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Ternary excess molar enthalpies for the mixtures of methanol and ethanol with tetrahydropyran or 1,4-dioxane at 298.15 K

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Abstract

Ternary excess molar enthalpies, H_m^E, at 298.15 K and atmospheric pressure measured by using a flow microcalorimeter are reported for the (methanol + ethanol + tetrahydropyran) and (methanol + ethanol + 1, 4-dioxane) mixtures. The pseudobinary excess molar enthalpies for all the systems are found to be positive over the entire range of compositions. The experimental results are correlated with a polynomial equation to estimate the coefficients and standard errors. The results have been compared with those calculated from a UNIQUAC associated solution model in terms of the self-association of alcohols as well as solvation between unlike alcohols and alcohols with tetrahydropyran or 1,4-dioxane. The association constants, solvation constants and optimally fitted binary parameters obtained solely from the pertinent binary correlation predict the ternary excess molar enthalpies with an excellent accuracy.

Keywords: Excess molar enthalpies; Tetrahydropyran; 1,4-Dioxane; Flow microcalorimeter; Association

1. Introduction

The thermodynamic properties of liquid mixtures provide important information for good design of industrial process, to improve the understanding of the molecular interactions existing in the liquid mixtures, and to test the predictive capability of the chemical models. The study of thermodynamic behavior for the mixtures of cyclic ethers and alkanols is of considerable interest because they represent a class of technically important compounds frequently used as solvents in the chemical industry. Cyclic polyethers have attracted interest as model substances for bio-systems and in relation to their use in synthetic methods in organic chemistry [1–3]. In addition, cycloethers such as 1,4-dioxane, 1,3-dioxolane, 1,3,5-trioxane, etc., might also serve as fuel additives in near future. The interaction between the hydroxyl group of alkanol and the oxygen atom of cycloether is not negligible [4,5]. The recent investigations [6–10] suggested a relatively strong association between the alkanol and the ether. Letcher and Govender [6] also showed that the interaction between alkanol and cycloether is generally greater than that of alkanol and branched ether.

Over the past few years, a large number of thermodynamic experimental results and theoretical investigations of binary mixtures involving a cyclic ether + a polar or nonpolar solvent has been devoted [11–25]. Some investigators have presented the binary excess molar enthalpies of tetrahydropyran or 1,4-dioxane and alkanols [6,20,26,27]. Although many excess molar enthalpy investigations of binary mixtures formed by tetrahydropyran or 1,4-dioxane have been made, less attention has been focused on the excess molar

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Nomenclature

a_{ij}	binary interaction parameters for i–j pair
A, B, C	methanol, ethanol, and tetrahydropyran or 1,4-dioxane
A_i, B_j	i-mer of methanol, and j-mer of ethanol
$\mathrm{A}_i\mathrm{B}_j$	complex between i-mer of methanol and j-mer of ethanol
$\mathrm{A}_i\mathrm{B}_j\mathrm{C}$	complex between i-mer of methanol and j-mer of ethanol and tetrahydropyran or 1,4-dioxane monomer
$\mathrm{A}_i\mathrm{C}$	complex between i-mer of methanol and tetrahydropyran or 1,4-dioxane monomer
b_j	coefficients of Eq. (4)
$\mathrm{B}_i\mathrm{C}$	complex between i-mer of ethanol and tetrahydropyran or 1,4-dioxane monomer
C_{ij}, D_{ij}	coefficients of Eq. (6)
F	objective function as defined by Eq. (7)
h_A	enthalpies of hydrogen bond formation of methanol or ethanol
h_AB	enthalpies of complex formation between unlike molecules
H_m^E	excess molar enthalpy
$H_{\mathrm{m},123}^\mathrm{E}$	excess molar enthalpies of ternary mixtures $(1+2+3)$
$H_{\mathrm{m},ij}^\mathrm{E}$	excess molar enthalpies of binary mixtures $(i+j)$
$\delta H_\mathrm{m}^\mathrm{E}$	deviation between experimental and calculated excess enthalpy value
$\Delta H_\mathrm{m}^\mathrm{E}$	excess molar enthalpies of pseudobinary mixtures
k	coefficient of Eq. (4)
K_A	self-association constants of methanol or ethanol
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

α_n	coefficients of Eq. (2)
δ	absolute arithmetic mean deviation
Δ_{123}	function as defined by Eq. (3)
σ	S.D.

Subscripts

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

Superscript

E	excess

enthalpy of ternary mixtures with tetrahydropyran or 1,4-dioxane [28,29].

The aforementioned aspects have greatly stimulated us to embark upon a program for the measurements of ternary excess molar enthalpies of two aliphatic lower alcohols and an alipahtic cyclic mono- or di-ether. In this work, we have presented the excess molar enthalpies of ternary mixtures formed by methanol and ethanol with tetrahydropyran or 1,4-dioxane. Literature searches reveal that excess molar enthalpy data for these ternary mixtures at 298.15 K and atmospheric pressure apparently seem not to exist. Binary excess molar enthalpies at 298.15 K for each of the five binary mixtures making up the two ternary systems of the present investigation have already been reported: (methanol + ethanol) [30]; (methanol + tetrahydropyran) [6]; (methanol + 1, 4-dioxane) [6,26]; (ethanol + tetrahydropyran) [6]; (ethanol + 1, 4-dioxane) [6,26].

