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Excess molar enthalpies for 1-propanol + acetone and 1-propanol + acetone + benzene mixtures at 298.15 K

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Abstract

Excess molar enthalpies for the 1-propanol + acetone and 1-propanol + acetone + benzene systems have been obtained using a flow microcalorimeter. The experimental values have been correlated with polynomial equations and compared with the predicted results derived from an association model with mole-fraction-based equilibrium constants and binary parameters alone.

Keywords: Acetone; Benzene; Binary system; Excess molar enthalpy; Model; Propanol; Self-association; Ternary system

1. List of symbols

$A_{n,ij}$	parameter of Eq. (1) or (2)
a_{JI}	binary interaction parameter for J–I pair
B_n	parameter of Eq. (4)
C_{JI}, D_{JI}	parameters of Eq. (17)
G_{JI}	parameter as defined by $\exp(-\alpha_{JI}\tau_{JI})$
H^E	excess molar enthalpy
h_2	enthalpy of hydrogen bond formation of open dimer
h	enthalpy of hydrogen bond formation of open *i*mer

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h_{AB}, h_{AC}	enthalpies of formation of chemical complexes A_iB and A_iC
K_2^0	equilibrium constant of open dimer formation
K_3^0	equilibrium constant of open chain trimer formation
K^0	equilibrium constant of open chain *i*mer formation, $i \geq 3$
K_{cy}^0	equilibrium constant for cyclization of open chain *i*mer, $i > 4$
K_{AB}^0, K_{AC}^0	equilibrium constants of chemical complexes A_iB and A_iC, $i \geq 1$
R	universal gas constant
S	stoichiometric sum
s	standard deviation
T	absolute temperature
x_I	liquid phase mole fraction of component I
z	coefficient as defined by $K^0 x_{A_1}$

1.1. Greek letters

α_{JI}	non-randomness parameter of NRTL equation for $J-I$ pair
Δ_m	ternary contribution function as defined by Eq. (4)
θ	constant related to K_{cy}^0
τ_{JI}	binary parameter as defined by a_{JI}/T

1.2. Subscripts

A	1-propanol
A_1, A_i	1-propanol monomer and open *i*mer
A_iB, A_iC	complex formation between 1-propanol open *i*mer and component B or C
chem	chemical
I, *J*, *K*	components
phys	physical

1.3. Superscripts

E	excess
*	pure 1-propanol

2. Introduction

Previously, excess molar enthalpies H^E for the methanol or ethanol + acetone and methanol or ethanol + acetone + benzene systems have been reported from this laboratory [1, 2]. This paper presents experimental H^E values for 1-propanol + acetone and 1-propanol + acetone + benzene mixtures, measured with a flow microcalorimeter at 298.15 K. The experimental H^E values will be correlated with polynomial equations and compared with those predicted from an association model with mole-fraction-based equilibrium constants and binary information without ternary parameters. H^E results for the two binaries making up the ternary mixture at 298.15 K are available in the literature and can be used in data analysis, namely 1-propanol + benzene [3] and acetone + benzene [4].

3. Experimental

1-Propanol (Wako Pure Chemical Industries Ltd., guaranteed reagent grade) was used directly. Acetone (Wako Pure Chemical Industries Ltd., guaranteed reagent grade) was fractionally distilled in a vacuum after drying over fresh potassium carbonate. Benzene (Kanto Chemical Co., first grade) was purified by repeated recrystallization. The densities of the chemicals used for experimental work, measured with an Anton Paar densimeter (DMA40) at 298.15 K, agreed well with published values [5]. Experimental H^E results were measured with a flow microcalorimeter, the details and operation of which have been described previously [6].

4. Results and data analysis

The experimental H^E values for 1-propanol(1) + acetone(2) at 298.15 K and the deviations $\delta H^E = (H^E - H^E_{ij})$ calculated from Eq. (1) are listed in Table 1. The present H^E results are compared with published values in Fig. 1 [7, 8]

$$H^E_{ij} = x_i x_j \sum_{n=1}^{m} A_{n,ij}(x_i - x_j)^{n-1} \tag{1}$$

The H^E data of 1-propanol(1) + benzene(3) were correlated with Eq. (2)

$$H^E_{13} = \frac{10^4 x_1 x_3}{\sum_{n=1}^{m} A_{n,13}(x_1 - x_3)^{n-1}} \tag{2}$$

