(10) Whitfield, M. *Geochim. Cosmochim. Acta* **1975**, *39*, 1545.
(11) Kelly, B.; Frederick, W. J. Jr. *Application of Chemical Engineering Principles in the Forest Products and Related Industries*; Kayihan, F., Krieger-Brackett, B., Eds.; AIChE Forest Products Division: Seattle, WA, 1986.
(12) Friedman, H. L. *Ionic Solution Theory*; Interscience: New York, 1962.
(13) Pitzer, K. S. *J. Solution Chem.* **1975**, *4*, 249.
(14) *IMSL Library Subroutine DMLIN*, 9th ed.; IMSL: Houston, TX June, 1982.
(15) Kim, H. T.; Frederick, W. J. Jr. *J. Chem. Eng. Data*, **1988**, *33*, 177.
(16) Harmer, W. J.; Wu, Y. C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047.
(17) Wu, Y. C.; Harmer, W. J. *J. Phys. Chem. Ref. Data* **1980**, *9*, 513.
(18) Goldberg, R. N.; *J. Phys. Chem. Ref. Data* **1981**, *10*, 671.
(19) Peiper, J. C.; Pitzer, K. S. *J. Chem. Thermodyn.* **1982**, *14*, 613.
(20) Goldberg, R. N.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1978**, *7*, 263.
(21) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959.
(22) Goldberg, R. N.; Nuttall, R. L.; Staples, B. R. *J. Phys. Chem. Ref. Data* **1979**, *8*, 923.
(23) Goldberg, R. N. *J. Phys. Chem. Ref. Data* **1979**, *8*, 1005.
(24) Libus, Z.; Sadowaska, T. *J. Chem. Thermodyn.* **1979**, *11*, 1151.
(25) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*, 3rd ed.; Reinhold: New York, 1958.
(26) Rush, R. M.; Johnson, J. S. *J. Phys. Chem.* **1968**, *72*, 767.
(27) Sankar, M.; Macaskill, J. B.; Bates, R. G. *J. Solution Chem.* **1981**, *10*, 169.
(28) Huston, R.; Butler, J. N. *Anal. Chem.* **1969**, *41*, 1695.
(29) Childs, C. W.; Downes, C. J.; Platford, R. F. *J. Solution Chem.* **1974**, *3*, 139.
(30) Robinson, R. A.; Wood, R. H.; Reilly, P. J. *J. Chem. Thermodyn.* **1971**, *3*, 461.
(31) Butler, J. N.; Huston, R. *Anal. Chem.* **1970**, *42*, 1308.
(32) Butler, J. N.; Huston, R. *J. Phys. Chem.* **1970**, *74*, 2976.
(33) Khoo, K. H.; Lim, T. K.; Chan, C. Y. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2037.
(34) Khoo, K. H.; Lim, T. K.; Chan, C. Y. *J. Solution Chem.* **1978**, *7*, 291.
(35) Khoo, K. H.; Chan, C.Y.; Lim, T. K. *J. Chem Soc., Faraday Trans. 1* **1978**, *74*, 837.
(36) Khoo, K. H.; Lim, T. K.; Chan, C. Y. *J. Solution Chem.* **1979**, *8*, 227.
(37) Roy, R. N.; Gibbons, J. J.; Owens, L. K.; Bliss, G. A.; Hartley, J. J. *J. Chem. Soc., Faraday Trans. 1* **1981**, *78*, 1405.
(38) Khoo, K. H.; Lim, T. K.; Chan, C. Y. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1067.
(39) Roy, R. N.; Gibbons, J. J.; Trower, J. K.; Lee, G. A. *J. Solution Chem.* **1980**, *9*, 535.
(40) Roy, R. N.; Gibbons, J. J.; Bliss, D. P. Jr.; Casebolt, R. G.; Baker, B. K. *J. Solution Chem.* **1980**, *9*, 911.
(41) Harned, H. S.; Paxton, T. R. *J. Phys. Chem.* **1953**, *57*, 531.
(42) Lim, T. K.; Khoo, K. H.; Chan, C. Y. *J. Solution Chem.* **1980**, *9*, 785.
(43) Rush, R. M.; Johnson, J. S. *J. Chem. Thermodyn.* **1971**, *3*, 779.
(44) Downes, C. J. *J. Chem Thermodyn.* **1974**, *6*, 317.
(45) Lindenbaum, S.; Rush, R. M.; Robinson, R. A. *J. Chem. Thermodyn.* **1972**, *4*, 381.
(46) Downes, C. J. *J. Chem. Eng. Data* **1975**, *18*, 412.
(47) Downes, C. J. *J Solution Chem.* **1975**, *4*, 191.
(48) Platford, R. F. *J. Chem Thermodyn.* **1971**, *3*, 319.
(49) Wu, Y. C.; Rush, R. M.; Scatchard, G. *J. Phys. Chem.* **1968**, *72*, 4048.
(50) Downes, C. J.; Pitzer, K. S. *J. Solution Chem.* **1976**, *5*, 389.
(51) White, D. R. Jr.; Bates, R. G. *Aust. J. Chem.* **1980**, *33*, 1903.
(52) Boyd, G. E. *J. Chem. Thermodyn.* **1978**, *10*, 415.
(53) Khoo, K. H. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1.
(54) Hintze, J. L. *Number Cruncher Statistical System (4.21)*; Number Cruncher Statistical Systems: Kaysville, UT, 1986.
(55) Khoo, K. H.; Chan, C. Y.; Lim, T. K. *J. Solution Chem.* **1977**, *6*, 651.
(56) Robinson, R. A.; Roy, R. N.; Bates, R. G. *J. Solution Chem.* **1974**, *3*, 837.

