International Journal of Thermophysics, Vol. 22, No. 6, November 2001 (© 2001)

Ternary Excess Molar Enthalpies of Alcohols with Methyl *t*-Butyl Ether at $T = 298.15$ K

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Received January 17, 2001

Ternary excess molar enthalpies $H_{\mathrm{m}}^{\mathrm{E}}$ at 298.15 K and atmospheric pressure measured in a flow microcalorimeter are reported for the methanol + 2-propanol + methyl *t*-butyl ether (MTBE) and ethanol + 1-propanol + MTBE systems. The ternary results have been correlated by means of a polynomial equation and used to construct constant excess enthalpy contours. Furthermore, the results have been compared with those calculated from a UNIQUAC associated-solution model taking into account molecular association of alcohols and solvation between unlike alcohols and alcohols with MTBE using only binary information.

KEY WORDS: alcohols; association; excess molar enthalpies; flow calorimeter; MTBE; solvation.

1. INTRODUCTION

The compositions of reformulated gasoline have received much attention by the Reformulated Gasoline Program of the United States, and stringent requirements have been placed on ozone-forming and air toxic emissions. These goals are achieved today by the addition of oxygenates such as light alcohols and aliphatic branched ethers because of their octane-enhancing and expected air pollution-reducing capabilities.

Methyl *t*-butyl ether (MTBE) as an octane enhancer in gasoline has been widely used over the last 10 years mostly as the result of the mandatory reduction in the use of organometal (e.g., tetra-ethyl lead, tetra-methyl lead, and methyl cyclopentadienyl manganese tricarbonyl) and aromatic compounds (e.g., benzene, toluene, xylenes, and ethylbenzene) in gasoline.

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MTBE is chiefly used as a motor fuel component because of its excellent blending octane number properties. It has outstanding physical properties such as low volatility, miscibility in gasoline, and storage stability. In addition to these properties, MTBE utilization offers ecological advantages, as it reduces the polluting components in exhaust gases such as CO, unburned hydrocarbon, ground-level ozone, and polynuclear aromatics. The economic advantages of the MTBE manufacturing process include lower investment [1], lower operating costs and energy consumption, besides its noteworthy octane properties. From the technological, ecological, and economical point of view, the need for information on the thermodynamic behavior of the liquid mixtures is significantly increasing, and an enormous amount of work [2–7] has been carried out to determine the mixing properties of the oxygenated additive. A reliable knowledge of thermodynamic excess properties for the additive is useful in the blending and refinery process.

We have undertaken a program on the measurements of the thermodynamic properties of ternary blends of oxygenated compounds such as two alcohols and an aliphatic branched ether. In this work, we have measured the ternary excess molar enthalpies of the methanol + 2-propanol + MTBE and ethanol + 1-propanol + MTBE systems at 298.15 K. Results for the corresponding six constituent binaries of the above two ternary systems at 298.15 K have already been reported: (methanol + 2-propanol) [8], (methanol + MTBE) [9], (ethanol + 1-propanol) [10], (ethanol + MTBE) [11], (1-propanol + MTBE) [12], and (2-propanol + MTBE) [12].

2. EXPERIMENTAL

The chemicals and their specifications are listed in Table I. The purities of the compounds analyzed by gas chromatography were of good

Table I. Specification and Density ($g \cdot cm^{-3}$) of the Chemicals at 298.15 K

Chemical	Supplier	Specification (mol%)	Density ($g \cdot cm^{-3}$)	
			Expt.	Lit.
Methanol	Wako Pure Chemical	G.C.: > 99.7	0.78665	0.78665 [7]
Ethanol	"	G.C.: > 99.5	0.78524	0.78530 [13]
1-Propanol	"	G.C.: > 99.5	0.79973	0.79975 [14]
2-Propanol	"	G.C.: > 99.5	0.78123	0.78129 [14]
MTBE	Kanto Chemical	G.C.: > 99.0	0.73538	0.73540 [15]

quality for the excess molar enthalpy measurements. The densities measured by a DMA 58 digital densimeter are in reasonable agreement with literature values [7, 13–15]. Liquids were stored in sealed dark bottles dried over molecular sieves (3A 1/16, 4A 1/16) for about 3 weeks before measurements to eliminate residual traces of water and avoid moisturizing. Just prior to use, the required amount of liquids was degassed for 10 min at about 298.15 K in an ultrasonic bath. During each experimental run the temperature was controlled by a thermostatic water bath within ±0.005 K. Excess molar enthalpies were determined by a flow microcalorimeter at 298.15 K. Details of the equipment and its operation were described previously [16]. Calibration of the calorimeter was carried out using test mixtures of (benzene + cyclohexane), and our results agreed with literature data [17, 18] to within 5 $J \cdot mol^{-1}$.