2. Experimental

Methanol, and ethanol used in the present investigation were the same as in our earlier work [8]. Tetrahydropyran, and 1,4-dioxane with mass fraction purities >0.990, and >0.998 were purchased from the Aldrich. Apart from degassing by ultrasonic technique at about 298.15 K, all of the components were used without further purification. All of the chemicals were manipulated under an inert nitrogen atmosphere. No significant peaks of impurities for all the components were detected by GC. The purity of solvents was further ascertained by comparing their density measured with DMA 58 digital densimeter (Anton Paar) at 298.15 K those are inserted in Table 1 along with the corresponding recent literature values [10,14,15,22,31,32].

The excess molar enthalpies, H_m^E, were measured using a flow-type microcalorimeter at $T = 298.15 \pm 0.005$ K. The detailed description of the experimental setup and operational procedure are given in previous publications [10,33]. For a test of the microcalorimeter, our H_m^E results measured for the (benzene + cyclohexane) mixture were in reasonable agreement with the literature values [33]. The experimental errors were estimated to be within $\pm 5 \times 10^{-3}$. H_m^E in excess molar enthalpies and $\pm 1 \times 10^{-4}$ in mole fraction. Ternary H_m^E measurements were carried out by adding tetrahydropyran or 1,4-dioxane to binary mixtures of $\{x'_1\text{methanol} + (1 - x'_1)\text{ethanol}\}$. The mixtures were prepared by mass using a balance (AEX-180, Shimadzu). Caution was taken to prevent evaporation and moisturization of the solutions during and after preparation. A ternary mixture can be considered as pseudobinary mixture forms tetrahydropyran or 1,4-dioxane and one binary alcohols mixture. Three experimental runs were performed by mixing tetrahydropyran or 1,4-dioxane with the initial binary mixtures (methanol + ethanol) whose three specified compositions are approximately 0.25, 0.50, and 0.75 in mole fraction of methanol. The excess molar enthalpies, $H_{m,123}^E$ of ternary mixture of composition x_1, x_2, and x_3 are expressed by:

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

where H_m^E is the molar enthalpy measured for the pseudobinary mixture, $H_{m,12}^E$ the molar enthalpy for the initial binary $\{x'_1\text{methanol} + (1 - x'_1)\text{ethanol}\}$ mixture, and x_3 the mole fraction of tetrahydropyran or 1,4-dioxane. The values of $H_{m,12}^E$ in Eq. (1) at three specified compositions were interpolated by means of a spline-fit method.

Table 1
Comparison of experimental densities, ρ (g cm^{-3}), for the pure liquids at 298.15 K

Component	Experimental	Literature
Methanol	0.78665	0.78665[a] 0.78656[b]
Ethanol	0.78524	0.78524[a] 0.78530[b]
Tetrahydropyran	0.87895	0.87891[c] 0.87916[d]
1,4-Dioxane	1.02795	1.02797[e] 1.02789[f]

[a] [10].
[b] [31].
[c] [14].
[d] [15].
[e] [22].
[f] [32].

3. Results and discussion

The binary experimental results for the mixtures of (methanol + 1, 4-dioxane), and (ethanol + 1, 4-dioxane) measured by the flow microcalorimeter [33] at 298.15 K are listed in Table 2 together with the deviations $\delta H_m^E = (H_m^E - H_{m,ij}^E)$ calculated from an equation of the form:

$$H_{m,ij}^E\ (\text{J mol}^{-1}) = x_i x_j \sum_{n=1}^{p} \alpha_n (x_i - x_j)^{n-1} \quad (2)$$

where α_n is the coefficient to be obtained by an unweighted least-squares method. Experimental H_m^E of binary alcohol–1,4-dioxane and values obtained from Eq. (2) are plotted in Fig. 1 and shown a comparison with the recent published experimental data [6,26]. Our binary excess molar enthalpy data for alcohol–1,4-dioxane mixtures are close to those of Letcher and Govender [6], but the experimental data obtained by Dai and Chao [26] show a large discrepancy between them. In order to obviate the alcohol–1,4-dioxane experimental values we have repeated the binary measurements.