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

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Excess molar enthalpies at 25 °C for methanol–1-butanol–benzene were measured with an isothermal dilution calorimeter. The experimental results agree well with those calculated from the UNIQUAC associated-solution model with two association constants for alcohols, three solvation constants for complex formation, and binary interaction parameters.

Introduction

Ternary excess molar enthalpies of 23 systems containing two aliphatic alcohols and one saturated hydrocarbon have been collected; however, those of systems of two alcohols with one unsaturated hydrocarbon are not filed in the compilation of Christensen et al. (*1*) and experimental results on only such two systems involving benzene at 25 °C have been reported from this laboratory: for ethanol–1-propanol–benzene (*2*) and for methanol–2-butanol–benzene (*3*). As part of a program to provide excess molar enthalpies on ternary systems formed by two alcohols and one unsaturated hydrocarbon, this paper reports the experimental results of the methanol–1-butanol–benzene system at 25 °C. The experimental results are compared with those calculated from the UNIQUAC associated-solution model (*2*). Excess molar enthalpies at 25 °C for the three binary systems forming the ternary system are available from the literature: methanol–1-butanol (*4*); methanol–benzene (*5*); 1-butanol–benzene (*5*).

Experimental Section

Analytical grade 1-butanol of specific purity 99.8 mol %, purchased from Wako Pure Chemical Industries Ltd., was directly used. C.P. methanol, treated with anhydrous copper sulfate, was distilled in a 1-m glass column packed with McMahon packing. C.P. benzene was purified by recrystallization three times. Densities of three chemicals at 25 °C, measured with an Anton Paar DMA40 densimeter, agreed excellently with the literature values (*6*). The isothermal dilution calorimeter as described by Nagata and Kazuma (*7*) was used to obtain ternary excess molar enthalpies. The experimental error involved in observed values was ±0.5% over the mole fraction range studied. Each experimental run was performed by adding benzene to a binary mixture of methanol and 1-butanol. A ternary mixture is regarded as a pseudobinary system made up of one binary mixture and benzene. One mole of the ternary mixture is prepared by mixing $(1 - x_3)$ of the initial binary mixture and x_3 of component 3. The ternary excess molar enthalpy H^E_{123} at x_1, x_2, and x_3 can be given as

