ciety of Mechanical Engineers: New York, 1981; Vol. II, p 298.
(10) Haar, L.; Gallagher, J. S.; Kell, G. S. *Proceedings of the 9th International Conference on the Properties of Steam*; Straub, J., Scheffler, K., Eds.; Pergamon: Oxford, 1980; p 89.
(11) Pitzer, K. S. *J. Solution Chem.* **1975**, *4*, 249.
(12) Pitzer, K. S. *J. Phys. Chem.* **1983**, *87*, 2360.
(13) Patterson, C. S.; Slocum, G. H.; Busey, R. H.; Mesmer, R. E. *Geochim. Cosmochim. Acta* **1982**, *46*, 1653.
(14) Patterson, C. S.; Busey, R. H.; Mesmer, R. E. *J. Solution Chem.* **1984**, *13*, 647.
(15) Holmes, H. F.; Mesmer, R. E. *J. Phys. Chem.* **1983**, *87*, 1242.
(16) Pitzer, K. S.; Mayorga, G. *J. Phys. Chem.* **1973**, *77*, 2300.

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Excess Molar Enthalpies for the 1-Butanol–Benzene–Cyclohexane System at 25 °C

Kazuhiro Tamura and Isamu Nagata*
Department of Chemical Engineering, Kanazawa University, Kanazawa 920, Japan

Excess molar enthalpies at 25 °C were measured for 1-butanol–benzene–cyclohexane by use of an isothermal dilution calorimeter. The experimental results were well correlated with the UNIQUAC associated-solution model, which includes the dimerization constant and the constant for formation of higher polymers for the alcohol, and one solvation constant between the alcohol and benzene and binary interaction parameters.

Introduction

Studies on the thermodynamic properties of 1-butanol mixtures are in progress in this laboratory. This work reports excess molar enthalpies for 1-butanol–benzene–cyclohexane at 25 °C, measured by using an isothermal dilution calorimeter. Excess molar enthalpies for all the binary systems constituting the ternary system have been already published: 1-butanol–benzene (*1*); 1-butanol–cyclohexane (*2*); benzene–cyclohexane (*3*). The experimental values are compared with those calculated from the UNIQUAC associated-solution model (*4*).

Experimental Section

Analytical grade 1-butanol and cyclohexane of specified purity 99.8 mol %, purchased from Wako Pure Chemical Industries Ltd., were used directly. C.P. benzene was recrystallized three times. Gas chromatographic analysis did not detect any appreciable impurities in the reagents used. Densities of these compounds, measured with an Anton Paar DMA40 densimeter, were in close agreement with literature values (*4*).

The isothermal dilution calorimeter used for excess enthalpy measurements at 25 °C was the same as described previously (*3*). The uncertainty in the obtained excess enthalpies is ±0.5%. Three experimental runs were carried out for ternary mixtures formed by adding 1-butanol to a binary mixture of benzene and cyclohexane. A ternary mixture may be considered as a pseudobinary mixture composed of 1-butanol (component 1) and one binary mixture.

Value of H^E_{123} for one mole of the ternary mixture of composition x_1, x_2, and x_3 can be given as

$$H^E_{123} = \Delta H_m + (1 - x_1)H^E_{23} \tag{1}$$

where ΔH_m is the measured molar enthalpy for the pseudobinary mixture and H^E_{23} is the molar enthalpy for the initial binary benzene (2)–cyclohexane (3) mixture. Values of H^E_{23} at three specified compositions were interpolated by use of a spline-fit method.

Table I gives experimental excess molar enthalpies for 1-butanol (1)–benzene (2)–cyclohexane (3). The measured results were correlated by

$$H^E_{123} = H^E_{12} + H^E_{13} + H^E_{23} + x_1x_2x_3\Delta_{123} \tag{2}$$

where Δ_{123} is expressed by

$$\frac{\Delta_{123}}{RT} = \frac{\sum_{i=1}^{5} b_i(1 - 2x_1)^{i-1}}{1 - k(1 - 2x_1)} \tag{3}$$

Smoothing equations for the binary excess enthalpy data are shown in Table II. The smoothing equations for 1-butanol–benzene and benzene–cyclohexane were taken from the literature (*1*, *3*). We did not use the smoothing equation described by Veselý and Pick (*2*), because their equation was not suited for correlating the ternary experimental data. An unweighted least-squares method provided the values of coefficients of eq 3 and the standard deviation σ: $b_1 = 1.3915$, $b_2 = 0.7319$, $b_3 = -1.8773$, $b_4 = -1.3453$, $b_5 = 3.4113$, $k = 0.9182$, and $\sigma = 10.5$ J mol^{-1}. Figure 1 shows lines of constant ternary excess molar enthalpies calculated from eq 2 and 3.