Ternary mixtures of the methanol + 2-propanol + MTBE or ethanol + 1-propanol + MTBE systems were prepared by mixing the binary mixtures of methanol (1) + 2-propanol (2) or ethanol (1) + 1-propanol (2) with MTBE. The compositions of three binary mixtures corresponding to A, B, and C in Fig. 1 were 25, 50, and 75 mol% of component 1 to cover complete composition ranges of the ternary mixtures. Consider 1 mol of a ternary mixture D prepared by mixing $(1-x_3)$ mol of binary mixture A and x_3 mole of component 3 (MTBE). The excess enthalpy for a mol of a

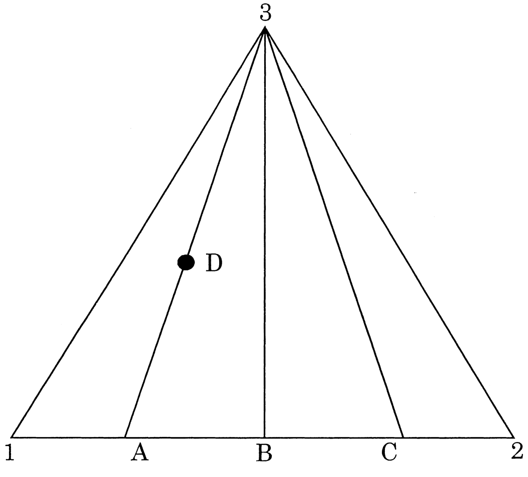

Fig. 1. Experimental procedure for the ternary system. A, B, and C correspond to compositions of binary mixture (1+2). D represents a composition of ternary mixture at which measurements were made.

ternary mixture of composition x_1, x_2, and x_3, corresponding to point D shown in Fig. 1, can be expressed as follows:

$$H^{\mathrm{E}}_{\mathrm{m},\,123} = \Delta H^{\mathrm{E}}_{\mathrm{m}} + (1 - x_3)_D\, H^{\mathrm{E}}_{\mathrm{m},\,A} \tag{1}$$

where $H^{\mathrm{E}}_{\mathrm{m},\,123}$ is the excess enthalpy per mol of ternary mixture D, and $\Delta H^{\mathrm{E}}_{\mathrm{m}}$ is the excess enthalpy measured for the pseudobinary mixture, which is obtained by mixing the binary mixture A with component 3. $H^{\mathrm{E}}_{\mathrm{m},\,A}$ is the excess enthalpy for the binary mixture A, whose value at a specified composition was interpolated by means of a spline-fit method. The same holds true with mixtures B and C as in mixture A.

3. RESULTS AND DISCUSSION

Experimental results for $\Delta H^{\mathrm{E}}_{\mathrm{m}}$ and the ternary excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m},\,123}$ are summarized in Table II for the (methanol + 2-propanol + MTBE) system and in Table III for the (ethanol + 1-propanol + MTBE) system. The measured values of the ternary mixtures were correlated using the following equation:

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

where $H^{\mathrm{E}}_{\mathrm{m},\,ij}$ were fitted to a polynomial equation of the form

$$H^{\mathrm{E}}_{\mathrm{m},\,ij}/(\mathrm{J \cdot mol^{-1}}) = x_i x_j \sum_{n=1}^{p} a_n (x_i - x_j)^{n-1} \tag{3}$$

where a_n is the coefficient calculated by using an unweighted least-squares method. The values of the coefficients for the six binary mixtures are listed in Table IV along with the standard deviations s defined by the formula $s = \{\sum_{i=1}^{m} (H^{\mathrm{E}}_{\mathrm{exp}} - H^{\mathrm{E}}_{\mathrm{cal}})^2/(m-p)\}^{0.5}$, where m is the number of experimental data points and p is the number of parameters. The term Δ_{123} of Eq. (2) is expressed by

