Thermodynamic Study of Liquid Phase Synthesis of Ethyl *tert*-Butyl Ether Using *tert*-Butyl Alcohol and Ethanol

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In this study, a detailed thermodynamic analysis of the ethyl *tert*-butyl ether (ETBE) synthesis reaction between *tert*-butyl alcohol (TBA) and ethanol is performed to determine a liquid phase equilibrium constant expression. The result is of practical significance in view of the imminent prominence of ETBE to be produced from TBA and ethanol, as a gasoline blending oxygenate. In this study, enthalpy of formation, Gibbs, enthalpy of vaporization, and heat capacities (as a function of temperature) of the reactants and products were estimated. At 298 K, the standard molar enthalpy of reaction for ETBE from TBA and ethanol was found as −1.23 kJ·mol^{-1}. The liquid phase nonideality of the system was tested, and it was found that the system approaches ideal conditions. The thermodynamic analysis approach given here is expected to be useful for other liquid-phase systems.

Introduction

New approaches in reformulation of gasoline were adopted following the regulations proposed by the U.S. Clean Air Act. Due to removal of alkyl−lead compounds from gasoline for environmental and public health reasons, oxygenated compounds have gained importance as octane enhancing fuel blending compounds.[1] Alcohols and ethers are among these oxygenated compounds, proposed as octane enhancers. Addition of oxygenates into gasoline also reduces exhaust emissions of CO and unburned hydrocarbons and helps to reduce the formation of atmospheric ozone.[2] Tertiary ethers are generally preferred to alcohols as gasoline blending components, due to their lower blending vapor pressures and their missibility advantages over gasoline. Alcohols have disadvantages arising from their properties such as phase separation in the presence of a small amount of water. Among the ethers suggested as fuel blending components, methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and *tert*-amyl ethyl ether (TAEE) are the best known oxygenates to be used to increase the octane level and to promote cleaner burning of gasoline and thus decrease harmful emissions from vehicles.[3] MTBE has become the major gasoline additive used in the last decade, due to the availability of methanol, produced starting from natural gas. There are many studies on MTBE.[4,5] However, MTBE has high water solubility, and it causes water pollution problems. Isobutene used in the production of MTBE is a petrochemical feedstock. In the synthesis of *tert*-ethers, the use of another compound (such as *tert*-butyl alcohol) instead of isobutene has attracted the attention of researchers. As a result, alternative oxygenates were being investigated.

ETBE has superior qualities as an octane enhancer compared to MTBE and could be produced from bioethanol, which is a renewable source. Its average octane value is 110. Thus, the production of ETBE reduces the dependence on methanol and also contributes to reduce the greenhouse effect. MTBE production technology can be extended easily to ETBE synthesis with similar benefits.[6]

Commercially, ETBE is synthesized by etherification reaction of isobutene with ethanol[7] at moderate temperatures and pressures in the liquid phase over sulfonated acidic ion-exchange resin catalysts, such as Amberlyst-15[8−11] and Lewatit K2631.[12−14]

$$(CH_3)_2C{=}CH_2 + CH_3CH_2OH \leftrightarrow (CH_3)_3COCH_2CH_3 \qquad \text{(I)}$$

However, the supply of isobutene, which is mostly derived from nonrenewable crude oil, is mainly limited from petroleum refining and also used in other chemical industries. Hence, reactants other than isobutene are being investigated in ETBE production. *tert*-Butyl alcohol (TBA), as a coproduct of propylene oxide production from isobutane and propylene in the ARCO process, is proposed as an alternative reactant, instead of isobutene, in ETBE synthesis.[15−23] There are two ways to produce ETBE from TBA, namely, an indirect and a direct method. In the indirect method, TBA is dehydrated to isobutene in the first reactor according to reaction II, and then isobutene is reacted with ethanol to form ETBE.

$$(CH_3)_3COH \leftrightarrow (CH_3)_2C{=}CH_2 + H_2O \qquad \text{(II)}$$

However, in the direct method, ETBE can be produced by reacting TBA directly with ethanol in a reactor in the presence of an acid catalyst, during which water is also formed as a byproduct

$$(CH_3)_3COH + CH_3CH_2OH \leftrightarrow (CH_3)_3COCH_2CH_3 + H_2O \qquad \text{(III)}$$

Synthesis of ETBE by using TBA and ethanol and utilizing concentrated sulfuric acid as the homogeneous catalyst was investigated by Habenicht et al.[20] Yin et al.[21] studied synthesis of ETBE from TBA and ethanol catalyzed by Amberlyst-15 and heteropoly acids (HPA) in a batch reactor. Heteropoly acids were found to yield superior selectivity; however, they were less attractive because of dissolution of these catalysts in polar solvents. Production of ETBE using TBA and ethanol was also