Data Analysis by means of the UNIQUAC Associated-Solution Model

The UNIQUAC associated-solution model (*5*) assumes that only the alcohol dimerization constant ($A_1 + A_1 = A_2$) is different and the other constants ($A_i + A_1 = A_{i+1}$, $i > 1$) are equal and the alcohol forms complexes with benzene ($A_i + B = A_iB$). The model gives ternary excess molar enthalpy for 1-butanol (A)–benzene (B)–cyclohexane (C) by

$$H^E_{123} = \frac{h_A x_A K_2 \Phi_{A_1}{}^2}{\Phi_A(1 - K_A\Phi_{A_1})^2}[1 + K_{AB}r_A\Phi_{B_1}] + \frac{h_{AB}x_AK_{AB}r_A\Phi_{A_1}\Phi_{B_1}}{\Phi_A}\left[1 + \frac{K_2\Phi_{A_1}}{(1 - K_A\Phi_{A_1})}\right] - \frac{h_Ax_AK_2\Phi^0{}_{A_1}{}^2}{(1 - K_A\Phi^0{}_{A_1})^2} - R\sum_I q_Ix_I\frac{\sum_J \theta_J \dfrac{\partial\tau_{JI}}{\partial(1/T)}}{\sum_J \theta_J\tau_{JI}} \tag{4}$$

Table I. Experimental Ternary Excess Molar Enthalpies for the 1-Butanol (1)-Benzene (2)-Cyclohexane (3) System at 25 °C[a]

x_1	x_2	H^E_{123}, J mol^{-1}	ΔH_m, J mol^{-1}
	$x_2' = 0.2501$, $H^E_{23} = 589.2$ J mol^{-1}		
0.0278	0.2431	861.1	288.3
0.0864	0.2285	995.5	457.3
0.1548	0.2114	1055.4	557.5
0.2453	0.1887	1069.3	624.7
0.3437	0.1641	1023.9	637.2
0.4296	0.1426	942.4	606.4
0.4935	0.1267	859.9	561.5
0.5448	0.1148	785.2	517.0
0.5867	0.1035	718.9	475.4
0.6502	0.0876	613.6	407.5
0.6968	0.0760	532.9	354.3
0.7336	0.0668	468.5	311.5
0.7556	0.0612	429.8	285.8
0.7779	0.0557	390.7	259.8
	$x_2' = 0.4996$, $H^E_{23} = 798.8$ J mol^{-1}		
0.0272	0.4860	1087.2	310.0
0.0976	0.4508	1270.0	549.1
0.1033	0.4030	1325.7	681.2
0.2947	0.3524	1287.6	724.1
0.3899	0.3048	1190.4	703.1
0.4574	0.2711	1092.4	658.9
0.5010	0.2493	1017.7	619.1
0.5396	0.2300	946.9	579.1
0.5711	0.2142	878.8	536.3
0.6327	0.1835	753.0	459.6
0.7015	0.1491	612.1	373.6
0.7317	0.1340	549.9	335.6
0.7569	0.1215	498.2	303.9
0.7793	0.1102	452.0	275.7
	$x_2' = 0.7488$, $H^E_{23} = 624.1$ J mol^{-1}		
0.0147	0.7377	827.6	212.7
0.0440	0.7160	1041.6	445.0
0.1021	0.6723	1221.7	661.4
0.1928	0.6044	1332.7	819.0
0.3032	0.5217	1319.0	884.2
0.3821	0.4627	1263.4	877.8
0.4486	0.4129	1178.3	834.1
0.4952	0.3780	1103.5	788.4
0.5308	0.3513	1037.3	744.4
0.5624	0.3277	964.9	691.8
0.6242	0.2814	830.0	595.4
0.6702	0.2470	729.0	523.2
0.7073	0.2192	647.2	464.5
0.7362	0.1975	583.3	418.6
0.7628	0.1776	524.4	376.4

[a] Ternary mixtures were prepared by mixing pure 1-butanol with $[(x_2')\text{benzene} + (1 - x_2')\text{cyclohexane}]$.

