J. Chem. Eng. Data **2000,** *45,* 319−323

tert-Amyl Methyl Ether (TAME). Thermodynamic Analysis of Reaction Equilibria in the Liquid Phase

Faisal H. Syed,† Christine Egleston,‡ and Ravindra Datta*,†

Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts 01609-2180, and Ifm efector, 805 Springdale Drive, Exton, Pennsylvania 19341

Ethers derived from C_5 olefin streams provide a good mix of octane-enhancing and carbon monoxide-reducing qualities and are, therefore, being considered as a replacement for the more common isobutylene-derived fuel additives such as methyl *tert*-butyl ether (MTBE). This paper provides data on the thermodynamic reaction equilibria for the synthesis of *tert*-amyl methyl ether (TAME), which is produced from the etherification reaction of 2-methyl-1-butene and 2-methyl-2-butene with methanol. Thermochemical parameters for the reaction mixture are experimentally verified, and expressions for the thermodynamic equilibrium constants as a function of temperature are developed. A corrected value for the Gibbs free energy of formation for TAME is provided.

Introduction

Ether-based oxygenates have seen a tremendous growth in the 1990s. Compared to alcohols, ethers have a lower Reid vapor pressure (RVP), while providing the benefits of increasing octane levels and reducing carbon monoxide emissions. Methyl *tert*-butyl ether (MTBE), produced from the addition reaction of methanol and isobutylene, has been the oxygenate of choice, mainly due to the economics and availability of the two feedstocks (Brockwell et al., 1991). However, over the past 5 years there has been a growing concern about contamination of groundwater by MTBE, due to leaking storage tanks and pipelines. California, which represents 25% of MTBE annual global demand, has already passed legislation for its phaseout by 2002 (Morse, 1999). The major factor affecting the impact of MTBE on drinking water stems from its high water solubility. Therefore, refiners are seeking alternative additives with lower water solubilities. *Tert*-amyl methyl ether (TAME), produced from methanol and C_5 tertiary olefins, is a promising candidate, although other ethers such as *tert*-amyl ethyl ether (TAEE) and *tert*-hexyl ethyl ethers (THEE1, THEE2, and THEE3) are also being actively investigated (Kitchaiya and Datta, 1995; Zhang and Datta, 1995). Not only are these ethers less water soluble, but they also have lower vapor pressures, which further aid in the reduction of air pollution for motor vehicles.

These tertiary ethers are industrially synthesized in the liquid phase over acid-functionalized ion-exchange resin catalysts. The reactions are thermodynamically limited, with equilibrium conversion declining at higher temperatures and as higher molecular weight olefin feeds are utilized (Datta et al., 1997). Several thermodynamic studies pertaining to MTBE, ETBE, TAEE, and ethanol-derived C_6 ethers are available in the literature (Colombo et al., 1983; Safronov et al., 1989; Rehfinger and Hoffmann, 1990; Izquierdo et al., 1992; Vila et al., 1993; Jensen and Datta, 1994; Zhang and Datta, 1995a; Kitchaiya and Datta, 1995; Zhang and Datta, 1995b). Although a number of thermodynamic studies have also been reported on TAME (Randriamahefa et al., 1988; Safronov et al., 1989; Rihko et al., 1994; Hwang and Wu, 1994; Oost et al., 1995; Piccoli and Lovisi, 1995), none of these have been able to provide satisfactory agreement between experiments and theory. Therefore, the aim of this paper is to provide a thermodynamic analysis of the reaction network involved in TAME synthesis and to investigate the cause(s) of the deviation between experiments and thermodynamic analysis, as well as some additional equilibrium data.

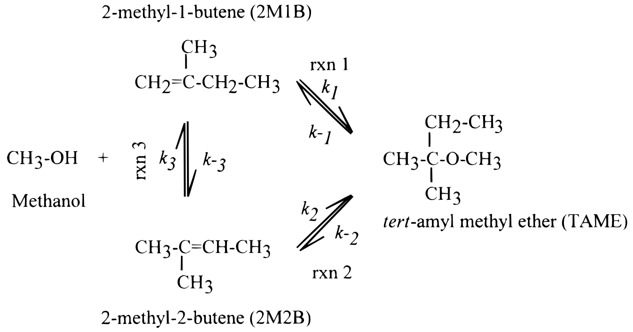

Figure 1. Simultaneous etherification and isomerization reactions involved in TAME synthesis.

