Excess Molar Enthalpies for Ethanol + 2-Propanol + Methyl *tert*-Butyl Ether and 1-Propanol + 2-Propanol + Methyl *tert*-Butyl Ether at the Temperature of 298.15 K

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Ternary excess molar enthalpies for the ethanol + 2-propanol + methyl *tert*-butyl ether (MTBE) and 1-propanol + 2-propanol + MTBE systems have been measured by a flow microcalorimeter at 298.15 K and ambient pressure. The pseudobinary excess molar enthalpies are positive over the whole range of composition. The ternary experimental results are correlated with a polynomial equation. The results have been compared with those calculated from a UNIQUAC associated-solution model taking into account the self-association of alcohols as well as the solvation between unlike alcohols and alcohols with MTBE using only binary parameters.

Introduction

Tertiary alkyl ethers are nontoxic, nonpolluting, and high octane number blending agents for gasoline; therefore, they are of great industrial interest, and mixtures containing such ethers have been extensively investigated, as recently reviewed by Marsh et al.[1] Methyl *tert*-butyl ether (MTBE) is one of the oxygenated additives used in gasoline to reduce the polluting components in exhaust gases such as CO, NO_x, unburned hydrocarbons, ground level ozone, and polynuclear aromatics.[2] It has outstanding physical properties such as volatility, miscibility in gasoline, and storage stability besides its noteworthy blending characteristics.[3,4] On the other hand, the most recent concern about health risks caused by the contamination of drinking water from MTBE into the ground makes it appear to be a somewhat controversial gasoline additive. The excess enthalpy data provide information about intermolecular interactions between component molecules as well as essential knowledge from an ecological point of view. The ternary excess enthalpies reflect differences in the molecular interactions among three components; therefore, it is of importance to use the ternary data for a prediction by model development. Following the above, it is desirable to know the thermodynamic properties of MTBE mixtures, and excess molar enthalpies of the ternary mixtures (ethanol or 1-propanol) + 2-propanol + MTBE at 298.15 K have been brought forward in this paper as a part of our systematic study.[5] Excess molar enthalpies of the binary mixtures making up the above two ternary systems at 298.15 K are available in the literature: ethanol + 2-propanol;[6] ethanol + MTBE;[7] 1-propanol + 2-propanol;[8] 1-propanol + MTBE;[9] and 2-propanol + MTBE.[9]

Experimental Section

Materials. Ethanol, 1-propanol, and 2-propanol were obtained from Wako Pure Chemical, and MTBE was from Kanto Chemical. Chemicals were kept in sealed dark bottles dried over molecular sieves 4A 1/16 (Wako Pure Chemical) for 2−3 weeks prior to their use to eliminate residual traces of water and avoid moisture gain. All of the chemicals were manipulated under a nitrogen atmosphere and degassed nearly at 298.15 K by using an ultrasonic technique. No further purification was performed as they did not show any significant peak of impurities by GC analysis. The purities of all the chemicals were estimated to be >99.7 mass %. Their densities were measured with a DMA 58 digital densimeter (Anton Paar) at 298.15 K, and the measured densities of the chemicals are compiled in Table 1 along with their recent published values.[5,10−13]

Table 1. Densities ρ/g·cm^{-3} for the Pure Liquids at 298.15 K

component	ρ/g·cm^{-3} this work	ρ/g·cm^{-3} lit.
ethanol	0.78524	0.78524[a] 0.78530[b]
1-propanol	0.79973	0.79973[a] 0.79975[c]
2-propanol	0.78123	0.78120[b] 0.78122[d]
methyl *tert*-butyl ether (MTBE)	0.73538	0.73538[a] 0.73540[e]

[a] Tamura et al.[5] [b] Tu et al.[10] [c] Nagata et al.[11] [d] Tamura et al.[12] [e] Tamura et al.[13]

Apparatus and Procedure. Excess molar enthalpies were determined by a flow microcalorimeter at 298.15 K. Details of its experimental setup and operational procedures were described previously.[12,14] Agreement between our results and the literature values for the benzene + cyclohexane mixtures[14,15] was good. Experimental uncertainties were <0.5% in H_m^E, 5 × 10^{-5} in mole fraction, and 3 mK in temperature over most of the range of experimental values.