Table 1

Experimental excess molar enthalpies for 1-propanol(1) + acetone(2) at 298.15 K

x_1	H^E/J mol^{-1}	δH^E/J mol^{-1}	x_1	H^E/J mol^{-1}	δH^E/J mol^{-1}
0.0500	300.0	3.6	0.5500	1382.3	2.5
0.1000	544.3	−3.9	0.6000	1346.1	0.8
0.1500	755.2	−4.8	0.6500	1284.8	−1.1
0.2000	929.9	−6.0	0.7000	1198.2	−2.1
0.2500	1074.0	−5.3	0.7500	1083.0	−3.6
0.3000	1194.1	1.0	0.8000	938.1	−4.4
0.3500	1285.5	5.8	0.8500	763.3	−2.0
0.4000	1346.7	6.0	0.9000	551.2	−0.4
0.4500	1384.9	7.5	0.9500	299.5	1.7
0.5000	1395.3	4.9			

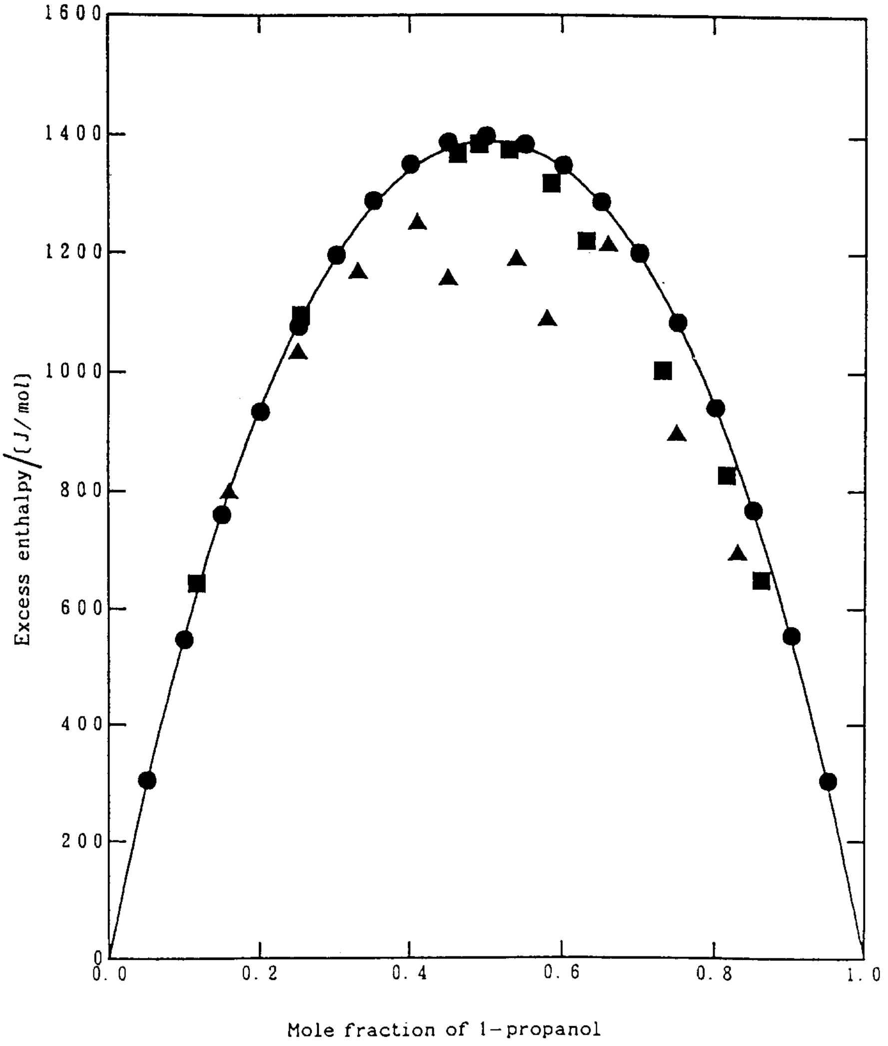

Fig. 1. Excess molar enthalpies for 1-propanol(1) + acetone(2) at 298.15 K. Experimental: ●, this work; ■, ref. 7; ▲, ref. 8; ——, calculated from Eq. (1)

and the H^E results of acetone(2) + benzene(3) were fitted to Eq. (1). Table 2 gives the parameters $A_{n,ij}$ of Eqs. (1) and (2).