Theoretical Analysis

TAME can be produced from either tertiary pentene, namely 2-methyl-1-butene (2M1B), or 2-methyl-2-butene (2M2B) and methanol over a protonated ion-exchange resin catalyst like Amberlyst-15. In addition to the two parallel etherification reactions, 2M1B also isomerizes to form 2M2B, and vice-versa, on the catalyst. The resulting reaction network is shown in Figure 1. The only significant side reaction observed is the production of *tert*-amyl alcohol if any water is present in the feed. The equilibrium analysis of Kitchaiya and Datta (1995) and Jensen and Datta (1995) is summarized below.

---

* Corresponding author. E-mail address: rdatta@wpi.edu.
† Worcester Polytechnic Institute.
‡ Ifm efector.

10.1021/je990191p CCC: $19.00

Table 1. Experimentally Determined Mole Fractions and Ideal K_{xi} and Nonideal K_i Equilibrium Constants for TAME Synthesis at Various Temperatures

T/K	$x_{\mathrm{MeOH,e}}$	$x_{\mathrm{2M1B,e}}$	$x_{\mathrm{2M2B,e}}$	$x_{\mathrm{TAME,e}}$	K_{x1}	K_{x2}	K_{x3}	K_1	K_2	K_3
298	0.159	0.009	0.152	0.680	451.40	28.23	8.91	119.80	7.45	16.08
308	0.174	0.012	0.164	0.650	311.61	22.74	9.65	85.94	6.23	13.79
318	0.187	0.015	0.174	0.625	229.22	19.27	10.56	65.38	5.47	11.96
328	0.242	0.023	0.217	0.519	95.37	9.89	13.70	29.39	3.03	9.70
348	0.271	0.027	0.241	0.461	62.74	7.04	15.98	19.97	2.23	8.96

For q liquid-phase reactions, the equilibrium constant K_i for the ith reaction, $\sum_{j=1}^{n} \nu_{ij} A_j$, can be written as

$$K_i = \exp\left(-\frac{\Delta G^\circ_{iT}}{RT}\right) = \prod_{j=1}^{n} a_{je}^{\nu_{ij}} = \left(\prod_{j=1}^{n} \gamma_{je}^{\nu_{ij}}\right)\left(\prod_{j=1}^{n} x_{je}^{\nu_{ij}}\right) = K_{\gamma i} K_{xi} \tag{1}$$

where $a_{je} = \gamma_{je} x_{je}$ is the activity of species j at equilibrium. The activity coefficient γ_{je} may be calculated from the equilibrium mole fraction x_{je} using an appropriate model. Columbo et al. (1983) and Izquierdo et al. (1992) have demonstrated the adequacy of the UNIFAC group contribution method for the highly nonideal MTBE reaction mixture. Furthermore, Jensen and Datta (1995), Kitchaiya and Datta (1995), and Zhang and Datta (1995), respectively, have shown the accuracy of the UNIFAC method for the ETBE, TAEE, and THEEx reaction systems. Therefore, this work assumes that the UNIFAC method is applicable to the TAME system.

The standard Gibbs free energy change and the standard enthalpy change for reaction i can be written as a function of temperature by relating them to the molar heat capacity $C^\circ_{\mathrm{P}j}$ of species j, given as a function of temperature by the usual form

$$C^\circ_{\mathrm{P}j} = a_j + b_j T + c_j T^2 + d_j T^3 \tag{2}$$

Thus

$$\Delta H^\circ_{iT} = I_{iH} + \Delta a_i T + \frac{\Delta b_i}{2} T^2 + \frac{\Delta c_i}{3} T^3 + \frac{\Delta d_i}{4} T^4 \tag{3}$$

