

Vapor–Liquid and Chemical Reaction Equilibria in the Synthesis of 2-Methoxy-2-methylbutane (TAME)

Liisa K. Rihko-Struckmann, Juha A. Linnekoski, and A. Outi I. Krause*

Helsinki University of Technology, Department of Chemical Technology, Kemistintie 1, FIN-02015 HUT, Finland

Oleg S. Pavlov

Jaroslav University of Technology, Russia

Isobaric vapor–liquid equilibrium (VLE) data (T - x - y) for the binary systems methanol/2-methoxy-2-methylbutane (TAME), methanol/2-methyl-2-butene, and methanol/2-methylbutane were obtained at 101.3 kPa. All systems showed a positive deviation from ideality with a minimum-boiling-point azeotrope. The activity coefficients were calculated with the use of the Wilson equation where the parameters of the binary systems were determined on the basis of the experimental data. Other VLE data relevant to TAME synthesis were collected from the literature, and the respective parameters were adjusted. Earlier reported results of the reaction equilibrium experiments on the liquid-phase formation of TAME were reanalyzed. On the basis of the experimental reaction equilibrium, a value of $-109.6 \text{ kJ}\cdot\text{mol}^{-1}$ is presented for the Gibbs energy of formation for TAME in the gas phase at 298 K.

Introduction

Tertiary ethers are used as octane-enhancing components in gasoline. Because of the relatively high solubility of 2-methoxy-2-methylpropane (methyl *tert*-butyl ether, MTBE) in water, a search is being made for substitutes posing less threat to the environment. Possible replacements are higher ethers, for example, 2-methoxy-2-methylbutane (*tert*-amyl methyl ether, TAME). Recently, several vapor–liquid equilibria (VLEs) studies of these ethers have been published.^{1–4}

TAME is synthesized in an acid-catalyzed equilibrium reaction of isoamylenes (2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B)) with methanol (MEOH).⁵ The third equilibrium in the system is that between the isoamylenes isomers, 2M1B and 2M2B. Typical side reactions are the dehydration of methanol to form methoxymethane (dimethyl ether, DME), the hydration of isoamylenes to yield 2-methyl-2-butanol (*tert*-amyl alcohol, TAOH), and the dimerization of isoamylenes to form branched C₁₀ alkenes (DIP).⁶

In our previous publication⁵ we measured the reaction equilibrium and calculated the reaction equilibrium constants for the formation of TAME. At the temperatures investigated, the equilibrium constants, having the activities calculated by the UNIQUAC method, were found to depend on the methanol mole fraction. The equilibrium constants were higher in experiments where the mole fraction of methanol in the equilibrium was below 0.02 than they were when the methanol mole fraction was above 0.02.

The aim of the present study was to measure the VLEs for the most important binary component pairs (MEOH/TAME, MEOH/2M2B) present in the TAME synthesis. The VLE of MEOH/IPEN (2-methylbutane, isopentane) was measured as well, because 2-methylbutane can be seen to

represent the C₅-inert in the TAME synthesis process. The available binary VLE data for 2M1B and for the side products (DME, TAOH, DIP) were taken from the literature. The parameters for the Wilson method were adjusted for our experimental data as well as for the data from the literature. The Wilson method was selected because it is particularly suitable for alcohol/hydrocarbon mixtures.^{7,8} In the second part of the work, the results of the reaction equilibrium experiments⁵ for the liquid-phase formation of TAME were recalculated using the Wilson method for the calculation of activity coefficients.

Experimental Section

Materials. The following chemicals were used in the VLE experiments: methanol (>99.95 mass %), 2-methyl-2-butene (>99.0 mass %, originating from 2-methylbutane dehydrogenation), 2-methylbutane (99.8 mass %), and TAME (>99.9 mass %, synthesized from methanol and isoamylenes). All chemicals were dried using molecular sieves. The water content was checked by the Fischer method, and it did not exceed 0.02 mass %.

Analysis. The samples were analyzed with a gas–liquid chromatograph LHM-80 equipped with a FID detector and a squalan capillary column (100 m, diameter 0.3 mm). The accuracy of the GC analysis was ± 0.5 mass %. The response factors of the compounds were determined with samples of known compositions.

Apparatus. The vapor–liquid equilibria of the binary pairs were measured in a glass still with vapor-phase circulation (modified Othmer-type still). A detailed description of the apparatus is given elsewhere.⁹ The still was operated under atmospheric pressure for about 1.5 to 2.0 h until the conditions were stabilized and the equilibrium was reached. The samples were analyzed every 15 min until no further change was observed in the compositions. The pressure was measured with a mechanical precision barometer with an accuracy of ± 0.13 kPa, and the tem-

* Corresponding author. Fax: +358-9-451 2622. E-mail: krause@polte.hut.fi.

