1.0192	2.3686
25.83	0.0899	0.3194	2.1518	1.0043	40.37	0.4993	0.7081	1.3426	1.2237	43.64	0.9151	0.9076	1.0149	2.4703
26.05	0.0997	0.3272	2.0038	1.0119	40.97	0.5496	0.7236	1.2649	1.3071	43.58	0.9301	0.9186	1.0093	2.6370
28.94	0.1485	0.4265	1.9485	1.0134	41.64	0.5990	0.7437	1.2122	1.3839	43.47	0.9460	0.9332	1.0055	2.7948
31.59	0.1997	0.5006	1.8572	1.0247	42.31	0.6532	0.7668	1.1649	1.4795	43.11	0.9754	0.9660	1.0012	3.0960
33.55	0.2482	0.5504	1.7446	1.0431	42.74	0.6996	0.7842	1.1234	1.5963	42.86	0.9903	0.9856	1.0002	3.2902
TAME (1) + 1-Butanol (2)														
9.31	0.0145	0.1617	2.4318	1.0011	26.28	0.2972	0.7745	1.6060	1.0659	38.37	0.7496	0.9118	1.0944	1.7079
10.47	0.0302	0.2647	2.1551	1.0037	28.33	0.3487	0.8015	1.5274	1.0916	39.34	0.7994	0.9248	1.0672	1.8636
12.80	0.0604	0.4161	2.0670	1.0057	30.20	0.4014	0.8237	1.4530	1.1246	40.10	0.8498	0.9366	1.0364	2.1387
13.89	0.0747	0.4696	2.0478	1.0064	31.98	0.4490	0.8432	1.4085	1.1507	40.92	0.8996	0.9521	1.0155	2.4672
15.04	0.0902	0.5181	2.0266	1.0074	33.35	0.4989	0.8573	1.3442	1.2005	41.12	0.9119	0.9565	1.0113	2.5658
15.75	0.1008	0.5445	1.9951	1.0090	34.44	0.5488	0.8685	1.2783	1.2686	41.48	0.9305	0.9649	1.0087	2.6454
18.83	0.1489	0.6363	1.8872	1.0170	35.63	0.5984	0.8810	1.2302	1.3351	42.01	0.9607	0.9784	1.0032	2.9115
21.59	0.1994	0.6977	1.7718	1.0305	36.93	0.6463	0.8943	1.1982	1.3952	42.23	0.9735	0.9850	1.0020	3.0166
24.24	0.2474	0.7443	1.7103	1.0410	37.32	0.6947	0.8986	1.1322	1.5662	42.51	0.9905	0.9942	1.0003	3.3140

$$a = \frac{0.42748R^2 T_c^2}{P_c} [1 + f_\omega(1 - T_r^{1/2})]^2$$

$$b = \frac{0.08664RT_c}{P_c}$$

$$f_\omega = 0.315 + 1.60\omega - 0.166\omega^2$$

We used here the modified vapor pressure function,  $f_\omega$ , proposed by Sim and Daubert (1980).

The initial mole fraction of the liquid phase ( $x_i^0$ ) and a true equilibrium liquid composition ( $x_i$ ) are calculated using eqs 14 and 15, respectively. The equilibrium compositions were calculated until the difference of calculated compositions on successive iteration was less than  $\pm 1 \times 10^{-8}$ .

$$x_1^0 = \frac{W_1/M_1}{(W_1/M_1) + (W_2/M_2)} \quad (14)$$

$$x_1 = \frac{n_1 - \Delta n_1}{(n_1 - \Delta n_1) + (n_2 - \Delta n_2)} \quad (15)$$

$$\Delta n_i = \frac{\text{vapor volume}(\text{headspace volume}/\text{cm}^3)}{v_i (\text{cm}^3 \text{ mol}^{-1})} \quad (16)$$

In the calculation of the amount of volatilization of component  $i$  in the vapor phase, the volume obtained from

