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Thermochimica Acta 437 (2005) 34–38
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Ternary excess molar enthalpies of (1-propanol + 2-propanol + 1,4-dioxane) mixture at 298.15 K

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Received 7 February 2005; received in revised form 29 April 2005; accepted 8 June 2005
Available online 15 July 2005

Abstract

Ternary excess molar enthalpies for (1-propanol + 2-propanol + 1,4-dioxane) mixture have been measured with a flow calorimeter at $T = 298.15$ K and atmospheric pressure. Constant contours for the ternary experimental results were calculated by a polynomial equation. Further, the results have been compared with those calculated from a UNIQUAC formalism taking into consideration the molecular self- and cross-association of two alcohols and the solvation among the alcohols and 1,4-dioxane. The results predicted by using binary parameters obtained from the corresponding binary results alone are in good agreement with the experimental values.

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Keywords: Excess molar enthalpies; 1,4-Dioxane; Flow calorimeter; Association; Solvation

1. Introduction

The liquid mixtures of cyclic ethers are highly non-ideal and a significant amount of work on thermodynamic properties of 1,4-dioxane mixtures with alcohols [1–6], hydrocarbons [7–9], and water [10] has been published. But very little attention has been paid to the excess molar enthalpies of ternary alcohol–cyclic ether mixtures. This prompted us to study the excess molar enthalpies of 1,4-dioxane or oxane ternary systems involving methanol, ethanol, 1-propanol or 2-propanol at $T = 298.15$ K. This paper presents the excess molar enthalpies of (1-propanol + 2-propanol + 1,4-dioxane) ternary mixtures at $T = 298.15$ K. The ternary results are compared with a UNIQUAC prediction. Excess enthalpies of the binary mixtures have been reported previously: (1-propanol + 2-propanol) [11]; (1-propanol + 1,4-dioxane) [2]; and (2-propanol + 1,4-dioxane) [4]. In the full concentration range the mixtures of (1-propanol + 2-propanol) are exothermic while those of 1,4-dioxane with either 1-propanol or 2-propanol are endothermic.

2. Experimental

1-Propanol and 2-propanol used in this investigation were the same as used in our earlier work [12] and 1,4-dioxane with mass fraction purity >0.998 was purchased from Aldrich Chemical Co. Chemicals were kept in sealed dark bottles dried over molecular sieves (3A 1/16, 4A 1/16) 2–3 weeks prior to their use to eliminate the residual traces of water. All of the chemicals were manipulated under an inert nitrogen atmosphere. No significant peaks of impurities for all the components were detected by gas chromatography.

Experimental measurements were carried out with a previously described [13,14] flow calorimeter at 298.15 ± 0.005 K. The errors in the excess molar enthalpy H_m^E were estimated to be less than ±0.5% from preliminary experiments on benzene + cyclohexane [14,15].

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0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.06.011

Three series of measurements were performed by adding 1,4-dioxane to binary mixtures composed of $\{x'_1$1-propanol $+ (1-x'_1)$2-propanol$\}$. The mixtures were prepared by mass using a balance (AEX—180, Shimadzu) ensuring accuracy in the mole fractions of 10^{-4}. Thus, the ternary excess molar enthalpy $H^{\mathrm{E}}_{\mathrm{m},123}$ can be expressed as

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

where $\Delta H^{\mathrm{E}}_{\mathrm{m}}$ is the measured excess molar enthalpy for the pseudobinary mixtures, $H^{\mathrm{E}}_{\mathrm{m},12}$ the excess molar enthalpy of the initial binary mixtures $\{x'_1$1-propanol $+ (1-x'_1)$2-propanol$\}$, and x_3 the mole fraction of 1,4-dioxane. 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) were interpolated by means of a spline–fit method.

3. Results and discussion

The experimental $\Delta H^{\mathrm{E}}_{\mathrm{m}}$ for the ternary mixture of (1-propanol + 2-propanol + 1,4-dioxane) at 298.15 K are presented in Table 1, along with $H^{\mathrm{E}}_{\mathrm{m},123}$ calculated from Eq. (1). The values were correlated using the following equation:

$$H^{\mathrm{E}}_{\mathrm{m},123} = H^{\mathrm{E}}_{\mathrm{m},12} + H^{\mathrm{E}}_{\mathrm{m},13} + H^{\mathrm{E}}_{\mathrm{m},23} + \frac{x_1x_2x_3\varDelta_{123}}{RT} \tag{2}$$

where $H^{\mathrm{E}}_{\mathrm{m},ij}$ are the binary excess molar enthalpies and were fitted to a polynomial equation of the form