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Table 1. Correlations of Equilibrium Constants, *K*, for ETBE Synthesis in the Literature

source	reactants	K
Vila et al.[28]	isobutene and ethanol	$K = \exp(1140 - 14580(T/\mathrm{K})^{-1} - 232.9 \ln(T/\mathrm{K}) + 1.087(T/\mathrm{K}) - 1.114\cdot10^{-3}(T/\mathrm{K})^2 + 5.538\cdot10^{-7}(T/\mathrm{K})^3)$
Jensen et al.[10]	isobutene and ethanol	(1) $K = \exp(10.387 + 4060.59(T/\mathrm{K})^{-1} - 2.89055 \ln(T/\mathrm{K}) - 1.91544\cdot10^{-2}(T/\mathrm{K}) + 5.28586\cdot10^{-5}(T/\mathrm{K})^2 - 5.32977\cdot10^{-8}(T/\mathrm{K})^3$ (2) $K = \exp(10.6162 + 4060.49(T/\mathrm{K})^{-1} - 2.89055 \ln(T/\mathrm{K}) + 1.91544\cdot10^{-2}(T/\mathrm{K}) + 5.28586\cdot10^{-5}(T/\mathrm{K})^2 - 5.32977\cdot10^{-8}(T/\mathrm{K})^3)$ (3) $K = \exp(0.558036 + 5345.01(T/\mathrm{K})^{-1} - 3.56724 \ln(T/\mathrm{K}) + 3.65829\cdot10^{-2}(T/\mathrm{K}) - 6.02157\cdot10^{-5}(T/\mathrm{K})^2 + 5.32295\cdot10^{-8}(T/\mathrm{K})^3)$
Assabumrungat et al.[17]	TBA and ethanol	$K = \exp(1140 - 14580(T/\mathrm{K})^{-1} + 232.9 \ln(T/\mathrm{K}) + 1.087(T/\mathrm{K}) - 1.114\cdot10^{-3}(T/\mathrm{K})^2 + 5.538\cdot10^{-7}(T/\mathrm{K})^3)$
Assabumrungat et al.[23]	TBA and ethanol	$K = \exp(1140 - 14580(T/\mathrm{K})^{-1} + 232.9 \ln(T/\mathrm{K}) + 1.087(T/\mathrm{K}) - 1.114\cdot10^{-3}(T/\mathrm{K})^2 + 5.538\cdot10^{-7}(T/\mathrm{K})^3)$
Kiatkittipong et al.[22]	TBA and ethanol	$K = \exp(1140 - 14580(T/\mathrm{K})^{-1} + 232.9 \ln(T/\mathrm{K}) + 1.087(T/\mathrm{K}) - 1.114\cdot10^{-3}(T/\mathrm{K})^2 + 5.538\cdot10^{-7}(T/\mathrm{K})^3)$

accomplished by reactive distillation in the study performed by Yang and Goto,[16] in which the combined process of pervaporation with reactive distillation had been investigated using Amberlyst-15. ETBE synthesis was further investigated by using Amberlyst 15, β-zeolite, and supported polyvinyl alcohol membrane by various researchers.[17,22,23] Yang et al.[19] also studied liquid phase etherification between ethanol and TBA under atmospheric pressure for the production of ETBE. Matouq et al.[24] employed $KHSO_4$, $NaHSO_4$, H_2SO_4, and Amberlyst-15 as catalysts for the production of ETBE from TBA and ethanol in a reactive distillation column. Umar et al.[18] studied this reaction in the liquid phase by using ion exchange resins, such as Purolite CT-124, CT-145H, CT-151, CT-175, CT-275, Amberlyst-15, and Amberlyst-35 wet.

A number of correlations have been proposed in the literature for the prediction of equilibrium constant, K, for the liquid phase MTBE synthesis reaction.[7,25–27] Unlike the case of MTBE, few studies have been published regarding to the thermodynamics of synthesis of ETBE from isobutene and ethanol. Vila et al.[28] reported a study of the equilibrium constant for liquid phase ETBE synthesis from isobutene and ethanol. Experimental equilibrium constant values were determined by direct measurement of the mixture composition at equilibrium at several temperatures. An equilibrium constant relationship for liquid phase ETBE synthesis reaction using isobutene and ethanol as the reactants was developed by Jensen and Datta,[10] using the thermodynamic pathways to obtain enthalpy and Gibbs free energy values.

In spite of the increasing interest in ETBE production from TBA and ethanol and its anticipated industrial importance, to our knowledge there is no published report on the thermodynamics of the liquid phase synthesis of ETBE from TBA and ethanol. Some researchers assumed the equilibrium constant relation of ETBE synthesis from isobutene and ethanol to be the same as the equilibrium constant relation of ETBE synthesis from TBA and ethanol. Assabumrungat et al.[17,23] and Kiatkittipong et al.[22] used the correlation of equilibrium constant for isobutene and ethanol reaction[28] also for TBA and ethanol reaction. The correlations for the equilibrium constant of ETBE synthesized from isobutene and ethanol are given in Table 1. The objective of this paper is to provide a detailed thermodynamic analysis of the liquid phase ETBE synthesis from TBA and ethanol and propose a relation for the equilibrium constant of this reaction. Also, a set of experimental results are obtained at different temperatures to check the equilibrium conversion value predicted from the derived expression.