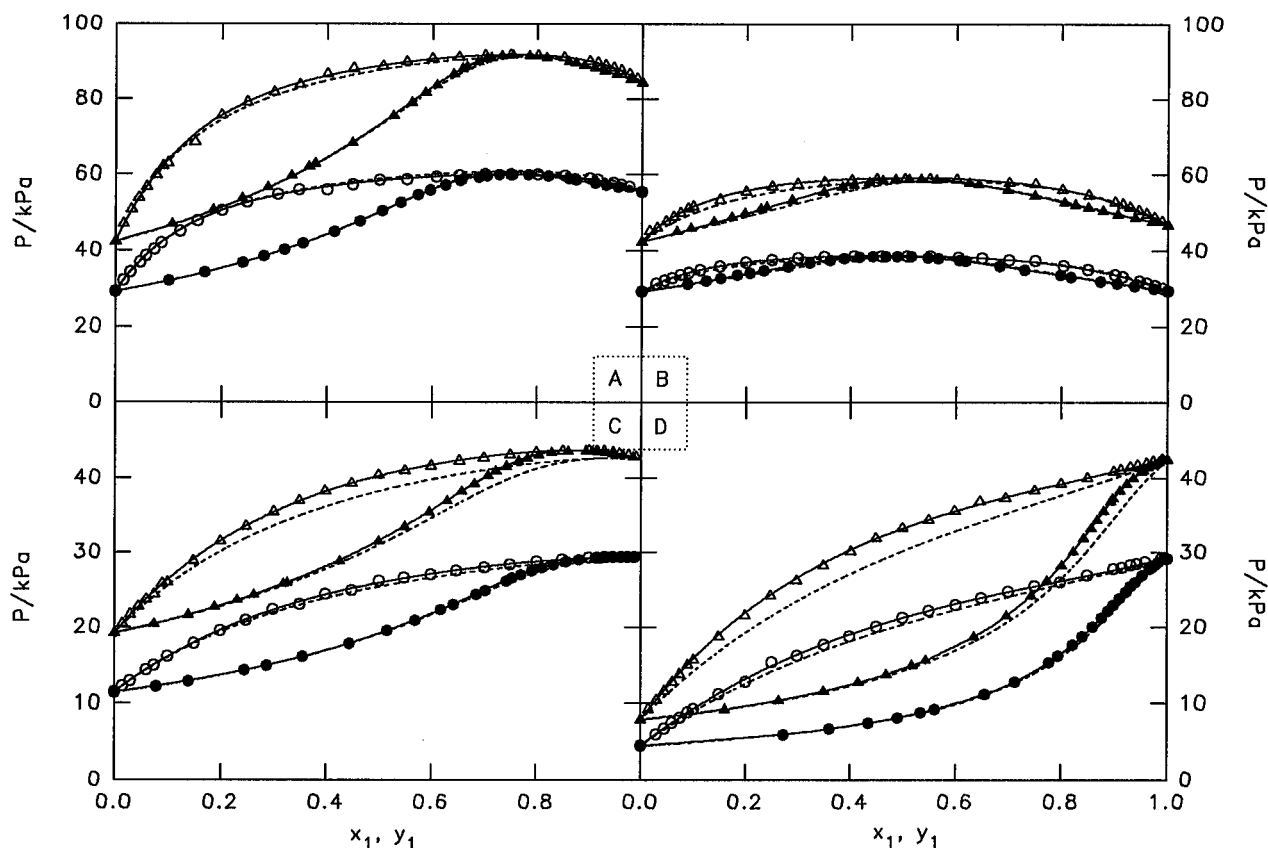
the ideal gas law was used as the initial volume, and the SRK equation of state and the Newton method (Rao, 1996) were introduced.

## Experimental Section

**Materials.** Commercial TAME and alcohols were obtained from Aldrich and Merck. They were dried with molecular sieves 3A (Aldrich) before use. The purity of each chemical was checked by GC and a digital vibrating densimeter (Anton Paar, DMA 48) with an accuracy of  $\pm 1 \times 10^{-4} \text{ g cm}^{-3}$ . The results of GC analysis, measured densities, and the Antoine constants of the chemicals are shown in Table 1.

**Apparatus and Procedures.** The HSGC system consists of a conventional gas chromatograph (Hewlett Packard, HP5890 series II) and a headspace sampler (HP 19395A), with an electropneumatic sampling system and a precision thermostat. For the sample analysis, a thermal conductivity detector and an HP-FFAP (Hewlett Packard, poly(ethylene glycol)-TPA modified) capillary column were used. Binary samples were prepared by means of the digital microbalance (AND Co. HA-202M) with an accuracy of  $\pm 1 \times 10^{-5} \text{ g}$ .

To decrease the experimental error due to the volatilization in preparing the binary samples, the less volatile component was injected into the glass vial (ca. 12 cm<sup>3</sup>) first, and then the more volatile material was injected. The glass vial with sample was placed in the thermostat, and then the liquid and vapor phases will be equilibrated in the vial. We allowed more than 2 h as the equilibration time. Since



**Figure 1.** Pressure–composition diagrams for (A) methanol (1) + TAME (2), (B) ethanol (1) + TAME (2), (C) TAME (1) + 1-propanol (2), and (D) TAME (1) + 1-butanol (2): (○)  $x_1$  and (●)  $y_1$  at 323.15 K; (△)  $x_1$  and (▲)  $y_1$  at 333.15 K; (—) Wilson equation and (---) modified UNIFAC (Dortmund) equation.