Three experimental runs of the measurements were carried out for ternary mixtures formed by adding MTBE to the initial binary mixtures of ethanol (1) and 2-propanol (2) or 1-propanol (1) and 2-propanol (2). Thus, a ternary mixture may be considered as a pseudobinary mixture composed of MTBE and one binary alcohol mixture. The

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

$x'_1 = 0.2501$, $H^E_{m,12} = -36.81$ J·mol^{-1}				$x'_1 = 0.5002$, $H^E_{m,12} = -45.30$ J·mol^{-1}				$x'_1 = 0.7499$, $H^E_{m,12} = -32.41$ 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}
0.2376	0.7124	103.9	68.9	0.4752	0.4748	87.1	44.1	0.7124	0.2376	69.9	39.1
0.2251	0.6749	202.4	169.2	0.4502	0.4498	170.4	129.7	0.6749	0.2251	137.5	108.3
0.2126	0.6374	294.4	263.1	0.4252	0.4248	250.8	212.3	0.6374	0.2126	206.7	179.1
0.2001	0.5999	380.1	350.6	0.4001	0.3999	326.9	290.3	0.5999	0.2001	274.0	248.1
0.1876	0.5624	458.0	430.4	0.3751	0.3745	396.4	362.5	0.5624	0.1876	336.2	311.9
0.1751	0.5249	525.6	499.9	0.3501	0.3499	459.8	428.1	0.5249	0.1751	394.8	372.1
0.1626	0.4874	587.4	563.5	0.3251	0.3249	517.2	487.8	0.4874	0.1626	447.9	426.9
0.1501	0.4499	637.5	615.4	0.3001	0.2999	564.5	537.3	0.4499	0.1501	490.5	471.0
0.1376	0.4124	675.5	655.3	0.2751	0.2749	601.5	576.9	0.4124	0.1376	529.5	511.7
0.1251	0.3749	700.6	682.2	0.2501	0.2499	628.0	604.9	0.3749	0.1251	555.1	538.9
0.1126	0.3374	723.2	706.6	0.2251	0.2249	649.4	629.0	0.3374	0.1126	576.2	561.6
0.1001	0.2999	728.1	713.4	0.2001	0.1999	657.9	639.8	0.3000	0.1000	589.0	576.0
0.0875	0.2625	719.5	706.7	0.1751	0.1749	654.7	638.8	0.2625	0.0875	587.9	576.6
0.0750	0.2250	697.4	686.3	0.1501	0.1499	637.9	624.3	0.2250	0.0750	576.4	566.6
0.0625	0.1875	656.4	647.2	0.1250	0.1250	603.2	591.8	0.1875	0.0625	548.3	540.2
0.0500	0.1500	595.0	587.6	0.1000	0.1000	550.3	541.2	0.1500	0.0500	506.4	499.9
0.0375	0.1125	510.9	505.4	0.0750	0.0750	471.8	465.0	0.1125	0.0375	437.4	432.5
0.0250	0.0750	405.4	401.7	0.0500	0.0500	368.8	364.2	0.0750	0.0250	352.3	349.1
0.0125	0.0375	260.6	258.7	0.0250	0.0250	232.0	229.8	0.0375	0.0125	220.8	219.2

[a] Ternary mixtures were prepared by mixing pure MTBE with {x'_1 ethanol + (1 − x'_1) 2-propanol}.