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

The values of the coefficients b_j and k, the absolute arithmetic-mean deviations $\delta(H^{\mathrm{E}}_{\mathrm{m}}) = \sum_{i=1}^{m} |H^{\mathrm{E}}_{\mathrm{exp}} - H^{\mathrm{E}}_{\mathrm{cal}}|/m$, and the standard deviations, s obtained in fitting Eqs. (3) and (4) to the experimental ternary $H^{\mathrm{E}}_{\mathrm{m},\,123}$ are listed in Table V. Constant $H^{\mathrm{E}}_{\mathrm{m},\,123}$ contours are plotted in Fig. 2 for the (methanol

Table II. Experimental Excess Molar Enthalpies of the Methanol (1) + 2-Propanol (2) + MTBE (3) Mixture at 298.15 K[a]

$x'_1 = 0.2505,\ H^E_{m,12} = -69.0\ J \cdot mol^{-1}$				$x'_1 = 0.4998,\ H^E_{m,12} = -75.7\ J \cdot mol^{-1}$				$x'_1 = 0.7501,\ H^E_{m,12} = -45.3\ J \cdot mol^{-1}$			
x_1	x_2	ΔH^E_m $(J \cdot mol^{-1})$	$H^E_{m,123}$ $(J \cdot mol^{-1})$	x_1	x_2	ΔH^E_m $(J \cdot mol^{-1})$	$H^E_{m,123}$ $(J \cdot mol^{-1})$	x_1	x_2	ΔH^E_m $(J \cdot mol^{-1})$	$H^E_{m,123}$ $(J \cdot mol^{-1})$
0.2380	0.7120	87.0	21.4	0.4748	0.4752	55.3	−16.7	0.7126	0.2374	21.1	−21.1
0.2255	0.6745	169.0	106.8	0.4498	0.4502	113.1	45.0	0.6751	0.2249	56.8	16.0
0.2129	0.6371	250.5	191.8	0.4249	0.4251	174.6	110.2	0.6376	0.2124	100.1	61.7
0.2004	0.5996	326.0	270.7	0.3999	0.4001	236.2	175.6	0.6001	0.1999	146.1	109.9
0.1879	0.5621	398.2	346.5	0.3749	0.3751	293.3	236.5	0.5626	0.1874	193.1	159.2
0.1754	0.5246	460.4	412.0	0.3499	0.3501	349.2	296.2	0.5251	0.1749	239.8	208.1
0.1628	0.4872	520.4	475.5	0.3249	0.3251	397.2	348.0	0.4876	0.1624	283.2	253.8
0.1503	0.4497	566.9	525.4	0.2999	0.3001	440.5	395.1	0.4501	0.1499	322.4	295.2
0.1378	0.4122	606.0	568.0	0.2749	0.2751	477.1	435.4	0.4126	0.1374	356.7	331.8
0.1253	0.3747	629.1	594.6	0.2499	0.2501	504.0	466.2	0.3751	0.1249	388.0	365.4
0.1127	0.3373	655.9	624.8	0.2249	0.2251	526.6	492.6	0.3376	0.1124	412.6	392.2
0.1002	0.2998	664.9	637.3	0.1999	0.2001	540.3	510.0	0.3001	0.0999	426.8	408.8
0.0877	0.2623	657.6	633.4	0.1749	0.1751	542.5	516.0	0.2626	0.0874	435.1	419.3
0.0752	0.2248	644.0	623.3	0.1499	0.1501	533.8	511.0	0.2250	0.0750	430.8	417.2
0.0626	0.1874	608.7	591.4	0.1250	0.1250	514.4	495.4	0.1875	0.0625	418.2	406.9
0.0501	0.1499	552.2	538.4	0.1000	0.1000	476.2	461.1	0.1500	0.0500	386.9	377.8
0.0376	0.1124	471.4	461.0	0.0750	0.0750	412.8	401.4	0.1125	0.0375	343.8	337.0
0.0250	0.0750	375.7	368.8	0.0500	0.0500	319.8	312.3	0.0750	0.0250	272.0	267.5
0.0125	0.0375	234.4	230.9	0.0250	0.0250	206.6	202.8	0.0375	0.0125	180.3	178.0

[a] Ternary mixtures were prepared by mixing pure MTBE with $[x'_1$ methanol $+ (1 - x'_1)$ 2-propanol$]$.