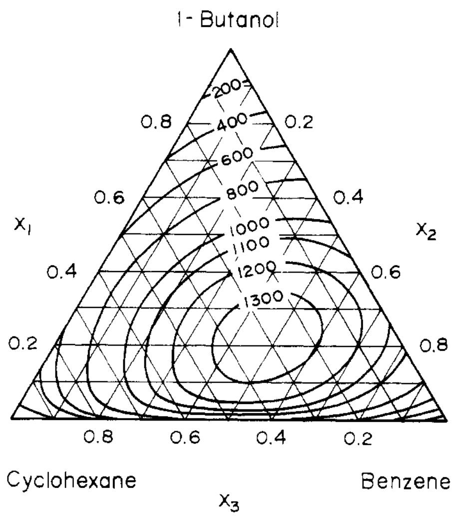

Figure 1. Curves of constant excess molar enthalpies at 25 °C.

Table II. Smoothing Equations for Three Binary Mixtures at 25 °C

mixture	H^E_{calcd}, J mol^{-1}	σ, J mol^{-1}	data source
1-butanol (1)–benzene (2)	$\dfrac{10^4 x_1 x_2}{2.3998 - 1.3476(x_2 - x_1) + 0.2829(x_2 - x_1)^2 - 0.4224(x_2 - x_1)^3 - 0.2194(x_2 - x_1)^4 - 0.1379(x_2 - x_1)^5}$		*1*
1-butanol (1)–cyclohexene (2)	$\dfrac{x_1 x_2[2357.93 - 1072.46(x_2 - x_1) - 648.65(x_2 - x_1)^2 - 234.55(x_2 - x_1)^3 + 217.09(x_2 - x_1)^4]^a}{1 - 0.9787(x_2 - x_1)}$	2.4	2
benzene (1)–cyclohexane (2)	$x_1 x_2[3200.34 - 162.91(x_2 - x_1) + 102.42(x_2 - x_1)^2 - 58.04(x_2 - x_1)^3]$	0.8	3

[a] The coefficients of the H^E equation for 1-butanol–cyclohexane were obtained by use of the method of least-squares and this equation is not identical with that given by Veselý and Pick (*2*).

Table III. Calculated Results for Three Binary Mixtures at 25 °C

mixture	no. of data points	abs arith mean dev, J mol^{-1}	parameters			
			C_A, K	C_B, K	D_A	D_B
1-butanol (A)–benzene (B)	10	6.8	-39.72	-34.21	0.7955	-1.4191
1-butanol (A)–cyclohexane (B)	26	6.3	52.43	-113.43	0.2791	-0.6381
benzene (A)–cyclohexane (B)	24	1.1	129.03	65.35	0.0963	-0.1206

where segment fraction Φ, surface fraction θ, and binary parameter τ are given by

$$\Phi_I = r_I x_I / \sum_J r_J x_J \tag{5}$$

$$\theta_I = q_I x_I / \sum_J q_J x_J \tag{6}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{7}$$

a_{JI} is assumed to be temperature-dependent linearly.

$$a_{JI} = C_I + D_I(T - 273.15) \tag{8}$$

The monomer segment fractions, Φ_{A_1} and Φ_{B_1}, are simultaneously obtained from eq 9 and 10 by using subroutine NOLBR built in a FACOM M-170F computer.

$$\Phi_A = \left[\Phi_{A_1} + \frac{K_2 \Phi_{A_1}{}^2 (2 - K_A \Phi_{A_1})}{(1 - K_A \Phi_{A_1})^2} \right] [1 + K_{AB} r_A \Phi_{B_1}] \tag{9}$$

$$\Phi_B = \Phi_{B_1} \left\{ 1 + K_{AB} r_B \Phi_{A_1} \left[1 + \frac{K_2 \Phi_{A_1}}{(1 - K_A \Phi_{A_1})} \right] \right\} \tag{10}$$

$\Phi^0{}_{A_1}$ is calculated from eq 11.