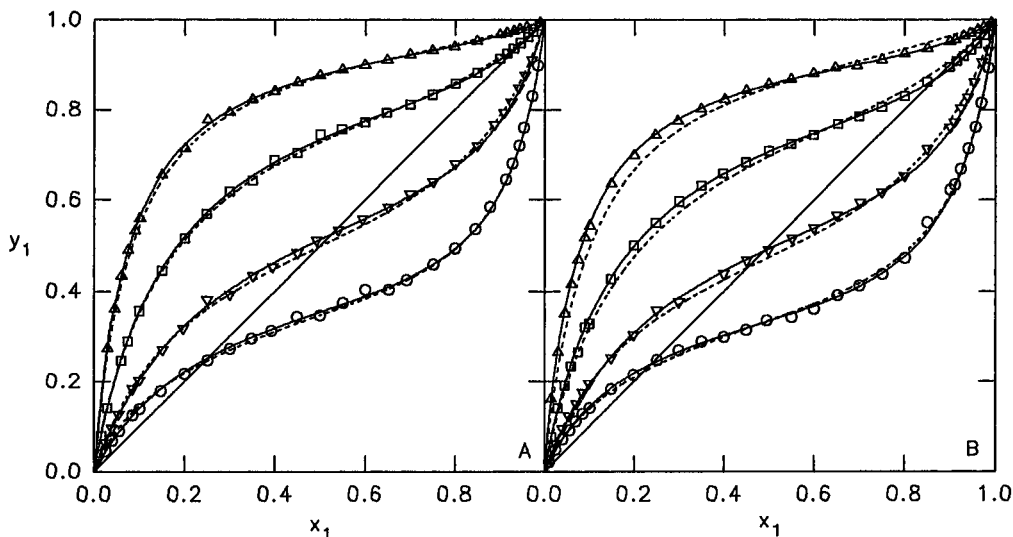
**Table 4.**  $G^E$  Model Parameters and Mean Deviation between the Calculated and Experimental Vapor Phase Mole Fraction ( $\Delta y_1$ )<sup>a</sup> for TAME + *n*-Alcohol ( $C_1$ – $C_4$ ) at 323.15 and 333.15 K

model eq	323.15 K				333.15 K			
	$A_{12}$	$A_{21}$	$\alpha$	$\Delta y_1$	$A_{12}$	$A_{21}$	$\alpha$	$\Delta y_1$
Methanol (1) + TAME (2)								
Margules	1.3932	1.2379		0.0049	1.3406	1.3696		0.0048
van Laar	1.4008	1.2387		0.0049	1.3406	1.3700		0.0048
Wilson	5794.5893	-1378.4441		0.0045	5536.0200	-849.5180		0.0043
NRTL	2212.7599	2781.6565	0.6656	0.0050	2689.3082	2575.4471	0.6462	0.0047
UNIQUAC	-777.3951	4336.3568		0.0053	-631.0612	4160.9098		0.0047
UNIFAC				0.0053				0.0078
Ethanol (1) + TAME (2)								
Margules	1.2580	0.9959		0.0049	1.2949	1.0073		0.0064
van Laar	1.2794	1.0029		0.0046	1.3256	1.0114		0.0064
Wilson	4856.9295	-1108.1902		0.0039	5186.1409	-1182.9301		0.0054
NRTL	1682.0528	2673.0074	0.7724	0.0041	592.3571	3126.6541	0.3000	0.0061
UNIQUAC	-2605.3312	-6797.3616		0.1270	-1043.4395	3421.2572		0.0066
UNIFAC				0.0075				0.0091
TAME (1) + 1-Propanol (2)								
Margules	0.7638	1.0625		0.0030	0.8454	1.1859		0.0032
van Laar	0.7789	1.0911		0.0028	0.8618	1.2205		0.0028
Wilson	-1044.3152	4088.0631		0.0027	-934.8000	4493.3186		0.0027
NRTL	2956.4471	-30.2373	0.3000	0.0027	2691.3120	1226.0750	0.7541	0.0040
UNIQUAC	2562.0039	-1053.4300		0.0029	2776.9450	-1080.9930		0.0030
UNIFAC				0.0036				0.0125
TAME (1) + 1-Butanol (2)								
Margules	0.6398	0.9843		0.0025	0.7921	1.1927		0.0031
van Laar	0.6604	1.0321		0.0023	0.8139	1.2470		0.0028
Wilson	-908.1701	3748.0080		0.0023	-597.8959	4198.1708		0.0027
NRTL	3286.4066	-508.3935	0.3000	0.0023	3637.7974	-197.8017	0.3000	0.0029
UNIQUAC	2238.6501	-1062.3311		0.0024	2428.4357	-1043.0089		0.0029
UNIFAC				0.0069				0.0204

