Excess Molar Enthalpies of Ternary Mixtures of Ethanol + 1-Propanol + Tetrahydropyran or 1,4-Dioxane at 298.15 K

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Excess molar enthalpies for the (ethanol + 1-propanol + tetrahydropyran) and (ethanol + 1-propanol + 1,4-dioxane) ternary mixtures and their binaries (ethanol + tetrahydropyran) have been measured by a flow microcalorimeter at 298.15 K and ambient pressure. The experimental results are correlated with a polynomial equation. The results have been compared with those calculated from a UNIQUAC associated-solution model. This model considers the self-association of like alcohols, cross-association of unlike alcohols, and solvation between alcohols and tetrahydropyran or 1,4-dioxane. The model with the association constants, solvation constants, and binary information alone could satisfactorily represent the ternary excess molar enthalpies.

Introduction

When two or more pure liquids mix, an enthalpy change will occur because of molecular interactions. The mixing or separation of substances is very common in chemical production and scientific research; in all such cases, excess enthalpies are involved. Excess enthalpy contains a substantial and significant amount of information about the nonidealities of liquid mixtures. A knowledge of the main factors involved in the strong nonideality of liquid mixtures is fundamental to a better understanding of excess enthalpies from the viewpoint of chemical engineering and is important because many kinds of strongly nonideal solutions are treated in chemical processes. Mixtures composed of alcohols and ethers comprise a substantial portion of liquid mixtures of practical importance. Tertiary alkyl ethers are nontoxic, nonpolluting high octane number blending agents for gasoline. Cyclic ethers represent a class of technically important compounds frequently used as solvents in the chemical industry.

The excess molar enthalpy of branched or cyclic ethers with polar or nonpolar compound binary mixtures has been the subject of a great number of investigations[1−15] over the past few years. In contrast to the large body of binary ether mixtures studied, theoretical and experimental investigations are sparse for ternary mixtures formed by two alcohols and an ether. Studies of the excess molar enthalpies of alcohol + ether mixtures are of interest in our laboratory, and some contributions have been made recently.[16−19] In continuation of our investigations on the excess molar enthalpies of two aliphatic lower alcohols and an aliphatic branched monoether or aliphatic cyclic mono- and diethers, we report the ternary excess molar enthalpies of ethanol + 1-propanol + tetrahydropyran or + 1,4-dioxane at 298.15 K and their constituent binaries ethanol + tetrahydropyran at 298.15 K.

Experimental Section

Materials. Ethanol and 1-propanol were obtained from Wako Pure Chemical, and tetrahydropyran and 1,4-dioxane were obtained from Aldrich Chemical Co. The stated mass purities of the chemicals are as shown in parentheses: ethanol (99.8%), 1-propanol (99.7%), tetrahydropyran (99%), and 1,4-dioxane (99.8%). Chemicals were kept in sealed, dark bottles and dried over molecular sieves (4Å $^{1}/_{16}$, Wako Pure Chemical) 2 to 3 weeks prior to their use in order to eliminate residual traces of water and avoid moisture. All of the chemicals were manipulated under a nitrogen atmosphere and degassed at a temperature close to 298.15 K by using an ultrasonic technique to avoid bubble formation. No further purification was carried out because they did not show any significant impurity peaks by GLC analysis. Their densities were measured with a DMA 58 digital densimeter (Anton Paar) at 298.15 K, and the measured densities of the chemicals were in good agreement with the recent literature values.[16,19,21−24]

Apparatus and Procedure. Excess molar enthalpies H_m^E were determined by a flow microcalorimeter at 298.15 K. Details of its experimental setup and operational procedures were described previously.[25] Agreement between our results and the literature values for the benzene + cyclohexane mixtures[25,26] was good. Experimental uncertainties were less than ±0.5% in H_m^E, $\pm 5 \times 10^{-5}$ in mole fraction, and ±3 mK in temperature over most of the range of experimental values.