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

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

The coefficient a_n of Eq. (3) and the standard deviation σ calculated for the three constituent binary mixtures are summarized in Table 2. Fig. 1 illustrates the experimental excess molar enthalpies of the constituent binary mixtures together with the calculated results from Eq. (3). The term $\varDelta_{123}$ in Eq. (2), stands for the ternary contribution to the magnitude was

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

$x'_1 = 0.2499$, $H^{\mathrm{E}}_{\mathrm{m},12} = -37.9$ (J mol^{-1})				$x'_1 = 0.5000$, $H^{\mathrm{E}}_{\mathrm{m},12} = -45.0$ (J mol^{-1})				$x'_1 = 0.7500$, $H^{\mathrm{E}}_{\mathrm{m},12} = -35.0$ (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})
0.2374	0.7126	415.1	379.1	0.4750	0.4750	395.3	348.8	0.7125	0.2375	374.1	340.9
0.2249	0.6751	795.8	761.7	0.4500	0.4500	766.0	722.0	0.6750	0.2250	723.0	691.5
0.2125	0.6375	1089.8	1057.6	0.4250	0.4250	1045.0	1003.3	0.6375	0.2125	996.3	966.6
0.2000	0.6000	1332.2	1301.8	0.4000	0.4000	1276.5	1237.3	0.6000	0.2000	1224.1	1196.1
0.1875	0.5625	1529.0	1500.6	0.3750	0.3750	1469.6	1432.9	0.5625	0.1875	1412.7	1386.5
0.1750	0.5250	1682.8	1656.3	0.3500	0.3500	1620.9	1586.6	0.5250	0.1750	1565.7	1541.2
0.1625	0.4875	1801.2	1776.5	0.3250	0.3250	1741.4	1709.6	0.4875	0.1625	1683.4	1660.6
0.1500	0.4500	1883.6	1860.8	0.3000	0.3000	1817.4	1788.0	0.4500	0.1500	1759.5	1738.5
0.1375	0.4125	1928.0	1907.1	0.2750	0.2750	1871.4	1844.5	0.4125	0.1375	1806.4	1787.1
0.1250	0.3750	1937.4	1918.4	0.2500	0.2500	1878.7	1854.2	0.3750	0.1250	1821.2	1803.7
0.1125	0.3375	1905.4	1888.3	0.2250	0.2250	1849.1	1827.0	0.3375	0.1125	1797.8	1782.1
0.1000	0.3000	1841.3	1826.2	0.2000	0.2000	1792.0	1772.5	0.3000	0.1000	1744.5	1730.5
0.0875	0.2625	1747.1	1733.8	0.1750	0.1750	1701.4	1684.3	0.2625	0.0875	1658.4	1646.1
0.0750	0.2250	1618.3	1606.9	0.1500	0.1500	1575.4	1560.7	0.2250	0.0750	1537.7	1527.2
0.0625	0.1875	1446.3	1436.8	0.1250	0.1250	1411.5	1399.3	0.1875	0.0625	1376.0	1367.3
0.0500	0.1500	1238.9	1231.3	0.1000	0.1000	1210.6	1200.8	0.1500	0.0500	1182.4	1175.4
0.0375	0.1125	1001.3	995.6	0.0750	0.0750	970.9	963.6	0.1125	0.0375	946.0	940.8
0.0250	0.0750	715.2	711.4	0.0500	0.0500	689.8	684.9	0.0750	0.0250	682.5	679.0
0.0125	0.0375	389.2	387.3	0.0250	0.0250	373.7	371.3	0.0375	0.0125	365.7	363.9

[a] Ternary mixtures were prepared by mixing pure 1,4-dioxane with $\{x'_1$1-propanol $+ (1-x'_1)$2-propanol$\}$.

Table 2
Coefficients a_n (J mol^{-1}) of Eq. (3) and standard deviations

System (1 + 2)	a_1	a_2	a_3	a_4	$\sigma(H^{\mathrm{E}}_{\mathrm{m}})$ (J mol^{-1})
1-Propanol + 2-propanol[a]	−195.64	14.56	3.16	−2.68	0.20
1-Propanol + 1,4-dioxane[b]	7076.00	17.80	845.00	508.30	3.17
2-Propanol + 1,4-dioxane[c]	8034.00	688.70	1074.50	−3.80	4.34

[a] [11].
[b] [5].
[c] [4].