Experimental Work

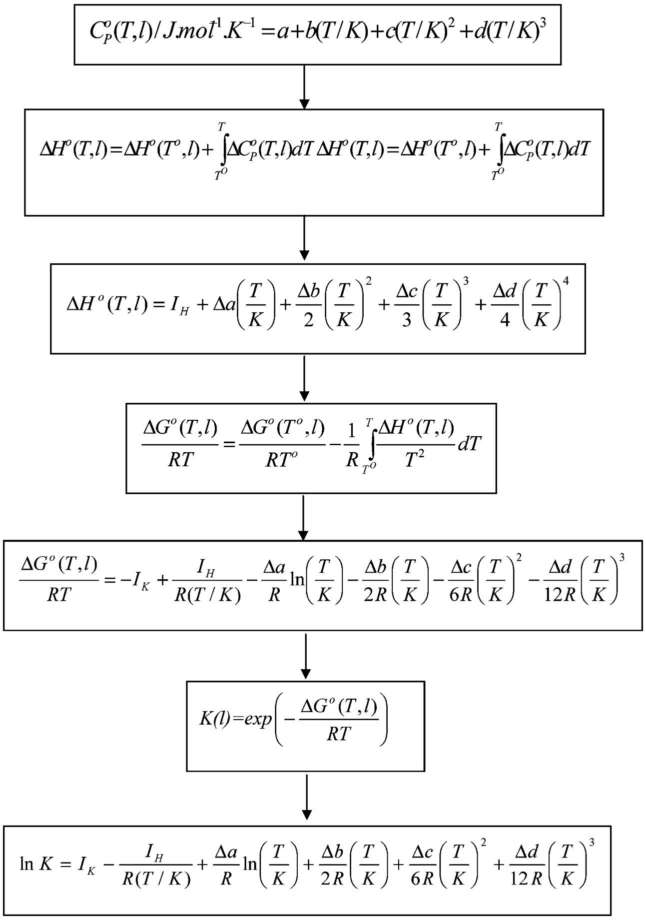
Materials. Analytic grade ethanol (Merck) and TBA (Merck) were used as reactants in the etherification reaction. The strongly acidic ion-exchange resin Amberlyst-15 (Merck) used as the catalyst is a macroporous sulfonated copolymer of styrene-divinylbenzene (DVB), containing a cross-linked matrix. Before the experiments, Amberlyst-15 was dried for 12 h at 383 K. Physical properties[29] of the catalyst used in this work are summarized in Table 2.

Table 2. Physical Properties of Amberlyst-15[29] [a]

s/m$^2\cdot$g^{-1}	ε	TIEC/meq of H$^+\cdot$g of dry material^{-1}	d_{avg}/m
59.2	0.32	5.2	$8.2\cdot10^{-8}$

[a] s is the surface area; ε is the macroporosity; d_{avg} is the average micrograin diameter; and TIEC is total ion exchange capacity. s and ε (ratio of macropore volume to total catalyst volume) values correspond to pores having diameters greater than $6.7\cdot10^{-9}$ m.

Continuous Flow Reactor Experiments. Liquid phase etherification of TBA with ethanol was investigated in a continuous



$$C_P^o(T,l)/J.mol^{-1}.K^{-1} = a + b(T/K) + c(T/K)^2 + d(T/K)^3$$

$$\Delta H^o(T,l) = \Delta H^o(T^o,l) + \int_{T^O}^{T} \Delta C_P^o(T,l)dT \; \Delta H^o(T,l) = \Delta H^o(T^o,l) + \int_{T^O}^{T} \Delta C_P^o(T,l)dT$$

$$\Delta H^o(T,l) = I_H + \Delta a\left(\frac{T}{K}\right) + \frac{\Delta b}{2}\left(\frac{T}{K}\right)^2 + \frac{\Delta c}{3}\left(\frac{T}{K}\right)^3 + \frac{\Delta d}{4}\left(\frac{T}{K}\right)^4$$

$$\frac{\Delta G^o(T,l)}{RT} = \frac{\Delta G^o(T^o,l)}{RT^o} - \frac{1}{R}\int_{T^O}^{T} \frac{\Delta H^o(T,l)}{T^2} dT$$

$$\frac{\Delta G^o(T,l)}{RT} = -I_K + \frac{I_H}{R(T/K)} - \frac{\Delta a}{R}\ln\left(\frac{T}{K}\right) - \frac{\Delta b}{2R}\left(\frac{T}{K}\right) - \frac{\Delta c}{6R}\left(\frac{T}{K}\right)^2 - \frac{\Delta d}{12R}\left(\frac{T}{K}\right)^3$$

$$K(l) = exp\left(-\frac{\Delta G^o(T,l)}{RT}\right)$$

$$\ln K = I_K - \frac{I_H}{R(T/K)} + \frac{\Delta a}{R}\ln\left(\frac{T}{K}\right) + \frac{\Delta b}{2R}\left(\frac{T}{K}\right) + \frac{\Delta c}{6R}\left(\frac{T}{K}\right)^2 + \frac{\Delta d}{12R}\left(\frac{T}{K}\right)^3$$

Figure 1. Flow scheme of the thermodynamic analysis.

Table 3. Gas Phase Thermochemical Data of TBA, Ethanol, ETBE, H_2O, and Constants for the Gas Phase Heat Capacity Equation (C_p(g)/J·mol^{-1}·K^{-1}) Term in Equations 7 and 8

	TBA[34]	ethanol[34]	ETBE[10]	H_2O[34]
$\Delta_f G°$/kJ·mol^{-1}	−177.8	−168.4	−121.15	−228.8
$\Delta_f H°$/kJ·mol^{-1}	−312.8	−235	−316.50	−242
a	−48.61	9.01	7.50	32.2
b	$7.172 \cdot 10^{-1}$	$2.141 \cdot 10^{-1}$	$6.293 \cdot 10^{-1}$	$1.924 \cdot 10^{-3}$
c	$-7.084 \cdot 10^{-4}$	$-8.390 \cdot 10^{-5}$	$-3.690 \cdot 10^{-4}$	$1.055 \cdot 10^{-5}$
d	$2.920 \cdot 10^{-7}$	$1.373 \cdot 10^{-9}$	$7.072 \cdot 10^{-9}$	$-3.596 \cdot 10^{-9}$