A ternary mixture may be considered to be a pseudobinary mixture composed of tetrahydropyran or 1,4-dioxane and one binary alcohol mixture. The ternary measurements were carried out by adding tetrahydropyran or 1,4-dioxane to binary mixtures of ethanol (1) + 1-propanol (2) having three different concentrations. Ternary excess molar enthalpies $H_{m,123}^E$ can be obtained from the following relation:

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$$H^{\mathrm{E}}_{\mathrm{m},123} = \Delta H^{\mathrm{E}}_{\mathrm{m}} + (1 - x_3)H^{\mathrm{E}}_{\mathrm{m},12} \qquad (1)$$

where $\Delta H^{\mathrm{E}}_{\mathrm{m}}$ is the molar enthalpy measured for the pseudobinary mixture when 1 mol of the ternary mixture is formed by mixing $(1 - x_3)$ mol of the binary mixture ethanol (1) + 1-propanol (2) and x_3 mol of tetrahydropyran or 1,4-dioxane, and $H^{\mathrm{E}}_{\mathrm{m},12}$ is the molar enthalpy for the initial constituent binary (x'_1ethanol + $(1 - x'_1)$1-propanol) mixture. The values of $H^{\mathrm{E}}_{\mathrm{m},12}$ at three specified compositions (approximate compositions of these mixtures were 25, 50, and 75 mol % of component 1) for the binary ethanol (1) + 1-propanol (2) mixture 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} with due precaution to minimize the evaporation loss.

Results

The experimental results measured by the flow microcalorimeter at 298.15 K for the constituent binary alcohol−cyclic ether mixture (ethanol + tetrahydropyran) are listed in Table 1. The binary results were correlated by the Redlich−Kister equation of the form

$$H^{\mathrm{E}}_{m,ij}/\mathrm{J{\cdot}mol^{-1}} = x_i x_j \sum_{n=1}^{p} a_n (x_i - x_j)^{n-1} \qquad (2)$$

where a_n is the coefficient to be obtained by an unweighted least-squares method. Experimental $H^{\mathrm{E}}_{\mathrm{m}}$ values of the binary mixture measured in the present work are highly endothermic. The experimental results and values obtained from eq 2 are plotted in Figure 1; recent literature values[14,15] are shown for comparison and are in fair agreement with our results.

The measured values of $\Delta H^{\mathrm{E}}_{\mathrm{m}}$ for the ternary mixtures of (ethanol + 1-propanol + tetrahydropyran) and (ethanol + 1-propanol + 1,4-dioxane) at 298.15 K are presented in Tables 2 and 3, respectively, along with $H^{\mathrm{E}}_{\mathrm{m},123}$ obtained from eq 1. The values were correlated using the following equation

$$H^{\mathrm{E}}_{\mathrm{m},123} = H^{\mathrm{E}}_{\mathrm{m},12} + H^{\mathrm{E}}_{\mathrm{m},13} + H^{\mathrm{E}}_{\mathrm{m},23} + x_1 x_2 x_3 \Delta_{123} \qquad (3)$$

where $H^{\mathrm{E}}_{\mathrm{m},ij}$ are the binary excess molar enthalpies calculated from eq 2. Table 4 presents the a_n coefficients of eq 2 for the five constituent binaries $H^{\mathrm{E}}_{\mathrm{m},ij}$. 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

$$\sigma(H^{\mathrm{E}}_{\mathrm{m}}) = \left\{ \sum_{i=1}^{m} \frac{(H^{\mathrm{E}}_{\mathrm{exp}} - H^{\mathrm{E}}_{\mathrm{cal}})^2}{(m - p)} \right\}^{1/2} \qquad (4)$$

where m is the number of experimental data points. The term Δ_{123} in eq 3, which stands for the ternary contribution to the magnitude, was correlated by the following expression:[16−19]