Table 1. Isobaric VLE Data, Temperature T , Liquid Phase x_1 and Vapor Phase y_1 Mole Fractions, and Experimental Activity Coefficients γ_i for Methanol (1)/TAME (2) Systems

T/K	x_1	y_1	γ_1	γ_2
337.55	100.00	100.00	1.002	
336.65	95.54	92.41	1.004	3.500
336.55	95.09	92.77	1.016	3.039
336.30	90.33	86.79	1.011	2.842
336.25	89.88	86.48	1.014	2.784
335.55	78.92	79.76	1.095	2.047
335.40	76.39	76.39	1.090	2.143
335.25	76.21	76.21	1.096	2.154
335.25	76.04	76.04	1.096	2.154
335.35	75.31	75.31	1.092	2.146
336.10	58.75	69.15	1.248	1.563
336.15	58.32	66.37	1.205	1.683
337.30	40.30	59.74	1.501	1.352
337.50	39.33	62.39	1.594	1.235
338.45	29.11	56.83	1.892	1.174
338.65	28.94	56.24	1.869	1.179
340.90	18.69	52.74	2.492	1.033
345.25	9.33	38.95	3.139	1.039
350.25	4.76	29.66	3.917	0.974
350.55	4.07	24.80	3.792	1.024
359.15	0.00	0.00		1.013

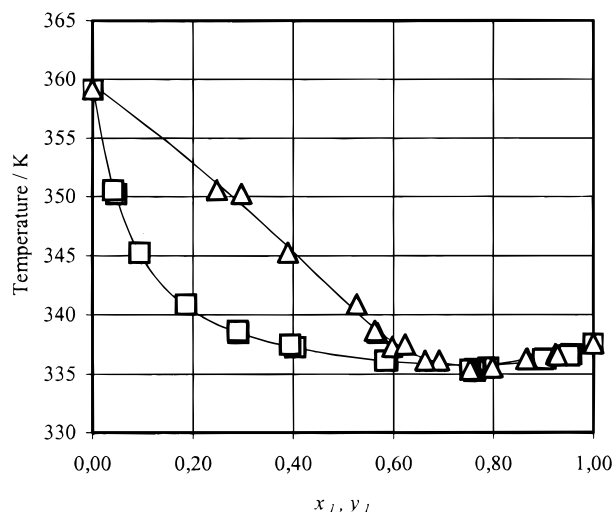
Table 2. Isobaric VLE Data, Temperature T , Liquid Phase x_1 and Vapor Phase y_1 Mole Fractions, and Experimental Activity Coefficients γ_i for Methanol (1)/2M2B (2) Systems

T/K	x_1	y_1	γ_1	γ_2
337.55	100.00	100.00	1.002	
334.70	99.44	87.58	0.986	11.221
334.65	99.31	87.14	0.985	9.442
325.40	97.05	58.38	0.984	9.289
325.25	96.84	60.15	1.023	8.340
317.65	93.68	40.00	0.978	7.907
317.75	93.37	40.40	0.987	7.464
312.75	88.41	32.95	1.066	5.634
312.70	88.09	33.66	1.096	5.434
308.20	74.17	24.70	1.180	3.302
308.25	73.82	25.95	1.243	3.198
307.40	61.49	23.56	1.411	2.310
307.30	61.14	23.21	1.404	2.307
307.00	48.21	21.40	1.666	1.790
306.85	34.22	22.15	2.447	1.403
306.85	33.84	24.43	2.729	1.354
306.75	21.43	21.10	3.741	1.195
306.75	21.26	20.98	3.749	1.194
306.70	20.82	20.48	3.746	1.197
306.70	20.58	20.33	3.762	1.196
306.70	18.72	20.57	4.185	1.165
306.65	18.44	19.89	4.118	1.173
307.00	11.24	18.77	6.269	1.080
306.90	10.81	17.23	6.012	1.098
307.25	5.43	16.48	11.258	1.033
307.35	5.16	17.07	12.212	1.019
307.35	5.07	15.99	11.642	1.032
311.80	0.00	0.00		1.004

perature was measured with a mercury thermometer with an accuracy of ± 0.2 K. The description of the apparatus which was used for the reaction equilibrium measurements can be found elsewhere.⁵

Results and Discussion

Vapor–Liquid Equilibrium. For the binary systems MEOH/TAME, MEOH/2M2B, and MEOH/IPEN, the T - x - y values were measured at atmospheric pressure. The liquid and vapor phase mole fractions of methanol along with the boiling points are presented in Tables 1–3. Figures 1–3 show the respective diagrams. The data were found to be thermodynamically consistent when they were tested by the method of Fredenslund.¹⁰ Second-order Legendre poly-

**Figure 1.** Temperature–composition diagram for the methanol (1)/TAME (2) system: experimental liquid-phase mole fraction of methanol x_1 (\square); vapor phase mole fraction of methanol y_1 (\triangle); calculated by the Wilson method (—).**Table 3. Isobaric VLE Data, Temperature T , Liquid Phase x_1 and Vapor Phase y_1 Mole Fractions, and Experimental Activity Coefficients γ_i for Methanol (1)/2-Methylbutane (2) Systems**