Table 4. Comparison of Enthalpy of Vaporization of TBA

reference	$\Delta_{vap}H°$/kJ·mol^{-1}
this work	46.21
Majer & Svoboda, 1985[35]	46.74
Polak & Benson, 1971[35]	46.94 ± 0.02
Skinner & Snelson, 1960[35]	46.02

Table 5. Comparison of Heat Capacity Values of TBA

reference	T/K	C_p/J·mol^{-1}·K^{-1}
this work	298	211.7
Caceres-Alonso & Costas, 1988[35]	298	215.4
Okano & Ogawa, 1978[35]	299	221.9
De Visser & Peron, 1977[36]	298	210.0
Murthy & Subrahmanyam, 1977[35]	298	224.9
Skold & Suurkuusk, 1976[35]	298	218.6
Parks & Anderson, 1926[37]	300	224.7
ChemCad v.5.2	298	224.8

Table 6. Comparison of Enthalpy of Formation of TBA in the Liquid Phase

Reference	$\Delta_f H°$/kJ·mol^{-1}
this work	−359
Wiberg & Hao, 1991[38]	−359.2 ± 0.84
Skinner & Snelson, 1960[35]	−359.3 ± 0.79
Taft & Riesz, 1955[39]	−356

flow reactor, which was made of a stainless steel tube in which 2.85 g of catalyst was packed. The reactor was immersed into a temperature-controlled furnace. TBA and ethanol (with a molar ratio of TBA/ethanol = 0.1; 0.3; 0.5) were mixed and sent to the system with pressurized nitrogen. Reaction was carried out at 1 atm pressure. A bypass line allowed the flow of reactants through the system without entering the reactor, when desired. The flow rate of the mixture was changed between (0.5 and 1) cm^3·min^{-1}. Etherification reaction experiments were performed in the temperature range of (373 to 383) K. Reaction products were analyzed by gas chromatography (Agilent 6890N) equipped with an FID and Poropak Q column. The column temperature was 473 K.

Table 9. Comparison of Some Thermochemical Properties of H_2O in the Liquid Phase

$\Delta_{vap}H°$/(kJ·mol^{-1})		$\Delta_f G°$/(kJ·mol^{-1})		$\Delta_f H°$/(kJ·mol^{-1})	
reference	value	reference	value	reference	value
this work	45.9	this work	−238.2	this work	−287.9
Murphy, 2005[44]	45.0	IAPWS[45]	−237.2	IAPWS[45]	−285.8
-	-	-	-	Cox et al., 1984[35]	−285.8 ± 0.04

Thermodynamic Analysis. Calculation of the Equilibrium Constant from Thermochemical Data. Thermodynamic equilibrium constant, K, for liquid phase (l) reaction, $\Sigma_{j=1}^{n} \nu_j N_j = 0$, among the n species N_j is given by

$$K(l) \equiv \prod_{j=1}^{n} a_{je}^{\upsilon_j} = \prod_{j=1}^{n} (\gamma_j)_e^{\upsilon_j} (x_j)_e^{\upsilon_j} = (\prod_{j=1}^{n} \gamma_{je}^{\upsilon_j})(\prod_{j=1}^{n} x_{je}^{\upsilon_j}) \equiv K_\gamma K_x \tag{1}$$

The activity of species j in the liquid phase, $a_j'\gamma_j x_j$, is calculated from its mole fraction, x_j, and the activity coefficient, γ_j, which can be determined through a UNIFAC method. υ_j is the stoichiometric coefficient of species j in reaction. Here, K_γ and K_x are equilibrium constants in terms of activity coefficients and mole fractions, respectively. The calculation method is indicated in a flow scheme in Figure 1. The detailed calculation process is given in the Appendix.

Prediction of Liquid Phase Thermochemical Data. Heat and free energy of formation values (at the standard state) of ethanol, isobutene, and ETBE are the thermochemical data to be evaluated to obtain an equilibrium constant. Molar heat capacities of the reactants and products are also obtained in the form of power functions. The enthalpy of formation of species j in the liquid phase is related to that in the gas phase by the following relation.[10]

$$\Delta_f H_j^o(T, l) = \Delta_f H_j^o(T, g) - \Delta_v H_j^o \tag{2}$$

Here, $\Delta_v H_j^o$ is the standard enthalpy of vaporization of species j at the temperature T and is obtained by the New Group Contribution Method[30] at T = 298.15 K.

$$\Delta_v H^o(298.15\ \mathrm{K}) = h_0 + \sum_{i=1}^{n_0} N_{h_{0,i}} C_{h_{0,i}} + w \sum_{j=1}^{m_0} M_{h_{0,j}} D_{h_{0,j}} + z \sum_{i=1}^{o_0} O_{h_{0,k}} E_{h_{0,k}} \tag{3}$$

Here, h_0 is an adjustable additional parameter, and $C_{h_{0,i}}$, $D_{h_{0,j}}$, $E_{h_{0,k}}$ are the first, second, and third level group contributions

Table 7. Comparison of Some Thermochemical Properties of Ethanol in the Liquid Phase

$\Delta_{vap}H°$/kJ·mol^{-1}		$\Delta_f G°$/kJ·mol^{-1}		$\Delta_f H°$/kJ·mol^{-1}	
reference	value	reference	value	reference	value
this work	41.6	this work	−174.7	this work	−276.6
Jensen & Datta, 1995[10]	42.6	Jensen & Datta, 1995[10]	−174.8	Jensen & Datta, 1995[10]	−277.5
-	-	-	-	Chao & Rossini, 1965[40]	−277.0 ± 0.3
-	-	-	-	Green, 1960[35]	−277.6 ± 0.42
-	-	-	-	Kelley, 1929[41]	−277.6
-	-	-	-	Parks, 1925[42]	−274.7