$$H^E_{123} = \Delta H_m + (1 - x_3)H^E_{12} \qquad (1)$$

where ΔH_m is the observed molar excess enthalpy for the

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

x_1	x_2	H^E_{123}, J·mol^{-1}	ΔH^E_m, J·mol^{-1}	x_1	x_2	H^E_{123}, J·mol^{-1}	ΔH^E_m, J·mol^{-1}
$x_1' = 0.2504$, $H^E_{12} = 87.1$ J·mol^{-1}							
0.2476	0.7412	106.8	20.6	0.0962	0.2879	999.3	965.8
0.2380	0.7127	175.6	92.7	0.0854	0.2557	1007.8	978.1
0.2232	0.6683	284.4	206.8	0.0774	0.2319	1005.6	978.7
0.2023	0.6055	441.7	371.3	0.0748	0.2238	1003.1	977.1
0.1798	0.5383	604.4	541.8	0.0739	0.2211	1001.3	975.6
0.1618	0.4845	724.9	668.5	0.0698	0.2088	995.1	970.8
0.1461	0.4375	818.2	767.3	0.0644	0.1929	982.4	960.0
0.1398	0.4185	851.8	803.1	0.0583	0.1747	963.2	942.9
0.1354	0.4053	873.7	826.6	0.0513	0.1536	933.0	915.1
0.1316	0.3941	890.9	845.1	0.0467	0.1397	908.4	892.1
0.1211	0.3624	934.4	892.3	0.0421	0.1260	879.3	864.7
0.1069	0.3199	978.1	940.9	0.0404	0.1211	867.9	853.8
$x_1' = 0.4994$, $H^E_{12} = 142.3$ J·mol^{-1}							
0.4936	0.4949	157.6	16.9	0.2177	0.2183	864.4	802.3
0.4574	0.4767	208.6	73.1	0.1971	0.1976	886.5	830.3
0.4479	0.4490	288.4	160.7	0.1792	0.1797	898.2	847.1
0.4164	0.4175	382.0	263.3	0.1716	0.1720	901.2	852.3
0.3820	0.3829	485.9	377.0	0.1702	0.1706	900.2	851.7
0.3504	0.3513	578.1	478.2	0.1570	0.1574	900.7	856.0
0.3255	0.3263	646.7	554.0	0.1399	0.1403	894.3	854.5
0.3032	0.3039	704.5	618.0	0.1221	0.1224	878.6	843.8
0.3021	0.3029	706.2	620.1	0.1069	0.1071	856.4	825.9
0.2889	0.2896	736.5	654.2	0.0966	0.0968	836.1	808.5
0.2667	0.2674	783.4	707.4	0.0902	0.0905	820.9	795.2
0.2427	0.2433	828.3	759.1				
$x_1' = 0.7501$, $H^E_{12} = 134.2$ J·mol^{-1}							
0.7372	0.2456	154.6	22.7	0.3635	0.1211	730.0	664.9
0.7142	0.2379	191.3	63.5	0.3286	0.1094	761.9	703.1
0.6781	0.2258	251.0	129.7	0.3163	0.1053	768.9	712.3
0.6342	0.2112	326.5	213.0	0.3000	0.0999	779.5	725.8
0.5886	0.1960	404.3	299.0	0.2993	0.0997	782.2	728.7
0.5464	0.1820	475.3	377.5	0.2816	0.0938	789.2	738.8
0.5108	0.1701	533.2	441.8	0.2564	0.0854	798.8	752.9
0.4847	0.1614	574.2	487.5	0.2315	0.0771	803.1	761.7
0.4956	0.1651	556.7	468.0	0.2063	0.0687	800.7	763.8
0.4723	0.1573	591.4	506.9	0.1891	0.0630	795.7	761.8
0.4389	0.1462	640.0	561.5	0.1859	0.0619	793.8	760.6
0.4011	0.1336	688.5	616.7				

[a] Ternary mixtures were prepared by mixing pure benzene with [x_1'methanol + $(1 - x_1')$1-butanol].

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

system	H^E_{calcd}, J·mol^{-1}	AAD, J·mol^{-1}	σ, J·mol^{-1}	ref
methanol (1)–1-butanol (2)	$x_1x_2[569.66 - 246.36(x_2 - x_1) + 79.06(x_2 - x_1)^2 - 35.52(x_2 - x_1)^3 + 17.11(x_2 - x_1)^4]$	0.2	0.3	*2*
methanol (1)–benzene (3)	$10^4x_1x_2/[4.0084 - 2.4775(x_3 - x_1) - 0.2986(x_3 - x_1)^2 - 0.4673(x_3 - x_1)^3 - 0.0729(x_3 - x_1)^4 - 0.0560(x_3 - x_1)^5]$	1.1	2.4	*3*
1-butanol (2)–benzene (3)	$10^4x_2x_3/[2.3998 - 1.3476\ (x_3 - x_2) + 0.2829(x_3 - x_2)^2 - 0.4224(x_3 - x_2)^3 - 0.2194(x_3 - x_2)^4 - 0.1379(x_3 - x_2)^5]$	2.9	6.8	*3*

pseudobinary mixture and H^E_{12} is the binary excess molar enthalpy of the methanol (1)–1-butanol (2) system. Values of H^E_{12} at three concentrations were interpolated by using a spline-fit method. Equation 1 does not involve any approximation (*8*).