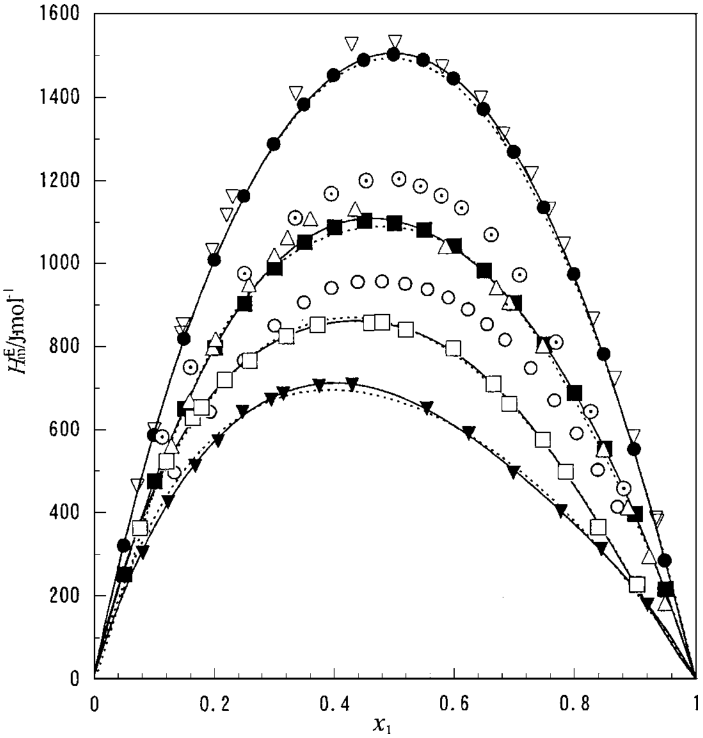

Fig. 1. Excess molar enthalpies H^E_m (J mol^{-1}) of constituent alcohol + ether binary mixtures at 298.15 K. Methanol (x_1) + 1, 4-dioxane (x_2): (■) this work; (△) Letcher and Govender [6]; (○) Dai and Chao [26]. Methanol (x_1) + tetrahydropyran (x_2): (▼) Letcher and Govender [6]. Ethanol (x_1) + 1, 4-dioxane (x_2): (●) this work; (▽) Letcher and Govender [6]; (⊙) Dai and Chao [26]. Ethanol (x_1) + tetrahydropyran (x_2): (□) Letcher and Govender [6]; (—) calculated from Eq. (2); (· · ·) correlated by the association model.

The experimental results for the ternary mixtures of (methanol + ethanol + tetrahydropyran) and (methanol + ethanol + 1, 4-dioxane) systems at 298.15 K are listed in Tables 3 and 4, respectively, along with the measured values of ΔH^E_m and the ternary experimental $H^E_{m,123}$ calculated from Eq. (1). The values were correlated using the following equation:

$$H^E_{m,123} = H^E_{m,12} + H^E_{m,13} + H^E_{m,23} + \frac{x_1 x_2 x_3 \Delta_{123}}{RT} \tag{3}$$

where $H^E_{m,ij}$ are the binary excess molar enthalpies and calculated from Eq. (2). Table 5 presents the coefficients of Eq. (2) for the five constituent binaries $H^E_{m,ij}$ and the S.D., calculated by using:

$$\sigma(H^E_m) = \left\{\sum_{i=1}^{m} \frac{(H^E_{exp} - H^E_{cal})^2}{m-p}\right\}^{0.5}$$

where m is the number of experimental data points and p the number of parameters. The term Δ_{123} in Eq. (3), stands for 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:

$$\delta(H^E_m) = \sum_{i=1}^{m} \frac{|H^E_{exp} - H^E_{cal}|}{m}$$

and the S.D. obtained in fitting Eqs. (3) and (4) to the experimental ternary H^E_m are $b_1 = -1.5673$, $b_2 = -0.4420$, $b_3 = -0.8495$, $b_4 = 0.4380$, $b_5 = 2.3471$, $b_6 = -1.3125$, $b_7 = -0.7974$, and $k = -1.1089$, $\delta(H^E_m) = 5.9$ J mol^{-1} and $\sigma(H^E_m) = 7.2$ J mol^{-1} for

Table 2
Binary excess molar enthalpies of alcohol + 1,4-dioxane mixtures at 298.15 K

x_1	H_m^E (J mol^{-1})	δH_m^E (J mol^{-1})
Methanol (1) + 1,4-dioxane (2)		
0.0500	250.81	−3.27
0.1000	475.42	6.62
0.1500	650.60	3.42
0.2000	796.29	4.17
0.2500	902.19	−4.22
0.3000	988.17	−4.45
0.3500	1050.15	−3.01
0.4000	1086.66	−3.50
0.4500	1102.02	−3.48
0.5000	1095.96	−4.76
0.5500	1079.90	2.84
0.6000	1040.92	5.58
0.6500	980.80	4.81
0.7000	902.79	3.80
0.7500	803.45	−0.37
0.8000	687.83	−1.64
0.8500	552.59	−1.79
0.9000	394.89	−1.51
0.9500	213.50	0.76
Ethanol (1) + 1,4-dioxane (2)		
0.0500	318.09	−0.14
0.1000	584.63	−2.63
0.1500	815.90	2.22
0.2000	1005.11	2.44
0.2500	1160.16	1.96
0.3000	1285.28	2.18
0.3500	1380.43	1.19
0.4000	1449.97	2.27
0.4500	1486.25	−2.61
0.5000	1499.37	−3.19
0.5500	1486.10	−2.15
0.6000	1441.50	−3.66
0.6500	1368.36	−4.02
0.7000	1265.97	−3.07
0.7500	1132.30	−2.18
0.8000	970.18	−1.84
0.8500	777.41	6.70
0.9000	549.24	6.92
0.9500	280.55	−4.08

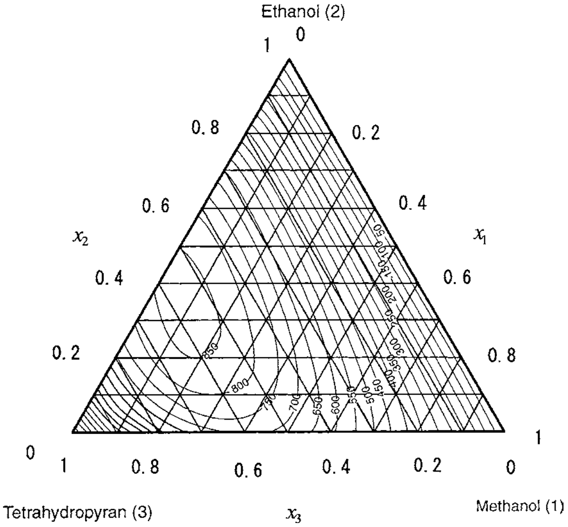

Fig. 2. Contours for constant values of $H^E_{m,123}$ (J mol^{-1}) for the (methanol + ethanol + tetrahydropyran) system at 298.15 K (—) calculated from Eq. (3).