which when used in the van't Hoff equation provides the standard Gibbs free energy change, or equivalently the equilibrium constant, for reaction i

$$-\frac{\Delta G^\circ_{iT}}{RT} = \ln K_i = I_{iK} - \frac{I_{iH}}{RT} + \frac{\Delta a_i}{R} \ln T + \frac{\Delta b_i}{2R} T + \frac{\Delta c_i}{6R} T^2 + \frac{\Delta d_i}{12R} T^3 \tag{4}$$

as a function of temperature. I_{iH} and I_{iK} are the respective integration constants, evaluated from thermochemical data at the standard temperature T° as

$$I_{iH} = \Delta H^\circ_{iT^\circ} - \Delta a_i T^\circ - \frac{\Delta b_i}{2}(T^\circ)^2 - \frac{\Delta c_i}{3}(T^\circ)^3 - \frac{\Delta d_i}{4}(T^\circ)^4 \tag{5}$$

and

$$I_{iK} = \ln K_{iT^\circ} + \frac{I_{iH}}{RT^\circ} - \frac{\Delta a_i}{R} \ln T^\circ - \frac{\Delta b_i}{2R} T^\circ - \frac{\Delta c_i}{6R}(T^\circ)^2 - \frac{\Delta d_i}{12R}(T^\circ)^3 \tag{6}$$

Experimental Section

The experimental study was carried out in a 300 mL Parr batch reactor. Amberlyst 15 ion-exchange resin catalyst (obtained from Sigma) was treated by washing the resin with ethanol, followed by 1.0 M HNO_3, and then with ethanol again to remove any excess free acid remaining on the resin beads. After drying for 12 h in an oven under vacuum at 105 °C, the resin was stored in a desiccator until time of use. One gram of catalyst was loaded into the reactor, and the reactor was evacuated using a vacuum pump before the desired reactant mixture was pumped in. TAME decomposition was studied by charging the reactor with TAME (97% purity, obtained from Aldrich). The reactor was heated to the desired reaction temperature and the mixture agitated using a built-in stirrer. The reactor was maintained at 1.03 MPa to ensure liquid-phase operation.

The reactor was operated in a recirculating mode, where the charged mixture was pumped continuously via a positive displacement pump (Gilson Medical, model 305) through an internal liquid-sampling injector (Valco model CL4WE) to a Perkin-Elmer AutoSystem gas chromatograph equipped with a Supelco capillary column (SPB-1, 0.25 mm i.d., 1.0 μm film thickness, 60 m length), before being recycled back to the reactor. A flame ionization detector (FID) operating at 250 °C was utilized. An oven temperature program starting at 35 °C for 4 min and then increased to 100 °C at a rate of 20 °C/min, where it was held for 1 min, was sufficient to provide the necessary separation. GC samples were taken until the successive reactor composition remained constant over time, at which point the temperature was set to the next desired value and GC sampling resumed.

Results and Discussion

Equilibrium constants were determined for the three individual reactions using eq 1. Equilibrium mole fractions x_{je} determined from GC analysis were used to calculate the species activity coefficients at equilibrium γ_{je} using the UNIFAC method. Table 1 lists the experimental results for the TAME decomposition reaction at different temperatures, along with ideal and nonideal equilibrium constants K_{xi} and K_i, respectively. Although K_{xi} and K_i follow similar trends, it is clear that the equilibrium reaction mixture significantly deviates from ideality. As the temperature increases, the equilibrium composition of TAME for both etherification reactions decreases, which is expected of exothermic reactions. The composition of 2M2B relative to 2M1B also decreases with increasing temperature. Furthermore, only two of the three reactions are independent, and their reaction equilibrium constants are, thus, related by

$$\ln K_1 = \ln K_2 + \ln K_3 \tag{7}$$

Theoretical reaction equilibrium constants at each temperature were calculated using eq 4 and the necessary liquid-phase thermochemical data. The thermochemical properties for the two iso-olefins were obtained from Kitchaiya and Datta (1995), and those of methanol, from Zhang and Datta (1995a). The standard enthalpy and standard Gibbs free energy for TAME at $T^\circ = 298.15$ K were obtained from the Thermodynamic Research Center