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

The coefficient k is used to represent the skewness of the curves. The values of coefficients b_j and k, the absolute arithmetic-mean deviation $\delta(H^{\mathrm{E}}_{\mathrm{m}}) = \sum_{i=1}^{m} |H^{\mathrm{E}}_{\mathrm{exptl}} - H^{\mathrm{E}}_{\mathrm{calcd}}|/m$, and the standard deviation obtained in fitting eqs 2, 3, and 5 to the experimental ternary $H^{\mathrm{E}}_{\mathrm{m}}$ are $b_1 = 0.6656$, $b_2 = 0.1444$, $b_3 = 0.8812$, $b_4 = 1.9893$, $b_5 = -3.8511$, $b_6 = -10.0564$, $b_7 = 6.0242$, $b_8 = 10.7014$, $k = -1.11689$, $\delta(H^{\mathrm{E}}_{\mathrm{m}}) = 5.8\ \mathrm{J{\cdot}mol^{-1}}$, and $\sigma(H^{\mathrm{E}}_{\mathrm{m}}) = 8.0\ \mathrm{J{\cdot}mol^{-1}}$ for the (ethanol + 1-propanol + tetrahydropyran) system and $b_1 = -0.3249$, $b_2 = 0.8746$, $b_3 = -0.8759$, $b_4 = -5.4467$, $b_5 = 8.6588$, $b_6 = 19.617$, $b_7 = -8.7538$, $b_8 = -18.080$, $k = -1.0743$, $\delta(H^{\mathrm{E}}_{\mathrm{m}}) = 3.0\ \mathrm{J{\cdot}mol^{-1}}$, and $\sigma(H^{\mathrm{E}}_{\mathrm{m}}) = 4.0\ \mathrm{J{\cdot}mol^{-1}}$ for the (ethanol + 1-propanol + 1,4-dioxane) system. Equations 2 and 5 were used to calculate contour lines of constant $H^{\mathrm{E}}_{\mathrm{m},123}$ plotted in Figure 2 for the (ethanol + 1-propanol + tetrahydropyran) system and in Figure 3 for the (ethanol + 1-propanol + 1,4-dioxane) system.

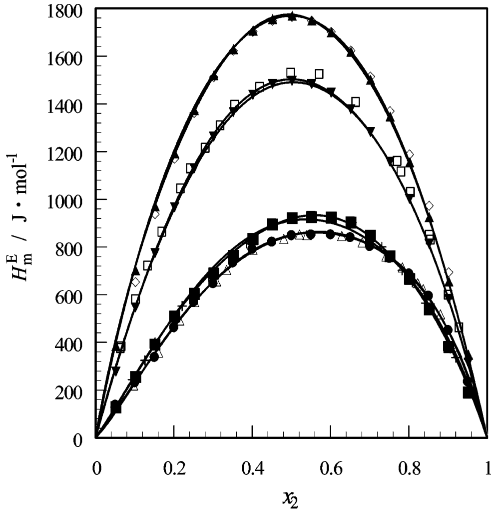

Figure 1. Comparison of excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m}}/\mathrm{J{\cdot}mol^{-1}}$ of the ternary constituent alcohol−ether binary mixtures at 298.15 K with literature values. Ethanol (x_1) + tetrahydropyran (x_2): ●, this work; △, Letcher et al., 1995. Ethanol (x_1) + 1,4-dioxane (x_2): ▼, Bhuiyan and Tamura, 2003; □, Letcher et al., 1995. 1-Propanol (x_1) + tetrahydropyran (x_2): ■, Tamura and Bhuiyan, 2003; +, Letcher et al., 1995. 1-Propanol (x_1) + 1,4-dioxane (x_2): ▲, Tamura and Bhuiyan, 2003; ◇, Calvo et al., 1999; —, calculated from eq 2; − − −, correlated by the association model.

Table 1. Experimental Excess Molar Enthalpies of the Constituent Binary Ethanol (1)−Tetrahydropyran (2) Mixture at 298.15 K

x_1	$H^{\mathrm{E}}_{\mathrm{m}}/\mathrm{J{\cdot}mol^{-1}}$	x_1	$H^{\mathrm{E}}_{\mathrm{m}}/\mathrm{J{\cdot}mol^{-1}}$
0.0500	236.15	0.5500	821.87
0.1000	451.36	0.6000	791.60
0.1500	595.28	0.6500	734.50
0.2000	688.62	0.7000	647.24
0.2500	753.64	0.7500	570.17
0.3000	803.36	0.8000	463.41
0.3500	840.66	0.8500	338.79
0.4000	852.47	0.9000	232.37
0.4500	852.05	0.9500	138.59
0.5000	849.10		

Data Reduction

The experimental excess molar enthalpies for the constituent binary mixtures were correlated, and those of ternary mixtures were calculated by means of the UNIQUAC associated-solution model.[27] This model assumes the linear self-association of ethanol (A) and 1-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 $B_i(A_jB_k)_l$, in terms of the hydrogen bond of the hydoxyl group of the alcohol, where the suffixes i, j, k, and l can be any integers from 1 to ∞. These alcohol polymers and copolymers form

Table 2. Experimental Excess Molar Enthalpies of Ethanol (1) + 1-Propanol (2) + Tetrahydropyran (3) Mixtures at 298.15 K[a]