Table III. Experimental Excess Molar Enthalpies of the Ethanol (1) + 1-Propanol (2) + MTBE (3) Mixture at 298.15 K[a]

$x'_1 = 0.2504$, $H^E_{m,12} = 13.9\ J \cdot mol^{-1}$				$x'_1 = 0.4999$, $H^E_{m,12} = 19.0\ J \cdot mol^{-1}$				$x'_1 = 0.7501$, $H^E_{m,12} = 15.9\ J \cdot mol^{-1}$			
x_1	x_2	ΔH^E_m $(J \cdot mol^{-1})$	$H^E_{m,123}$ $(J \cdot mol^{-1})$	x_1	x_2	ΔH^E_m $(J \cdot mol^{-1})$	$H^E_{m,123}$ $(J \cdot mol^{-1})$	x_1	x_2	ΔH^E_m $(J \cdot mol^{-1})$	$H^E_{m,123}$ $(J \cdot mol^{-1})$
0.2374	0.7126	57.5	70.7	0.4753	0.4747	57.0	75.0	0.7125	0.2375	54.6	69.7
0.2249	0.6751	118.9	131.5	0.4503	0.4497	117.1	134.2	0.6750	0.2250	112.0	126.3
0.2124	0.6376	183.3	195.2	0.4253	0.4247	177.6	193.8	0.6375	0.2125	170.1	183.6
0.1999	0.6001	243.5	254.6	0.4002	0.3998	238.4	253.6	0.6000	0.2000	229.2	241.9
0.1874	0.5626	301.2	311.6	0.3752	0.3748	294.0	308.3	0.5625	0.1875	285.7	297.6
0.1749	0.5251	355.3	365.0	0.3502	0.3498	348.3	361.6	0.5250	0.1750	340.3	351.4
0.1624	0.4876	406.0	415.1	0.3252	0.3248	397.5	409.9	0.4875	0.1625	388.1	398.4
0.1499	0.4501	448.0	456.4	0.3002	0.2998	439.4	450.8	0.4500	0.1500	428.7	438.2
0.1374	0.4126	482.9	490.6	0.2752	0.2748	474.1	484.6	0.4125	0.1375	465.6	474.3
0.1250	0.3750	516.6	523.6	0.2502	0.2498	496.9	506.4	0.3750	0.1250	492.4	500.3
0.1125	0.3375	536.8	543.0	0.2251	0.2249	520.0	528.6	0.3375	0.1125	514.1	521.3
0.1000	0.3000	547.6	553.2	0.2001	0.1999	532.6	540.2	0.3000	0.1000	527.2	533.5
0.0875	0.2625	546.7	551.6	0.1751	0.1749	534.8	541.4	0.2625	0.0875	530.8	536.3
0.0750	0.2250	534.3	538.5	0.1501	0.1499	524.3	530.0	0.2250	0.0750	519.0	523.8
0.0625	0.1875	508.0	511.4	0.1251	0.1249	500.5	505.2	0.1875	0.0625	497.6	501.6
0.0500	0.1500	464.5	467.3	0.1001	0.0999	459.6	463.4	0.1500	0.0500	456.3	459.5
0.0375	0.1125	401.8	403.9	0.0750	0.0750	401.1	404.0	0.1125	0.0375	403.2	405.6
0.0250	0.0750	311.3	312.7	0.0500	0.0500	325.2	327.1	0.0750	0.0250	320.3	321.9
0.0125	0.0375	190.5	191.2	0.0250	0.0250	207.2	208.1	0.0375	0.0125	194.4	195.2

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

Table IV. Coefficients of Eq. (3) and Standard Deviations, s

Mixture	a_1	a_2	a_3	a_4	s ($J \cdot mol^{-1}$)
Methanol + 2-propanol[a]	−302.63	125.72	−8.07	1.05	0.0
Methanol + MTBE[b]	1152.20	−929.30	55.30	−635.10	1.8
Ethanol + 1-propanol[c]	76.72	11.34	8.69	−1.58	0.1
Ethanol + MTBE[d]	1947.30	−901.61	578.29	−760.01	4.3
1-Propanol + MTBE[e]	2136.60	−1007.80	361.70	−372.20	1.1
2-Propanol + MTBE[e]	3106.10	−914.70	598.40	−629.70	3.4

[a] From Ref. 8.
[b] From Ref. 9.
[c] From Ref. 10.
[d] From Ref. 11.
[e] From Ref. 12.