Table 2. Liquid-Phase Thermochemical Data Reported in the Literature for the TAME Reaction System

component	heat capacity coefficients/ kJ·mol^{-1}·K^{-1} $C^\circ_{Pj} = a_j + b_jT + c_jT^2 + d_jT^3$					
j	$10a_j$	10^4b_j	10^7c_j	$10^{10}d_j$	$\Delta G^\circ_{fjT^\circ}$/ kJ·mol^{-1}	$\Delta H^\circ_{fjT^\circ}$/ kJ·mol^{-1}
methanol[a]	0.077	1.62	2.06	2.87	−166.64	−238.91
2M1B[b]	1.27	−0.609	5.08	1.69	65.00	−62.47
2M2B[b]	1.33	−1.48	7.51	−0.882	58.40	−69.91
TAME	1.73[c]	2.29[c]	−6.00[c]	20.0[c]	−108.20[d]	−334.90[d]

[a] Zhang and Datta (1995a). [b] Kitchaiya and Datta (1995). [c] Estimated by the Missenard method (Reid et al., 1987). [d] TRC (1992).

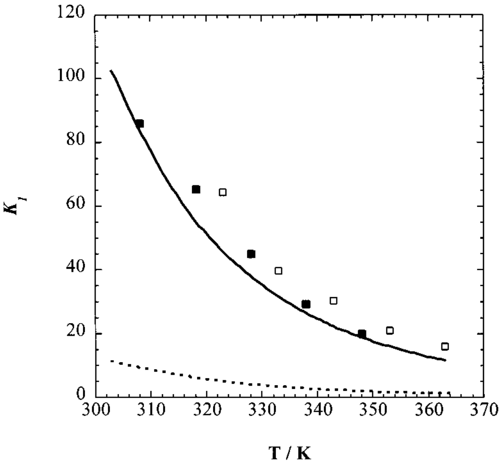

Figure 2. Experimental (■, this study; □, Rihko et al., 1994) and theoretical reaction equilibrium constant as a function of temperature for TAME synthesized from methanol and 2M1B using literature (dotted line) and regressed (solid line) $\Delta H^\circ_{iT^\circ}$ and $\Delta G^\circ_{iT^\circ}$ values from Table 3.

(TRC), while the heat capacity information was estimated using the Missenard method described by Reid et al. (1987). This method is a group contribution method providing estimates with <5% error. The thus obtained thermochemical data for all components are summarized in Table 2.

The experimental and theoretical reaction equilibrium constants for the TAME reaction system as a function of temperature are plotted in Figures 2−4, along with the data of Rihko et al. (1994), who studied TAME synthesis as well as decomposition using different feed mixtures. The experimental results of this study are similar to the results obtained by Rihko et al. (1994). However, experimental results for both of the etherification reactions are approximately an order of magnitude higher than the results predicted using the literature thermochemical data listed in Table 2. However, the equilibrium constant for the isomerization reaction agrees well with predictions. The disagreement between theory and experiments raises questions about the accuracy of the thermochemical data listed in Table 2. It is known that slight changes in the enthalpy and the Gibbs free energy of formation values can cause significant changes in the equilibrium constant. Rihko et al. (1994) found that an increase of 1% in the enthalpy of formation of TAME caused the value of the equilibrium constant to increase by as much as 3-fold. Furthermore, Kitchaiya and Datta (1995) found that the equilibrium constant is fairly insensitive to errors in the heat capacity data, but a 1 kJ/mol difference in the standard Gibbs free energy can result in a 50% difference in the thermodynamic equilibrium constant.