T/K	x_1	y_1	γ_1	γ_2
337.55	100.00	100.00	1.002	
318.95	97.57	43.15	0.956	13.503
319.10	97.39	44.32	0.977	12.261
307.50	93.59	27.53	1.077	9.188
307.20	93.11	28.53	1.139	8.510
301.00	86.34	18.83	1.100	5.953
300.80	85.88	16.36	0.971	5.974
299.00	76.39	16.84	1.231	3.772
298.25	61.75	16.92	1.590	2.386
298.15	61.18	15.12	1.441	2.410
297.95	50.30	14.20	1.663	1.916
297.80	35.31	14.57	2.450	1.473
297.85	35.05	15.21	2.570	1.454
297.75	24.69	14.55	3.508	1.268
297.70	14.78	14.78	5.969	1.119
297.65	14.32	14.32	5.984	1.121
297.70	14.12	14.12	5.969	1.119
297.70	14.08	14.08	5.969	1.119
297.70	10.10	12.03	7.110	1.095
297.75	9.33	12.27	7.830	1.081
298.00	4.58	11.01	14.130	1.033
298.10	4.09	12.15	17.371	1.011
300.70	0.00	0.00		1.012

nomials were obtained for the three binary systems. The mean deviations between the experimental and calculated vapor-phase mole fraction compositions were 0.0082 (MEOH/TAME), 0.0083 (MEOH/2M2B), and 0.0090 (MEOH/IPEN). The Antoine equation and the coefficients from Table 4 for TAME and the Wagner equation for MEOH, 2M2B, and 2-methylbutane⁷ were used in the calculation of vapor pressures.

All the measured systems showed positive deviations from ideality, having a minimum-boiling azeotrope. The azeotropic compositions and boiling points are summarized in Table 5. The azeotropic boiling points and the mole fractions of the binary systems obtained in the experiments were in good agreement with the values found in the literature (see Table 5). The azeotropic point for MEOH/2M2B was estimated also from the results of Budantseva et al.,¹⁷ the agreement with our results being satisfactory.

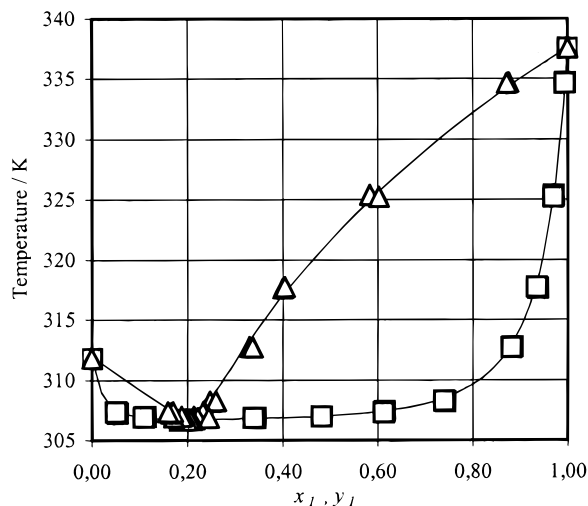


Figure 2. Temperature–composition diagram for the methanol (1)/2M2B (2) system: experimental liquid-phase mole fraction of methanol x_1 (\square); vapor-phase mole fraction of methanol y_1 (Δ); calculated by the Wilson method (—).

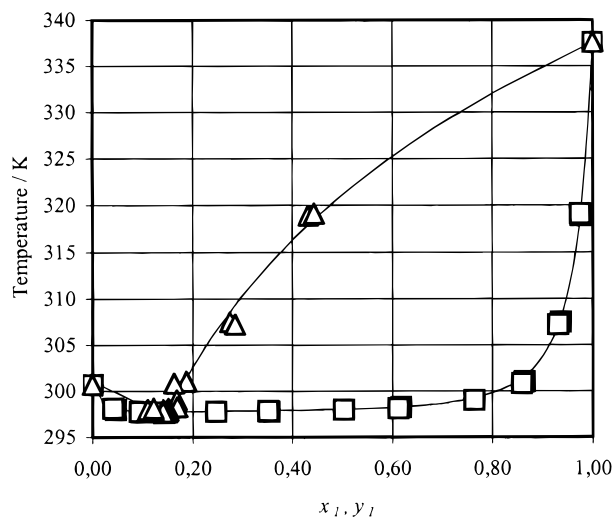


Figure 3. Temperature–composition diagram for the methanol (1)/isopentane (2) system: experimental liquid-phase mole fraction of methanol x_1 (\square); vapor-phase mole fraction of methanol y_1 (Δ); calculated by the Wilson method (—).

Table 4. Coefficients of the Antoine Equation for TAME

compound	A^a	B	C
TAME	5.976 31 ^b	1208.391	-55.243

^a Equation: $\log P$ (kPa) = $A - B/(TK) + C$. ^b Cervenková and Boublik.¹¹

The experimental activity coefficient of the liquid phase, γ_i , was calculated by the following equation:

$$\frac{y_i}{x_i} = \frac{\gamma_i p_i^S \phi_i^S PF}{\phi_i^V P} \quad (1)$$

where x_i and y_i are the measured mole fractions of the liquid and vapor phases, ϕ_i^S and ϕ_i^V are the fugacity coefficients of the liquid and vapor phases, PF is the Poynting factor, p_i^S is the vapor pressure of component i , and P is the total pressure. The fugacity coefficients of the vapor and liquid phases were calculated with the Soave–Redlich–Kwong (SRK) equation of state.

