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Excess molar enthalpies of ternary mixtures formed by methanol and methyl *tert*-butyl ether with ethanol or 1-propanol at 298.15 K

Kazuhiro Tamura*, Mohammad M.H. Bhuiyan, Toshiro Yamada

Department of Chemistry and Chemical Engineering, Division of Physical Sciences, 40-20 Kodatsuno 2-chome,
Kanazawa University, Kanazawa, Ishikawa 920-8667, Japan

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Abstract

Ternary excess molar enthalpies for (methanol + ethanol + methyl *tert*-butyl ether (MTBE)) and (methanol + 1-propanol + MTBE) mixtures have been measured with a flow microcalorimeter at $T = 298.15$ K and atmospheric pressure. Constant contours for the ternary experimental results were calculated by a polynomial equation. Further, the results have been compared with those calculated from a UNIQUAC associated-solution model taking into account the molecular self- and cross-association of two alcohols and the solvation among the alcohols and MTBE. The results predicted by using binary parameters obtained from the corresponding experimental binary results alone are in good agreement with the experimental values. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Excess molar enthalpies; MTBE; Flow calorimeter; Association; Solvation

1. Introduction

Before the Clean Air Act Amendments of 1990, organo-metal (e.g. tetra-ethyl lead, tetra-methyl lead, methyl cyclopentadienyl manganese tricarbonyl, etc.) and aromatics (e.g. benzene, toluene, xylenes, ethylbenzene, etc.) were frequently used as octane enhancers for automobiles and vehicles. From the recent increasing concerns about the environmental problems and health risks for human, however, oxygenated organic compounds such as light alcohols and aliphatic branched ethers are being considered and/or mandated for addition to gasoline because of their expected air pollution-reducing capabilities.

Methyl *tert*-butyl ether (MTBE) is one of the oxygenated additives into gasoline to reduce the polluting component in exhaust gases like CO, NO_x, unburned hydrocarbons, polynuclear aromatics. The economic advantages of the MTBE manufacturing process include lower investment [1], operating costs, and energy consumption, besides its noteworthy octane properties. Therefore, the blending characteristics of MTBE additive in a new gasoline formulation have been investigated extensively [2,3]. The MTBE mixtures with lower alcohols have outstanding properties such as miscibility in gasoline, storage stability, and potential compatibilities with the emission restriction by the clean air legislation. Following these incentives, we have measured the ternary excess

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* Corresponding author. Tel.: +81-76-234-4804;
fax: +81-76-234-4829.
E-mail address: tamura@t.kanazawa-u.ac.jp (K. Tamura).

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Nomenclature

a_{ji}	binary interaction parameters for i–j pair
a_n	coefficients of Eq. (3)
A, B, C	methanol, ethanol or 1-propanol, and MTBE
A_i, B_j	i-mer of methanol and j-mer of ethanol or 1-propanol
A_iB_j	complex between i-mer of methanol and j-mer of ethanol or 1-propanol
A_iB_jC	complex between i-mer of methanol and j-mer of ethanol or 1-propanol and MTBE monomer
A_iC	complex between i-mer of methanol and MTBE monomer
b_j	coefficients of Eq. (4)
B_iC	complex between i-mer of ethanol or 1-propanol and MTBE monomer
C_{ji}, D_{ji}	coefficients of Eq. (6)
h_A	enthalpies of hydrogen-bond formation of methanol or ethanol or 1-propanol
h_{AB}	enthalpies of complex formation between unlike molecules
H_m^E	excess molar enthalpy
$H_{m,123}^E$	excess molar enthalpies of ternary mixtures $(1+2+3)$
$H_{m,ij}^E$	excess molar enthalpies of binary mixtures $(i+j)$
δH_m^E	deviation between experimental and calculated excess enthalpy value
ΔH_m^E	excess molar enthalpies of pseudobinary mixtures
k	coefficient of Eq. (4)
K_A	self-association constants of methanol or ethanol or 1-propanol
K_{AB}	solvation constants between unlike molecules
m	number of experimental data points
p	number of parameters
q	molecular geometric area parameter of pure component
r	molecular geometric volume parameter of pure component
R	gas constant
T	absolute temperature
x_I	liquid mole fraction of component I
x'_I	liquid mole fraction of component I in a binary mixture