$x'_1 = 0.2495$, $H^E_{m,12} = 13.6$ J·mol^{-1}				$x'_1 = 0.5000$, $H^E_{m,12} = 19.3$ J·mol^{-1}				$x'_1 = 0.7498$, $H^E_{m,12} = 15.6$ 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}
0.2371	0.7129	159.55	172.44	0.4750	0.4750	187.37	205.65	0.7123	0.2377	162.62	177.47
0.2246	0.6754	293.70	305.91	0.4500	0.4500	296.56	313.88	0.6748	0.2252	274.88	288.95
0.2121	0.6379	414.13	425.66	0.4250	0.4250	411.33	427.69	0.6373	0.2127	388.92	402.21
0.1996	0.6004	528.00	538.85	0.4000	0.4000	522.28	537.68	0.5998	0.2002	494.38	506.89
0.1871	0.5629	630.33	640.50	0.3750	0.3750	620.52	634.95	0.5624	0.1876	589.55	601.27
0.1747	0.5253	718.23	727.73	0.3500	0.3500	706.01	719.48	0.5249	0.1751	672.29	683.23
0.1622	0.4878	790.31	799.13	0.3250	0.3250	777.23	789.74	0.4874	0.1626	743.04	753.20
0.1497	0.4503	846.70	854.84	0.3000	0.3000	821.96	833.51	0.4499	0.1501	797.49	806.87
0.1372	0.4128	885.78	893.24	0.2750	0.2750	870.61	881.20	0.4124	0.1376	837.80	846.40
0.1248	0.3752	909.92	916.70	0.2500	0.2500	895.13	904.75	0.3750	0.1250	864.17	871.99
0.1123	0.3377	914.56	920.66	0.2250	0.2250	902.61	911.27	0.3374	0.1126	872.52	879.55
0.0998	0.3002	905.39	910.82	0.2000	0.2000	896.17	903.87	0.2999	0.1001	869.69	875.95
0.0873	0.2627	877.38	882.13	0.1750	0.1750	870.68	877.42	0.2624	0.0876	849.82	855.29
0.0749	0.2251	830.55	834.62	0.1500	0.1500	826.58	832.35	0.2249	0.0751	812.29	816.98
0.0624	0.1876	765.61	769.00	0.1250	0.1250	762.81	767.62	0.1875	0.0625	753.89	757.80
0.0499	0.1501	677.18	679.89	0.1000	0.1000	675.52	679.37	0.1500	0.0500	672.37	675.50
0.0374	0.1126	563.36	565.39	0.0750	0.0750	565.68	568.57	0.1125	0.0375	562.84	565.18
0.0250	0.0750	418.40	419.76	0.0500	0.0500	423.71	425.63	0.0750	0.0250	422.39	423.95
0.0125	0.0375	246.17	246.85	0.0250	0.0250	243.73	244.69	0.0375	0.0125	244.39	245.17

[a] Ternary mixtures were prepared by mixing pure tetrahydropyran with (x'_1ethanol + (1 − x'_1)1-propanol).

Table 3. Experimental Excess Molar Enthalpies of Ethanol (1) + 1-Propanol (2) + 1,4-Dioxane (3) Mixtures at 298.15 K[a]