Table 5. Boiling Points and Mole Fraction of Methanol, x_1 , of the Azeotropes

system	P /kPa	T /K	x_1
MEOH–TAME	101.3	335.25	0.7613
	101.3	335.45	0.7613 ^a
	101.3	335.41	0.7710 ^b
	101.3	335.37	0.7674 ^c
MEOH–2M2B	101.3	335.34	0.749 ^d
	101.3	306.7	0.2058
	101.3	306.25	0.22 ^e
	101.3	306.25	0.216 ^f
MEOH–IPEN	101.3	297.65	0.1432
	101.3	297.35	0.1440 ^f

^a Evans and Edlund.¹² ^b Cervenková and Boublik.¹¹ ^c Palczewska-Tulinska et al.¹³ ^d Arce et al.¹⁴ ^e Kudryavtseva et al.¹⁵ ^f Ogorodnikov et al.¹⁶

The activity coefficients were calculated by the Wilson method.¹⁸ The molar volume for each component was estimated from the density and molar mass. The adjustable parameters in the Wilson method are the differences in the parameters λ_{ij} and λ_{ji} for each binary component pair. The program VLEFIT was used in the optimization.¹⁹ The differences $(\lambda_{ij} - \lambda_{ji})$ were adjusted for the T - x - y or P - x - y data by using the Davidon method to minimize the objective function:

$$OF = (\gamma_L^{\text{meas}} - \gamma_L^{\text{calc}})^2 \quad (2)$$

For the sets of isothermic P - x data, the differences between measured and calculated total pressures were minimized as follows:

$$OF = (P^{\text{meas}} - P^{\text{calc}})^2 \quad (3)$$

The lines in Figures 1–3 represent vapor-phase mole fractions calculated by the Wilson method using the parameters obtained in the optimization. As can be seen, the method describes the activities of the studied systems well.

The Wilson parameters $(\lambda_{ij} - \lambda_{ji})$ obtained for MEOH/2M2B, MEOH/TAME, and MEOH/IPEN are summarized in Table 6. To be able to calculate the component activities for the reaction equilibrium results in the next section, the parameters for the other compounds present in the TAME synthesis are included. T - x - y type data were available for MEOH/2M1B¹⁶ and MEOH/DIP;²⁰ P - x - y type data were available for MEOH/DME²¹ and TAME/DIP;²² and P - x type data were available for MEOH/TAOH.²³ For 2M1B/TAME, 2M2B/TAME, and TAME/IPEN, P - x type data of TAME/pentane²⁴ and, for 2M1B/TAOH, 2M2B/TAOH, and TAOH/IPEN, P - x type data of TAOH/pentane²⁴ were used. The parameters for the nearly ideal binary pair 2M1B/2M2B, 2M1B/IPEN, or 2M2B/IPEN are based on P - x type data of n -pentane/2M2B.²⁵ For some component pairs (e.g. TAME/DME, 2M2B/DME, 2M2B/DIP), no VLE data were found, and ideal behavior between the components was assumed. The Wilson parameters were adjusted for the above data and are summarized in Table 6.

Chemical Reaction Equilibrium. The equilibrium constants for the reactions of MEOH and 2M1B to TAME (R1) and of MEOH and 2M2B to TAME (R2) are the following:

$$R_i: K_{ai} = \frac{\alpha_{\text{TAME}}}{\alpha_{\text{MeOH}}\alpha_{\text{2M2B}}} = \frac{\gamma_{\text{TAME}}}{\gamma_{\text{MeOH}}\gamma_{\text{2M2B}}} \frac{x_{\text{TAME}}}{x_{\text{MeOH}}x_{\text{2M2B}}} \quad (4)$$

For isomerization of 2M1B to 2M2B, the equilibrium

Table 6. Wilson Parameters ($\lambda_{ij} - \lambda_{ii}$)/J·mol⁻¹

<i>i</i>	<i>j</i>							
	MEOH	2M1B	2M2B	TAME	DME	TAOH	DIP	IPEN
MEOH	0.0	12510.2	9030.9	6556.5	4630.6	104.7	11216.4	9822.2
2M1B	935.7	0.0	-94.2	584.9		85.8		-94.2
2M2B	1490.9	504.9	0.0	584.9		85.8		-94.2
TAME	-1660.9	-218.1	-218.1	0.0		-775.3	-432.1	-218.1
DME	-701.7				0.0			
TAOH	528.4	3479.2	3479.2	3509.9		0.0		3479.2
DIP	1658.0			1150.1			0.0	
IPEN	2221.9	504.9	504.9	584.9		85.8		0.0

Table 7. Experimental Reaction Conditions (Initial Mole Ratio of Methanol/Isoamylene, Temperature), Mole Fractions of Methanol (1), 2-Methyl-1-butene (2), 2-Methyl-2-butene (3), TAME (4), Dimethyl Ether (5), *tert*-Amyl Alcohol (6), and Diisopentane (7) in Equilibrium, Activity Coefficients by Wilson for Methanol (1), 2-Methyl-1-butene (2), 2-Methyl-2-butene (3), and TAME (4), and the Reaction Equilibrium Constants