Greek letters

δ	absolute arithmetic-mean deviation
Δ_{123}	function as defined by Eq. (2)
σ	standard deviation

Subscripts

A	methanol or ethanol or 1-propanol
AB	complex between unlike molecules
cal	calculated
chem	chemical
exp	experimental
i, j, k, l	i, j, k, and l-mer of methanol, ethanol, and 1-propanol
phys	physical

Superscript

E	excess

molar enthalpies of (methanol + ethanol + MTBE) and (methanol + 1-propanol + MTBE) systems at 298.15 K. Binary excess molar enthalpies at 298.15 K for each of the five mixtures making up the two ternary systems of our present interest have already been reported: (methanol + ethanol) [4]; (methanol + 1-propanol) [4]; (methanol + MTBE) [5]; (ethanol + MTBE) [6]; (1-propanol + MTBE) [7].

2. Experimental

All the alcohols used in this research were purchased from Wako Pure Chemical, and MTBE from Kanto Chemical. The quoted mass purities of these chemicals are as shown in parentheses: methanol (99.7%), ethanol (99.8%), 1-propanol (99.7%), and MTBE (99%). Chemicals were kept in dark bottles dried over molecular sieves (3A 1/16, 4A 1/16) 2–3 weeks prior to their use to eliminate the residual traces of water and avoid moisturizing. The chemicals were degassed by the ultrasonic technique and their densities were calculated with a DMA 58 digital densimeter (Anton Paar). The solvent purities were analyzed in comparison with our observed and recent published values [8–15], and are given in Table 1. Experimental measurements were carried out using a flow microcalorimeter [16]. The temperature was monitored by a calibrated quartz thermometer

Table 1
Comparison of experimental densities ρ for the pure liquids at 298.15 K

Component	ρ (g cm^{-3})		
	Experimental value	Literature	
		Value	Reference
Methanol	0.78665	0.78665	[8]
		0.78668	[9]
Ethanol	0.78524	0.78504	[10]
		0.78530	[11]
1-Propanol	0.79973	0.79975	[12]
		0.79965	[13]
MTBE	0.73538	0.73540	[14]
		0.73529	[15]

(DMT-610BG, Tokyo Denpa). During each experimental run, the temperature in the mixing system was maintained at 298.15 ± 0.005 K. The errors in the excess molar enthalpy $H_{\mathrm{m}}^{\mathrm{E}}$ were estimated to be less than ±0.5% from preliminary experiments for the measurements of (benzene + cyclohexane) [17–19] and (1-propanol + MTBE) [7] systems.

Three experimental series of the measurements were performed by adding MTBE to binary mixtures composed of $\{x_1'$ methanol $+ (1 - x_1')$(ethanol or 1-propanol)$\}$. The mixtures were prepared by mass using a balance (AEX-180, Shimadzu) ensuring accuracy in the mole fractions of 10^{-4}. Thus, the ternary excess molar enthalpy $H_{\mathrm{m},123}^{\mathrm{E}}$ can be expressed as

$$H_{\mathrm{m},123}^{\mathrm{E}} = \Delta H_{\mathrm{m}}^{\mathrm{E}} + (1 - x_3) H_{\mathrm{m},12}^{\mathrm{E}} \tag{1}$$

where $\Delta H_{\mathrm{m}}^{\mathrm{E}}$ is the measured excess molar enthalpy for the pseudobinary mixtures, $H_{\mathrm{m},12}^{\mathrm{E}}$ the excess molar enthalpy of the initial binary mixtures $\{x_1'$ methanol $+ (1 - x_1')$(ethanol or 1-propanol)$\}$, and x_3 the mole fraction of MTBE. The values of $H_{\mathrm{m},12}^{\mathrm{E}}$ at three specified compositions (approximate compositions of these mixtures were 25, 50, and 75 mol% of component 1) were interpolated by means of a spline-fit method.