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

$x'_1 = 0.2501$, $H^E_{m,12} = -37.93$ J·mol^{-1}				$x'_1 = 0.5005$, $H^E_{m,12} = -48.95$ J·mol^{-1}				$x'_1 = 0.7499$, $H^E_{m,12} = -35.02$ 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}
0.2376	0.7124	97.7	61.6	0.4755	0.4745	93.8	47.2	0.7125	0.2375	81.4	48.1
0.2251	0.6749	199.0	164.9	0.4504	0.4496	182.6	138.6	0.6750	0.2250	158.6	127.0
0.2126	0.6374	296.6	264.3	0.4254	0.4246	265.9	224.0	0.6375	0.2125	235.4	205.6
0.2001	0.5999	386.6	356.2	0.4004	0.3996	348.5	309.4	0.6000	0.2000	307.2	279.2
0.1876	0.5624	466.7	438.2	0.3754	0.3746	422.1	385.4	0.5625	0.1875	373.1	346.8
0.1751	0.5249	537.7	511.1	0.3503	0.3497	486.8	452.6	0.5250	0.1750	436.4	411.9
0.1626	0.4874	603.4	578.7	0.3253	0.3247	544.7	512.9	0.4875	0.1625	491.3	468.6
0.1500	0.4499	652.7	630.0	0.3003	0.2997	592.8	563.5	0.4500	0.1500	536.9	515.9
0.1376	0.4124	692.9	672.1	0.2753	0.2747	628.9	602.0	0.4125	0.1375	571.4	552.1
0.1251	0.3750	720.8	701.8	0.2502	0.2498	650.7	626.2	0.3750	0.1250	593.9	576.4
0.1125	0.3375	737.2	720.1	0.2252	0.2248	672.5	650.4	0.3375	0.1125	614.7	598.9
0.1000	0.3000	741.4	726.2	0.2002	0.1998	679.2	659.6	0.3000	0.1000	623.4	609.4
0.0875	0.2625	732.5	719.2	0.1752	0.1748	674.3	657.2	0.2625	0.0875	619.0	606.7
0.0750	0.2250	707.0	695.7	0.1501	0.1499	653.5	638.8	0.2250	0.0750	601.5	591.0
0.0625	0.1875	661.7	652.2	0.1251	0.1249	615.7	603.5	0.1875	0.0625	567.8	559.0
0.0500	0.1500	598.9	591.3	0.1001	0.0999	558.9	549.2	0.1500	0.0500	516.7	509.7
0.0375	0.1125	512.8	507.2	0.0751	0.0749	478.4	471.0	0.1125	0.0375	440.7	435.4
0.0250	0.0750	396.7	392.9	0.0500	0.0500	368.7	363.8	0.0750	0.0250	344.8	341.3
0.0125	0.0375	242.7	240.8	0.0250	0.0250	222.6	220.2	0.0375	0.0125	210.1	208.4

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

value of $H^E_{m,123}$ for 1 mol of the ternary mixture of composition x_1, x_2, and x_3 can be obtained from the relationship

$$H^E_{m,123} = \Delta H^E_m + (1 - x_3)H^E_{m,12} \qquad (1)$$

where ΔH^E_m is the molar enthalpy measured for the pseudobinary mixture, $H^E_{m,12}$ the molar enthalpy for the initial binary ethanol (1) + 2-propanol (2) or 1-propanol (1) + 2-propanol (2) mixture, and x_3 the mole fraction of MTBE. The values of $H^E_{m,12}$ 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. The mixtures were prepared by mass using an analytical balance (LIBROR AEX-180, Shimadzu) ensuring accuracy in the mole fractions of 10^{-4}.

Results and Discussion

The experimental ΔH^E_m for the ternary mixtures of (ethanol + 2-propanol + MTBE) and (1-propanol + 2-propanol + MTBE) at 298.15 K are presented in Tables 2 and 3, respectively, along with $H^E_{m,123}$ calculated from eq 1. The values were correlated using the equation

$$H^E_{m,123} = H^E_{m,12} + H^E_{m,13} + H^E_{m,23} + x_1x_2x_3\Delta_{123}/RT \qquad (2)$$

where $H^E_{m,ij}$ were fitted to a polynomial equation of the form

$$H^E_{m,ij}/(\text{J·mol}^{-1}) = x_ix_j\sum_{n=1}^{p} a_n(x_i - x_j)^{n-1} \qquad (3)$$

In each case, the optimum number of coefficients p was ascertained from an examination of the variation of the standard deviation σ with the number of parameters n

$$\sigma(H^E_m) = \{\sum_{i=1}^{m}(H^E_{\text{exptl}} - H^E_{\text{calcd}})^2/(m - p)\}^{1/2} \qquad (4)$$

where m is the number of experimental data points. The coefficients a_n of eq 3 and the standard deviation σ

Table 4. Coefficients a_n of Equation 3 and Standard Deviations

system (1 + 2)	a_1	a_2	a_3	a_4	$\sigma(H^E_m)$ / $J \cdot mol^{-1}$
ethanol + 2-propanol[a]	−181.80	23.33	−11.64	6.88	0.3
ethanol + MTBE[b]	1947.30	−901.61	578.29	−760.01	4.3
1-propanol + 2-propanol[c]	−195.64	14.56	3.16	−2.68	0.2
1-propanol + MTBE[d]	2136.60	−1007.80	361.70	−372.20	1.1
2-propanol + MTBE[d]	3106.10	−914.70	598.40	−629.70	3.4