the (methanol + ethanol + tetrahydropyran) system and $b_1 = -0.7067$, $b_2 = 0.9056$, $b_3 = -2.9187$, $b_4 = -7.5159$, $b_5 = 16.8310$, $b_6 = 28.2754$, $b_7 = -17.2889$, $b_8 = -27.7939$, and $k = -1.1199$, $\delta(H_m^E) = 5.3\,\mathrm{J\,mol^{-1}}$ and $\sigma(H_m^E) = 7.6\,\mathrm{J\,mol^{-1}}$ for the (methanol + ethanol + 1, 4-dioxane) system. Constant $H^E_{m,123}$ contours calculated from Eq. (3) are depicted in Figs. 2 and 3 for the (methanol + ethanol + tetrahydropyran) and (methanol + ethanol + 1, 4-dioxane) systems, respectively.

The measured pseudobinary excess molar enthalpies, ΔH_m^E, have been found to be positive for all the systems over the whole range of compositions.

It is well known that alcohol molecules are self- and cross-associated through hydrogen bonding of

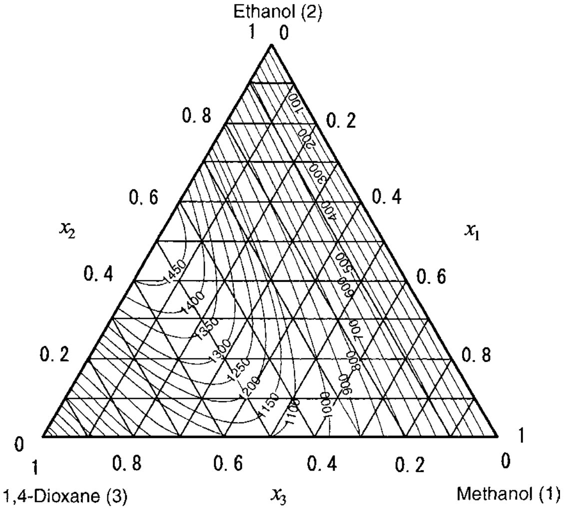

Fig. 3. Contours for constant values of $H^E_{m,123}$ (J mol^{-1}) for the (methanol + ethanol + 1, 4-dioxane) system at 298.15 K (—) calculated from Eq. (3).

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

$x'_1 = 0.2500$, $H^{\mathrm{E}}_{\mathrm{m},12} = 2.6$ (J mol^{-1})				$x'_1 = 0.4999$, $H^{\mathrm{E}}_{\mathrm{m},12} = 4.5$ (J mol^{-1})				$x'_1 = 0.7502$, $H^{\mathrm{E}}_{\mathrm{m},12} = 4.0$ (J mol^{-1})			
x_1	x_2	$\Delta H^{\mathrm{E}}_{\mathrm{m}}$ (J mol^{-1})	$H^{\mathrm{E}}_{\mathrm{m},123}$ (J mol^{-1})	x_1	x_2	$\Delta H^{\mathrm{E}}_{\mathrm{m}}$ (J mol^{-1})	$H^{\mathrm{E}}_{\mathrm{m},123}$ (J mol^{-1})	x_1	x_2	$\Delta H^{\mathrm{E}}_{\mathrm{m}}$ (J mol^{-1})	$H^{\mathrm{E}}_{\mathrm{m},123}$ (J mol^{-1})
0.2378	0.7122	112.51	115.01	0.4749	0.4751	100.66	104.94	0.7127	0.2373	88.58	92.41
0.2253	0.6747	219.67	222.04	0.4499	0.4501	199.00	203.05	0.6752	0.2248	179.45	183.08
0.2128	0.6372	319.45	321.69	0.4249	0.4251	291.66	295.49	0.6377	0.2123	266.55	269.98
0.2003	0.5997	410.06	412.17	0.3999	0.4001	377.18	380.78	0.6002	0.1998	346.69	349.91
0.1878	0.5622	494.20	496.17	0.3749	0.3751	455.82	459.20	0.5627	0.1873	420.42	423.44
0.1752	0.5248	569.11	570.95	0.3499	0.3501	527.27	530.42	0.5252	0.1748	488.79	491.61
0.1627	0.4873	636.94	638.65	0.3249	0.3251	588.12	591.05	0.4877	0.1623	551.75	554.37
0.1502	0.4498	693.00	694.58	0.2999	0.3001	640.61	643.31	0.4501	0.1499	601.68	604.10
0.1377	0.4123	734.73	736.18	0.2749	0.2751	683.21	685.69	0.4126	0.1374	641.79	644.01
0.1252	0.3748	764.99	766.31	0.2499	0.2501	715.16	717.41	0.3751	0.1249	671.46	673.48
0.1127	0.3373	782.30	783.48	0.2249	0.2251	733.97	736.00	0.3376	0.1124	690.38	692.19
0.1001	0.2999	785.96	787.01	0.1999	0.2001	739.63	741.43	0.3001	0.0999	696.98	698.59
0.0876	0.2624	773.98	774.90	0.1750	0.1750	730.20	731.77	0.2626	0.0874	690.14	691.55
0.0751	0.2249	745.75	746.54	0.1500	0.1500	705.02	706.37	0.2251	0.0749	668.03	669.24
0.0626	0.1874	698.24	698.90	0.1250	0.1250	662.33	663.46	0.1876	0.0624	628.23	629.24
0.0501	0.1499	627.72	628.25	0.1000	0.1000	598.52	599.42	0.1500	0.0500	575.05	575.86
0.0376	0.1124	537.00	537.39	0.0750	0.0750	513.82	514.50	0.1125	0.0375	4891.64	489.76
0.0250	0.0750	410.15	410.41	0.0500	0.0500	394.55	395.00	0.0750	0.0250	377.14	377.54
0.0125	0.0375	242.14	242.27	0.0250	0.0250	236.01	236.24	0.0375	0.0125	225.46	225.66