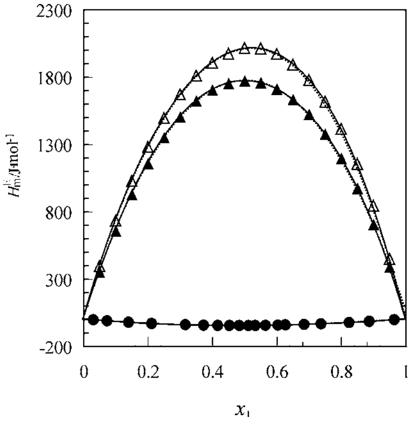

Fig. 1. Excess molar enthalpies H^E_m(J mol^{-1}) of constituent binary mixtures at 298.15 K. 1-Propanol (x_1) + 2-propanol (x_2): (●) Polak et al. [11]; 1-propanol (x_1) + 1,4-dioxane (x_2): (▲) Tamura and Bhuiyan [2]; 2-propanol (x_1) + 1,4-dioxane (x_2): (△) Bhuiyan and Tamura [4]; (—) calculated from Eq. (3); (···) correlated by the association model.

correlated by the following expression:

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

The values of the coefficients b_j and k, the absolute arithmetic mean deviation, and the standard deviation obtained in fitting Eqs. (2) and (4) to the experimental ternary H^E_m are $b_1 = -0.1876$, $b_2 = 1.3148$, $b_3 = -1.1959$, $b_4 = -4.7629$, $b_5 = 9.2818$, $b_6 = 17.127$, $b_7 = -8.3762$, $b_8 = -15.495$, $k = -1.0823$, $\delta(H^E_m) = 3.5$ J mol^{-1}, and $\sigma(H^E_m) = 4.6$ J mol^{-1} for the (1-propanol + 2-propanol + 1,4-dioxane) system. Eq. (2) was used to calculate contour lines of constant $H^E_{m,123}$ plotted in Fig. 2 for the (1-propanol + 2-propanol + 1,4-dioxane) system.

The excess enthalpy ΔH^E_m reported is mainly resulted 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 $C_4H_8O_2$···HO–hydrogen-bonded complexes.

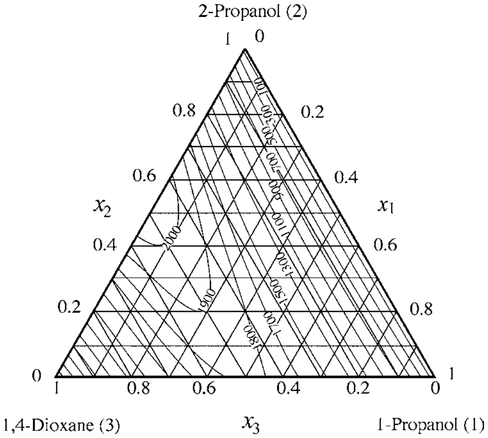

Fig. 2. Contours for constant values of $H^E_{m,123}$(J mol^{-1}) for the (1-propanol + 2-propanol + 1,4-dioxane) system at 298.15 K (—) calculated from Eq. (2).

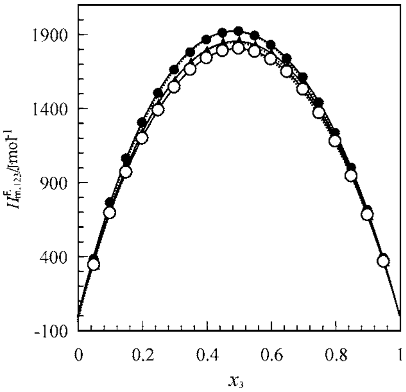

Fig. 3. Excess molar enthalpies $H^E_{m,123}$(J mol^{-1}) for the ternary mixtures of {1-propanol (x_1) + 2-propanol (x_2) + 1,4-dioxane (x_3)} at 298.15 K: (●) $x'_1 = 0.25$; (▲) $x'_1 = 0.50$; (○) $x'_1 = 0.75$; (—) calculated from Eq. (2); (···) predicted from the association model.

The positive excess enthalpy of the pseudobinary mixtures as shown in Table 1 indicates the predominance of the disruption of the existing hydrogen bonds of the alkanol multimers over the formation of weak hydrogen bonds between linear alkanol multimers and cyclic 1,4-dioxane molecules during the mixing process.

Fig. 3 compares the experimental ternary H^E_m with the results calculated from Eq. (2) for the (1-propanol + 2-propanol + 1,4-dioxane) system.