3. Results and discussion

The experimental results for the ternary mixtures of (methanol + ethanol + MTBE) and (methanol + 1-propanol + MTBE) systems at 298.15 K are listed in Tables 2 and 3, respectively, along with the measured values of $\Delta H_{\mathrm{m}}^{\mathrm{E}}$ and the ternary experimental $H_{\mathrm{m},123}^{\mathrm{E}}$ calculated from Eq. (1). The values were correlated using the following equation:

$$H_{\mathrm{m},123}^{\mathrm{E}} = H_{\mathrm{m},12}^{\mathrm{E}} + H_{\mathrm{m},13}^{\mathrm{E}} + H_{\mathrm{m},23}^{\mathrm{E}} + \frac{x_1 x_2 x_3 \Delta_{123}}{RT} \tag{2}$$

where $H_{\mathrm{m},ij}^{\mathrm{E}}$ are the binary excess molar enthalpies (in J mol^{-1}) and calculated from a polynomial equation of the form

$$H_{\mathrm{m},ij}^{\mathrm{E}} = x_i x_j \sum_{n=1}^{p} a_n (x_i - x_j)^{n-1} \tag{3}$$

where a_n is the coefficient to be obtained by an unweighted least-squares method. Table 4 presents the coefficients of Eq. (3) for the five binary mixtures and the standard deviation calculated by using $\sigma(H_{\mathrm{m}}^{\mathrm{E}}) = \left\{ \sum_{i=1}^{m} (H_{\mathrm{exp}}^{\mathrm{E}} - H_{\mathrm{cal}}^{\mathrm{E}})^2 / (m - p) \right\}^{0.5}$, where m is the number of experimental data points and p the number of parameters. The term Δ_{123} in Eq. (2), representing the ternary contribution to the magnitude, was correlated by the following expression:

$$\frac{\Delta_{123}}{RT} = \frac{\sum_{j=1}^{p} b_j (1 - 2x_3)^{j-1}}{1 - k(1 - 2x_3)} \tag{4}$$

The values of the coefficients b_j and k, the absolute arithmetic-mean deviation calculated by $\delta(H_{\mathrm{m}}^{\mathrm{E}}) = \sum_{i=1}^{m} |H_{\mathrm{exp}}^{\mathrm{E}} - H_{\mathrm{cal}}^{\mathrm{E}}| / m$, and the standard deviation obtained in fitting Eqs. (2) and (4) to the experimental ternary $H_{\mathrm{m}}^{\mathrm{E}}$ are $b_1 = -0.8778$, $b_2 = -0.6007$, $b_3 = -0.5331$, $b_4 = -1.0022$, $b_5 = -0.7695$, and $k = -1.1189$, $\delta(H_{\mathrm{m}}^{\mathrm{E}}) = 1.9$ J mol^{-1} and $\sigma(H_{\mathrm{m}}^{\mathrm{E}}) = 3.0$ J mol^{-1} for (methanol + ethanol + MTBE) system and $b_1 = -1.0877$, $b_2 = -0.5932$, $b_3 = -0.2046$, $b_4 = -0.5876$, $b_5 = 0.6687$, $b_6 = -0.9762$, and $k = -1.0708$, $\delta(H_{\mathrm{m}}^{\mathrm{E}}) = 3.0$ J mol^{-1} and $\sigma(H_{\mathrm{m}}^{\mathrm{E}}) = 3.9$ J mol^{-1} for (methanol + 1-propanol + MTBE) system. Constant $H_{\mathrm{m},123}^{\mathrm{E}}$ contors calculated from Eq. (2) are plotted in Figs. 1 and 2 for (methanol + ethanol + MTBE) and (methanol + 1-propanol + MTBE) systems, respectively. The maximum value of $H_{\mathrm{m},123}^{\mathrm{E}}$ was 520.1 J mol^{-1} for (methanol + ethanol + MTBE) system at the mole fraction of $x_1 = 0.035$ and $x_2 = 0.327$, and that of (methanol + 1-propanol + MTBE) system was 566.5 J mol^{-1} at $x_1 = 0.025$ and $x_2 = 0.359$.