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

Table 4
Experimental excess molar enthalpies of methanol (1) + ethanol (2) + 1,4-dioxane (3) mixture at 298.15 K[a]

$x'_1 = 0.2498$, $H^{\mathrm{E}}_{\mathrm{m},12} = 2.6$ (J mol^{-1})				$x'_1 = 0.4995$, $H^{\mathrm{E}}_{\mathrm{m},12} = 4.5$ (J mol^{-1})				$x'_1 = 0.7496$, $H^{\mathrm{E}}_{\mathrm{m},12} = 4.0$ (J mol^{-1})			
x_1	x_2	$\Delta H^{\mathrm{E}}_{\mathrm{m}}$ (J mol^{-1})	$H^{\mathrm{E}}_{\mathrm{m},123}$ (J mol^{-1})	x_1	x_2	$\Delta H^{\mathrm{E}}_{\mathrm{m}}$ (J mol^{-1})	$H^{\mathrm{E}}_{\mathrm{m},123}$ (J mol^{-1})	x_1	x_2	$\Delta H^{\mathrm{E}}_{\mathrm{m}}$ (J mol^{-1})	$H^{\mathrm{E}}_{\mathrm{m},123}$ (J mol^{-1})
0.2373	0.7127	241.70	244.20	0.4746	0.4754	211.11	215.38	0.7121	0.2379	184.04	187.87
0.2248	0.6752	522.90	525.26	0.4496	0.4504	471.72	475.77	0.6746	0.2254	424.26	427.89
0.2123	0.6377	736.28	738.51	0.4246	0.4254	660.95	664.78	0.6372	0.2128	596.21	599.64
0.1998	0.6002	908.60	910.70	0.3996	0.4004	809.03	812.63	0.5997	0.2003	739.12	742.35
0.1873	0.5627	1050.40	1052.37	0.3747	0.3753	941.18	944.56	0.5622	0.1878	862.38	865.41
0.1748	0.5252	1166.39	1168.23	0.3497	0.3503	1048.43	1051.58	0.5247	0.1753	960.54	963.36
0.1623	0.4877	1260.35	1262.06	0.3247	0.3253	1137.68	1140.61	0.4872	0.1628	1040.05	1042.67
0.1499	0.4501	1326.63	1328.20	0.2997	0.3003	1201.46	1204.16	0.4498	0.1502	1099.57	1101.99
0.1374	0.4126	1363.80	1365.24	0.2747	0.2753	1239.10	1241.57	0.4123	0.1377	1134.93	1137.15
0.1249	0.3751	1377.43	1378.75	0.2498	0.2502	1254.19	1256.44	0.3748	0.1252	1159.88	1161.90
0.1124	0.3376	1373.29	1374.47	0.2248	0.2252	1254.38	1256.41	0.3373	0.1127	1160.63	1162.45
0.0999	0.3001	1341.54	1342.59	0.1998	0.2002	1229.71	1231.51	0.2998	0.1002	1136.99	1138.61
0.0874	0.2626	1282.41	1283.33	0.1748	0.1752	1179.54	1181.12	0.2624	0.0876	1094.22	1095.63
0.0749	0.2251	1195.31	1196.10	0.1499	0.1501	1104.04	1105.40	0.2249	0.0751	1025.47	1026.68
0.0624	0.1876	1082.90	1083.56	0.1249	0.1251	1000.89	1002.01	0.1874	0.0626	932.51	933.52
0.0500	0.1500	937.02	937.54	0.0999	0.1001	869.67	870.57	0.1499	0.0501	812.55	813.35
0.0375	0.1125	757.63	758.03	0.0749	0.0751	707.95	708.63	0.1124	0.0376	657.14	657.74
0.0250	0.0750	554.81	555.07	0.0500	0.0500	515.25	515.70	0.0750	0.0250	480.09	480.50
0.0125	0.0375	304.74	304.87	0.0250	0.0250	289.81	290.04	0.0375	0.0125	270.34	270.54

[a] Ternary mixtures were prepared by mixing pure 1,4-dioxane with $\{x'_1\text{methanol} + (1 - x'_1)\text{ethanol}\}$.