[a] Pflug et al.[6] [b] Nagata.[7] [c] Polak et al.[8] [d] Nagata et al.[9]

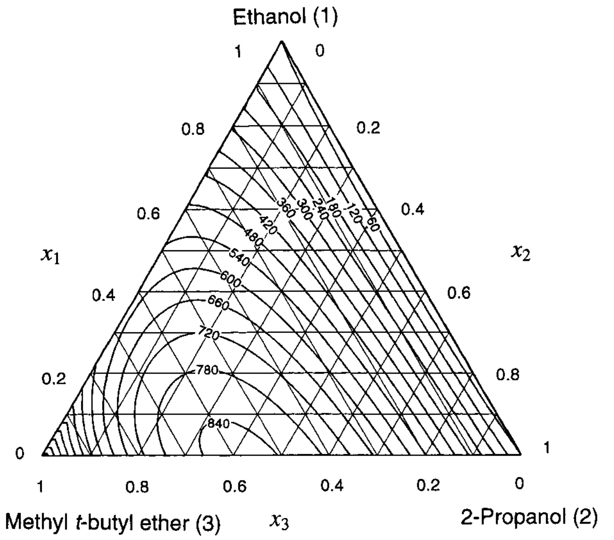

Figure 1. Contours of excess molar enthalpies for the ternary mixtures of {ethanol (x_1) + 2-propanol (x_2) + MTBE (x_3)} at 298.15 K.

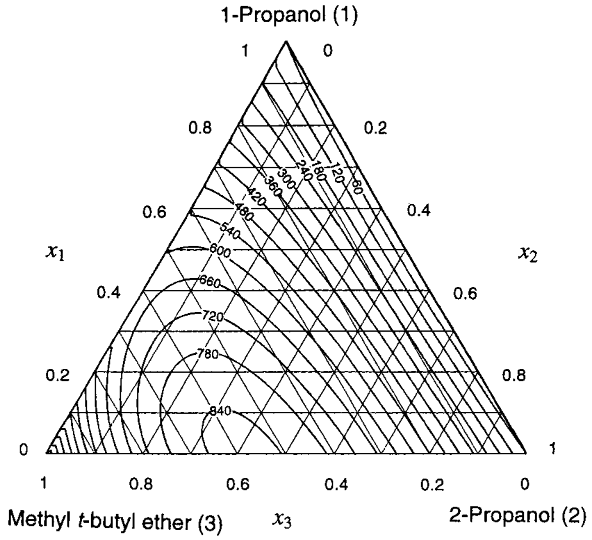

Figure 2. Contours of excess molar enthalpies for the ternary mixtures of {1-propanol (x_1) + 2-propanol (x_2) + MTBE (x_3)} at 298.15 K.

calculated from eq 4 for the five constituting binary mixtures are summarized in Table 4. The term Δ_{123} in eq 2, which stands for the ternary contribution to the magnitude, was correlated by the following expression:

$$\Delta_{123}/RT = \sum_{j=1}^{p} b_j(1 - 2x_3)^{j-1}/\{1 - k(1 - 2x_3)\} \qquad (5)$$

The values of the coefficients b_j and k, the absolute arithmetic-mean deviation $\delta(H^E_m) = \sum_{i=1}^{m}|H^E_{exptl} - H^E_{calcd}|/m$, and the standard deviation obtained in fitting eqs 2, 3, and 5 to the experimental ternary H^E_m are $b_1 = -1.0555$, $b_2 = 0.0510$, $b_3 = -0.4045$, $b_4 = -1.2666$, $b_5 = 1.4373$, $k = -1.0931$, $\delta(H^E_m) = 3.3$ J·mol^{-1}, and $\sigma(H^E_m) = 4.8$ J·mol^{-1} for the ethanol + 2-propanol + MTBE system and $b_1 = -1.0049$, $b_2 = 0.2401$, $b_3 = 0.0409$, $b_4 = -1.4779$, $b_5 = 0.8516$, $k = -1.0817$, $\delta(H^E_m) = 2.5$ J·mol^{-1}, and $\sigma(H^E_m) = 3.3$ J·mol^{-1} for the 1-propanol + 2-propanol + MTBE system. Equation 2 was used to calculate contour lines of constant $H^E_{m,123}$ plotted in Figure 1 for the ethanol + 2-propanol + MTBE system and in Figure 2 for the 1-propanol + 2-propanol + MTBE system.