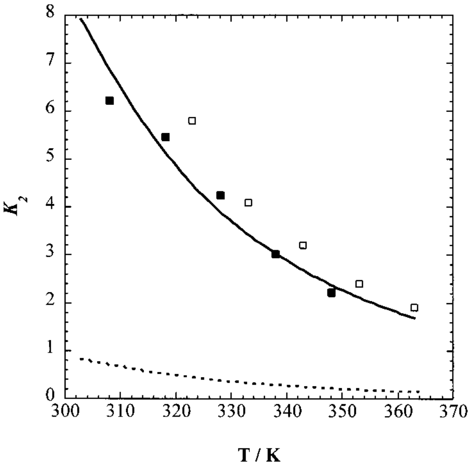

Figure 3. Experimental (■, this study; □, Rihko et al., 1994) and theoretical reaction equilibrium constant as a function of temperature for TAME synthesized from methanol and 2M2B using literature (dotted line) and regressed (solid line) $\Delta H^\circ_{iT^\circ}$ and $\Delta G^\circ_{iT^\circ}$ values from Table 3.

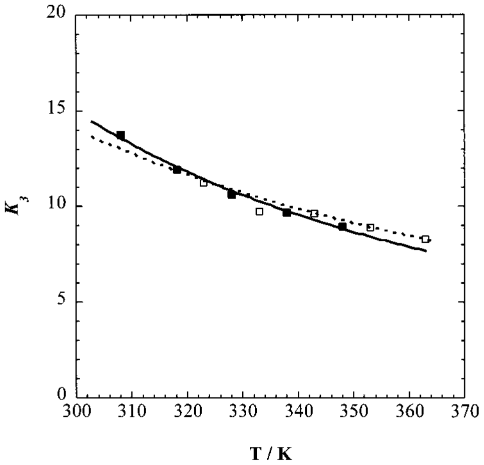

Figure 4. Experimental (■, this study; □, Rihko et al., 1994) and theoretical reaction equilibrium constant as a function of temperature for the isomerization of 2M1B to 2M2B using literature (dotted line) and regressed (solid line) $\Delta H^\circ_{iT^\circ}$ and $\Delta G^\circ_{iT^\circ}$ values from Table 3.

To obtain more accurate values of the standard enthalpy change $\Delta H^\circ_{iT^\circ}$ and the standard Gibbs free energy change $\Delta G^\circ_{iT^\circ}$ for reaction i at $T^\circ = 298.15$ K, eqs 5 and 6 for the constants I_{iH} and I_{iK} are substituted into eq 4 to obtain

$$\ln K_i - \frac{\phi_i}{R} = K_{iT^\circ} + \frac{\Delta H^\circ_{iT^\circ}}{R}\left(\frac{1}{T^\circ} - \frac{1}{T}\right) \tag{8}$$

where

$$\phi_i \equiv \left(\Delta a_i T^\circ + \frac{\Delta b_i}{2}(T^\circ)^2 + \frac{\Delta c_i}{3}(T^\circ)^3 + \frac{\Delta d_i}{4}(T^\circ)^4\right) \times \left(\frac{1}{T} - \frac{1}{T^\circ}\right) + \Delta a_i \ln\frac{T}{T^\circ} + \frac{\Delta b_i}{2}(T - T^\circ) + \frac{\Delta c_i}{6}(T^2 - (T^\circ)^2) + \frac{\Delta d_i}{12}(T^3 - (T^\circ)^3) \tag{9}$$

A plot of the LHS of eq 8, using experimentally determined values for K_i, versus $(1/T^\circ - 1/T)$ results in a straight line, as shown in Figure 5, with a slope of $\Delta H^\circ_{iT^\circ}/R$ and an intercept equal to K_{iT°. The resulting standard enthalpy $\Delta H^\circ_{iT^\circ}$ and standard Gibbs free energy $\Delta G^\circ_{iT^\circ}$ of reaction for

Table 3. Standard Enthalpy and Gibbs Free Energy of Reaction *i* at $T° = 298.15$ K

	regressed from eq 8		determined from literature values	
reaction *i*	$\Delta G^\circ_{iT^\circ}$/kJ·mol^{-1}	$\Delta H^\circ_{iT^\circ}$/kJ·mol^{-1}	$\Delta G^\circ_{iT^\circ}$/kJ·mol^{-1}	$\Delta H^\circ_{iT^\circ}$/kJ·mol^{-1}
1	−12.00	−32.96	−6.56	−33.52
2	−5.50	−23.50	0.04	−26.08
3	−6.76	−9.46	−6.60	−7.44