init ratio	<i>T</i>	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₄	<i>x</i> ₅	<i>x</i> ₆	<i>x</i> ₇	γ_1	γ_2	γ_3	γ_4	<i>K</i> _{a1}	<i>K</i> _{a2}
<i>a</i>	323	0.195	0.015	0.166	0.604	0.009	0.010	0.001	2.629	1.416	1.351	1.069	59.14	5.62
1.0	323	0.202	0.014	0.152	0.618	0.000	0.013	0.000	2.530	1.436	1.373	1.077	64.72	6.23
<i>a</i>	333	0.220	0.019	0.194	0.557	0.000	0.010	0.000	2.471	1.448	1.371	1.076	39.90	4.15
0.1	333	0.003	0.071	0.736	0.133	0.000	0.013	0.045	12.853	1.103	1.008	1.092	55.91	5.86
0.5	333	0.047	0.041	0.416	0.481	0.000	0.014	0.001	5.505	1.154	1.083	1.013	39.60	4.15
1.0	333	0.221	0.021	0.187	0.560	0.000	0.011	0.000	2.444	1.452	1.377	1.079	36.78	4.33
2.5	333	0.636	0.005	0.054	0.298	0.001	0.005	0.000	1.190	3.082	3.012	1.710	41.33	4.14
5.0	333	0.794	0.003	0.026	0.174	0.001	0.003	0.000	1.059	4.646	4.696	2.241	37.28	3.84
10	333	0.900	0.001	0.011	0.085	0.001	0.001	0.000	1.014	6.571	6.906	2.802	37.97	3.38
<i>a</i>	343	0.242	0.023	0.207	0.510	0.000	0.018	0.000	2.280	1.482	1.399	1.092	30.12	3.49
1.0	343	0.271	0.021	0.204	0.491	0.003	0.009	0.001	2.173	1.537	1.447	1.105	27.99	3.13
<i>a</i>	353	0.267	0.029	0.247	0.447	0.002	0.007	0.001	2.243	1.505	1.405	1.085	18.64	2.34
0.1	353	0.007	0.072	0.646	0.127	0.000	0.012	0.135	11.430	1.080	1.005	1.089	23.32	2.81
0.13	353	0.011	0.071	0.634	0.172	0.004	0.010	0.097	10.352	1.088	1.010	1.072	20.94	2.53
0.5	353	0.080	0.051	0.447	0.403	0.004	0.011	0.004	4.663	1.181	1.098	1.008	18.02	2.22
1.0	353	0.274	0.027	0.243	0.446	0.001	0.008	0.000	2.192	1.523	1.422	1.093	19.38	2.35
2.5	353	0.634	0.009	0.081	0.268	0.004	0.004	0.000	1.207	2.943	2.829	1.639	20.75	2.50
5.0	353	0.804	0.005	0.038	0.147	0.004	0.002	0.000	1.058	4.599	4.577	2.206	18.36	2.16
10	353	0.900	0.002	0.017	0.078	0.003	0.001	0.000	1.016	6.332	6.525	2.729	18.97	2.16
<i>a</i>	363	0.290	0.032	0.257	0.400	0.009	0.011	0.001	2.109	1.541	1.433	1.098	14.70	1.95

^a Initial feed TAME.constant can be calculated from *K*_{a1} and *K*_{a2},

$$\text{R3: } K_{a3} = \frac{a_{2\text{M2B}}}{a_{2\text{M1B}}} = \frac{K_{a1}}{K_{a2}} \quad (5)$$

The mole fractions of the main components MEOH, 2M1B, 2M2B, and TAME in the equilibrium measurements were reported earlier.⁵ To allow a closer analysis, Table 7 presents the results of the equilibrium measurements in detail, including the mole fractions of the side products DME, TAOH, and DIP. The Wilson method using the parameters ($\lambda_{ij} - \lambda_{ii}$) from Table 6 was used in the calculation of the activity coefficients for MEOH, 2M1B, 2M2B, and TAME in a multicomponent system. The mole fractions of the side products (Table 7) and the respective Wilson parameters in Table 6 were included in the calculation. The effect of the side products on the activity of methanol was significant in experiments where the methanol mole fraction was low. In the case when the methanol activity is high (over 10), it is sensitive to the mole fractions of the other compounds present in the system or to the parameters ($\lambda_{ij} - \lambda_{ii}$) used in the calculation. In Table 7 the activity coefficients and equilibrium constants *K*_{a1} and *K*_{a2} for each experiment are presented. After applying the *r*-criterion²⁶ to the experimental data, the equilibrium constants calculated from the experiment with the methanol equilibrium mole fraction 0.003 at 333 K were omitted. At 333 K the average equilibrium constant *K*_{a1} by the Wilson method was 38.8 with standard deviation 1.72 and *K*_{a2} was 4.00 with standard deviation 0.3. For comparison,

the respective equilibrium constants by the UNIQUAC method were 44.7 (*K*_{a1}) and 4.3 (*K*_{a2}) with standard deviations of 4.0 and 0.2.