Table I lists the ternary excess molar enthalpies H^E_{123} of the methanol (1)–1-butanol (2)–benzene (3) system at 25 °C. The values of H^E_{123} were adequately correlated by

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

where

$$\Delta_{123}/RT = \sum_{i=1}^{6} b_i(1 - 2x_3)^{i-1} \tag{3}$$

Equation 2 was used by Van Ness and his co-workers (*9*, *10*) in correlating their ternary excess molar enthalpy results. Equation 3 is different from that suggested by Van Ness and his co-workers and was used in our previous papers (*2*, *3*). Table II gives expressions for H^E_{12}, H^E_{13}, and H^E_{23} taken from the literature (*4*, *5*). The coefficients of eq 3 together with the absolute arithmetic mean deviation AAD and standard deviation σ were obtained from an unweighted least-squares method: $b_1 = -2.6201$, $b_2 = 2.2693$, $b_3 = -1.2294$, $b_4 = 5.4605$, $b_5 = -14.1932$, $b_6 = 8.9962$, AAD = 3.0 J·mol^{-1}, and $\sigma = 3.9$ J·mol^{-1}. Figure 1 shows lines of constant ternary excess molar enthalpies calculated by use of eq 2 and 3.

Data Analysis

The UNIQUAC associated-solution model (*11*–*14*) is based on the UNIQUAC model of Abrams and Prausnitz (*15*). The UNIQUAC associated-solution model works much better than the original UNIQUAC model in the correlation of binary vapor–liquid equilibrium and excess enthalpy data and the prediction of ternary vapor–liquid, liquid–liquid equilibrium, and excess molar enthalpy data from binary data for mixtures containing one alcohol. The UNIQUAC associated-solution model

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

system	K_{AB}(50 °C)	$-h_{AB}$, kJ·mol^{-1}	no. of data points	ADD, J·mol^{-1}	σ, J·mol^{-1}	parameters			
						C_{BA}, K	C_{AB}, K	D_{BA}	D_{AB}
methanol (A)–1-butanol (B)	85	23.2	19	1.1	2.4	130.99	117.28	0.1551	0.4395
methanol (A)–benzene (B)	4	8.3	10	1.7	2.6	1260.71	−190.34	2.1743	−0.3827
1-butanol (A)–benzene (B)	2.5	8.3	10	9.3	13.2	618.02	361.31	1.6777	1.3346

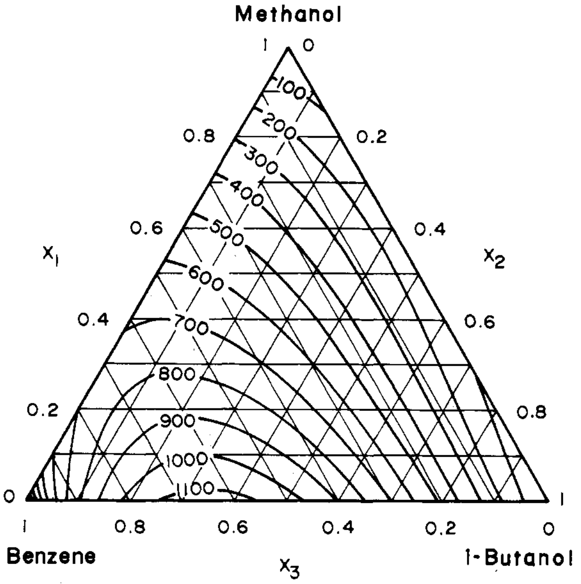

Figure 1. Curves of constant excess molar enthalpies at 25 °C.

has been revised to obtain improved calculated results of thermodynamic properties for mixtures involving two alcohols (*2*, *16*, *17*). The UNIQUAC associated-solution model for ternary mixtures including two alcohols and one active nonassociating component (*2*) assumes that the two alcohols (A and B) and benzene (C) form linear chemical complexes: A_i, B_i, $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$, $B_i(A_jB_k)_l$, A_iC, B_iC, $(A_iB_j)_kC$, $A_i(B_jA_k)_lC$, $(B_iA_j)_kC$, and $B_i(A_jB_k)_lC$, where the indices i, j, k, and l go from one to infinity. Further assumptions are that the association constants of the alcohols are independent of the degree of association and the solvation constants are also not concerned with the degree of association and solvation. Thus the model includes totally five equilibrium constants: K_A, K_B, K_{AB}, K_{AC}, and K_{BC}. The model gives the ternary excess molar enthalpy of the system as the sum of the chemical and physical contributions

$$H^E = H^E_{chem} + H^E_{phys} \tag{4}$$

Expressions for H^E_{chem} and H^E_{phys} are not reproduced here to save space. The temperature dependence of the energy parameters in H^E_{phys} is assumed to be given by