Table 5
Coefficients α_n (J mol^{-1}) of Eq. (2) and S.D.

System (1 + 2)	α_1	α_2	α_3	α_4	α_5	$\sigma(H_m^E)$ (J mol^{-1})
Methanol + ethanol[a]	17.7462	6.9218	0.6257	1.0390		0.09
Methanol + tetrahydropyran[b]	2730.90	−1067.79	345.44	108.37	599.22	5.94
Methanol + 1,4-dioxane[c]	4402.90	−575.56	630.82	113.70		4.20
Ethanol + tetrahydropyran[b]	3390.11	−686.08	581.82	−1341.04		6.10
Ethanol + 1,4-dioxane[c]	6010.22	−7.47	414.39	−475.99		3.75

[a] [8].
[b] [6].
[c] This work.

their hydroxyl groups. In the mixing process of alcohols–cyclic ether, the significant intermolecular order of both alcohols and ether is deeply modified. Therefore, the experimental ΔH_m^E data can be interpreted qualitatively by taking into account the two kinds of opposite contributions. The positive contributions to the excess molar enthalpies are:

(i) breaking or stretching of hydrogen bonds in the self-associated alkanol multimers due to the hydroxyl group of alcohol molecule;
(ii) disruption of ether–ether interactions;
(iii) geometrical factor that hinders the component molecules to come closer to each other.

The negative one is:

(i) Solvation and complex formation between unlike molecules. This occurs through the complex formation of hydrogen bonding between unlike alkanol multimers and the complex formation between alkanol multimers and tetrahydropyran or 1,4-dioxane.

The high endothermic values of pseudobinary mixtures, ΔH_m^E for both the {(methanol + ethanol) + tetrahydropyran} and {(methanol + ethanol) + 1, 4-dioxane} systems reflect that the positive contributions to excess enthalpies outweigh the negative one as given in Tables 2 and 3, respectively. This is mainly explained by considering that the cyclic molecular shape of tetrahydropyran or 1,4-dioxane is not ideal to accept the hydroxyl groups of alkanol multimers that restrict the extent of interaction between alkanol multimers and cyclic ether molecules.

4. Data analysis

The experimental excess molar enthalpies for binary mixtures were correlated and those of ternary mixtures were predicted by means of the UNIQUAC associated solution model [34]. This model assumes the linear self-association of methanol (A) and ethanol (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 integers from 1 to ∞. These alcohol polymers and copolymers form 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 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.

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

$$H^E = H_{chem}^E + H_{phys}^E \quad (5)$$

The chemical contribution term is related to the enthalpies of complex formation in the mixing system whose derivation is presented previously [34]. On the other hand, 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 [35], which has two adjustable energy parameters a_{ij} for each binary i–j pair. In fitting the model to binary ΔH_m^E data, the energy parameters a_{ij} in H_{phys}^E are assumed to be a linear function of temperature as given by:

$$\frac{a_{ij}}{R} = C_{ij} + D_{ij}\left\{\left(\frac{T}{K}\right) - 273.15\right\} \tag{6}$$

The coefficients C_{ij} and D_{ij} were obtained by using the simplex method [36] and the objective function is given by:

$$F = \sum_{k}^{m} (H_{exp}^E - H_{cal}^E)_k^2 \tag{7}$$

4.1. Binary correlation

The association parameters of methanol, $K_A = 173.9$, and ethanol $K_B = 110.4$ at 323.15 K were taken from [37]. The enthalpy of H-bonding formation for all alcohols is assumed to be $h_A = h_B = h_{AB} = -23.2\,\mathrm{kJ\,mol^{-1}}$, which is same as the enthalpy of dilution of ethanol in *n*-hexane [38] at 298.15 K. The enthalpy of complex formation between alcohols and tetrahydropyran or 1,4-dioxane is estimated as $-18.5\,\mathrm{kJ\,mol^{-1}}$ or $-16.3\,\mathrm{kJ\,mol^{-1}}$ from the difference between the enthalpy of dilution of ethanol in *n*-hexane and those of ethanol in tetrahydropyran or 1,4-dioxane. Table 6 summarizes the solvation constants and enthalpies of complex formation between unlike molecules. Pure component molecular size parameters r and q were calculated using the method of Vera et al. [39]. The binary coefficients and the absolute arithmetic mean deviations $\langle|H_m^E|\rangle$ between the binary experimental and calculated values are included in Table 7. Fig. 1 shows a comparison of the experimental binary H_m^E for the mixtures of (methanol + tetrahydropyran), (methanol + 1, 4-dioxane), (ethanol + tetrahydropyran), and (ethanol + 1, 4-dioxane) with those calculated by the association model. The correlated values for (methanol + ethanol) are available elsewhere [8,40,41].

Table 6
Values of solvation constants and enthalpies of complex formation between unlike molecules

System (A + B)	K_{AB}	$-h_{AB}$ ($\mathrm{kJ\,mol^{-1}}$)	T (K)
Methanol + ethanol[a]	99.0	23.2	323.15
Methanol + tetrahydropyran[b]	27.0	18.5	298.15
Methanol + 1,4-dioxane[b]	51.5	16.3	298.15
Ethanol + tetrahydropyran[b]	20.0	18.5	298.15
Ethanol + 1,4-dioxane[b]	47.9	16.3	298.15

[a] [8].
[b] This work.