$$\Phi^0{}_{A_1} + \frac{K_2 \Phi^0{}_{A_1}{}^2 (2 - K_A \Phi^0{}_{A_1})}{(1 - K_A \Phi^0{}_{A_1})^2} = 1 \tag{11}$$

The values of K_2 and K_A for 1-butanol were taken from the previous paper (*5*): $K_2 = 29.4$ and $K_A = 72.0$ at 50 °C. We used $h_A = -23.2$ kJ mol^{-1}, which is the enthalpy of dilution of ethanol in *n*-hexane at 25 °C (*6*). This value fixes the temperature dependence of the association constants by the van't Hoff relation. The solvation constant and enthalpy of complex formation for 1-butanol–benzene were obtained from Nagata (*7*): $K_{AB} = 2.5$ at 50 °C and $h_{AB} = -8.3$ kJ mol^{-1}. Pure-component structural constants, r and q, were estimated in accordance with the method of Vera et al. (*8*): for 1-butanol, $r = 2.77$ and $q = 2.42$; for benzene, $r = 2.56$ and $q = 2.05$; for cyclohexane, $r = 3.18$ and $q = 2.55$. Table III lists the results of fitting the UNIQUAC associated-solution model to the binary excess molar enthalpies for three mixtures. The absolute arithmetic-mean deviation between the experimental and calculated values is 14.2 J mol^{-1} and the absolute relative mean deviation is 1.6 % for 43 data points. Agreement is considered to be good.

Glossary

A, B, C	1-butanol, benzene, and cyclohexane
a_{JI}	binary interaction parameter
b_i	coefficient of eq 3
C_I, D_I	coefficients of eq 8
H^E_{123}	excess molar enthalpy for ternary mixture
H^E_{IJ}	excess molar enthalpy for binary I–J mixture
ΔH_m	excess molar enthalpy for pseudobinary mixture composed of 1-butanol and binary benzene–cyclohexane mixture
h_A	enthalpy of formation of 1 mol of hydrogen bond
h_{AB}	enthalpy of complex formation between alcohol and aromatic hydrocarbon
K_2	association constant for dimer $(\Phi_{A_2}/2\Phi_{A_1}{}^2)$
K_A	association constant for *i*-mer $(\Phi_{A_{i+1}}/\Phi_{A_i}\Phi_{A_1})[i/(i + 1)]$
K_{AB}	solvation constant $(\Phi_{A_iB}/\Phi_{A_i}\Phi_{B_1})[i/(ir_A + r_B)]$
k	coefficient of eq 3
q	pure-component area parameter
R	universal gas constant
r	pure-component volume parameter
T	absolute temperature
x	liquid-phase mole fraction

Greek Letters

Δ_{123}	function defined by eq 3
θ_I	area fraction of component I
σ	standard deviation
τ_{IJ}	$\exp(-a_{IJ}/T)$
Φ_{A_1}	segment fraction of alcohol monomer in mixture
$\Phi^0{}_{A_1}$	segment fraction of alcohol monomer in pure alcohol solution
Φ_{B_1}	segment fraction of benzene monomer
Φ_I	segment fraction of component I

Registry No. 1-BuOH, 71-36-3; C_6H_6, 71-43-2; C_6H_{12}, 110-82-7.

Literature Cited

(1) Mrazek, R. V.; Van Ness, H. C. *AIChE J.* **1961**, *7*, 190–5.
(2) Veselý, F.; Pick, J. *Int. Data Ser. Ser. A* **1983**, 169–70.
(3) Nagata, I.; Kazuma, K. *J. Chem. Eng. Data* **1977**, *22*, 79–84.
(4) Riddick, J.; Bunger, W. B. *Organic Solvents*, 3rd ed.; Wiley-Interscience: New York, 1970; pp 77, 107, 151.
(5) Nagata, I.; Inaguma, K. *Thermochim. Acta* **1986**, *97*, 51–60.
(6) Stokes, R. H.; Burfitt, C. *J. Chem. Thermodyn.* **1973**, *5*, 623–31.
(7) Nagata, I. *Fluid Phase Equilib.* **1985**, *19*, 153–74.
(8) Vera, J. H.; Sayegh, S. G.; Ratcliff, G. A. *Fluid Phase Equilib.* **1977**, *1*, 113–35.

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