Table 4. Calculated Standard Gibbs Free Energy and Standard Enthalpy of Formation for TAME at $T° = 298.15$ K

	regressed from eq 8		lit. values (TRC)		exp at 298.15 K
reaction *i*	$\Delta G^\circ_{fiT^\circ}$/kJ·mol^{-1}	$\Delta H^\circ_{fiT^\circ}$/kJ·mol^{-1}	$\Delta G^\circ_{fiT^\circ}$/kJ·mol^{-1}	$\Delta H^\circ_{fiT^\circ}$/kJ·mol^{-1}	$\Delta G^\circ_{fiT^\circ}$/kJ·mol^{-1}
1	−113.9	−334.32	−108.2	−334.9	−113.5
2	−113.7	−332.34			−113.2

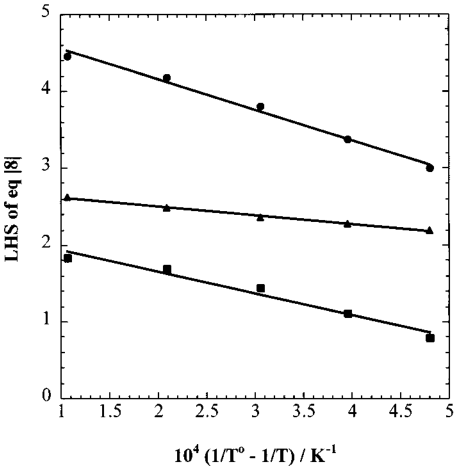

Figure 5. Estimation of standard enthalpy change and standard Gibbs free energy change of reaction at $T° = 298.15$ K using eq 8 for reaction 1 (●), reaction 2 (■), and reaction 3 (▲).

all three reactions are shown in Table 3, along with values obtained using the thermochemical data in Table 2. A much better fit between theory and experiments is obtained if the $\Delta H^\circ_{iT^\circ}$ and $\Delta G^\circ_{iT^\circ}$ values thus obtained from eq 8 are used in eqs 4−6, as shown in Figures 2−4 (corrected). The resulting equilibrium constants for the TAME reaction network can thus be written in their final form:

$$\ln K_1 = -39.065 + \frac{5018.61}{T} + 4.6866 \ln T + 0.00773T - (2.635 \times 10^{-5})T^2 + (1.547 \times 10^{-8})T^3 \quad (10)$$

$$\ln K_2 = -34.798 + \frac{3918.02}{T} + 3.9168 \ln T + 0.01293T - (3.121 \times 10^{-5})T^2 + (1.805 \times 10^{-8})T^3 \quad (11)$$

$$\ln K_3 = -4.159 + \frac{1100.69}{T} + 0.7698 \ln T - 0.00521T + (4.865 \times 10^{-6})T^2 - (2.580 \times 10^{-9})T^3 \quad (12)$$

On average, eqs 10−12 provide values with errors of 9.6%, 9.2%, and 1.8%, respectively, within the studied temperature range.

Since studies by Zhang and Datta (1995) and Kitchaiya and Datta (1995) have demonstrated the accuracy of the thermochemical parameters for methanol and the C_5 isoolefins, respectively, those for TAME are likely the cause of the discrepancy between theory and experiments. Thus, the reaction was conducted at $T° = 298.15$ K to directly determine the standard Gibbs free energy of formation of TAME from the equilibrium composition. This is compared to the value obtained from the regression of eq 8 in Table 4, and the two are seen to be in excellent agreement. In comparison to the literature values, the $\Delta H^\circ_{fiT^\circ}$ value is similar, but the $\Delta G^\circ_{fiT^\circ}$ value differs significantly. Thus, it appears that a more accurate value for $\Delta G^\circ_{fiT^\circ}$ for TAME is −113.8 kJ/mol, rather than the −108 kJ/mol value reported in the literature (TRC, 1992).