4.2. Ternary prediction

The excess molar enthalpies for the ternary systems are predicted 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 predicted ones are $20.8\,\mathrm{J\,mol^{-1}}$ for the (methanol + ethanol + tetrahydropyran) system and $15.5\,\mathrm{J\,mol^{-1}}$ for the (methanol + ethanol + 1, 4-dioxane) system. Comparison between the ternary experimental H_m^E and predicted results obtained from the association model are shown in Fig. 4 for the (methanol + ethanol + tetrahydropyran) system and in Fig. 5 for the (methanol + ethanol + 1, 4-dioxane) system.

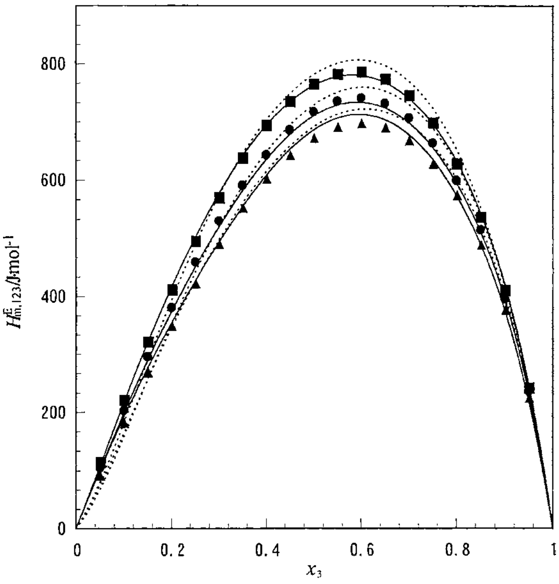

Fig. 4. Excess molar enthalpies $H_{m,123}^E$ ($\mathrm{J\,mol^{-1}}$) for the ternary mixtures of {methanol (x_1) + ethanol (x_2) + tetrahydropyran (x_3)} at 298.15 K. (■) $x'_1 = 0.25$; (●) $x'_1 = 0.50$; (▲) $x'_1 = 0.75$; (—) calculated from Eq. (3); (···) predicted from the association model.

Table 7
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 + tetrahydropyran[b]	19	−742.97	−398.05	−2.8868	−1.5238	6.94
Methanol + 1,4-dioxane[b]	19	−67.41	413.76	0.1999	−0.5346	11.90
Ethanol + tetrahydropyran[b]	19	−363.03	−671.28	−1.6402	−2.5014	5.93
Ethanol + 1,4-dioxane[b]	19	−189.50	463.76	−0.5784	−0.5020	8.20

[a] [8].
[b] This work.

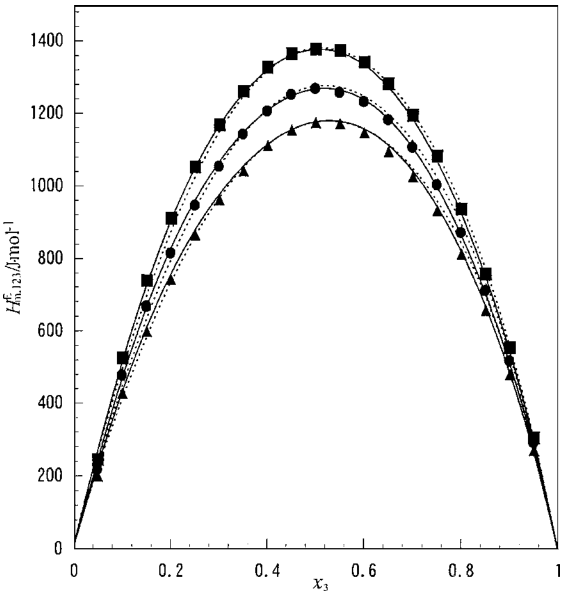

Fig. 5. Excess molar enthalpies $H^E_{m,123}$ (J mol^{-1}) for the ternary mixtures of {methanol (x_1) + ethanol (x_2) + 1, 4-dioxane (x_3)} at 298.15 K. (■) $x_1' = 0.25$; (●) $x_1' = 0.50$; (▲) $x_1' = 0.75$; (—) calculated from Eq. (3); (···) predicted from the association model.

5. Conclusions

We presented the binary excess molar enthalpies for the (methanol+1, 4-dioxane), (ethanol+1, 4-dioxane) systems and ternary excess molar enthalpies for the (methanol + ethanol + tetrahydropyran), (methanol + ethanol+1, 4-dioxane) systems measured at 298.15 K. The binary experimental results were correlated and ternary experimental ones were predicted by using only optimally fitted binary parameters with the UNIQUAC associated solution model. The correlated and predicted values show a fair agreement with the experimental data.