Table 2
Experimental excess molar enthalpies of methanol (1) + ethanol (2) + MTBE (3) mixture at 298.15 K[a]

$x'_1 = 0.2493$, $H^E_{m,12} = 2.6\,J\,mol^{-1}$				$x'_1 = 0.5008$, $H^E_{m,12} = 4.5\,J\,mol^{-1}$				$x'_1 = 0.7494$, $H^E_{m,12} = 4.0\,J\,mol^{-1}$			
x_1	x_2	ΔH^E_m (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})	x_1	x_2	ΔH^E_m (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})	x_1	x_2	ΔH^E_m (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})
0.2368	0.7132	34.8	37.3	0.4758	0.4742	18.2	22.5	0.7119	0.2381	4.9	8.7
0.2244	0.6756	77.5	79.9	0.4507	0.4493	53.1	57.2	0.6745	0.2255	31.3	35.0
0.2119	0.6381	129.8	132.1	0.4257	0.4243	96.1	99.9	0.6370	0.2130	67.6	71.0
0.1994	0.6006	183.1	185.2	0.4006	0.3994	141.4	145.0	0.5995	0.2005	109.0	112.2
0.1870	0.5630	232.0	233.9	0.3756	0.3744	187.7	191.1	0.5621	0.1879	152.1	155.1
0.1745	0.5255	284.7	286.5	0.3506	0.3494	234.8	238.0	0.5246	0.1754	194.9	197.8
0.1620	0.4880	329.4	331.1	0.3255	0.3245	277.9	280.9	0.4871	0.1629	235.9	238.5
0.1496	0.4504	369.6	371.1	0.3005	0.2995	317.9	320.7	0.4496	0.1504	273.0	275.4
0.1371	0.4129	405.1	406.5	0.2754	0.2746	352.6	355.1	0.4122	0.1378	306.2	308.4
0.1246	0.3754	436.3	437.6	0.2504	0.2496	381.5	383.8	0.3747	0.1253	334.9	337.0
0.1122	0.3378	459.5	460.7	0.2254	0.2246	405.2	407.3	0.3372	0.1128	357.2	359.0
0.0997	0.3003	472.0	473.1	0.2003	0.1997	421.3	423.1	0.2998	0.1002	376.1	377.8
0.0873	0.2627	477.2	478.1	0.1753	0.1747	443.0	444.6	0.2623	0.0877	381.9	383.3
0.0748	0.2252	472.2	473.0	0.1502	0.1498	430.4	431.7	0.2248	0.0752	380.4	381.6
0.0623	0.1877	451.9	452.5	0.1252	0.1248	410.8	412.0	0.1874	0.0626	369.4	370.4
0.0499	0.1501	417.4	417.9	0.1002	0.0998	379.1	380.0	0.1499	0.0501	342.0	342.8
0.0374	0.1126	362.2	362.6	0.0751	0.0749	330.8	331.5	0.1124	0.0376	300.9	301.5
0.0249	0.0751	283.7	283.9	0.0501	0.0499	248.8	249.3	0.0749	0.0251	233.0	233.4
0.0125	0.0375	179.4	179.5	0.0250	0.0250	164.7	164.9	0.0375	0.0125	156.2	156.4

[a] Ternary mixtures were prepared by mixing pure MTBE with {x'_1 methanol + $(1 - x'_1)$ethanol}.

Table 3
Experimental excess molar enthalpies of methanol (1) + 1-propanol (2) + MTBE (3) mixture at 298.15 K[a]