The excess molar enthalpies of the constituent binary alcohol mixtures, ethanol + 2-propanol[6] and 1-propanol + 2-propanol,[8] are completely exothermic, whereas for ethanol + MTBE,[7] 1-propanol + MTBE,[9] and 2-propanol + MTBE[9] these values are highly endothermic. Figure 3 illustrates the experimental excess molar enthalpies of the above constituting binary mixtures together with the calculated results from eq 3.

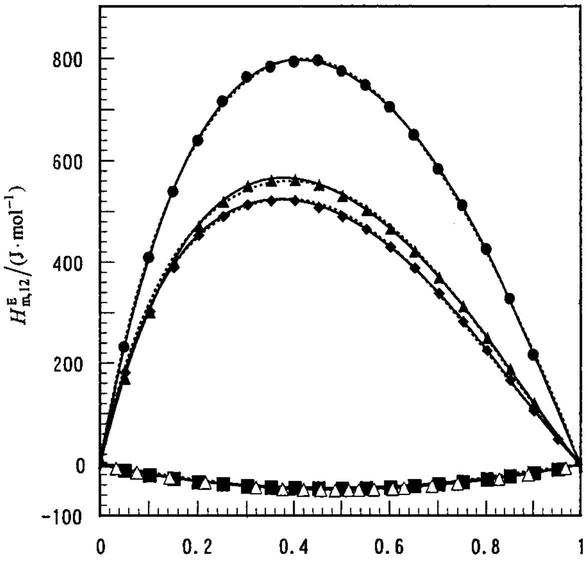

Figure 3. Excess molar enthalpies of constituting binary mixtures: ■, ethanol (x_1) + 2-propanol (x_2); △, 1-propanol (x_1) + 2-propanol (x_2); ◆, ethanol (x_1) + MTBE (x_3); ▲, 1-propanol (x_1) + MTBE (x_3); ●, 2-propanol (x_2) + MTBE (x_3); −, calculated from eq 3; · · ·, obtained from the association model.

The excess enthalpy ΔH^E_m reported results mainly from two contributions of opposite signs: (i) a positive term due to the disruption of alkanol−alkanol hydrogen bonds and (ii) a negative term due to the formation of $-OH\cdots O(CH_3)C(CH_3)_3$ hydrogen-bonded complexes.

The positive excess enthalpy of the pseudobinary mixtures as shown in Tables 2 and 3 indicates the predominance of the disruption of the existing hydrogen bonds of the alkanol multimers over the formation of weak hydrogen

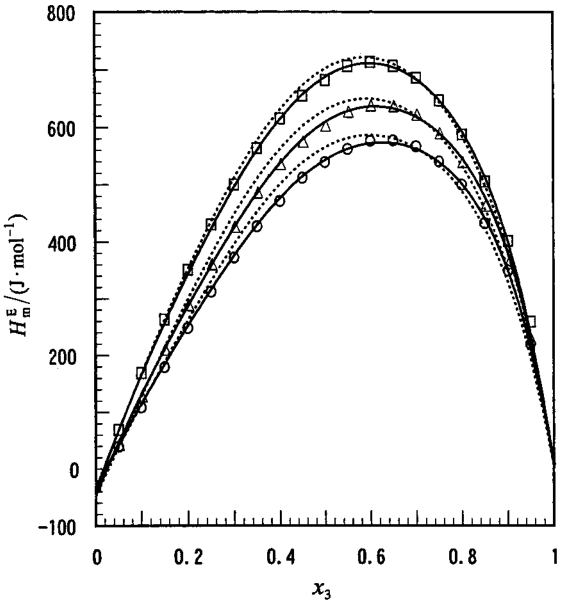

Figure 4. Excess molar enthalpies for the ternary mixtures of {ethanol (x_1) + 2-propanol (x_2) + MTBE (x_3)} at 298.15 K: □, $x_1' = 0.25$; △, $x_1' = 0.50$; ○, $x_1' = 0.75$; −, calculated from eq 2; · · ·, predicted from the association model.