Parts a and b of Figure 4 show the reaction equilibrium constants *K*_{a1} and *K*_{a2} obtained by the Wilson method as a function of methanol mole fraction at equilibrium. For comparison, the equilibrium constants calculated by the UNIQUAC⁵ method are included. As can be seen, at MEOH mole fractions above 0.05, the equilibrium constants obtained by the Wilson method are on the same level as the values obtained by the UNIQUAC method. At the point where the methanol mole fraction was 0.0026 (at 333 K), the equilibrium constants calculated with the Wilson method were closer to the average than the ones calculated with the UNIQUAC method. Our results reinforce the view of the Wilson method being a good estimation method for hydrocarbon/alcohol mixtures.^{7,8}

Equilibrium Constants. The equilibrium constant *K*_a at temperature *T* is defined by the equation

$$K_a = \exp\left(\frac{-\Delta G_R^L(T)}{RT}\right) = \prod_{i=1}^N a_i^{\nu_i} \quad (6)$$

where $-\Delta G_R^L(T)$ is the Gibbs energy change for the liquid-phase reaction at the temperature *T*. We wanted to calculate the respective value for the Gibbs energy change of TAME formation in the liquid phase at 298 K, ΔG_{TAME}^L , and the corresponding value in the gas phase, ΔG_{TAME}^G , that would agree with our experimental results. From the Gibbs–Helmholtz equation the temperature dependence of

Table 8. Thermodynamic Data for Methanol, 2-Methyl-1-butene, 2-Methyl-2-butene, and TAME

quantity	units	MEOH	2M1B	2M2B	TAME
$\Delta H_f(\text{gas})^a$	$\text{kJ}\cdot\text{mol}^{-1}$	-201.3 ^c	-36.34 ^c	-42.58 ^c	-305.4 ^h
$\Delta G_f(\text{gas})^a$	$\text{kJ}\cdot\text{mol}^{-1}$	-162.6 ^c	65.65 ^c	59.7 ^c	
$\Delta H_f(\text{vap})^a$	$\text{kJ}\cdot\text{mol}^{-1}$	37.53 ^d	25.8 ^f	27.1 ^f	35.3 ^h
T_c	K	512.6 ^c	465 ^c	470 ^c	531.2 ⁱ
P_c	kPa	8090 ^c	3450 ^c	3450 ^c	3250 ⁱ
ω		0.556 ^c	0.236 ^c	0.244 ^c	0.246 ⁱ
$c_p(\text{liq})^a$	$\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	0.0816 ^d	0.1569 ^d	0.1523 ^d	0.2192 ^g
$c_p(\text{liq})^b$	$a \times 10^2$	10.76 ^e	14.951 ^e	15.4 ^e	7.83 ^e
	$b \times 10^5$	-38.06 ^e	-24.763 ^e	-29.335 ^e	44.92 ^e
	$c \times 10^7$	9.79 ^e	9.1849 ^e	9.794 ^e	

^a At 298.15 K. ^b The equation of temperature dependence for $c_p = a + bT + cT^2$. ^c Reid et al., 1988.⁷ ^d CRC, 1983.²⁷ ^e Daubert and Danner, 1992.²⁸ ^f Smith and Srivastava, 1986.²⁹ ^g TRC, 1986.³⁰ ^h Rozhnov et al., 1991.³¹ ⁱ Palczewska-Tulinska et al., 1990.¹³

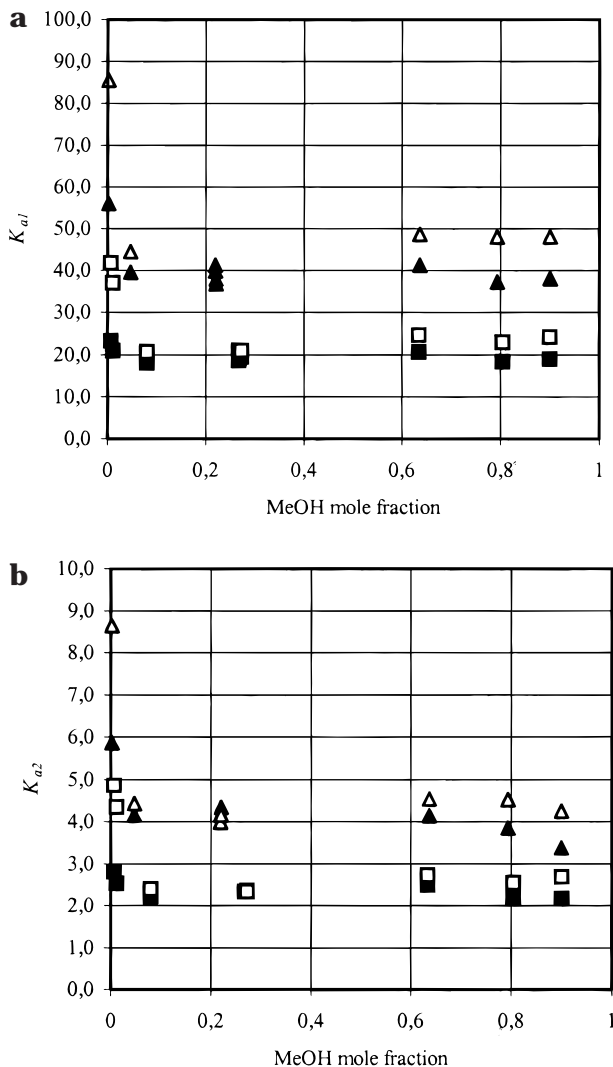


Figure 4. (a) K_{a1} as a function of MEOH mole fraction x in the equilibrium state: K_{a1} at 333 K (\blacktriangle) and at 353 K (\blacksquare) calculated by the Wilson method; K_{a1} at 333 K (\triangle) and at 353 K (\square) calculated by UNIQUAC method taken from Rihko et al.⁵ (b) K_{a2} as a function of MEOH mole fraction x in the equilibrium state: K_{a2} at 333 K (\blacktriangle) and at 353 K (\blacksquare) calculated by the Wilson method; K_{a2} at 333 K (\triangle) and at 353 K (\square) calculated by the UNIQUAC method taken from Rihko et al.⁵

the equilibrium constants is derived

$$\ln \frac{K_a}{K_{a0}} = \int_{T_0}^T \frac{\Delta H_R^L(T)}{RT^2} dT \quad (7)$$