Table 8. Comparison of Some Thermochemical Properties of ETBE in the Liquid Phase

$\Delta_{vap}H°$/kJ·mol^{-1}		$\Delta_f G°$/kJ·mol^{-1}		$\Delta_f H°$/kJ·mol^{-1}	
reference	value	reference	value	reference	value
this work	32.4	This work	−125.6	This work	−348.9
Majer & Svoboda, 1985[35]	33.0	Jensen & Datta, 1995[10]	−126.8	Jensen & Datta, 1995[10]	−357.5
Jensen & Datta, 1995[10]	41.0	-	-	Sharonov et al. 1995[43]	−350.8 ± 2.6

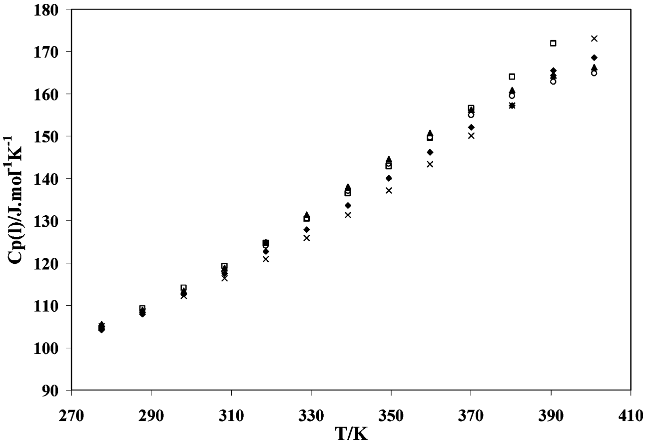


Figure 2. Comparison of liquid phase heat capacities for ethanol. ◆, this work; □, ref 10; ▲, ref 26; ○, ref 28; ×, ChemCad v5.2.

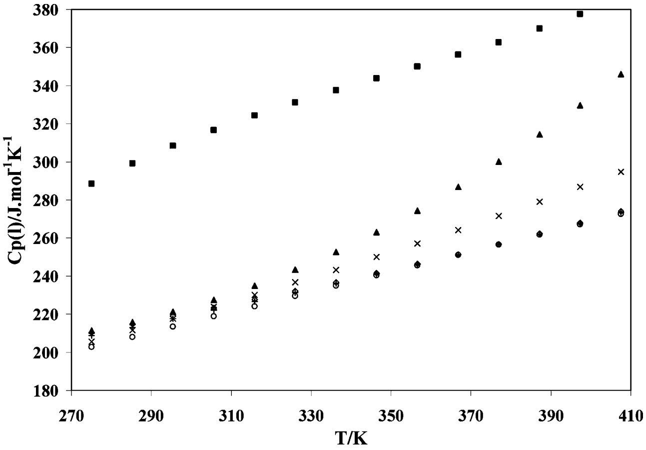


Figure 3. Comparison of liquid phase heat capacities for ETBE. ◇, This work; ■, ref 33; +, ref 26; ×, ref 10; ▲, ref 13; ○, ChemCad v5.2.

Table 10. Liquid Phase Thermochemical Data of TBA, Ethanol, ETBE, H_2O, and Constants for the Liquid Phase Heat Capacity Equation (C_p(g)/J·mol^{-1}·K^{-1}) Term in Equations 7 and 8

	TBA	ethanol	ETBE	H_2O
$\Delta_f G°$/kJ·mol^{-1}	−185.25	−174.70	−125.57	−238.15
$\Delta_f H°$/kJ·mol^{-1}	−359.01	−276.60	−348.93	−287.91
a	−2971.14	−386.058	18.79	44.56
b	24.74	3.4299	1.251	0.450
c	−0.0637	−0.0081	$-3.015\cdot10^{-3}$	$-1.64\cdot10^{-3}$
d	$5.543\cdot10^{-5}$	$7.379\cdot10^{-6}$	$3.637\cdot10^{-6}$	$1.786\cdot10^{-6}$

of types i, j, and k in eq 3. $N_{h_{0,i}}$, $M_{h_{0,j}}$, and $O_{h_{0,k}}$ are the number of occurrences of the first, second, and third level groups in eq 3.

Another expression for $\Delta_v H_j^o$ is Pitzer's approximation[31]

$$\frac{\Delta_v H_j^o}{RT_c} = 7.08(1 - T_r)^{0.354} + 10.95\omega(1 - T_r)^{0.456} \tag{4}$$

Here, T_c, T_r, and ω are critical temperature, reduced temperature (T/T_c), and acentric factor, respectively.