The thermodynamic excess properties of ternary mixtures reflect differences in the molecular size, shape, and interactions among three components; therefore, it is of importance to use ternary data for testing models for the prediction. The experimental ternary H^E_ms were compared with those predicted by a UNIQUAC associated-solution model [16]. The model assumes linear associating polymers of 1-propanol (A) and 2-propanol (B) molecules and the multisolvation of polymers result in homopolymers (A_i and B_i) and copolymers $\{(A_iB_j)_k$, $A_i(B_jA_k)_l$, $(B_iA_j)_k$, and $B_i(A_jB_k)_l\}$. The resulting homopolymers, copolymers and 1,4-dioxane (C) as an active nonassociating component form other complexes: A_iC, B_iC, $A_i(B_jA_k)_lC$ and $B_i(A_jB_k)_lC$. Here subindices i, j, k, and l go from one to infinity. The equilibrium constants for these chemical complex-forming reactions are assumed to be independent of the degree of self-association, cross-association, and multisolvation. The equilibrium constants are tempera-

Table 3
Values of solvation constants and enthalpies of complex formation between unlike molecules

System (A + B)	K_{AB}	$-h_{AB}$ (kJ mol^{-1})	T (K)
1-Propanol + 2-propanol[a]	36.1	23.2	323.15
1-Propanol + 1,4-dioxane[b]	45.0	16.3	298.15
2-Propanol + 1,4-dioxane[c]	21.0	16.3	298.15

[a] [12,13].
[b] [5].
[c] [4].

Table 4
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})
1-Propanol + 2-propanol[a]	19	204.09	29.25	0.7856	0.0339	0.07
1-Propanol + 1,4-dioxane[b]	19	−60.01	594.88	−0.3380	−0.4143	6.80
2-Propanol + 1,4-dioxane[c]	19	−305.00	420.38	−1.7526	1.0451	11.80

[a] [12,13].
[b] [5].
[c] [4].

ture dependent and are fixed by means of the following van't Hoff's equation:

$$\frac{\delta \ln K}{\delta(1/T)} = -\frac{h}{R} \tag{5}$$

The enthalpies of hydrogen bond formation are assumed to be independent of temperature.

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

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

The chemical contribution term is related to the enthalpy of complex formation in the mixing [16]. The physical contribution term is derived by applying the Gibbs–Helmholtz relation to the residual term of the UNIQUAC equation [17]. The equilibrium association constants at 323.15 K and the enthalpies of hydrogen bond formation of alcohols A and B were taken from the refs. [18,19]. The structural parameters of complexes are expressed as the sum of parameters of each monomer. The monomer structural size and surface parameters r and q were calculated according to the Vera et al. method [20]. The cross-association constants and enthalpies of hydrogen bond formation for alcohols are available elsewhere [12,13]. The solvation constants and enthalpies of complex formation between alcohols and 1,4-dioxane were recently reported [4,5]. The values of the solvation constants summarized in Table 3 [4,5,12,13] are treated as adjustable parameters to give the best fit to the experimental data. The enthalpies of complex formation for all alcohols $h_A = h_B = h_{AB} = -23.2$ kJ mol is the same as the enthalpy of dilution of ethanol in n-hexane [19]. The enthalpies of complex formation for the (alcohols + l,4-dioxane) systems are estimated as −18.5 kJ mol. The estimation is made from the difference between the enthalpy of dilution of ethanol in n-hexane and those of ethanol in 1,4-dioxane. In fitting the association model to the binary experimental H_m^E values, the energy parameter a_{ji} in H^E_{phys} is assumed to be a linear function of temperature as expressed by

$$\frac{a_{ji}}{R} = C_{ji} + D_{ji}\left\{\left(\frac{T}{K}\right) - 273.15\right\} \tag{7}$$

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

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

The binary coefficients and the absolute arithmetic mean deviations $\langle|H_m^E|\rangle$ between the binary experimental and calculated values are inserted in Table 4. Fig. 1 shows a comparison of the experimental binary H_m^E with those calculated by the association model. The model with the association and solvation constants and binary parameters obtained solely from the corresponding binary correlation predicted the ternary excess molar enthalpies. The absolute arithmetic mean deviations between the experimental and calculated excess molar enthalpies were 10.8 J mol^{-1} for the (1-propanol + 2-propanol + 1,4-dioxane) system. Comparison between the ternary experimental H_m^E and predicted results obtained from the association model are shown in Fig. 3 for the system. The correlated and predicted values show a fair agreement with the experimental data.

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