The ternary experimental H^E values of 1-propanol(1) + acetone(2) + benzene(3) are shown in Table 3 and were fitted to Eq. (3)

$$H^E = H^E_{12} + H^E_{13} + H^E_{23} + x_1x_2x_3\Delta_m \tag{3}$$

where

$$\Delta_m/RT = B_0 - B_1x_1 - B_2x_2 - B_3x_1^2B - B_4x_2^2 - B_5x_1x_2 - B_6x_1^3 \tag{4}$$

Table 2
Binary parameters of Eqs. (1) and (2) and standard deviations

Mixture ($i+j$)	$A_{1,ij}$	$A_{2,ij}$	$A_{2,ij}$	$A_{4,ij}$	$A_{5,ij}$	$A_{6,ij}$	s
1-Propanol + acetone	5561.64	49.483	856.60	−40.970			4.6
1-Propanol + benzene	2.6287	1.5119	0.2274	0.5056	−0.1927	0.666	
Acetone + benzene	554.95	−46.97	171.91	23.93	23.23	−172.88	0.9

Table 3
Experimental ternary excess molar enthalpies for 1-propanol(1) + acetone(2) + benzene(3) mixtures at 298.15 K

x_1	x_2	H^E/J mol^{-1}	x_1	x_2	H^E/J mol^{-1}	x_1	x_2	H^E/J mol^{-1}
$x'_2=0.2497$ [a]			$x'_2=0.5002$ [a]			$x'_2=0.7510$ [a]		
0.0500	0.2373	492.5	0.0500	0.4747	455.8	0.0500	0.7135	411.2
0.1000	0.2248	727.2	0.1000	0.4498	686.3	0.1000	0.6789	646.3
0.1500	0.2123	885.1	0.1500	0.4248	869.0	0.1500	0.6384	836.8
0.2000	0.1998	992.2	0.2000	0.3998	1006.3	0.2000	0.6008	996.3
0.2500	0.1873	1061.3	0.2500	0.3748	1105.6	0.2500	0.5633	1118.3
0.3000	0.1748	1109.9	0.3000	0.3498	1176.6	0.3000	0.5257	1211.1
0.3500	0.1623	1130.8	0.3500	0.3248	1214.9	0.3500	0.4882	1274.1
0.4000	0.1498	1127.6	0.4000	0.2998	1231.8	0.4000	0.4506	1312.7
0.4500	0.1374	1107.1	0.4500	0.2748	1223.8	0.4500	0.4131	1330.3
0.5000	0.1249	1068.7	0.5000	0.2499	1216.1	0.5000	0.3755	1325.6
0.5500	0.1124	1027.3	0.5500	0.2249	1174.7	0.5500	0.3380	1298.2
0.6000	0.0999	957.3	0.6000	0.1999	1111.2	0.6000	0.3004	1242.4
0.6500	0.0874	878.5	0.6500	0.1749	1025.5	0.6500	0.2629	1170.7
0.7000	0.0749	783.0	0.7000	0.1499	939.8	0.7000	0.2253	1079.3
0.7500	0.0624	679.2	0.7500	0.1249	831.5	0.7500	0.1878	964.3
0.8000	0.0499	558.3	0.8000	0.0999	700.2	0.8000	0.1502	824.4
0.8500	0.0375	437.3	0.8500	0.0750	539.9	0.8500	0.1127	661.8
0.9000	0.0250	300.8	0.9000	0.0500	374.2	0.9000	0.0751	475.4
0.9500	0.0125	157.1	0.9500	0.0250	195.3	0.9500	0.0376	246.7

[a] Ternary mixtures were obtained by mixing pure methanol with [x'_2 acetone + $(1-x'_2)$benzene].

Equation (4) was used by Van Ness et al. [9, 10] in the correlation of ternary H^E values for acetone-chloroform-methanol and chloroform + ethanol + n-heptane, and they give five to seven significant figures for 10 coefficients (B_0–B_9 of Eq. (4)). The parameters of Eq. (4) were calculated by the method of unweighted least squares: $B_0=-6.5835$, $B_1=27.4180$, $B_2=8.0046$, $B_3=-43.1955$, $B_4=-5.0369$, $B_5=-14.9720$ and $B_6=24.4180$. The absolute mean deviation of the experimental values from calculated results is 6.9 J mol^{-1} and the standard deviation $s=9.3$. Figure 2 shows contours of the ternary H^E values calculated from Eqs. (3) and (4).