$$a_{JI} = C_{JI} + D_{JI}(T - 273.15) \tag{5}$$

The association constants of alcohols at 50 °C were taken from Brandani (*18*): for methanol, 173.9; for 1-butanol, 69.5. The enthalpy of hydrogen-bond formation was set as −23.2 kJ·mol^{-1} for the alcohols (*19*), being independent of temperature. This value fixes the temperature dependence of the association constants according to the van't Hoff relation. Pure-component molecular structure constants were estimated by the method of Vera et al. (*20*): for methanol, r = 1.15 and q = 1.12; for 1-butanol, r = 2.77 and q = 2.42; for benzene, r = 2.56 and q = 2.05. Table III presents the absolute arithmetic mean deviations and standard deviations between the experimental values and calculated results obtained in fitting the model to the binary experimental excess enthalpy data by means of the simplex method (*21*), together with the solvation constants and enthalpies of complex formation.

The absolute arithmetic mean deviation and standard deviation between the ternary experimental and calculated values are respectively 8.9 and 10.4 J·mol^{-1}, and the absolute relative mean deviation is 1.6% for 70 data points, showing that agreement is good.

Glossary

a_{JI}	binary interation parameter
b_i	coefficient of eq 3
C_{JI}, D_{JI}	coefficient of eq 5
H^E	excess molar enthalpy
H^E_{chem}	chemical contribution term to excess molar enthalpy
H^E_{phys}	physical contribution term to excess molar enthalpy
H^E_{123}	excess molar enthalpy for ternary mixture
H^E_{IJ}	excess molar enthalpy for I–J binary mixture
ΔH^E_m	excess molar enthalpy for pseudobinary mixture composed of benzene and binary methanol–1-butanol mixture
K_A, K_B	association constants
K_{AB}, K_{AC}, K_{BC}	solvation constants
q	pure component area parameter
r	pure component volume parameter
T	absolute temperature
x	liquid-phase mole fraction
Δ	function defined by eq 3

Registry No. Methanol, 67-56-1; 1-butanol, 71-36-3; benzene, 71-43-2.

Literature Cited

(1) Christensen, C.; Gmehling, J.; Rasmussen, P.; Weidlich, U. *Heats of Mixing Data Collection, Binary and Multicomponent System, Chemistry Data Series*; DECHEMA: Frankfurt am Main, 1984; Vol. III, Part 2.
(2) Nagata, I.; Tamura, K.; Gotoh, K. *Thermochim. Acta* **1986**, *104*, 179.
(3) Nagata, I.; Tamura, K. *Fluid Phase Equilib.*, in press.
(4) Pope, A. E.; Pflug, H. D.; Dacre, H.; Benson, G. C. *Can. J. Chem.* **1967**, *45*, 2655.
(5) Mrazek, R. V.; Van Ness, H. C. *AIChE J.* **1961**, *7*, 190.
(6) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986; pp 135, 190, 198.
(7) Nagata, I.; Kazuma, K. *J. Chem. Eng. Data* **1977**, *22*, 79.
(8) Ramalho, R. S.; Ruel, M. *Can. J. Chem. Eng.* **1968**, *46*, 467.
(9) Morris, J. W.; Mulvey, P. J.; Abbott, M. M.; Van Ness, H. C. *J. Chem. Eng. Data* **1975**, *20*, 403.
(10) Shatas, Jr. J. P.; Abbott, M. M.; Van Ness, H. C. *J. Chem. Eng. Data* **1975**, *20*, 406.
(11) Nagata, I.; Kawamura, Y. *Z. Phys. Chem. Neue Folge* **1977**, *107*, 141.
(12) Nagata, I.; Kawamura, Y. *Chem. Eng. Sci.* **1979**, *34*, 601.
(13) Nagata, I. *Fluid Phase Equilib.* **1985**, *19*, 153.
(14) Nagata, I.; Inaguma, K. *Thermochim. Acta* **1986**, *97*, 51.
(15) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(16) Nagata, I.; Ohtsubo, K. *Thermochim. Acta* **1986**, *102*, 185.
(17) Nagata, I.; Gotoh, K. *Thermochim. Acta* **1986**, *102*, 207.
(18) Brandani, V. *Fluid Phase Equilib.* **1983**, *12*, 87.
(19) Stokes, R. H.; Burfitt, C. *J. Chem. Thermodyn.* **1973**, *5*, 623.
(20) Vera, J. H.; Sayegh, S. G.; Ratcliff, G. A. *Fluid Phase Equilib.* **1977**, *1*, 113.
(21) Nelder, J. A.; Mead, R. *Compt. J.* **1965**, *7*, 308.

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