$x'_1 = 0.2504$, $H^E_{m,12} = 52.9\,J\,mol^{-1}$				$x'_1 = 0.4999$, $H^E_{m,12} = 82.3\,J\,mol^{-1}$				$x'_1 = 0.7501$, $H^E_{m,12} = 72.1\,J\,mol^{-1}$			
x_1	x_2	ΔH^E_m (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})	x_1	x_2	ΔH^E_m (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})	x_1	x_2	ΔH^E_m (J mol^{-1})	$H^E_{m,123}$ (J mol^{-1})
0.2379	0.7121	41.5	91.8	0.4750	0.4750	21.1	99.3	0.7125	0.2375	4.5	73.0
0.2254	0.6746	92.4	140.0	0.4500	0.4500	55.0	129.1	0.6750	0.2250	26.5	91.4
0.2129	0.6371	143.9	188.9	0.4250	0.4250	95.9	165.8	0.6375	0.2125	58.9	120.2
0.2004	0.5996	198.9	241.2	0.4000	0.4000	139.5	205.4	0.6000	0.2000	96.8	154.4
0.1878	0.5622	249.6	289.3	0.3750	0.3750	184.8	246.5	0.5625	0.1875	137.0	191.1
0.1753	0.5247	299.1	336.2	0.3500	0.3500	229.4	287.1	0.5250	0.1750	178.3	228.8
0.1628	0.4872	345.4	379.8	0.3250	0.3250	271.6	325.1	0.4875	0.1625	217.9	264.8
0.1503	0.4497	385.6	417.3	0.3000	0.3000	309.0	358.4	0.4500	0.1500	254.5	297.8
0.1377	0.4123	418.4	447.5	0.2750	0.2750	342.4	387.7	0.4125	0.1375	286.3	326.0
0.1252	0.3748	446.6	473.0	0.2500	0.2500	368.1	409.3	0.3750	0.1250	317.6	353.7
0.1127	0.3373	469.2	493.0	0.2250	0.2250	391.8	428.8	0.3375	0.1125	340.8	373.2
0.1002	0.2998	481.0	502.2	0.2000	0.2000	408.7	441.6	0.3000	0.1000	357.5	386.3
0.0877	0.2623	485.4	503.9	0.1750	0.1750	415.9	444.7	0.2625	0.0875	367.0	392.2
0.0751	0.2249	476.0	491.9	0.1500	0.1500	413.4	438.1	0.2250	0.0750	367.0	388.7
0.0626	0.1874	459.4	472.7	0.1250	0.1250	400.7	421.2	0.1875	0.0625	356.1	374.1
0.0501	0.1499	416.5	427.1	0.1000	0.1000	371.1	387.6	0.1500	0.0500	334.9	349.3
0.0376	0.1124	366.3	374.2	0.0750	0.0750	322.0	334.4	0.1125	0.0375	292.5	303.3
0.0250	0.0750	290.0	295.3	0.0500	0.0500	258.3	266.5	0.0750	0.0250	238.6	245.8
0.0125	0.0375	179.9	182.5	0.0250	0.0250	167.2	171.3	0.0375	0.0125	155.4	159.0

[a] Ternary mixtures were prepared by mixing pure MTBE with {x'_1 methanol + $(1 - x'_1)$1-propanol}.

Table 4
Coefficients a_n (in J mol^{-1}) of Eq. (3) and standard deviations

System (1 + 2)	a_1	a_2	a_3	a_4	$\sigma(H_m^E)$ (J mol^{-1})
Methanol + ethanol[a]	17.7462	6.9218	0.6257	1.0390	0.09
Methanol + 1-propanol[a]	328.57	99.02	23.94	9.03	0.17
Methanol + MTBE[b]	1152.20	−929.30	55.30	−635.01	1.80
Ethanol + MTBE[c]	1947.30	−901.61	578.29	−760.01	4.30
1-Propanol + MTBE[d]	2136.80	−1007.80	361.70	−372.20	1.10

[a] [4].
[b] [5].
[c] [6].
[d] [7].

The measured pseudobinary excess molar enthalpies ΔH_m^E are shown in Fig. 3 for (methanol + ethanol + MTBE) system and in Fig. 4 for (methanol + 1-propanol + MTBE) system along with their constituting binary alcohols–MTBE [5–7] excess molar enthalpies H_m^E against the mole fraction of MTBE. The pseudobinary excess enthalpies have been found to be positive for all the systems measured over the whole range of compositions. The experimental ΔH_m^E data may be interpreted qualitatively by two kinds of opposing factors. The positive factors to the excess molar enthalpies are as follows:

1. Disruption or stretching of hydrogen bonds in the self-associated alkanol multimers due to the hydroxy group of alcohol molecule.
2. Geometrical factor caused by steric effect hinders the component molecules to come closer to each other.