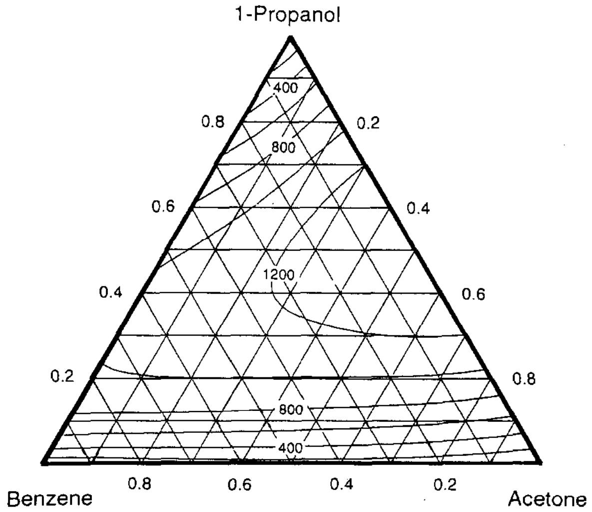

Fig. 2. Curves of constant excess molar enthalpies for 1-propanol(1) + acetone(2) + benzene(3) at 298.15 K; —, calculated from Eq. (3).

An association model [11] was used to reproduce the three sets of binary H^E results and then to predict the ternary H^E data. The model assumes that open alcohol chains of any length, as well as cyclic chains, exist in a ternary mixture of alcohol (A), acetone (B) and benzene (C), and that open polymeric species are formed between the terminal hydroxyl group of alcohol chains and active non-associating components (B or C). The four association constants and the enthalpies of hydrogen bond formation for alcohol open chains are K_2^0 and h_2 for $A_1 + A_1 = A_2$; K_3^0 and $(2h - h_2)$ for $A_2 + A_1 = A_3$; K^0 and h for $A_i = A_1 = A_{i+1}$, where $i \geq 3$; $K_{cy}^0 = \theta / i$ and h for A_i(open) $= A_i$(cyclic), where $i > 4$, θ being independent of i. The solvation constants and the enthalpies of complex formation between open chains (A_i) and one molecule of acetone (B) or benzene (C) are K_{AB}^0 and h_{AB} for A_i(open) $+ B_1 = A_iB$, where $i \geq 1$; K_{AC}^0 and h_{AC} for A_i(open) $+ C_1 = A_iC$, where $i \geq 1$. All the equilibrium constants are defined in terms of the mole fraction of chemical species present. The ternary H^E is expressed by the sum of the chemical and physical contribution terms

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

$$\begin{aligned} H_{\text{chem}}^E = {} & \{(1 + K_{AB}^0 x_{B_1} + K_{AC}^0 x_{C_1})[h_2 K_2^0 x_{A_1}^2 + h K_2^0 K_3^0 x_{A_1}^3 (2 - z)/(1 - z)^2] \\ & + h K_2^0 K_3^0 K^{02} \theta x_{A_1}^5 (1 - z) + (h_{AB} K_{AB}^0 x_{B_1} + h_{AC} K_{AC}^0 x_{C_1})[x_{A_1} + K_2^0 x_{A_1}^2 \\ & + K_2^0 K_3^0 x_{A_1}^3 / 1(1 - z)]\}/S - x_A [h_2 K_2^0 x_{A_1}^{*2} + h K_2^0 K_3^0 x_{A_1}^{*3} \\ & \times (2 - z^*)/(1 - z^*)^2 + h K_2^0 K_3^0 K^{02} \theta x_{A_1}^{*5} (1 - z^*)]/S^* \end{aligned} \tag{6}$$

where $z = K^0 x_{A_1}$ and S is the stoichiometric sum given by

$$S = (1 + K^0_{AB}x_{B_1} + K^0_{AC}x_{C_1})[x_{A_1} + 2K^0_2x^2_{A_1} + K^0_2K^0_3x^3_{A_1}(3-2z)/(1-z)^2] + K^0_2K^0_3K^{02}x^5_{A_1}/(1-z) + (K^0_{AB}x_{B_1} + K^0_{AC}x_{C_1})[x_{A_1} + K^0_2x^2_{A_1} + K^0_2K^0_3x^3_{A_1}/(1-z)] + x_{B_1} + x_{C_1} \quad (7)$$

The sum of the mole fractions of all chemical species is equal to unity

$$(1 + K^0_{AB}x_{B_1} + K^0_{AC}x_{C_1})[x_{A_1} + K^0_2x^2_{A_1} + K^0_2K^0_3x^3_{A_1}/(1-z)] - (K^0_2K^0_3\theta/K^{03})[\ln(1-z) + z + z^2/2 + z^3/3 + z^4/4] + x_{B_1} + x_{C_1} = 1 \quad (8)$$