The liquid phase Gibbs free energy of formation of species j can be obtained from the gas phase by[10]

$$\frac{\Delta_f G_j^o(T,l)}{RT} = \frac{\Delta_f G_j^o(T,g)}{RT} + \frac{1}{R}\int_{T_{bj}}^{T} \frac{\Delta_v H_j^o(T,l)}{T^2}\mathrm{d}T \tag{5}$$

The liquid phase heat capacity may be related to that in the gas phase by the Bondi and Rowlinson correlation[32]

$$C_P^o(T,l) = R\left[2.56 + \frac{0.436}{(1 - T_r)} + \omega\left[2.91 + 4.28(1 - T_r)^{1/3}/T_r + \frac{0.296}{(1 - T_r)}\right]\right] \tag{6}$$

An alternative procedure is the Sternling and Brown correlation[10]

$$\frac{C_P^o(T,l) - C_P^o(T,g)}{R} = (0.51 + 2.2\omega)\left[3.67 + \frac{11.64}{(1 - T_r)^4} + 0.634(1 - T_r)^{-1}\right] \tag{7}$$

Equations 6 and 7 are for nonpolar liquids. They are accurate to within 8 % except for $T_r > 0.95$ for polar compounds, such as ethanol and TBA. There is an alternative correlation given by Yuan and Stiel for polar compounds.[33]

$$C_{Pj}^o(l) - C_{Pj}^o(g) = \Delta C_P^{(0)} + w\Delta C_P^{(1)} + x\Delta C_P^{(2)} + x^2\Delta C_P^{(3)} + w^2\Delta C_P^{(4)} + xw\Delta C_P^{(5)} \tag{8}$$

Here (0), (1), and (2) are fluid function and correction terms, and (3), (4), and (5) are coefficients for higher-order terms.

Here, x is the fourth parameter and P_r is reduced vapor pressure, given by the following expression.

$$x = \log P_r|_{T_r=0.6} + 1.70\omega + 1.552 \tag{9}$$

Results and Discussion

Gas phase thermodynamic data are available for a large number of species.[31] However, there are not sufficient data for liquid phase applications. There are insufficient thermodynamic data for ETBE synthesis from TBA and ethanol in the literature. In this study, liquid phase data were estimated from gas phase thermodynamic data.

Table 3 shows the values for the gas phase thermochemical data and the coefficients of the equation for molar heat capacity of the components (TBA, ethanol, ETBE, and water) in the vapor phase.[10,34] The liquid phase data for the Gibbs free energy and the heat capacity of TBA as a function of temperature are not available in the literature. So, enthalpy of vaporization was estimated by the group contribution method[31] at $T = 298$ K according to eq 3 and compared with the literature[35] (Table 4). The estimated value of enthalpy of vaporization was used for the calculation of Gibbs free energy of TBA (−185.254

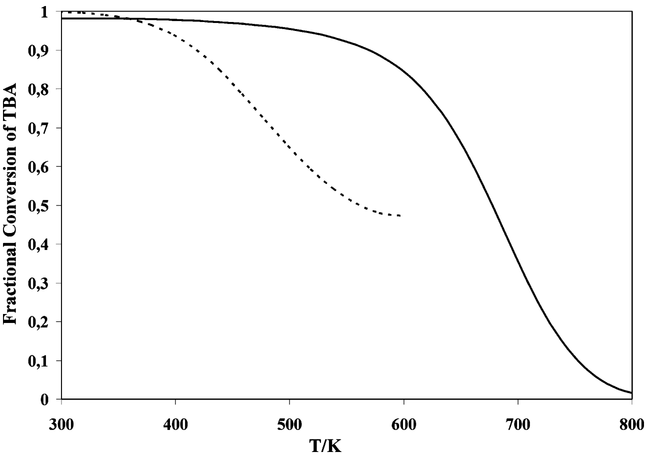


Figure 4. Equilibrium conversions of TBA versus temperature. —, This work (TBA + Ethanol reaction); - - - -, ref 10 (Isobutene + Ethanol reaction).

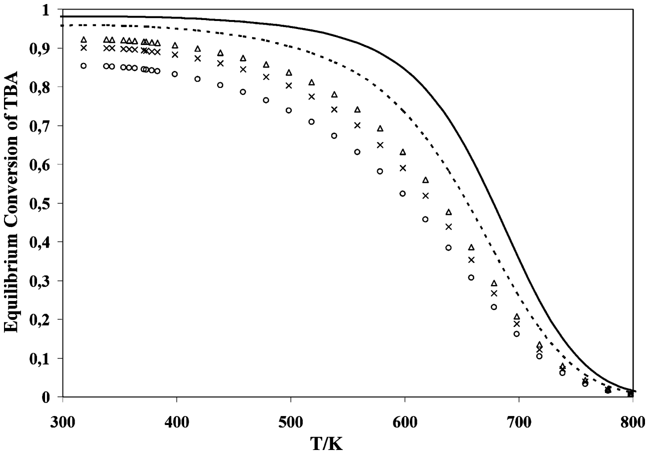


Figure 5. Equilibrium conversions of TBA as a function of temperature for different TBA/Ethanol ratios. —, TBA/Ethanol = 0.1; - - -, TBA/Ethanol = 0.2; Δ, TBA/Ethanol = 0.3; ×, TBA/Ethanol = 0.4; ○, TBA/Ethanol = 0.5.

Table 11. Comparison of Experimental Equilibrium Conversions at Different Space Times with Equilibrium Conversion (T = 373 K)

space time ($g \cdot min \cdot cm^{-3}$)	0.05	0.3	0.5	1	5.7	[a]
TBA conversion (%)	30	78	91	92	96	97

[a] Theoretically evaluated using eq 10.

