J. Chem. Eng. Data **1996,** *41,* 593−597

Excess Molar Enthalpies of Ternary Systems Butan-1-ol or Butan-2-ol + Aniline + Propanone and of Binary Systems Butan-1-ol or Butan-2-ol + Propanone at the Temperature 298.15 K

Isamu Nagata,* Kazuhiro Tamura, and Hideo Kataoka

Department of Chemistry and Chemical Engineering, Division of Physical Sciences, Kanazawa University,
40-20, Kodatsuno 2-chome, Kanazawa, Ishikawa 920, Japan

Andrzej Ksiażczak

Department of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland

The excess molar enthalpies at the temperature 298.15 K for ternary systems butan-1-ol + aniline + propanone and butan-2-ol + aniline + propanone and their constituent binary systems butan-1-ol + propanone and butan-2-ol + propanone, measured with an isothermal dilution calorimeter, are reported. The experimental results have been analyzed and compared with a polynomial equation and the UNIQUAC-associated solution model with binary and ternary additional parameters.

Introduction

A series of studies on specific molecular interactions between alcohol and aniline in a nonassociated component have been conducted in our laboratory. We recently reported excess molar enthalpies of binary and ternary mixtures formed by alcohol and aniline with propanone (Nagata, 1994a,b; Nagata and Ksiażczak, 1995). As an extension of our research, we present the excess molar enthalpies at 298.15 K for ternary systems butan-1-ol + aniline + propanone and butan-2-ol + aniline + propanone and for their constituent binary systems butan-1-ol + propanone and butan-2-ol + propanone. Excess molar enthalpies of binary mixtures relevant to the ternary ones at 298.15 K had been published previously: butan-1-ol + aniline (Nagata, 1993; Chao and Dai, 1989); butan-1-ol + propanone (Murakami and Fujishiro, 1966; Coomber and Wormald, 1976; Battler and Rowley, 1985); aniline + propanone (Nagata and Ksiażczak, 1995); butan-2-ol + aniline (Nagata, 1994c; Chao and Dai, 1989).

Experimental Section

All the chemicals used were purchased from Wako Pure Chemical Industries Ltd. except for aniline (Kanto Chemical Co.). Analytical grade butan-1-ol, butan-2-ol, and aniline, with stated minimum purities of 99.5, 99.5, and 99.3 mol %, respectively, were used without further purification. Analytical grade propanone (stated purity >99.8 mol %) was dried from anhydrous copper sulfate and fractionally distilled in a packed column apparatus (HP-9000B, Shibata Scientific Technology Ltd.). The purity was checked by using glc, and no appreciable peaks of impurities for the assay were detected. Densities of pure components measured by an Anton-Paar vibrating-tube densimeter (DMA55) at the temperature $T = 298.15$ K were in good agreement with the literature values (Riddick et al., 1986).

Excess molar enthalpy H_m^E data were measured using an isothermal dilution calorimeter at the temperature (298.15 ± 0.005) K under ambient pressure. Details of the apparatus and operation of the calorimeter were described earlier (Nagata and Kazuma, 1977). Before the present measurements, calibration of the calorimeter was carried out by measuring the excess molar enthalpies of the standard system benzene + cyclohexane at 298.15 K. By comparing with the literature values (Nagata and Kazuma, 1977; Tanaka et al., 1972, 1975), the experimental error of excess molar enthalpies was estimated to be less than ±0.5% of H_m^E over most of mole fraction range and that of the mole fraction was within $\pm 1 \times 10^{-4}$.

Results

The experimental excess molar enthalpy H_m^E results of binary systems butan-1-ol + propanone and butan-2-ol + propanone at $T = 298.15$ K and atmospheric pressure are presented in Table 1, along with the deviations $\delta H_m^E = \{H_{m(exp)}^E - H_{m(calc)}^E\}$ between the experimental results and values calculated from a polynomial equation of the form

$$H_{m,ij}^E/\mathrm{J\cdot mol^{-1}} = x_i x_j \sum_{n=1}^{m} a_{ij,n}(x_i - x_j)^{n-1} \qquad (1)$$