References

[1] D.J. Cram, J.M. Cram, Science 183 (1974) 803–809.
[2] R.F. Jameson, in: H.A. Skinner (Ed.), Thermochemistry and Thermodynamics, MTP International Review of Science, Butterworths, London, 1972.
[3] H.V. Kehiaian, in: H.A. Skinner (Ed.), Thermochemistry and Thermodynamics, MTP International Review of Science, Butterworths, London, 1972.
[4] E.M. Arnett, L. Joris, E. Mitchell, T.S.S.R. Murty, T.M. Gorrie, P.V.R. Schleyer, J. Am. Chem. Soc. 92 (1970) 2365–2377.
[5] C.N.R. Rao, P.C. Dwivedi, H. Ratajczak, W.J. Orville-Thomas, J. Chem. Sco., Faraday Trans. Part 2 71 (1975) 955–966.
[6] T.M. Letcher, U.P. Govender, J. Chem. Eng. Data 40 (1995) 1097–1100.
[7] T.M. Letcher, P.U. Govender, J. Chem. Eng. Data 40 (1995) 997–1000.
[8] K. Tamura, M.M.H. Bhuiyan, T. Yamada, Thermochim. Acta 376 (2001) 9–16.
[9] M.M.H. Bhuiyan, K. Tamura, T. Yamada, J. Chem. Eng. Data 46 (2001) 1499–1503.
[10] K. Tamura, M.M.H. Bhuiyan, T. Yamada, Int. J. Thermophys. 22 (2001) 1739–1753.
[11] A. Amigo, R. Bravo, M. Pintos, J. Chem. Eng. Data 38 (1993) 141–142.
[12] M. Pintos, A. Amigo, R. Bravo, J. Chem. Thermodyn. 25 (1993) 337–341.
[13] I. Castro, M. Pintos, A. Amigo, R. Bravo, M.I. Paz Andrade, J. Chem. Thermodyn. 26 (1994) 29–33.
[14] I. Castro, E. Calvo, R. Bravo, M. Pintos, A. Amigo, J. Chem. Eng. Data 40 (1995) 230–232.
[15] A. Inglese, J.-P.E. Grolier, E. Wilhelm, J. Chem. Eng. Data 28 (1983) 124–127.
[16] R. Bravo, M. Pintos, A. Amigo, Can. J. Chem. 73 (1995) 375–379.
[17] A. Inglese, E. Wilhelm, J.-P.E. Grolier, H.V. Kehiaian, J. Chem. Thermodyn. 12 (1980) 217–222.
[18] P. Brocos, E. Calvo, A. Amigo, R. Bravo, M. Pintos, J. Chem. Eng. Data 43 (1998) 112–116.
[19] E. Calvo, P. Brocos, R. Bravo, M. Pintos, A. Amigo, A.H. Roux, G. Roux-Desgranges, J. Chem. Eng. Data 43 (1998) 105–111.

[20] V. Alonso, E. Calvo, R. Bravo, M. Pintos, A. Amigo, J. Chem. Eng. Data 39 (1994) 926–928.

[21] A. Penas, E. Calvo, M. Pintos, A. Amigo, R. Bravo, J. Chem. Eng. Data 45 (2000) 682–685.

[22] R. Francesconi, C. Castellari, F. Comelli, J. Chem. Eng. Data 46 (2001) 577–581.

[23] E. Calvo, A. Penas, M. Pintos, R. Bravo, A. Amigo, J. Chem. Eng. Data 46 (2001) 692–695.

[24] H. Ohji, K. Tamura, H. Ogawa, J. Chem. Thermodyn. 32 (2000) 319–328.

[25] P. Brocos, A. Piñeiro, R. Bravo, A. Amigo, A.H. Roux, G. Roux-Desgranges, J. Chem. Eng. Data 47 (2002) 351–358.

[26] M. Dai, J.-P. Chao, Fluid Phase Equilb. 23 (1985) 321–326.

[27] E. Calvo, P. Brocos, A. Piñeiro, M. Pintos, A. Amigo, R. Bravo, A.H. Roux, G. Roux-Desgranges, J. Chem. Eng. Data 44 (1999) 948–954.

[28] J. Gmehling, T. Holderbaum, Heats of Mixing Data Collection, Chemistry Data Series, vol. III, Part 3, Frankfurt am Main, April 1991.

[29] J.J. Christensen, R. L. Rowley, R. M. Izatt, Handbook of Heats of Mixing, Wilely/Interscience, New York, April 1988.

[30] H.D. Pflug, A.E. Pope, G.C. Benson, J. Chem. Eng. Data 13 (1968) 408–410.

[31] J.M. Resa, C. Gonzlez, S.O. de Landaluce, J. Lanz, J. Chem. Eng. Data 47 (2002) 435–440.

[32] M.C. Kinart, W. Kinart, A. Ćwiklińska, J. Chem. Eng. Data 47 (2002) 23–25.

[33] I. Nagata, K. Tamura, S. Ozaki, Thermochim. Acta 209 (1992) 31–41.

[34] I. Nagata, K. Tamura, K. Gotoh, Thermochim. Acta 104 (1986) 179–202.

[35] D.S. Abrams, J.M. Prausnitz, Am. Inst. Chem. Eng. J. 21 (1975) 116–128.

[36] J.A. Nelder, R. Mead, Comput. J. 7 (1965) 308–313.

[37] V.A. Brandani, Fluid Phase Equilib. 12 (1983) 87–104.

[38] R.H. Stokes, C. Burfitt, J. Chem. Thermodyn. 5 (1973) 623–631.

[39] J.H. Vera, S.G. Sayegh, G.A. Ratcliff, Fluid Phase Equilib. 1 (1977) 113–135.

[40] I. Nagata, K. Tamura, K. Miyai, Fluid Phase Equilib. 149 (1998) 147–161.

[41] K. Tamura, M. Saito, T. Yamada, J. Chem. Eng. Data 44 (1999) 626–630.