The stoichiometric mole fractions of the components, x_A, x_B and x_C, are related to the monomeric mole fractions of the components, x_{A_1}, x_{B_1} and x_{C_1}, and the equilibrium constants

$$x_A = \{(1 + K^0_{AB}x_{B_1} + K^0_{AC}x_{C_1})[x_{A_1} + 2K^0_2x^2_{A_1} + K^0_2K^0_3x^3_{A_1}(3-2z)/(1-z)^2] + K^0_2K^0_3K^{02}x^5_{A_1}/(1-z)\}/S \quad (9)$$

$$x_B = \{x_{B_1} + K^0_{AB}x_{B_1}[x_{A_1} + K^0_2x^2_{A_1} + K^0_2K^0_3x^3_{A_1}/(1-z)]\}/S \quad (10)$$

$$x_C = \{x_{C_1} + K^0_{AC}x_{C_1}[x_{A_1} + K^0_2x^2_{A_1} + K^0_2K^0_3x^3_{A_1}/(1-z)]\}/S \quad (11)$$

The values of x_{A_1}, x_{B_1} and x_{C_1} can be solved simultaneously from Eqs. (9)–(11). At pure alcohol state, $z^* = K^0x^*_{A_1}$, $x^*_{A_1}$ and S^* are obtained from Eqs. (12) and (13)

$$x^*_{A_1} + K^0_2x^{*2}_{A_1} + K^0_2K^0_3x^{*3}_{A_1}/(1-z^*) - (K^0_2K^0_3\theta/K^{03})[\ln(1-z^*) + z^* + z^{*2}/2 + z^{*3}/3 + z^{*4}/4] = 1 \quad (12)$$

$$S^* = x^*_{A_1} + 2K^0_2x^{*2}_{A_1} + K^0_2K^0_3x^{*3}_{A_1}(3-2z^*)/(1-z^*)^2 + K^0_2K^0_3K^{02}\theta x^{*5}_{A_1}/(1-z^*) \quad (13)$$

Thus physical contribution term is given by application of the Gibbs–Helmholtz equation to the NRTL equation for the excess Gibbs free energy [12]

$$H^E_{\text{phys}} = R\sum_I x_I \left[\frac{\sum_J x_J \dfrac{\partial(\tau_{JI}G_{JI})}{\partial(1/T)}}{\sum_K G_{KI}x_K} - \frac{\sum_J \tau_{JI}G_{JI}x_J \sum_K \dfrac{\partial G_{KI}}{\partial(1/T)}}{(\sum_K G_{KI}x_K)^2}\right] \quad (14)$$

where τ_{JI} and G_{JI} are defined by

$$\tau_{JI} = a_{JI}/T \quad (15)$$

$$G_{JI} = \exp(-\alpha_{JI}\tau_{JI}) \quad (16)$$

and the non-randomness parameter α_{JI} is set as 0.3 for all binary mixtures. The energy parameters a_{JI} are assumed to be linearly temperature-dependent

$$a_{JI} = C_{JI} + D_{JI}(T - 273.15) \quad (17)$$

The parameters C_{JI} and D_{JI} were determined using a simplex method [13].

Table 4
Binary calculated results based on the association model

Mixture (A + B)	C_{BA}/K	C_{AB}/K	D_{BA}	D_{AB}	Abs. arith. mean dev./J mol^{-1}
1-Propanol + acetone	1169.62	−295.35	−4.5201	−1.7821	16.7
1-Propanol + benzene	−1135.43	594.67	−3.8897	2.0141	7.9
Acetone + benzene	553.16	513.11	1.7149	1.6470	1.0

The association parameters are $K_2^0 = 35$, $K_3^0 = 90$, $K^0 = 40$ and $\theta = 75$ at 298.15 K, and $h_2 = -21.2$ kJ mol^{-1} and $h = -23.5$ kJ mol^{-1}. The solvation parameters are $K_{AB}^0 = 22$ at 298.15 K, $h_{AB} = -21.0$ kJ mol^{-1}, $K_{AB}^0 = 3.2$ at 298.15 K and $h_{AC} = -8.2$ kJ mol^{-1}. Table 4 gives the binary calculated results based on the association model. The ternary H^E predictions were performed using only binary information: the absolute arithmetic mean deviation between the experimental and calculated values for 57 data points is 14.8 J mol^{-1} and the root-mean squared deviation is 18.5 J mol^{-1}, indicating that agreement is good [11].

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