The coefficients of eq 1 and the absolute arithmetic mean deviations $\delta(H_m^E)$ and standard deviations $\sigma(H_m^E)$ obtained by the unweighted least-squares method are shown in Table 2. Figure 1 compares H_m^E's of the binary system butan-1-ol + propanone with the literature values. Our results were about 200 J·mol^{-1} higher than those reported by Murakami and Fujishiro (1966) and Battler and Rowley (1985), and 150 J·mol^{-1} higher than those of Coomber and Wormald (1976) near the middle mole fraction range. The deviations of our results from three sets of the experimental data seem to be excessive. To ensure the justification of our experimental results, we can refer to excess molar enthalpies of the binary systems methanol + propanone and butan-1-ol + acetonitrile which were measured previously using the same dilution calorimeter in our laboratory (Nagata and Tamura, 1983, 1988) and were in good agreement with the literature values. However, a similar difference, whose excess molar enthalpies of butan-1-ol + acetonitrile reported by Murakami and Fujishiro (1966)

---

* To whom correspondence should be addressed. e-mail: tamura@heikou1.ch.t.kanazawa-u.ac.jp. Fax: 762-34-4829.

0021-9568/96/1741-0593$12.00/0

Table 1. Binary Excess Molar Enthalpies at T = 298.15 K

x_1	H_m^E/J·mol^{-1}	δH_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	δH_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	δH_m^E/J·mol^{-1}
			x_1Butan-1-ol + x_2Propanone					
0.0234	195.4	−0.2	0.3840	1729.9	3.2	0.6989	1456.0	0.5
0.0714	554.0	1.0	0.4101	1751.8	−0.3	0.7470	1307.6	0.6
0.1221	871.7	0.6	0.4583	1774.8	−0.2	0.7959	1124.9	−0.9
0.1755	1145.2	−0.8	0.5057	1768.0	−0.1	0.8454	908.8	−1.1
0.2314	1372.0	−1.9	0.5535	1733.1	0.4	0.8971	647.1	−0.0
0.2843	1536.4	−1.8	0.6015	1669.8	0.4	0.9493	341.0	0.3
0.3338	1650.7	0.2	0.6498	1577.8	0.2			
			x_1Butan-2-ol + x_2Propanone					
0.0489	343.6	−1.8	0.3434	1652.5	0.1	0.6920	1669.8	−1.4
0.0978	650.6	−0.8	0.3913	1751.3	−0.0	0.7591	1468.1	−1.9
0.1468	921.4	0.7	0.4384	1816.9	−2.5	0.8241	1198.0	−0.3
0.1963	1156.9	0.8	0.4861	1854.5	−4.4	0.8863	860.5	1.9
0.2457	1356.6	0.8	0.5539	1868.9	5.8	0.9442	461.8	−0.9
0.2949	1521.9	0.8	0.6234	1803.4	1.8			

Table 2. Coefficients $a_{ij,k}$ of Eq 1 and Abolute Arithmetic Mean Deviations $\delta(H_m^E)$ and Standard Deviations $\sigma(H_m^E)$

system ($i + j$)	$a_{ij,1}$	$a_{ij,2}$	$a_{ij,3}$	$a_{ij,4}$	$a_{ij,5}$	$a_{ij,6}$	$\delta(H_m^E)$/ J·mol^{-1}	$\sigma(H_m^E)$/ J·mol^{-1}	ref
$x_1$butan-1-ol + $x_2$aniline	4077.28	−726.58	297.00	−118.49	−228.37	−118.42	0.5	0.8	Nagata (1993)
$x_1$butan-2-ol + $x_2$aniline	6190.92	849.55	752.87	340.09	416.96	154.99	0.7	1.1	Nagata (1994a)
$x_1$butan-1-ol + $x_3$propanone	7081.68	−745.69	834.59	−10.03			0.7	1.2	this work
$x_1$butan-2-ol + $x_3$propanone	7641.74	649.41	799.55	163.56			1.7	2.6	this work
$x_2$aniline + $x_3$propanone	−4895.20	1098.30	811.95	−428.67	−932.02		4.9	8.1	Nagata and Ksiażczak (1955)