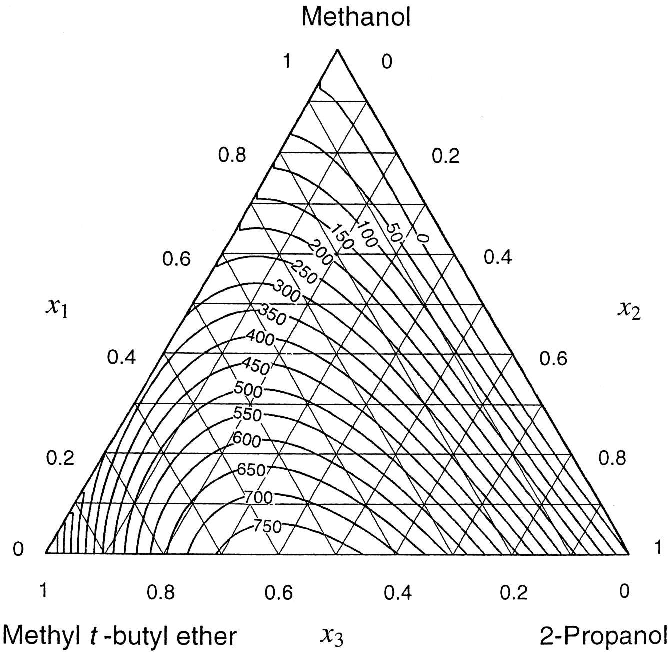

Fig. 2. Contours of excess molar enthalpies for the ternary mixture of methanol + 2-propanol + MTBE at 298.15 K. (——) Calculated from Eqs. (3) and (4).

Table V. Coefficients of Eq. (4), Absolute Arithmetic-Mean Deviations, $\delta(H_{\mathrm{m}}^{\mathrm{E}})$, and Standard Deviations, s

Mixture	b_1	b_2	b_3	b_4	b_5	b_6	k	$\delta(H_{\mathrm{m}}^{\mathrm{E}})$ $(\mathrm{J \cdot mol^{-1}})$	s $(\mathrm{J \cdot mol^{-1}})$
Methanol + 2-propanol + MTBE	−1.4467	−0.5481	−0.1828	−1.2183	0.8622		−1.0876	3.2	4.1
Ethanol + 1-propanol + MTBE	−0.9434	−0.1086	−0.5215	−0.8841	1.3647	−0.6145	−1.0680	2.3	3.0

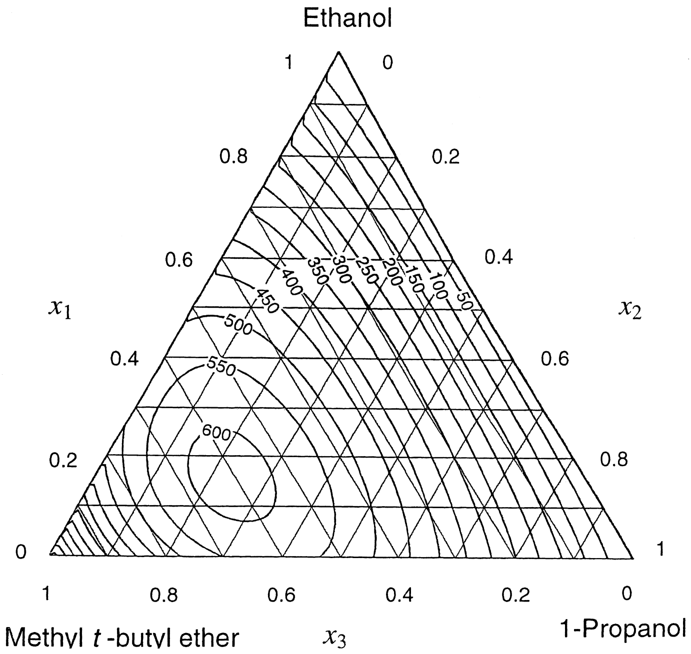

Fig. 3. Contours of excess molar enthalpies for the ternary mixture of ethanol + 1-propanol + MTBE at 298.15 K. (——) Calculated from Eqs. (3) and (4).

+ 2-propanol + MTBE) system and in Fig. 3 for the (ethanol + 1-propanol + MTBE) system using Eqs. (3) and (4).

Figure 4 shows the plot of the binary excess molar enthalpy H_m^E against the mole fraction of pure alcohol (x_1) for the six constituent binaries: methanol (1) + 2-propanol (2), methanol (1) + MTBE (2), 2-propanol (1) + MTBE (2), ethanol (1) + 1-propanol (2), ethanol (1) + MTBE (2), and 1-propanol (1) + MTBE (2). The measured values of pseudobinary excess molar enthalpies ΔH_m^E are plotted in Fig. 5 for the (methanol + 2-propanol + MTBE) system and in Fig. 6 for the (ethanol + 1-propanol + MTBE) system as a function of the mole fraction of MTBE. The experimental pseudobinary excess molar enthalpies are positive for all the studied systems over the whole range of composition. The measured ΔH_m^E data may be interpreted qualitatively by postulating that the excess molar enthalpy is the result of two opposing effects:

(i) The positive contribution to ΔH_m^E arises from the breaking, or stretching, of hydrogen bonds in the self-associated alkanol multimers due to the hydroxy groups.