$kJ \cdot mol^{-1}$) in the liquid phase by the method of Jensen and Datta,[10] according to eq 5. The molar heat capacities of TBA in the liquid phase at different temperatures were estimated by the Yuan and Stiel method[33] for polar liquids using eq 8. By substituting the CurveExpert 1.3 program, the molar heat capacities were expressed as a function of temperature in cubic polynomial form. They were also estimated at 298 K by using ChemCad v.5.2. The heat capacity value at 298 K was compared in Table 5 with the literature[35−37] to justify the temperature dependence form. The liquid phase enthalpy of formation of TBA was available in the literature.[35,38,39] It was also determined from eq 2 and compared with the literature values in Table 6. The estimation methods were also used for the calculations of enthalpy of vaporization, liquid phase Gibbs free energy, and enthalpy of formation of ethanol, ETBE, and H_2O and compared with literature values in Tables 7, 8, and 9, respectively. The coefficients for the liquid phase heat capacity of ethanol and H_2O were estimated by eq 8, and the coefficients for ETBE were estimated by the Sternling and Brown correlation according to eq 7. They were also compared with the literature in Figures 2 and 3. Liquid phase heat capacities of ETBE are different for separate studies. Small variations as stated in Figure 3 were shown except for the curve obtained in Yuan and Stiel's work.[33] ETBE is a polar compound. As far as polar compounds are considered, some factors such as short-range intermolecular forces and quantum effects for low molecular weight substances may cause deviations.[33] Especially at low reduced temperatures, the experimental data tend to scatter. Table 10 shows all these liquid phase thermochemical data. Employing the calculation method of the equilibrium constant from thermochemical data in Table 10, the following expression results

$$\ln K(l) = -2101.93 + \frac{38672.73}{T/\mathrm{K}} + 411.41 \ln\left(\frac{T}{\mathrm{K}}\right) - 1.592\left(\frac{T}{\mathrm{K}}\right) + 1.345 \cdot 10^{-3}\left(\frac{T}{\mathrm{K}}\right)^2 - 5.7517 \cdot 10^{-7}\left(\frac{T}{\mathrm{K}}\right)^3 \quad (10)$$

Equilibrium conversion of TBA to ETBE was estimated by using the equilibrium constant relation (eq 10) derived above in a temperature range of (300 to 800) K, and the data plotted are given in Figure 4. A typical curve obtained with a TBA/ethanol feed ratio of 0.1 is given in Figure 4. In this analysis, activity coefficients are estimated from the UNIFAC program. In the same figure, equilibrium conversion values estimated by using the equilibrium constant relation proposed by Jensen and Datta[10] for the isobutene−ethanol reaction is also given. As seen in this figure, in the temperature range lower than about 380 K, the predictions of both correlations are quite close. However, at higher temperatures the equilibrium conversion estimated by the correlation proposed in this work for the TBA−ethanol reaction is much higher than the equilibrium conversion plotted according to Jensen and Datta's correlation[10] for the isobutene−ethanol reaction. This deviation is reasonable since those two curves are for different reaction systems.

Equilibrium conversion of TBA at different TBA/ethanol ratios (0.1 to 0.5) estimated by the correlation proposed in this work is given in Figure 5. In this figure, it is clearly seen that equilibrium conversion of TBA has reached the highest value for a molar ratio of TBA/ethanol = 0.1 which corresponds to the mostly used feed range in industry.

Experimental equilibrium TBA conversion results obtained at 373 K at different space times, in the range of (0.05 to 5.7) $min \cdot g \cdot cm^{-3}$, are reported in Table 11. At long space times, equilibrium is closely approached. The comparison between experimental equilibrium conversions and theoretically calculated equilibrium conversions in the presence of various TBA/ethanol molar ratios (0.1, 0.3, and 0.5) is given in Table 12. For TBA/ethanol = 0.1, the experimental equilibrium conversion value (0.96) obtained at a space time of 5.7 $min \cdot g \cdot cm^{-3}$ was very close to the corresponding predicted equilibrium conversion value (0.97). All these values quite agree with each other. Experimental and predicted equilibrium conversion values at different temperatures in the range of (373 to 383) K are reported in Table 12. Due to deactivation of Amberlyst-15 at around 393 K, maximum reaction temperature was selected as 383 K.

Conclusions

A new equilibrium constant relation was derived for the synthesis of ETBE from TBA and ethanol. The present study was thought to be a new and necessary approach for liquid phase applications considering the scarcity of liquid phase thermo-

Table 12. Comparison of Experimental Equilibrium Conversions with Equilibrium Conversions From Predicted Correlation (Equation 10) (Space Time = 5.7 $g \cdot min \cdot cm^{-3}$)

TBA/ethanol molar ratio	0.1		0.3		0.5	
T/K	equilibrium conversion of TBA (experimental) (%)	equilibrium conversion of TBA (from correlation) (%)	equilibrium conversion of TBA (experimental) (%)	equilibrium conversion of TBA (from correlation) (%)	equilibrium conversion of TBA (experimental) (%)	equilibrium conversion of TBA (from correlation) (%)
373	96	97	92	92	84	84
378	95	97	91	91	83	84
383	94	97	91	91	83	84

dynamic data for this reaction. Thermodynamic data for the formation enthalpy, Gibbs free energy, vaporization enthalphy, and specific heat capacity were calculated for reactants and products with the aid of an approach obtained by the combination of various methods. It was shown that the equilibrium conversion values of the TBA−ethanol reaction are much higher than the isobutene−ethanol reaction at temperatures over 380 K. Predicted conversion values agreed well with the experimental results in the temperature range of (373 to 383) K.