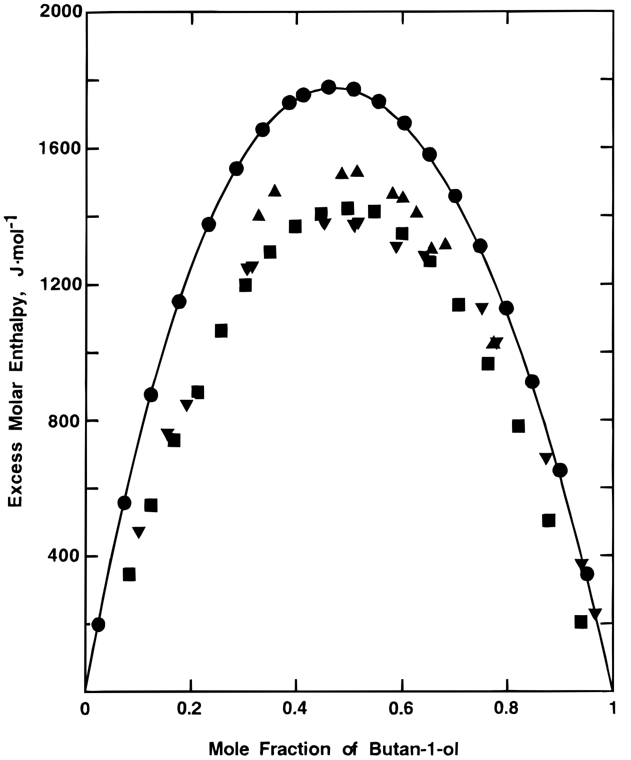

Figure 1. Excess molar enthalpy H_m^E results for the binary system butan-1-ol (1) + propanone (2) at 298.15 K. Experimental results: (●) this work; (■) Battler and Rowley (1985); (▲) Coomber and Wormald (1976); (▼) Murakami and Fujishiro (1966). Curve (—): calculated from eq 1 with the parameters given in Table 2.

were approximately 250 J·mol^{-1} lower than our results near the equimolar composition, was shown in our previous paper (Nagata and Tamura, 1988). Therefore these systematic discrepancies in the excess molar enthalpies for the binary system butan-1-ol + propanone observed in Figure 1 could be characterized by the calorimeters used in their measurements. Murakami and Fujishiro (1966) measured using a twin-type calorimeter. Battler and Rowley (1985) used a commercial Tronac flow calorimeter. Coomber and Womald (1976) employed a stirred flow calorimeter. In their flow measurements, good enough mixing could be required for measuring the excess molar enthalpies of these viscous mixtures, because the viscosity of butan-1-ol is quite high compared to that of methanol, acetonitrile, or propanone.

Ternary excess molar enthalpy $H_{m,123}^E$, measured by adding butan-1-ol or butan-2-ol to binary x_2'aniline + (1 − x_2')propanone mixtures having a fixed composition, is obtained from the relation

$$H_{m,123}^E = \Delta H_m^E + (1 - x_1)H_{m,23}^E \qquad (2)$$

where ΔH_m^E is the excess molar enthalpy measured for the pseudobinary mixture and $H_{m,23}^E$ is the excess molar enthalpy at three specified compositions of x_2'aniline + (1 − x_2')propanone mixtures and is interpolated from experimental values of Nagata and Ksiażczak (1995) by using a spline-fit method. The experimental ternary values for butan-1-ol (1) + aniline (2) + propanone (3) and butan-2-ol (1) + aniline (2) + propanone (3) systems at 298.15 K and atmospheric conditions are presented in Table 3 and fitted to an equation of the form

$$H_{m,123}^E = H_{m,12}^E + H_{m,13}^E + H_{m,23}^E + x_1x_2x_3\Delta_{123} \qquad (3)$$

where $H_{m,ij}^E$ is calculated using eq 1 with the coefficients given in Table 2 and Δ_{123} is expressed by

$$\Delta_{123}/RT = b_0 - b_1x_1 - b_2x_2 - b_3{x_1}^2 - b_4{x_2}^2 - b_5x_1x_2 - b_6{x_1}^3 \qquad (4)$$

The values of coefficients, absolute arithmetic mean deviations $\delta(H_m^E)$, and standard deviations $\sigma(H_m^E)$ fitting eqs 3 and 4 to the experimental ternary H_m^E results are b_0 = −5.6969, b_1 = 4.2263, b_2 = −13.1374, b_3 = −9.1121, b_4 = 10.9045, b_5 = −1.4875, b_6 = 9.6536, $\delta(H_m^E)$ = 4.7 J·mol^{-1}, and $\sigma(H_m^E)$ = 6.1 J·mol^{-1} for the butan-1-ol + aniline + propanone system and b_0 = −1.1552, b_1 = 12.6040, b_2 = 1.6140, b_3 = −32.1631, b_4 = −2.9608, b_5 = −1.9890, b_6 = 36.0519, $\delta(H_m^E)$ = 9.5 J·mol^{-1}, and $\sigma(H_m^E)$ = 12.1 J·mol^{-1} for the butan-2-ol + aniline + propanone system.