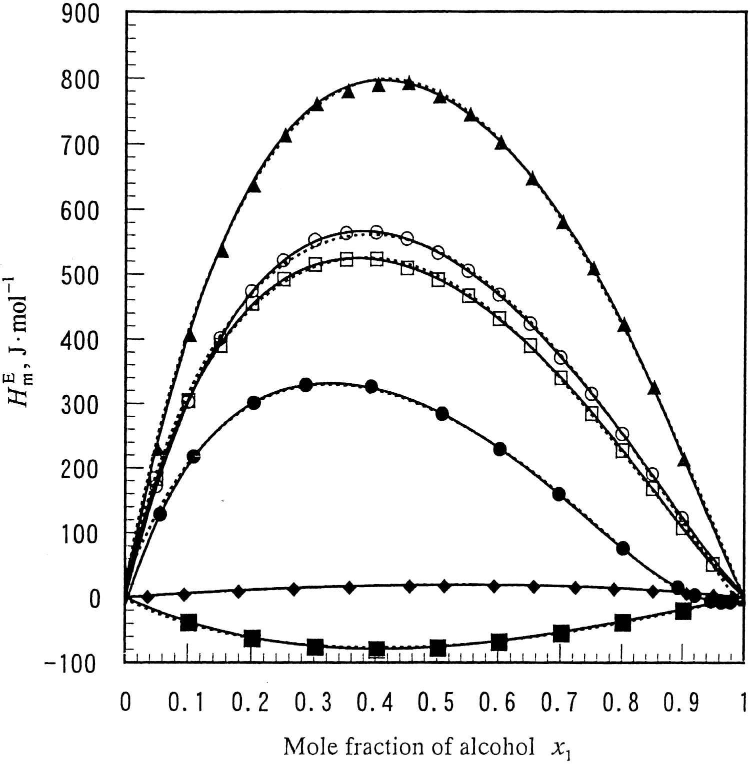

Fig. 4. Excess molar enthalpies H_m^E for the six binary mixtures at 298.15 K: (▲) 2-propanol + MTBE, (○) 1-propanol + MTBE, (□) ethanol + MTBE, (●) methanol + MTBE, (◆) ethanol + 1-propanol, and (■) methanol + 2-propanol. (···) Obtained from the model.

(ii) The negative contribution to ΔH_m^E arises from the cross-association between unlike alkanol multimers and the solvation between alkanol multimers and MTBE through hydrogen bonding.

The positive experimental results for both systems suggest generally that the hydrogen bonds of the alkanol multimers broken by the addition of MTBE predominate over the weak hydrogen bonds formed between alkanol multimers and sterically hindered MTBE molecules.

4. EXCESS ENTHALPY PREDICTION

The experimental determination of multicomponent properties is considerably more tedious and complicated compared to that of binaries if the