<sup>a</sup>  $\Delta y_1 = |y_{1,\text{exp}} - y_{1,\text{cal}}|/n$ ,  $n$  = number of data. Units for parameters of equations of Wilson, NRTL, and UNIQUAC are J mol<sup>-1</sup>.

the volume of the liquid sample was small (ca. 3 cm<sup>3</sup>) and the equilibrium cell was also small, 2 h is sufficient to reach equilibrium between the liquid and vapor phases. When

equilibrium was achieved, the equilibrium vapor composition was shifted to the sample loop by an electropneumatic sampling system. The collected equilibrium vapor phase



**Figure 2.** Comparison of VLE data between TAME (1) + *n*-alcohol (2) at 323.15 K (A) and at 333.15 K (B): (○) methanol; (▽) ethanol; (□) 1-propanol; (△) 1-butanol; (—) Wilson equation and (---) modified UNIFAC (Dortmund) equation.

in the sample loop was automatically transferred to the GC for analysis.

## Results

The true liquid phase composition in a glass vial was calculated using the SRK equation of state. For TAME, we used a mean value of critical pressures, calculated by the Lydersen (1955), Joback (1984), and Ambrose (1980) methods, and the acentric factor was calculated from the Lee–Kesler equation (Lee and Kesler, 1975). The calculated critical temperature, critical pressure, and acentric factor were 534.0 K, 3.1051 MPa, and 0.324, respectively.

The measured isothermal VLE data at 323.15 and 333.15 K for TAME + *n*-alcohol ( $C_1$ – $C_4$ ) binary mixtures are listed in Tables 2 and 3. In this method, the equilibrium total pressure was not the measured value but the calculated value. The  $x$ – $y$ – $P$  data for TAME + *n*-alcohol ( $C_1$ – $C_4$ ) systems at 323.15 and 333.15 K are plotted in Figure 1. Each of the mixtures except the TAME + 1-butanol binary mixture has a minimum boiling azeotrope. The experimental VLE data were correlated with common  $G^E$  models. The solid lines in the figure indicate the calculated values by the best correlated equation. The predicted VLE data with the modified UNIFAC (Dortmund) equation were also plotted, which are shown as dashed lines in each of the diagrams. The calculated and predicted vapor phase mole fractions were compared with the experimental data. Their deviations between experimental values and predicted values by the modified UNIFAC (Dortmund) method were less than  $1 \times 10^{-2}$ , while that of TAME + 1-propanol and + 1-butanol mixtures at 333.15 K were  $2 \times 10^{-2}$ . These comparisons were listed in Table 4 with the fitted  $G^E$  model parameters. In Table 4, parameters ( $A_{ij}$ ) for the Wilson, NRTL, and UNIQUAC equations were

$$\text{Wilson: } A_{ij} = (\lambda_{ij} - \lambda_{ji})$$

$$\text{NRTL: } A_{ij} = (g_{ij} - g_{ji})$$

$$\text{UNIQUAC: } A_{ij} = (u_{ij} - u_{ji})$$

The equilibrium liquid and vapor phase compositions are shown in Figure 2, in which TAME was regarded as the (1) component for easy comparison. As shown in Figure 2, as the carbon number of the alcohols increased, the azeotropic point moved to the alcohol-rich region, and the deviation from Raoult's law was increased.

## Conclusions

TAME is used as an octane booster for lead-free or low-leaded gasoline because of its octane-enhancing and pollution-reducing capabilities. Isothermal VLE were measured by the headspace gas chromatography (HSGC) method for TAME + *n*-alcohol ( $C_1$ – $C_4$ ) binary mixtures at 323.15 and 333.15 K. The critical pressure and acentric factor of TAME were calculated by the Lydersen, Joback, Ambrose, and Lee–Kesler methods. All the binaries showed positive deviations from Raoult's law. Except for the TAME + 1-butanol system, they have a minimum boiling azeotrope. Experimental data were compared with the calculated values by  $G^E$  models and predicted values by modified UNIFAC (Dortmund). Most of the deviations of the vapor phase mole fraction were less than 1%. When TAME was component 1, with the increasing carbon number of the alcohols, the azeotropic point moved to the alcohol-rich region and the deviation from Raoult's law increased.

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