Table 3. Ternary Excess Molar Enthalpies for Butan-1-ol (1) + Aniline (2) + Propanone (3) and Butan-2-ol (1) + Aniline (2) + Propanone (3) Systems at T = 298.15 K

x_1	x_2	ΔH_m^E/ J·mol^{-1}	$H_{m,123}^E$/ J·mol^{-1}	x_1	x_2	ΔH_m^E/ J·mol^{-1}	$H_{m,123}^E$/ J·mol^{-1}	x_1	x_2	ΔH_m^E/ J·mol^{-1}	$H_{m,123}^E$/ J·mol^{-1}
x_1Butan-1-ol + x_2Aniline + x_3Propanone[a]											
$x_2' = 0.24494$				$x_2' = 0.4989$				$x_2' = 0.7475$			
$H_{m,23}^E = -983.9$ J·mol^{-1}				$H_{m,23}^E = -1226.5$ J·mol^{-1}				$H_{m,23}^E = -813.4$ J·mol^{-1}			
0.0450	0.2382	280.0	−659.6	0.0502	0.4738	284.6	−880.5	0.0428	0.7155	222.9	−555.6
0.0919	0.2265	535.0	−358.5	0.1028	0.4476	538.7	−561.8	0.0956	0.6760	459.1	−277.5
0.1473	0.2127	793.9	−45.0	0.1565	0.4208	758.4	−276.2	0.1575	0.6298	683.8	−1.5
0.2050	0.1983	1014.9	232.7	0.2120	0.3931	945.0	−21.5	0.2154	0.5865	851.3	213.1
0.2632	0.1837	1193.0	468.1	0.2681	0.3651	1096.9	199.3	0.2704	0.5454	976.7	383.3
0.3153	0.1708	1316.3	642.6	0.3252	0.3366	1213.7	386.1	0.3188	0.5092	1061.5	507.4
0.3574	0.1602	1393.0	760.8	0.3816	0.3085	1297.4	538.9	0.3677	0.4727	1123.9	609.5
0.4079	0.1477	1458.2	875.7	0.4348	0.2820	1345.8	652.6	0.4171	0.4357	1164.6	690.5
0.4572	0.1354	1496.2	962.2	0.4636	0.2676	1359.1	701.2	0.4665	0.3988	1183.4	749.5
0.4884	0.1276	1506.1	1002.8	0.4827	0.2581	1364.6	730.1	0.4913	0.3803	1184.7	770.9
0.5340	0.1162	1502.3	1043.8	0.5160	0.2415	1361.2	767.5	0.5043	0.3705	1183.3	780.1
0.5821	0.1042	1473.2	1062.0	0.5592	0.2199	1344.7	804.1	0.5546	0.3329	1161.7	799.4
0.6316	0.0919	1418.6	1056.2	0.6052	0.1970	1307.0	822.7	0.6021	0.2974	1121.2	797.5
0.6857	0.0784	1328.4	1019.2	0.6498	0.1747	1252.1	822.6	0.6505	0.2612	1062.3	778.1
0.7115	0.0720	1273.6	989.7	0.6929	0.1532	1178.3	801.7	0.6982	0.2256	984.4	738.9
0.7248	0.0686	1241.8	971.1	0.7335	0.1329	1091.8	765.0	0.7349	0.1982	911.6	695.9
0.7460	0.0633	1186.1	936.2	0.7546	0.1224	1039.8	738.9	0.7747	0.1684	818.5	635.2
0.7843	0.0537	1068.8	856.9	0.7940	0.1027	928.3	675.7	0.8172	0.1367	703.5	554.8
0.8284	0.0428	914.1	745.3	0.8324	0.0836	802.8	596.6	0.8416	0.1184	629.1	500.2
0.8518	0.370	819.2	673.4	0.8582	0.0707	707.8	533.9	0.8610	0.1039	566.3	453.2
				0.8681	0.0658	669.1	507.4	0.8697	0.0974	536.2	430.3
x_1Butan-2-ol + x_2Aniline + x_3Propanone[b]											
$x_2' = 0.2498$				$x_2' = 0.5002$				$x_2' = 0.7494$			
$H_{m,23}^E = -985.0$ J·mol^{-1}				$H_{m,23}^E = -1225.2$ J·mol^{-1}				$H_{m,23}^E = -808.5$ J·mol^{-1}			