The negative ones are as follows:

1. Solvation and complex formation between unlike molecules. This occurs through the complex formation of hydrogen bonding between unlike

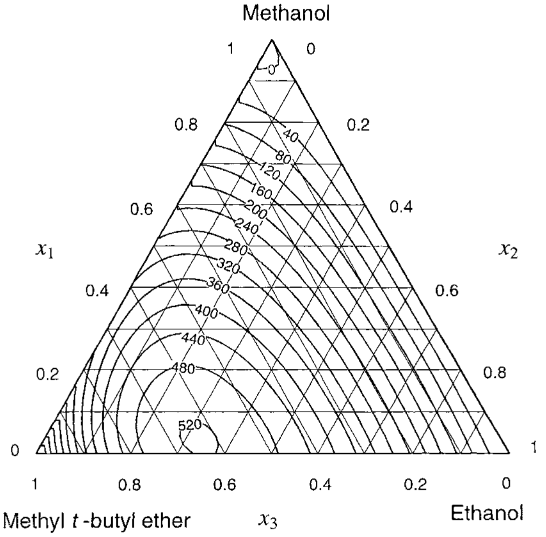

Fig. 1. Contours for constant values of $H_{m,123}^E$ (J mol^{-1}) for the (methanol + ethanol + MTBE) system at 298.15 K (—) calculated from Eq. (2).

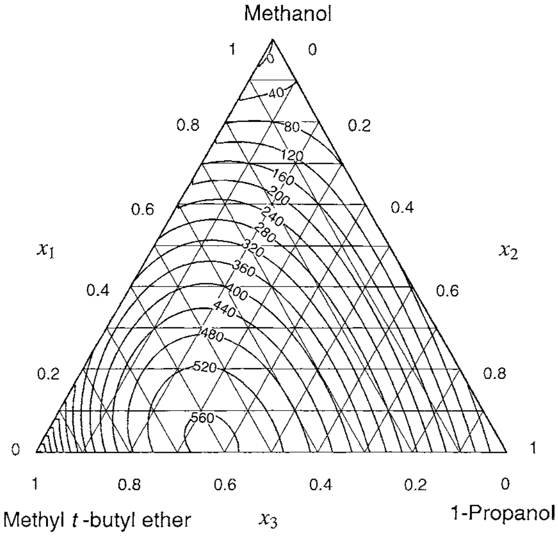

Fig. 2. Contours for constant values of $H_{m,123}^E$ (J mol^{-1}) for the (methanol + 1-propanol + MTBE) system at 298.15 K (—) calculated from Eq. (2).

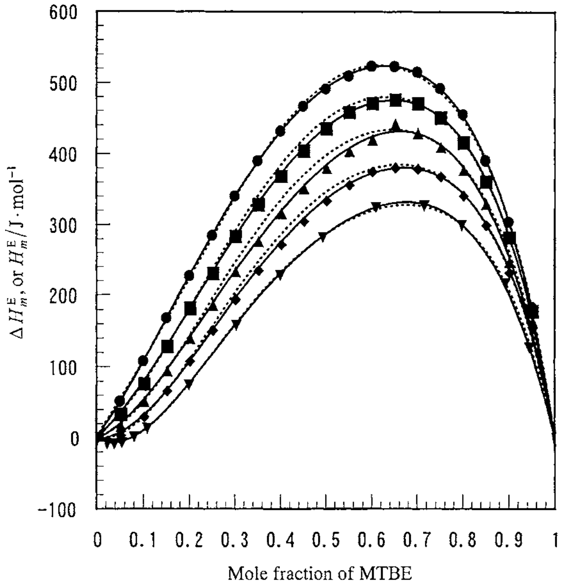

Fig. 3. Pseudobinary excess molar enthalpies ΔH_m^E (J mol^{-1}) for the ((methanol + ethanol) + MTBE) system and its constituting alcohols–MTBE binary excess molar enthalpies H_m^E (J mol^{-1}) at 298.15 K: (■) $x_1' = 0.25$; (▲) $x_1' = 0.50$; (◆) $x_1' = 0.75$; (▼) methanol + MTBE; (●) ethanol + MTBE; (···) obtained from the model.