The $\Delta H_R^L(T)$ was calculated with the $\Delta H_f^L(298 \text{ K})$, the heat of vaporization, $\Delta H_f^{\text{VAP}}(298 \text{ K})$, and the liquid-phase

heat capacities of each compound (Table 8). The experimental K_{ai} values at 323 to 363 K were compared to the values that were calculated with eqs 6 and 7. The ΔG_{TAME}^L was adjusted minimizing the difference between the experimental equilibrium constants and the ones from thermodynamic data.

The gas-phase Gibbs energies ΔG_i^G for the formation of TAME were calculated from the liquid-phase values ΔG_i^L by the equation

$$\Delta G_i^G = \Delta G_i^L - RT \ln \left(\frac{\phi_i^s p_i^s PF}{P} \right) \quad (8)$$

where ϕ_i^s is the component fugacity coefficient at the vapor pressure p_i^s of component i and P is the atmospheric pressure. The Poynting factor, PF , was assumed to have a value of 1 under these conditions. The fugacity coefficients were calculated with the SRK equation of state using the critical temperatures and acentric factors for the components from Table 8. A value of $-115.5 \pm 0.1 \text{ kJ}\cdot\text{mol}^{-1}$ was obtained for ΔG_{TAME}^L , corresponding by eq 7 to a gas-phase value ΔG_{TAME}^G of $-109.6 \pm 0.1 \text{ kJ}\cdot\text{mol}^{-1}$ at 298 K.

Our experimental value of ΔG_{TAME}^G is 5.4% lower than the value $-104.0 \text{ kJ}\cdot\text{mol}^{-1}$ reported in the literature.³⁰ Our value for ΔG_{TAME}^L agrees with the values $-114.65 \text{ kJ}\cdot\text{mol}^{-1}$ ³² and with the value $-113.8 \text{ kJ}\cdot\text{mol}^{-1}$, published recently by Syed et al. (2000).³³ The differences are likely due to the different thermodynamic data used in the calculation.

Conclusions

The isobaric vapor-liquid equilibrium data (T - x - y) were measured for three binary mixtures: methanol/2-methoxy-2-methylbutane (TAME), methanol/2-methyl-2-butene, and methanol/2-methylbutane. On the basis of experimental findings, we adjusted the binary parameters for the Wilson method of activity coefficient estimation. The reaction equilibrium constants were recalculated for the liquid-phase synthesis of TAME by using the Wilson method. The nonideality was well described with the Wilson method, and the equilibrium constants remained more invariable than those calculated earlier with the UNIQUAC method. On the basis of the experimental equilibrium results, a value of $-109.6 \text{ kJ}\cdot\text{mol}^{-1}$ is proposed for the formation of TAME in the gas phase, ΔG_{TAME}^G , at 298 K.

Literature Cited

- (1) Marsh, K. N.; Niamskul, P.; Gmehling, J.; Böltz, R. Review of Thermophysical Property Measurement on Mixtures Containing MTBE, TAME, and Other Ethers with Nonpolar Solvents. *Fluid Phase Equilib.* **1999**, *156*, 207-227.