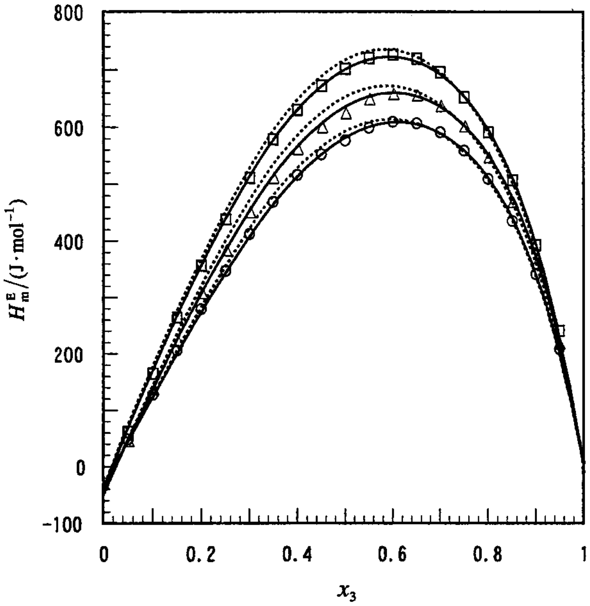

Figure 5. Excess molar enthalpies for the ternary mixtures of {1-propanol (x_1) + 2-propanol (x_2) + MTBE (x_3)} at 298.15 K: □, $x_1' = 0.25$; △, $x_1' = 0.50$; ○, $x_1' = 0.75$; −, calculated from eq 2; · · ·, predicted from the association model.

bonds between alkanol multimers and sterically hindered MTBE molecules during the mixing process.

Figures 4 and 5 compare the experimental ternary H^E_m with the results calculated from eq 2 for the ethanol + 2-propanol + MTBE and 1-propanol + 2-propanol + MTBE systems, respectively.

Data Analysis

In our present investigation, the ternary excess molar enthalpies containing two alcohols and an active nonassociating component were analyzed by means of a UNIQUAC associated-solution model.[16] The model assumes the linear self-association of ethanol (A) and 1-propanol or 2-propanol (B) to form pure *i*-mers, A_i and B_i, and multisolvated copolymers, $(A_iB_j)_k$, $A_i(B_jA_k)_l$, $(B_iA_j)_k$, and $B_i(A_jB_k)_l$, where the suffixes *i*, *j*, *k*, and *l* can be any integer from 1 to infinity. These alcohol polymers and copolymers form ternary complexes with C (MTBE as active nonassociating component): $(A_iB_j)_kC$, $A_i(B_jA_k)_lC$, $(B_iA_j)_kC$, and $B_i(A_jB_k)_lC$. The equilibrium constants for these chemical complex-forming reactions are also assumed to be independent of the degree of self-association, cross-association, and multisolvation. Thus, the model includes totally five equilibrium constants: K_A, K_B, K_{AB}, K_{AC}, and K_{BC}. The temperature dependence of the equilibrium constants is fixed by the van't Hoff equation, and the enthalpies of complex formation are independent of temperature.

Table 5. Values of Solvation Constants and Enthalpies of Complex Formation between Unlike Molecules

		$-h_{AB}$	T
mixture (A + B)	K_{AB}	kJ·mol^{-1}	K
ethanol + 2-propanol[a]	47.6	23.2	323.15
ethanol + MTBE[b]	18.0	19.5	298.15
1-propanol + 2-propanol[a]	36.1	23.2	323.15
1-propanol + MTBE[b]	6.0	19.5	298.15
2-propanol + MTBE[c]	5.0	19.5	298.15

[a] Tamura et al.[12] [b] Tamura et al.[5] [c] This work.

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

$$H^E = H^E_{chem} + H^E_{phys} \tag{6}$$

The chemical contribution term is related to the enthalpies of complex formation in the mixing system the derivation of which was presented previously.[16] On the other hand, the physical contribution term is derived by applying the Gibbs−Helmholtz relationship to the residual term of excess Gibbs free energy given by the UNIQUAC model,[17] which has two adjustable energy parameter a_{ij} for each binary $i-j$ pair. The association parameters of alcohols A and B expressed in K_A and K_B at 323.15 K were taken from ref 18. The enthalpy of H-bonding formation for all alcohols is assumed to be $h_A = h_B = h_{AB} = -23.2$ kJ·mol^{-1}, which is the same as the enthalpy of dilution of ethanol in *n*-hexane[19] at 298.15 K. The enthalpy of complex formation between alcohols and MTBE is estimated as −19.5 kJ·mol^{-1} from the difference between the enthalpy of dilution of ethanol in *n*-hexane and that of ethanol in MTBE. Table 5 summarizes the solvation constants and enthalpies of complex formation between unlike molecules. Pure component molecular size parameters were calculated using the method of Vera et al.[20] In fitting the model to binary H^E_m data, the energy parameters a_{ij} in H^E_{phys} are assumed to be a linear function of temperature as given by