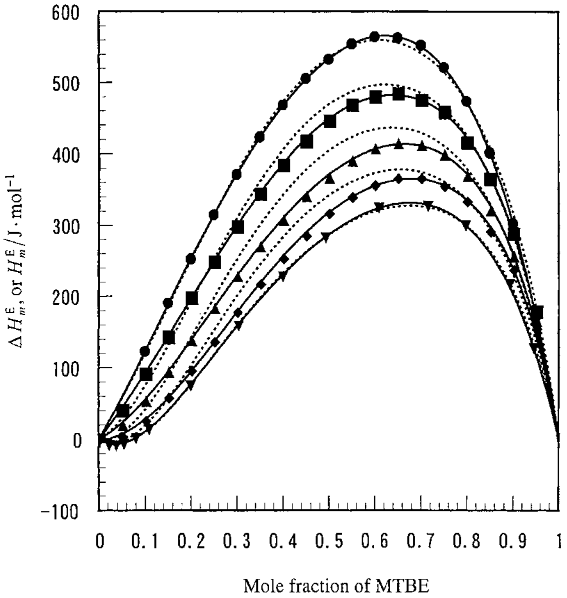

Fig. 4. Pseudobinary excess molar enthalpies ΔH_m^E (J mol^{-1}) for the ((methanol + propanol) + MTBE) system and its constituting alcohols–MTBE binary excess molar enthalpies H_m^E (J mol^{-1}) at 298.15 K: (■) $x_1' = 0.25$; (▲) $x_1' = 0.50$; (◆) $x_1' = 0.75$; (▼) methanol + MTBE; (●) 1-propanol + MTBE; (···) obtained from the model.

alkanol multimers and the complex formation between alkanol multimers and MTBE.

2. Change of the free volumes in the mixture.

The experimental ΔH_m^E for the pseudobinary mixtures indicates that the positive contributions to excess enthalpies outweigh the negative ones as shown in Figs. 3 and 4. This is mainly explained by considering that the sterically hindered MTBE molecules can restrict the extent of interaction between alkanol multimers and MTBE molecules.

4. Data analysis

The experimental ternary H_m^E were further compared with those predicted by a UNIQUAC associated-solution model [20]. The model assumes the linear associating polymers of methanol (A) and ethanol or 1-propanol (B) molecules, and the multisolvation of polymers results in homopolymers (A_i and B_i) and copolymers ($(A_iB_j)_k$, $A_i(B_jA_k)_l$, $(B_iA_j)_k$, and $B_i(A_jB_k)_l$). The resulting homopolymers, copolymers, and MTBE (C) as an active non-associating component form other complexes: A_iC, B_iC, $A_i(B_jA_k)_lC$, and $B_i(A_jB_k)_lC$. Here subindices i, j, k, and l are from one to infinity. The equilibrium constants for these chemical complex-forming reactions are assumed to be independent of the degree of self-association, cross-association, and multisolvation. The temperature dependence of the equilibrium constants is fixed by the van't Hoff equation. The enthalpies of hydrogen-bond formation are assumed to be independent of temperature.

The model gives the ternary excess molar enthalpy for the systems as the sum of the chemical and physical contributions:

$$H^E = H^E_{\text{chem}} + H^E_{\text{phys}} \tag{5}$$

The chemical contribution term is related to the enthalpy of complex formation in the mixing system whose derivation is presented previously [20]. The physical contribution term is derived by applying the Gibbs–Helmholtz relation to the residual term of the

Table 5
Values of self-association constants of alcohols at 323.15 K and enthalpies of hydrogen-bond formation

Component	K_A[a]	$-h_A$[b] (kJ mol^{-1})
Methanol	173.9	23.2
Ethanol	110.4	23.2
1-Propanol	87.4	23.2

[a] [22].
[b] [23].