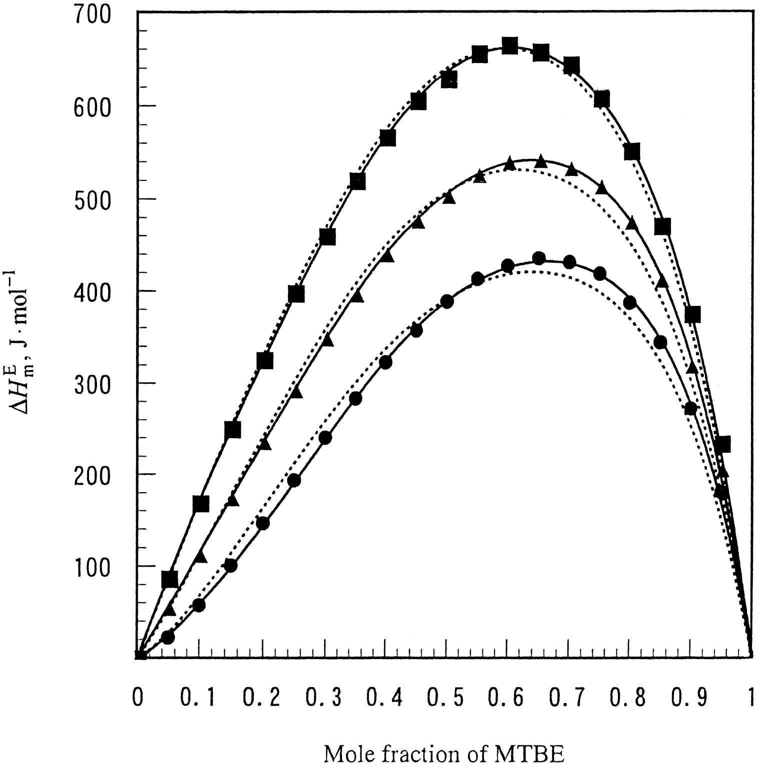

Fig. 5. Excess molar enthalpies ΔH_m^E for the pseudobinary mixtures of [(methanol + 2-propanol) + MTBE] at 298.15 K: (■) $x_1' = 0.25$, (▲) $x_1' = 0.50$, and (●) $x_1' = 0.75$. (···) Obtained from the model.

data have to be known at any composition. For this reason a practical method of predicting the thermodynamic properties of multicomponent systems from binary data has been proposed. We use a UNIQUAC associated-solution model [19] to express the ternary excess molar enthalpies of the mixtures containing two alcohols and an active nonassociating component.

A and B stand for two alcohols (methanol and 2-propanol or ethanol and 1-propanol) and C denotes methyl *t*-butyl ether (MTBE) as an active nonassociating component. The model assumes that the two alcohols A and B undergo self- and cross-association and solvation with C to form linear complexes: A_i, B_j, $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$, $B_i(A_jB_k)$, A_iC, B_iC, $(A_iB_j)_k$ C, $A_i(B_jA_k)_l$ C, $(B_iA_j)_k$ C, and $B_i(A_jB_k)$ C, where i, j, k, and l go from 1 to ∞. Further assumptions are that the association constants of

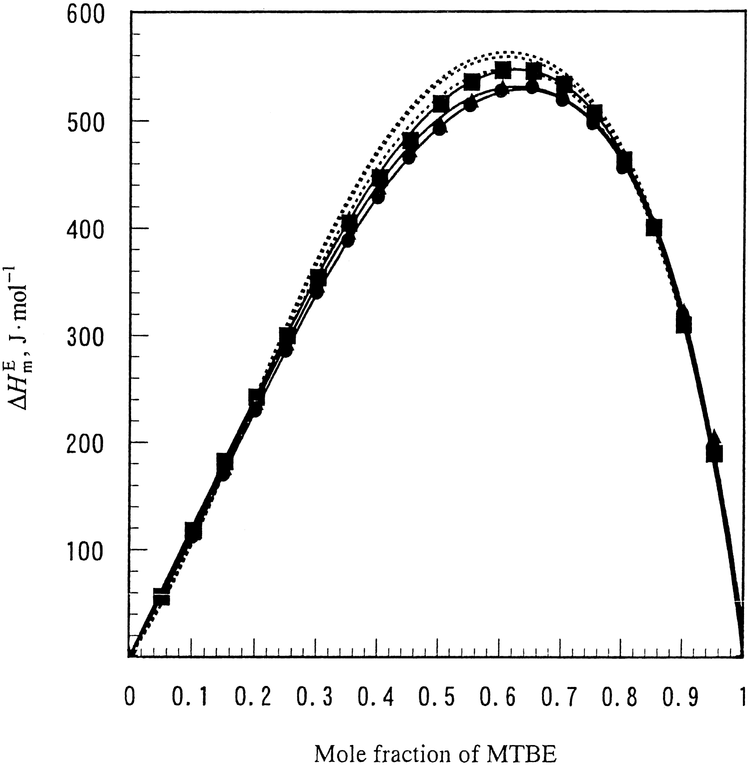

Fig. 6. Excess molar enthalpies ΔH^{E}_{m} for the pseudobinary mixtures of [(ethanol + 1-propanol) + MTBE] at 298.15 K: (■) $x'_1 = 0.25$, (▲) $x'_1 = 0.50$, and (●) $x'_1 = 0.75$. (···) Obtained from the model.

the alcohols are independent of the degree of association and the solvation constants are also not concerned with the degree of association and solvation. Thus, the model includes a total of five equilibrium constants: K_A, K_B, K_{AB}, K_{AC}, and K_{BC}. The equilibrium constants of the preceding chemical complex forming reactions are defined in terms of the segment fractions and the molecular geometric volume parameters of the chemical species so that the equilibrium constants are dimensionless.