$$a_{ij}/R = C_{ij} + D_{ij}\{(T/K) - 273.15\} \tag{7}$$

The coefficients C_{ij} and D_{ij} were obtained by using the simplex method,[21] and the objective function is given by

$$F = \sum_k^m (H^E_{exptl} - H^E_{calcd})^2_k \tag{8}$$

The binary coefficients and the absolute arithmetic-mean deviations $\langle|H^E_m|\rangle$ between the binary experimental and calculated values are given in Table 6. Figure 3 shows a comparison of the experimental binary H^E_m with those calculated by the association model. The model with the association and solvation constants and binary parameters

Table 6. Results of Fitting the Models to H_m^E for Binary Mixtures

system (A + B)	no. of data points	model[d]	C_{BA}/K	C_{AB}/K	D_{BA}	D_{AB}	$\delta(H_m^E)$/J·mol^{-1}
ethanol + 2-propanol[a]	19	I	104.21	95.60	0.3495	0.3014	2.3
		II	75.31	42.19	0.3563	0.1284	0.4
ethanol +MTBE[b]	19	I	839.30	515.83	2.6866	0.7471	3.2
		II	483.56	−212.28	0.5521	−0.7435	5.7
1-propanol + 2-propanol[a]	19	I	204.09	29.25	0.7856	0.0339	0.7
		II	168.56	−21.52	0.6249	−0.0423	0.2
1-propanol + MTBE[b]	18	I	264.91	377.01	0.7462	0.7250	5.4
		II	299.95	21.51	0.1421	0.2319	4.3
2-propanol + MTBE[c]	18	I	283.78	316.54	0.6814	0.3358	3.9
		II	399.10	29.81	0.4195	−0.0169	3.6

[a] Tamura et al.[12] [b] Tamura et al.[5] [c] This work. [d] I, UNIQUAC associated-solution; II, UNIQUAC.

alone predicted the ternary excess molar enthalpies. The absolute arithmetic-mean deviations between the experimental and calculated excess molar enthalpies were 12.8 J·mol^{-1} for the ethanol + 2-propanol + MTBE system and 9.8 J·mol^{-1} for the 1-propanol + 2-propanol + MTBE system. Comparison between the ternary experimental H_m^E and predicted results obtained from the association model are shown in Figure 4 for the ethanol + 2-propanol + MTBE system and in Figure 5 for the 1-propanol + 2-propanol + MTBE system. On the other hand, the absolute arithmetic-mean deviations in ternary predictions by the original UNIQUAC model with the binary parameters given in Table 6 were 21.7 J·mol^{-1} for the ethanol + 2-propanol + MTBE system and 32.9 J·mol^{-1} for the 1-propanol + 2-propanol + MTBE system.

Conclusion

Excess molar enthalpies at 298.15 K have been presented for the ethanol + 2-propanol + MTBE and 1-propanol + 2-propanol + MTBE systems, and the experimental results compare well with those calculated by using the polynomial equation. Furthermore, the ternary excess molar enthalpies of the mixtures formed by two lower alcohols and an active nonassociating component were predicted by the UNIQUAC associated-solution model with sufficient accuracy by using the binary parameters obtained solely from the binary correlation.

Literature Cited

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

(2) Fadopé, C. M. Washington Meeting Examines the Safety of MTBE. *Chem. Eng. (N. Y.)* **1995**, *102* (4), 49.

(3) Chang, E. J. Which Oxygenate is Right for You? *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1994**, *39*, 330−336.

(4) Brockwell, H. L.; Sarathy, P. R.; Trotta, R. Synthesize Ethers: Understanding of Etherification Technology Benefits MTBE Reactor Design. *Hydrocarbon Process.* **1991**, *9*, 133−141.