Conclusions

The thermodynamic equilibrium constants for the simultaneous etherification and isomerization reactions involved in the liquid-phase synthesis of TAME are analyzed. Experimental equilibrium constants were calculated by studying TAME decomposition in a recirculating batch reactor at different temperatures with activity coefficients determined using the UNIFAC method. Comparison of experimental data and theoretical predictions revealed the possibility of erroneous values reported in the literature for the standard Gibbs free energy of formation for TAME.

Experiments conducted at $T° = 298.15$ K, coupled with the linear regression of data at other temperatures, revealed that the actual value of $\Delta G^\circ_{fiT^\circ}$ for TAME is closer to −113.8 kJ/mol, rather than to −108 kJ/mol reported in the literature (TRC) and used by all studies on TAME. The use of these values in the thermodynamic analysis results in a much better agreement between experiments and theory, allowing for the determination of more accurate expressions for the equilibrium constants for the TAME reaction network.

Nomenclature

a_j, b_j, c_j, d_j = coefficients of molar heat capacity expression
a_j = activity of species j, $\equiv \gamma_j x_j$
C°_{Pj} = molar heat capacity of species j, J/mol·K
I_{iH} = constant of integration
I_{iK} = constant of integration
K_i = thermodynamic equilibrium constant of reaction i
R = gas constant, 8.3143 J/mol·K
T = temperature, K
$T°$ = standard temperature, 298.15 K
x_j = mole fraction of species j

Greek Letters

γ_j = activity coefficient of species j
$\Delta a_i \equiv \sum_{j=1}^{n} \nu_{ij} a_j$
$\Delta b_i \equiv \sum_{j=1}^{n} \nu_{ij} b_j$
$\Delta c_i \equiv \sum_{j=1}^{n} \nu_{ij} c_j$
$\Delta d \equiv \sum_{j=1}^{n} \nu_{ij} d_j$
ΔC°_{iP} = liquid-phase heat capacity difference between products and reactants of reaction i, $\Delta C^\circ_{iP} \equiv \sum_{j=1}^{n} \nu_{ij} C^\circ_{Pj}$, J/(mol·K)
ΔG°_{fjT} = standard Gibbs energy of formation of species j in the liquid phase at temperature T, kJ/mol

ΔG°_{iT} = standard Gibbs energy change for reaction i in the liquid phase at temperature T, $\Delta G^\circ_{iT} \equiv \sum_{j=1}^{n} \nu_{ij} \Delta G^\circ_{\mathrm{f}jT}$, kJ/mol
$\Delta H^\circ_{\mathrm{f}jT}$ = standard enthalpy of formation of species j in the liquid phase at temperature T, kJ/mol
ΔH°_{iT} = standard enthalpy change for reaction i in the liquid phase at temperature T, $\Delta H^\circ_{iT} \equiv \sum_{j=1}^{n} \nu_{ij} \Delta H^\circ \sum_{j=1}^{n} \nu_{ij} \Delta H^\circ_{\mathrm{f}iT}$, kJ/mol
ν_{ij} = stoichiometric coefficient of species j in reaction i

Subscripts

e = at equilibrium
f = of formation
i = of reaction i
j = of species j
T = at temperature T
T° = at standard temperature

Abbreviations

2M1B = 2-methyl-1-butene
2M2B = 2-methyl-2-butene
RVP = Reid vapor pressure
ETBE = ethyl *tert*-butyl ether
MTBE = methyl *tert*-butyl ether
TAEE = *tert*-amyl ethyl ether
TAME = *tert*-amyl methyl ether
THEE = *tert*-hexyl ethyl ethers

Literature Cited

Brockwell, H. L.; Sarathy, P. R.; Trotta, R. Synthesize Ethers. *Hydrocarbon Process.* **1991**, *70* (9), 133−141.

Colombo, F.; Cori, L.; Dallora, L.; Delogu, P. Equilibrium Constant for the Methyl *tert*-Butyl Ether Liquid-Phase Synthesis by use of UNIFAC. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 219−223.