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Appendix

The equilibrium constant can be related to the thermodynamic properties of the system for a reaction occurring at the reaction temperature T, using eq A1

$$K(l) = \exp\left(-\frac{\Delta G^{o}(T, l)}{RT}\right) \tag{A1}$$

The standard Gibbs energy change for the liquid phase reaction is computed from eq A2

$$\Delta G^{o}(T, l) = \sum_{j=1}^{n} \upsilon_j \Delta_f G_j^{o}(T, l) \tag{A2}$$

Here, $\Delta_f G_j^{o}(T,l)$ is the Gibbs energy of formation of species j in the liquid phase at the reaction temperature T. R is the gas constant, 8.3143 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

The enthalpy of reaction at the temperature T is given by eq 4.

$$\Delta H^{o}(T, l) \equiv \sum_{j=1}^{n} \upsilon_j \Delta_f H_j^{o}(T, l) \tag{A3}$$

The standard Gibbs free energy change for the liquid phase reaction can also be obtained from the standard enthalpy and entropy changes ($S^{o}(T,l)$)

$$\Delta G^{o}(T, l) = \Delta H^{o}(T, l) - T\Delta S^{o}(T, l) \tag{A4}$$

Temperature dependence of standard Gibbs free energy change of reaction at constant pressure is obtained from

$$\frac{\Delta G^{o}(T, l)}{RT} = \frac{\Delta G^{o}(T^{o}, l)}{RT^{o}} - \frac{1}{R}\int_{T^{o}}^{T} \frac{\Delta H^{o}(T, l)}{T^{2}}\mathrm{d}T \tag{A5}$$

Here, $\Delta H^{o}(T,l)$, the standard enthalpy of reaction at temperature T, may be written in terms of the enthalpy of reaction at $T = T^{o}$, $\Delta H^{o}(T^{o},l)$, and the dependence of $\Delta H^{o}(T,l)$ on temperature can be computed by integration of the Kirchoff equation.

$$\Delta H^{o}(T, l) = \Delta H^{o}(T^{o}, l) + \int_{T^{o}}^{T} \Delta C_P^{o}(T, l)\mathrm{d}T \tag{A6}$$

Here, ΔC_P^{o} is the difference between the molar heat capacities of the products and reactants of the reaction and is given by

$$\Delta C_P^{o}(T, l) \equiv \sum_{j=1}^{n} \upsilon_j \Delta C_{Pj}^{o}(T, l) \tag{A7}$$

The molar heat capacities in the liquid phase of the species take part in the reaction and are usually expressed in the polynomial form.[31]

$$C_P^{o}(T, l)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = a + b(T/\text{K}) + c(T/\text{K})^2 + d(T/\text{K})^3 \tag{A8}$$

Here $C_P^{o}(T,l)$ is the liquid phase molar heat capacity of the species, and a, b, c, and d are the coefficients of molar heat capacity expression. Integrating eq A6 and taking into account eq A7 and eq A8 provides the following expressions[10]

$$\Delta H^{o}(T, l) = I_{\text{H}} + \Delta a\left(\frac{T}{\text{K}}\right) + \frac{\Delta b}{2}\left(\frac{T}{\text{K}}\right)^2 + \frac{\Delta c}{3}\left(\frac{T}{\text{K}}\right)^3 + \frac{\Delta d}{4}\left(\frac{T}{\text{K}}\right)^4 \tag{A9}$$

Here, I_{H} is the constant of integration

$$I_{\text{H}} \equiv \Delta H^{o}(T^{o}, L) - \Delta a\left(\frac{T^{o}}{\text{K}}\right) - \frac{\Delta b}{2}\left(\frac{T^{o}}{\text{K}}\right)^2 - \frac{\Delta c}{3}\left(\frac{T^{o}}{\text{K}}\right)^3 - \frac{\Delta d}{4}\left(\frac{T^{o}}{\text{K}}\right)^4 \tag{A10}$$

and

$$\Delta a \equiv \sum_{j=1}^{n} \upsilon_j a_j \Delta b \equiv \sum_{j=1}^{n} \upsilon_j b_j \Delta c \equiv \sum_{j=1}^{n} \upsilon_j c_j \Delta d \equiv \sum_{j=1}^{n} \upsilon_j d_j \tag{A11}$$

Using eq A9 in eq A5 yields

$$\frac{\Delta G^{o}(T, l)}{RT} = -I_{\text{K}} + \frac{I_{\text{H}}}{R(T/\text{K})} - \frac{\Delta a}{R}\ln\left(\frac{T}{\text{K}}\right) - \frac{\Delta b}{2R}\left(\frac{T}{\text{K}}\right) - \frac{\Delta c}{6R}\left(\frac{T}{\text{K}}\right)^2 - \frac{\Delta d}{12R}\left(\frac{T}{\text{K}}\right)^3 \tag{A12}$$

where I_{K} is the constant of integration

$$I_{\text{K}} \equiv \ln K_{T^{o}} + \frac{I_{\text{H}}}{R(T^{o}/\text{K})} - \frac{\Delta a}{R}\ln\left(\frac{T^{o}}{\text{K}}\right) - \frac{\Delta b}{2R}\left(\frac{T^{o}}{\text{K}}\right) - \frac{\Delta c}{6R}\left(\frac{T^{o}}{\text{K}}\right)^2 - \frac{\Delta d}{12R}\left(\frac{T^{o}}{\text{K}}\right)^3 \tag{A13}$$

The use of eq A12 in eq A1 results in

$$\ln K = I_{\text{K}} - \frac{I_{\text{H}}}{R(T/\text{K})} + \frac{\Delta a}{R}\ln\left(\frac{T}{\text{K}}\right) + \frac{\Delta b}{2R}\left(\frac{T}{\text{K}}\right) + \frac{\Delta c}{6R}\left(\frac{T}{\text{K}}\right)^2 + \frac{\Delta d}{12R}\left(\frac{T}{\text{K}}\right)^3 \tag{A14}$$

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