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

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

The chemical contribution term is related to the enthalpy of complex formation in the mixing system whose derivation was presented previously

[19]. The physical contribution term is derived by applying the Gibbs–Helmholtz relation to the residual term of the UNIQUAC equation [20]. The association constants of alcohols A and B expressed as K_A and K_B at 323.15 K taken from Ref. 21 are 173.9 for methanol, 110.4 for ethanol, 87.0 for 1-propanol, and 49.1 for 2-propanol. The enthalpy of H-bonding formation is assumed to be $h_A = h_B = h_{AB} = -\ 23.2\ \mathrm{kJ \cdot mol^{-1}}$ for all alcohols [22], and the enthalpy of complex formation between alcohols and MTBE is estimated as $-19.5\ \mathrm{kJ \cdot mol^{-1}}$. Table VI summarizes the solvation constants [23] and enthalpies of complex formation between unlike molecules. The temperature dependence of the equilibrium constants is fixed by the van't Hoff relation and the enthalpies of chemical complex formation are assumed to be independent of temperature. The equilibrium constants at 298.15 K required for the excess enthalpy calculation were obtained according to the van't Hoff equation. The structural parameters of complexes are expressed as the sum of parameters of each monomer. The monomer structural parameters, r and q , were calculated using the method of Vera et al. [24]. In fitting the model to binary H_m^E data, from a practical point of view the energy parameters a_{ij} in H_{phys}^E are assumed to be a linear function of temperature as given by $a_{ij}/R = C_{ij} + D_{ij}\{(T/\mathrm{K}) - 273.15\}$. The coefficients C_{ij} and D_{ij} were obtained by minimizing the sum of squares between the experimental H_m^E and the values calculated by using the model of a simplex method [25]. The binary parameters and the absolute arithmetic-mean deviations $\delta(H_m^E)$ between the binary experimental and the calculated values are given in Table VII. The model with the association and solvation constants and binary parameters alone was used to predict the ternary excess molar enthalpies. The absolute arithmetic-mean deviations of the excess molar enthalpies between the experimental and the calculated values were 11.2 $\mathrm{J \cdot mol^{-1}}$ for the methanol +

Table VI. Values of Solvation Constants and Enthalpies of Complex Formation Between Unlike Molecules

Mixture (A + B)	$K_{AB}(T)$	$-h_{AB}$ ($\mathrm{kJ \cdot mol^{-1}}$)	T (K)
Methanol + 2-propanol[a]	70.0	23.2	323.15
Methanol + MTBE[b]	22.0	19.5	298.15
Ethanol + 1-propanol[a]	49.0	23.2	323.15
Ethanol + MTBE[b]	18.0	19.5	298.15
1-Propanol + MTBE[b]	6.0	19.5	298.15
2-Propanol + MTBE[b]	5.0	19.5	298.15

[a] From Ref. 23.

[b] From this work.

Table VII. Binary Parameters and Absolute Arithmetic-Mean Deviations

Mixture (A + B)	No. of data points	C_{BA} (K)	C_{AB} (K)	D_{BA}	D_{AB}	$\delta(H^E_m)$ $(J \cdot mol^{-1})$
Methanol + 2-propanol[a]	9	−68.29	−293.12	−0.3051	−1.0499	2.2
Methanol + MTBE[b]	14	−95.19	371.97	−0.0301	0.1757	2.5
Ethanol + 1-propanol[a]	15	259.75	193.98	0.9548	0.7018	0.2
Ethanol + MTBE[b]	19	839.30	515.83	2.6866	0.7471	3.2
1-Propanol + MTBE[b]	18	264.91	377.01	0.7462	0.7250	5.4
2-Propanol + MTBE[b]	18	283.78	316.54	0.6814	0.3358	3.9

[a] From Ref. 23.
[b] From this work.

2-propanol + MTBE system and 14.7 $J \cdot mol^{-1}$ for the ethanol + 1-propanol + MTBE system.

5. CONCLUSION

Ternary excess molar enthalpies have been determined for the methanol + 2-propanol + MTBE and ethanol + 1-propanol + MTBE systems at 298.15 K, and the results compare well with those calculated by using a polynomial equation. Furthermore, the experimental results were represented satisfactorily by the UNIQUAC associated-solution model using only binary parameters.

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