$x'_1 = 0.2503$, $H^E_{m,12} = 13.6$ J·mol^{-1}				$x'_1 = 0.5009$, $H^E_{m,12} = 19.3$ J·mol^{-1}				$x'_1 = 0.7501$, $H^E_{m,12} = 15.6$ 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}
0.2378	0.7122	335.71	348.63	0.4759	0.4741	316.85	335.13	0.7126	0.2374	295.06	309.90
0.2253	0.6747	660.26	672.50	0.4508	0.4492	620.67	637.99	0.6751	0.2249	600.90	614.96
0.2128	0.6372	909.87	921.43	0.4258	0.4242	865.98	882.34	0.6376	0.2124	828.68	841.95
0.2003	0.5997	1122.17	1133.04	0.4007	0.3993	1064.98	1080.38	0.6001	0.1999	1017.92	1030.41
0.1878	0.5622	1291.65	1301.84	0.3757	0.3743	1236.63	1251.06	0.5626	0.1874	1183.46	1195.17
0.1752	0.5248	1437.33	1446.85	0.3506	0.3494	1365.61	1379.09	0.5251	0.1749	1309.88	1320.81
0.1627	0.4873	1546.40	1555.24	0.3256	0.3244	1476.52	1489.03	0.4876	0.1624	1408.80	1418.95
0.1502	0.4498	1622.28	1630.44	0.3005	0.2995	1549.94	1561.49	0.4501	0.1499	1489.72	1499.10
0.1377	0.4123	1671.65	1679.12	0.2755	0.2745	1599.96	1610.54	0.4126	0.1374	1532.65	1541.24
0.1252	0.3748	1686.60	1693.40	0.2504	0.2496	1605.02	1614.64	0.3751	0.1249	1545.71	1553.52
0.1127	0.3373	1666.74	1672.86	0.2254	0.2246	1595.99	1604.65	0.3376	0.1124	1533.25	1540.27
0.1001	0.2999	1623.72	1629.16	0.2004	0.1996	1556.20	1563.89	0.3001	0.0999	1495.25	1501.50
0.0876	0.2624	1547.55	1552.31	0.1753	0.1747	1484.23	1490.97	0.2625	0.0875	1429.85	1435.31
0.0751	0.2249	1434.80	1438.88	0.1503	0.1497	1382.06	1387.84	0.2250	0.0750	1328.41	1333.10
0.0626	0.1874	1291.02	1294.42	0.1252	0.1248	1245.64	1250.45	0.1875	0.0625	1201.22	1205.13
0.0501	0.1499	1114.45	1117.17	0.1002	0.0998	1073.43	1077.28	0.1500	0.0500	1034.48	1037.60
0.0376	0.1124	896.59	898.62	0.0751	0.0749	853.61	856.50	0.1125	0.0375	836.15	838.50
0.0250	0.0750	640.69	642.05	0.0501	0.0499	620.96	622.88	0.0750	0.0250	606.73	608.29
0.0125	0.0375	353.62	354.30	0.0250	0.0250	343.23	344.19	0.0375	0.0125	330.54	331.32

[a] Ternary mixtures were prepared by mixing pure 1,4-dioxane with (x'_1ethanol + (1 − x'_1)1-propanol).

Table 4. Coefficients a_n/J·mol^{-1} of Equation 2 and Standard Deviations

system (1 + 2)	a_1	a_2	a_3	a_4	$\sigma(H^E_m)$/J·mol^{-1}
ethanol + 1-propanol[a]	76.72	11.34	8.69	−1.58	0.10
ethanol + tetrahydropyran[b]	3390.11	−686.08	581.82	−1341.04	6.10
ethanol + 1,4-dioxane[b]	6010.22	−7.47	414.39	−475.99	3.75
1-propanol + tetrahydropyran[c]	3687.20	−882.56	−70.45	−9.93	7.57
1-propanol + 1,4-dioxane[c]	7076.03	17.81	845.02	508.34	3.17

[a] Tamura et al.[17] [b] Bhuiyan and Tamura.[18] [c] This work.

ternary complexes with C (tetrahydropyran or 1,4-dioxane): $(A_iB_j)_kC$, $A_i(B_jA_k)_lC$, $(B_iA_j)_kC$, and $B_i(A_jB_k)_lC$. The self-association of tetrahyrdopyran or 1,4-dioxane can be disregarded because of the weaker dipole−dipole intermolecular interaction of the cyclic ethers compared to the hydrogen bonding of alcohols.

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 a total of 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.

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

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

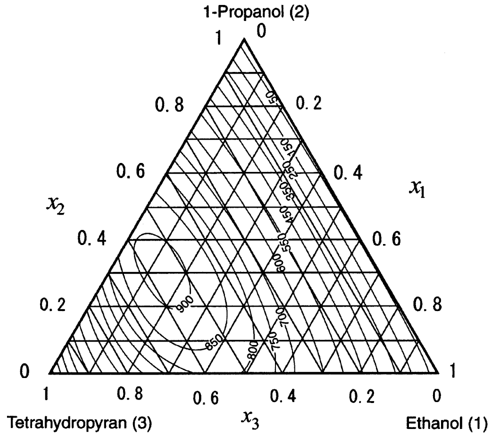

Figure 2. Contours for constant values of $H^{E}_{m,123}$/J·mol^{-1}for the (ethanol + 1-propanol + tetrahydropyran) system at 298.15 K: —, obtained using eqs 2 and 5.