Table 6
Molecular size and surface parameter of pure component

Component	r[a]	q[a]
Methanol	1.15	1.12
Ethanol	1.69	1.55
1-Propanol	2.23	1.98
MTBE	3.26	2.81

[a] [24].

Table 7
Values of solvation constants and enthalpies of complex formation between unlike molecules

System (A + B)	K_{AB}	$-h_{AB}$ (kJ mol^{-1})	T (K)
Methanol + ethanol[a]	99	23.2	323.15
Methanol + 1-propanol[b]	72	23.2	323.15
Methanol + MTBE[c]	22	19.5	298.15
Ethanol + MTBE[c]	18	19.5	298.15
1-Propanol + MTBE[c]	6	19.5	298.15

[a] [25].
[b] [9,25].
[c] This work.

UNIQUAC equation [21]. The equilibrium association constants at 323.15 K and the enthalpies of hydrogen-bond formation of alcohols A and B taken from [22,23] are shown in Table 5. The structural parameters of complexes are expressed as the sum of parameters of each monomer. The monomer structural size and surface parameters r and q were calculated according to the Vera et al. method [24] and listed in Table 6. The cross-association constants and enthalpies of hydrogen-bond formation for alcohols were reported [9,25] in the recent past. The solvation constants and enthalpies of complex formation between alcohols and MTBE are fixed in this work. The values of the solvation constants summarized in Table 7 are treated as adjustable parameters to give the better fit to the experimental data and the enthalpies of complex formation between unlike molecules estimated from the difference between the enthalpies of the dilution of ethanol in n-hexane [23] and those of ethanol in MTBE. In fitting the association model to the binary experimental H_m^E values, the energy parameter a_{ji} in H_{phys}^E is assumed to be a linear function of temperature (in K) as expressed by

$$\frac{a_{ji}}{R} = C_{ji} + D_{ji}(T - 273.15) \tag{6}$$

Table 8 presents the binary parameters C_{ji}, D_{ji}, and the absolute arithmetic-mean deviations obtained by minimizing the sum of squares of the deviations between the experimental and calculated H_m^E values for all data points by means of the simplex method [26]. The absolute arithmetic-mean deviation and root-mean square deviation between experimental H_m^E and values predicted from the association model are $\langle|\delta(H_m^E)|\rangle = 6.3\,\text{J mol}^{-1}$ and $\langle|\delta(H_m^E)|^2\rangle^{1/2} = 8.1$ J mol^{-1} for (methanol + ethanol + MTBE) system and $\langle|\delta(H_m^E)|\rangle = 14.3\,\text{J mol}^{-1}$ and $\langle|\delta(H_m^E)|^2\rangle^{1/2} =$

Table 8
Binary parameters and absolute arithmetic-mean deviations

System (A + B)	No. of data points	C_{BA} (K)	C_{AB} (K)	D_{BA}	D_{AB}	$\delta(H_m^E)$ (J mol^{-1})
Methanol + ethanol[a]	15	170.14	169.22	0.6285	0.6159	0.11
Methanol + 1-propanol[b]	21	185.93	47.36	0.7190	0.0854	0.52
Methanol + MTBE[c]	14	−95.19	371.97	−0.0301	0.1757	2.45
Ethanol + MTBE[c]	19	839.30	515.83	2.6866	0.7471	3.20
1-Propanol + MTBE[c]	18	264.91	377.01	0.7462	0.7250	5.35

[a] [25].
[b] [9,25].
[c] This work.

$17.1\,\mathrm{J\,mol^{-1}}$ for (methanol + 1-propanol + MTBE) system.

5. Conclusion

Excess molar enthalpies measured at 298.15 K have been reported for the ternary systems containing two alcohols (methanol, ethanol or 1-propanol) and MTBE. The experimental results were compared well with those calculated by using the polynomial equation. The UNIQUAC associated-solution model employed in this study shows a good workability in the prediction of ternary excess enthalpy for the (methanol + ethanol + MTBE) and (methanol + 1-propanol + MTBE) systems by using only the binary parameters.

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