CRC Handbook of Chemistry and Physics, 73rd ed.; Lide, D., Ed.; CRC: Boca Raton, FL, 1992.

Datta, R.; Jensen, K.; Kitchaiya, P.; Zhang, T. Thermodynamic Transition-State Theory and Extrathermodynamic Correlations for the Liquid-Phase Kinetics of Ethanol Derived Ethers. In *Dynamics of Surfaces and Reaction Kinetics in Heterogeneous Catalysis*; Froment, G. F., Waugh, K. C., Eds.; Elsevier: Amsterdam, 1997; pp 559−564.

Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals, Data Compilation*; Hemisphere Publishing Corp.: Washington, DC, 1992.

Hwang, W. S.; Wu, J. C. Kinetics and Thermodynamics of Synthesis of Tertiary-Amyl Methyl Ether Catalyzed by Ion-Exchange Resin. *J. Chin. Chem. Soc.* **1994**, *41*, 181−186.

Ignatius, J.; Järvelin, H.; Lindqvist, P. Use TAME and Heavier Ethers to Improve Gasoline Properties. *Hydrocarbon Process.* **1995**, *74* (2), 51−53.

Izquierdo, J. F.; Cunill, F.; Vila, M.; Tejero, J.; Iborra, M. Equilibrium Constants for Methyl *tert*-Butyl Ether Liquid Phase Synthesis. *J. Chem. Eng. Data* **1992**, *37*, 339−343.

Jensen, K. L.; Datta, R. Ethers from Ethanol. 1. Equilibrium Thermodynamic Analysis of the Liquid-Phase Ethyl *tert*-Butyl Ether Reaction. *Ind. Eng. Chem. Res.* **1995**, *34*, 392−399.

Kitchaiya, P.; Datta, R. Ethers from Ethanol. 2. Reaction Equilibria of Simultaneous *tert*-Amyl Ethyl Ether Synthesis and Isoamylene Isomerization. *Ind. Eng. Chem. Res.* **1995**, *34*, 1092−1101.

Morse, P. M. Producers Brace for MTBE Phaseout. *Chem. Eng. News* **1999**.

Piccoli, R. L.; Lovisi, H. Kinetics and Thermodynamic Study of the Liquid-Phase Etherification of Isoamylenes with Methanol. *Ind. Eng. Chem. Res.* **1995**, *34*, 510−515.

Rehfinger, A.; Hoffmann, U. Kinetics of Methyl Tertiary Butyl Ether Liquid Phase Synthesis Catalyzed by Ion Exchange Resin-I. Intrinsic Rate Expression in Liquid-Phase Activities. *Chem. Eng. Sci.* **1990**, *45*, 1605−1617.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

Rihko, L.; Linnekoski, J. A.; Krause, 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.

Safronov, V. V.; Sharanov, K. G.; Rozhnov, A. M.; Alenin, V. J.; Sidorov, S. A. Thermodynamics of Sythesis of *tert*-Amyl Methyl Ether. *Zh. Prikl. Khim. (Leningrad)* **1989**, *62*, 824−828.

TRC Thermodynamic Tables, Hydrocarbons and Nonhydrocarbons; Thermodynamic Research Center: Texas A&M University, College Station, TX, 1992; Vol. 5.

Vila, M.; Cunill, F.; Izquierdo, J. F.; Tejero, J.; Iborra, M. Equilibrium Constants For Ethyl *tert*-Butyl Ether Liquid-Phase Synthesis. *Chem. Eng. Commun.* **1993**, *124*, 223−232.

Zhang, T.; Datta, R. Integral Analysis of Methyl *tert*-Butyl Ether Synthesis Kinetics. *Ind. Eng. Chem. Res.* **1995a**, *34*, 730−740.

Zhang, T.; Datta, R. Ethers from Ethanol. 3. Equilibrium Conversion and Selectivity Limitations in the Liquid-Phase Synthesis of Two *tert*-Hexyl Ethyl Ethers. *Ind. Eng. Chem. Res.* **1995b**, *34*, 2237−2246.

Received for review July 12, 1999. Accepted December 8, 1999.

JE990191P