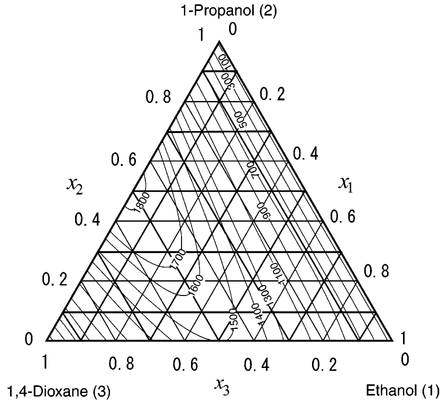

Figure 3. Contours for constant values of $H^{E}_{m,123}$/J·mol^{-1}for the (ethanol + 1-propanol + 1,4-dioxane) system at 298.15 K: —, obtained using eqs 2 and 5.

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

system (A + B)	K_{AB}	$-h_{AB}$/kJ·mol^{-1}	T/K
ethanol + 1-propanol[a]	49.0	23.2	323.15
ethanol + tetrahydropyran[b]	20.0	18.5	298.15
ethanol + 1,4-dioxane[b]	47.9	16.3	298.15
1-propanol + tetrahydropyran[c]	10.0	18.5	298.15
1-propanol + 1,4-dioxane[c]	45.0	16.3	298.15

[a] Tamura et al.[17] [b] Bhuiyan and Tamura.[18] [c] This work.

The chemical contribution term is related to the enthalpies of complex formation in the mixing system whose derivation was presented previously.[27] However, the physical contribution term is derived by applying the Gibbs−Helmholtz relation to the residual term of excess Gibbs free energy given by the UNIQUAC model,[28] which has two adjustable energy parameters a_{ij} for each binary $i-j$ pair. 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

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

The coefficients C_{ij} and D_{ij} were obtained by using the simplex method,[29] and the objective function is given by

$$F = \sum_{k}^{m}(H^{E}_{exptl} - H^{E}_{calcd})^{2}_{k} \tag{8}$$

Binary Correlation. The association parameters of ethanol, $K_A = 110.4$, and 1-propanol, $K_B = 87.4$, at 323.15 K were taken from ref 30. 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 same as the enthalpy of dilution of ethanol in n-hexane[31] at 298.15 K. The enthalpy of complex formation between alcohols and tetrahydropyran or 1,4-dioxane is estimated to be −18.5 kJ·mol^{-1}or −16.3 kJ·mol^{-1} from the difference between the enthalpy of dilution of ethanol in n-hexane and that of ethanol in tetrahydropyran or 1,4-dioxane.[18] The solvation constants between 1-propanol + tetrahydropyran and + 1,4-dioxane were adjusted in fitting the model to the experimental results accurately, and those of ethanol + the cyclic ethers were taken from ref 18. Table 5 summarizes the solvation constants and enthalpies of complex formation between unlike molecules. 1,4-Dioxane contains two oxygen atoms in the ring; therefore, the values of K_{AB} between the alcohol + 1,4-dioxane that were obtained were relatively higher than those of the alcohol + tetrahydropyran. This trend may be explained by the number of active sites that are able to solvate with alcohol.

Pure-component molecular size parameters r and q used in the UNIQUAC model were calculated using the method of Vera et al.[32] The binary coefficients and the absolute arithmetic-mean deviations $\delta(H^{E}_{m})$ between the binary experimental and calculated values are included in Table 6. Figure 1 shows a comparison of the experimental binary H^{E}_{m} for the mixtures of (ethanol + tetrahydropyran), (ethanol + 1,4-dioxane), (1-propanol + tetrahydropyran), and (1-propanol + 1,4-dioxane) with those calculated by the association model. The correlated values for the (ethanol + 1-propanol) mixture are available elsewhere.[17,33,34]

Ternary Prediction. The excess molar enthalpies for the ternary systems are reproduced by use of the association model with the association constants, solvation constants, and optimally fitted binary parameters obtained solely from the corresponding binary correlation. The values of the absolute arithmetic-mean deviations between the experimental and calculated values are 18.4 J·mol^{-1} for the (ethanol + 1-propanol + tetrahydropyran) system and 11.4 J·mol^{-1} for the (ethanol + 1-propanol + 1,4-dioxane) system. The magnitude of the deviations obtained for the ethanol + 1-propanol + tetrahydropyran or + 1,4-