- (2) Loras, S.; Aucejo, A.; Muñoz, R. Vapor-Liquid Equilibria in the Systems 3-Methylpentane + Methyl 1,1-Dimethylethyl Ether and 3-Methylpentane + Methyl 1,1-Dimethylpropyl Ether at 101.3 kPa. *Fluid Phase Equilib.* **1999**, *156*, 185–195.
- (3) Heine, A.; Fischer, K.; Gmehling, J. Various Thermodynamic Properties for Binary Systems with Tertiary Ethers. *J. Chem. Eng. Data* **1999**, *44*, 373–378.
- (4) Chamorro, C. R.; Segovia, J. J.; Martín, M. C.; Montero, E. A.; Villamañán, M. A. Phase Equilibrium Properties of Binary and Ternary Systems Containing *tert*-Amylmethyl Ether (TAME) as Oxygenate Additive and Gasoline Substitution Hydrocarbons at 313.15 K. *Fluid Phase Equilib.* **1999**, *156*, 73–87.
- (5) Rihko, L. K.; Linnekoski, J. A.; Krause, A. O. I. Reaction Equilibria in the Synthesis of 2-Methoxy-2-methylbutane and 2-Ethoxy-2-methylbutane in the Liquid Phase. *J. Chem. Eng. Data* **1994**, *39*, 700–704.
- (6) Kiviranta-Pääkkönen, P. K.; Struckmann, L. K.; Linnekoski, J. A.; Krause, A. O. I. Dehydration of the Alcohol in the Etherification of Isoamylenes with Methanol and Ethanol. *Ind. Eng. Chem. Res.* **1998**, *37*, 18–24.
- (7) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases & Liquids*, 4th ed.; McGraw-Hill Book Company: Singapore, 1988.
- (8) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection*; Chem. Data Series, Vol. I, Part 1; Dechema: Frankfurt, 1977.
- (9) Pavlov, S. Yu. *Isolation and Purification of Monomers for Synthetic Rubber* (in Russian); Chimiya: Leningrad, 1987.
- (10) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria using UNIFAC a group contribution method*; Elsevier Scientific Publishing Company: Amsterdam, 1986.
- (11) Cervenková, I.; Boublik, T. Vapor Pressures, Refractive Indexes, and Densities at 20.0 °C, and Vapor-Liquid Equilibrium at 101.325 kPa, in the *tert*-Amyl Methyl Ether-Methanol System. *J. Chem. Eng. Data* **1984**, *29*, 425–427.
- (12) Evans, T. W.; Edlund, K. R. Tertiary Alkyl Ethers Preparation and Properties. *Ind. Eng. Chem.* **1936**, *28*, 1186–1188.
- (13) Palczewska-Tulinska, M.; Wyrzykowska-Stankiewicz, D. Isobaric Vapor-Liquid Equilibrium in Two Binary Systems Involving *tert*-Amyl Methyl Ether. *Fluid Phase Equilib.* **1990**, *54*, 57–68.
- (14) Arce, A.; Martínez-Ageitos, J.; Soto, A. VLE Measurements of Binary Mixtures of Methanol, Ethanol, 2-Methoxy-2-methylpropane, and 2-Methoxy-2-methylbutane at 101.32 kPa. *J. Chem. Eng. Data* **1996**, *41*, 718–723.
- (15) Kudryavtseva, L. S.; Eizen, O. G.; Susarev, M. P. *Zh. Fiz. Khim.* **1966**, *40*, 1285.
- (16) Ogorodnikov, S. K.; Kogan, V. B.; Nemtsov, M. S. *Zh. Prikl. Khim.* **1960**, *33*, 2685.
- (17) Budantseva, L. S.; Lesteva, T. M.; Nemtsov, M. S. *Zh. Fiz. Khim.* **1975**, *49*, 1847.
- (18) 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.
- (19) Aittamaa, J.; Salminen, K. K.; Järveläinen, M. Calculation of Vapor-Liquid Equilibria for Multicomponent Mixtures. Part I. Methods (in Finn.). *Kemia-Kemi* **1987**, *5*, 511–514.
- (20) Pavlov, O. S. To be published.
- (21) Chang, E.; Calado, J. C. C.; Street, W. B. *J. Chem. Eng. Data* **1982**, *27*, 293.
- (22) Antosik, M.; Sandler, S. I. Vapor-Liquid Equilibria of Hydrocarbons and *tert*-Amyl Methyl Ether. *J. Chem. Eng. Data* **1994**, *39*, 584–587.
- (23) Barton, D. P.; Bhethanabotla, V. R.; Campbell, S. W. Binary Total Pressure Measurements for Methanol with 1-Pentanol, 2-Pentanol, 3-Pentanol, 2-Methyl-1-butanol, 2-Methyl-2-butanol, 3-Methyl-1-butanol, and 3-Methyl-2-butanol at 313.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1138–1140.
- (24) Semar, S.; Sandler, S. I.; Antosik, M. Total Pressure Measurements of Binary Mixtures Containing *tert*-Amyl Methyl Ether and *tert*-Amyl Alcohol. *J. Chem. Eng. Data* **1995**, *40*, 712–718.
- (25) Gumpert, H. J.; Koehler, H.; Schille, W.; Bittrich, H. *J. Wiss. Z. Technol. Hochsch. Chem. Leuna-Merseburg* **1973**, *15*, 179.
- (26) Nalimov, V. V. *The Application of Mathematical Statistics to Chemical Analysis*; Pergamon Press: London, 1963.
- (27) *CRC Handbook of Chemistry and Physics*, 64th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1983; D-63–64, D-151.
- (28) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals, Data Compilation*, Part 2; Hemisphere Publishing Corporation: Washington, DC, 1992.
- (29) Smith, B. D.; Srivastava, R. *Thermodynamic Data for Pure Compounds*, Part A; Elsevier Scientific Publishing Company: Amsterdam, 1986.
- (30) *TRC Thermodynamic Tables*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1986; Vol. V, p 6090, 6101.
- (31) Rozhnov, A. M.; Safronov, V. V.; Verevkin, S. P.; Sharanov, K. G.; Alenin, V. I. Enthalpy of Combustion and Enthalpy of Vaporization of 2-Ethyl-2-methoxypropane and Thermodynamics of its Gas-Phase Synthesis from (Methanol + a 2-Methylbutene). *J. Chem. Thermodyn.* **1991**, *23*, 629–635.
- (32) Thiel, C.; Hoffmann, U. Zur Frage der chemischen Gleichgewichtslage der Synthese von *tert*-Amyl-methyl ether (TAME). *Chem.-Ing.-Tech.* **1996**, *68*, 1317–1320.
- (33) Syed, F. H.; Egleston, C.; Datta, R. *tert*-Amyl Methyl Ether (TAME). Thermodynamic Analysis of Reaction Equilibria in the Liquid Phase. *J. Chem. Eng. Data* **2000**, *45*, 319–323.

Received for review September 8, 1999. Accepted July 10, 2000.

JE990245V