(5) Tamura, K.; Bhuiyan, M. M. H.; Yamada, T. Excess Molar Enthalpies of Ternary Mixtures Formed by Methanol and Methyl *tert*-Butyl Ether with Ethanol or 1-Propanol at 298.15 K. *Thermochim. Acta* **2001**, *376*, 9−16.

(6) Nagata, I.; Tamura, K.; Miyai, K. Excess Molar Enthalpies H^E of Ternary Mixtures of (Methanol + Ethanol + 1-Propanol or 2-Propanol) at 298.15 K. *Fluid Phase Equilib.* **1998**, *149*, 147−161.

(7) Nagata, I. Excess Enthalpies for (Ethanol + 1,1-Dimethylethyl Methyl Ether) and (Ethanol + 1,1-Dimethylethyl Methyl Ether + Benzene) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 1137−1142.

(8) Polak, J.; Murakami, S.; Benson, G. C.; Pflug, H. D. Excess Enthalpy, Volumes, and Gibbs Free Energy of *n*-Propanol-2-Propanol Mixtures at 25 °C. *Can. J. Chem.* **1970**, *48*, 3782−3785.

(9) Nagata, I.; Tamura, K. Excess Enthalpies for (Propan-1-ol or Propan-2-ol + 1,1-Dimethylethylmethyl Ether + Benzene) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1995**, *27*, 1091−1095.

(10) Tu, C.-H.; Ku, H.-C.; Wang, W.-F.; Chou, Y.-T. Volumetric and Viscometric Properties of Methanol, Ethanol, Propano-2-ol, and 2-Methylpropan-2-ol with a Synthetic C_{6+} Mixture from 298.15 K to 318.15 K. *J. Chem. Eng. Data* **2001**, *46*, 317−321.

(11) Nagata, I.; Tamura, K.; Miyai, K. Isothermal Vapor-Liquid Equilibria of Mixtures of (Methanol + Ethanol + 1-Propanol or 2-Propanol) at 333.15 K. *Fluid Phase Equilib.* **2000**, *170*, 37−48.

(12) Tamura, K.; Saito, M.; Yamada, T. Ternary Excess Molar Enthalpies for Methanol or Ethanol + 1-Propanol + 2-Propanol at the Temperature 298.15 K. *J. Chem. Eng. Data* **1999**, *44*, 626−630.

(13) Tamura, K.; Chen, Y.; Tada, K.; Yamada, T. Liquid−Liquid Equilibria for Quaternary Mixtures of Water, Ethanol, and 2,2,4-Trimethylpentane with Fuel Additives. *Fluid Phase Equilib.* **2000**, *171*, 115−126.

(14) Nagata, I.; Tamura, K.; Ozaki, S.; Myohen, K. Ternary Excess Molar Enthalpies of Chloroform + Acetone + Cyclohexane Mixtures at 298.15 K. *Thermochim. Acta* **1992**, *209*, 31−41.

(15) Elliott, K.; Wormald, C. J. A Precision Differential Flow Calorimeter. The Excess Enthalpy of Benzene + Cyclohexane Between 280.15 and 393.15 K. *J. Chem. Thermodyn.* **1976**, *8*, 881−893.

(16) Nagata, I.; Tamura, K.; Gotoh, K. Thermodynamics of Alcohol Solutions. Excess Molar Enthalpies of Ternary Mixtures Containing Two Alcohols and One Active Nonassociating Component. *Thermochim. Acta* **1986**, *104*, 179−202.

(17) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *Am. Inst. Chem. Eng. J.* **1975**, *21*, 116−128.

(18) Brandani, V. A. Continuous Linear Association Model for Determining the Enthalpy of Hydrogen-Bond Formation and the Equilibrium Constant for Pure Hydrogen-Bonded Liquids. *Fluid Phase Equilib.* **1983**, *12*, 87−104.

(19) Stokes, R. H.; Burfitt, C. Enthalpies for Dilution and Transfer of Ethanol in Non-Polar Solvents. *J. Chem. Thermodyn.* **1973**, *5*, 623−631.

(20) Vera, J. H.; Sayegh, S. G.; Ratcliff, G. A. A Quasi-Lattice-Local Composition Model for the Excess Gibbs Free Energy of Liquid Mixtures. *Fluid Phase Equilib.* **1977**, *1*, 113−135.

(21) Nelder, J. A.; Mead, R. Simplex Method for Minimization. *Comput. J.* **1965**, *7*, 308−313.

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