Table 6. Binary Parameters and Absolute Arithmetic-Mean Deviations Between Experimental and Correlated Values

system (A + B)	no. of data points	C_{BA}/K	C_{AB}/K	D_{BA}	D_{AB}	$\delta(H^{E}_{m})$/J·mol^{-1}
ethanol + 1-propanol[a]	15	259.75	193.98	0.9548	0.7018	0.2
ethanol + tetrahydropyran[b]	19	−363.03	−671.28	−1.6402	−2.5014	5.9
ethanol + 1,4-dioxane[b]	19	−189.50	463.76	−0.5784	−0.5020	8.2
1-propanol + tetrahydropyran[c]	19	−126.01	554.06	−0.8703	1.4661	11.5
1-propanol + 1,4-dioxane[c]	19	−60.01	594.88	−0.3380	−0.4143	6.8

[a] Tamura et al.[17] [b] Bhuiyan and Tamura.[18] [c] This work.

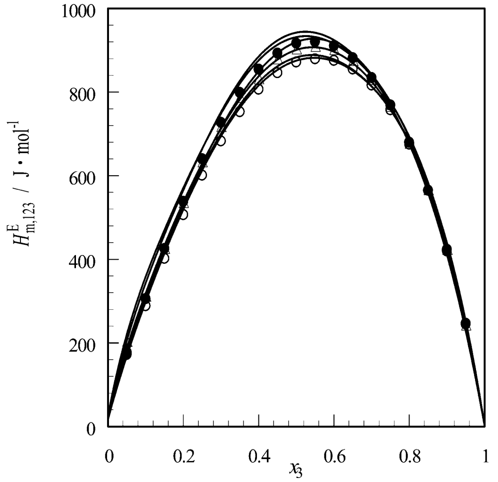

Figure 4. Excess molar enthalpies $H^E_{m,123}$/J·mol^{-1} for the ternary mixtures of {ethanol (x_1) + 1-propanol (x_2) + tetrahydropyran (x_3)} at 298.15 K: ●, x'_1 = 0.25; △, x'_1 = 0.50; ○, x'_1 = 0.75; —, calculated from eq 3; – – –, calculated from the association model.

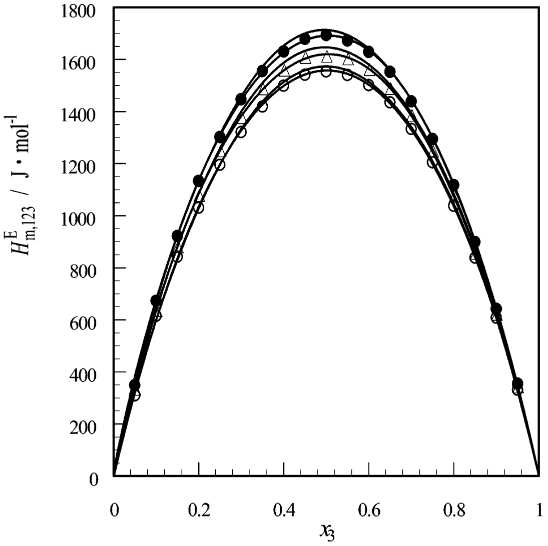

Figure 5. Excess molar enthalpies $H^E_{m,123}$/J·mol^{-1}for the ternary mixtures of {ethanol (x_1) + 1-propanol (x_2) + 1,4-dioxane (x_3)} at 298.15 K: ●, x'_1 = 0.25; △, x'_1 = 0.50; ○, x'_1 = 0.75; —, calculated from eq 3; – – –, calculated from the association model.

dioxane systems was comparable to that of the calculated results reported previously.[16−19] A comparison between the ternary experimental H^E_m and calculated results obtained from the association model is shown in Figure 4 for the (ethanol + 1-propanol + tetrahydropyran) system and in Figure 5 for the (ethanol + 1-propanol + 1,4-dioxane) system.

Conclusions

The excess molar enthalpies at 298.15 K have been presented for the ternary (ethanol + 1-propanol + tetrahydropyran) and (ethanol + 1-propanol + 1,4-dioxane) systems and the binary (ethanol + tetrahydropyran) system. The experimental results compared well with those calculated by using the polynomial equation. Furthermore, the ternary excess molar enthalpies of the mixtures formed by two lower *n*-alcohols (C_2−C_3) and a cyclic ether were calculated satisfactorily by the UNIQUAC associated-solution model with sufficient accuracy using the binary parameters only.

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