0.0413	0.2395	283.1	−661.2	0.0492	0.4756	313.7	−851.3	0.0563	0.7072	335.3	−427.7
0.0834	0.2293	539.8	−364.1	0.0981	0.4511	595.0	−510.0	0.1129	0.6648	631.2	−86.0
0.1238	0.2189	773.9	−89.1	0.1469	0.4267	843.8	−201.4	0.1692	0.6226	885.9	214.3
0.1652	0.2086	982.2	159.9	0.1970	0.4016	1063.0	79.2	0.2254	0.5805	1098.6	472.4
0.2066	0.1982	1156.9	384.5	0.2460	0.3771	1246.9	323.1	0.2807	0.5391	1274.6	693.1
0.2481	0.1878	1328.0	587.4	0.2943	0.3530	1400.9	536.3	0.3345	0.4987	1414.2	876.2
0.2897	0.1774	1466.4	766.8	0.3410	0.3296	1525.1	717.7	0.3877	0.4589	1519.3	1024.2
0.3299	0.1674	1580.1	920.1	0.3869	0.3067	1620.9	869.7	0.4384	0.4209	1591.5	1137.5
0.3697	0.1575	1672.0	1051.2	0.4316	0.2843	1690.3	993.8	0.4873	0.3842	1633.6	1219.1
0.4121	0.1469	1748.3	1169.3	0.4748	0.2627	1736.2	1092.7	0.5314	0.3512	1650.1	1271.3
0.4502	0.1373	1797.7	1256.2	0.5527	0.2237	1747.2	1199.2	0.5839	0.3118	1641.3	1304.9
0.4897	0.1275	1828.0	1325.3	0.6131	0.1935	1715.5	1241.5	0.6320	0.2758	1604.2	1306.7
0.5349	0.1162	1838.9	1380.8	0.6552	0.1725	1664.5	1242.1	0.6820	0.2383	1518.5	1261.4
0.5800	0.1049	1820.0	1406.3	0.6947	0.1527	1594.2	1220.1	0.7096	0.2177	1467.6	1232.8
0.6206	0.0948	1785.3	1411.9	0.7254	0.1373	1523.6	1187.2	0.7356	0.1982	1409.1	1195.3
0.6505	0.0873	1745.3	1401.1	0.7519	0.1241	1450.5	1146.5	0.7543	0.1842	1360.4	1161.7
0.6784	0.0803	1692.9	1376.2	0.7989	0.1006	1282.8	1036.5	0.7831	0.1625	1261.3	1086.0
0.7029	0.0742	1638.0	1345.3	0.8258	0.0871	1168.8	955.4	0.8147	0.1389	1143.5	993.7
0.7206	0.0698	1592.6	1317.5	0.8456	0.0772	1076.0	886.9	0.8386	0.1210	1042.6	912.1
0.7440	0.0640	1530.6	1278.4	0.8582	0.0709	1013.0	839.2	0.8563	0.1077	961.0	844.8
0.7735	0.0566	1432.8	1209.6					0.8710	0.0967	887.7	783.4
0.7976	0.0506	1339.4	1140.0								
0.8182	0.0454	1250.6	1071.5								
0.8345	0.0413	1174.2	1011.2								
0.8518	0.0370	1086.7	940.7								

[a] Ternary mixtures were prepared by mixing pure butan-1-ol with {x_2'aniline + (1 − x_2')propanone}. [b] Ternary mixtures were prepared by mixing pure butan-2-ol with {x_2'aniline + (1 − x_2')propanone}.

Lines of constant values of $H_{m,123}^E$ for the ternary mixtures are shown in Figure 2 for the butan-1-ol (1) + aniline (2) + propanone (3) system and in Figure 3 for the butan-2-ol (1) + aniline (2) + propanone (3) system.

Data Analysis

The experimental H_m^E results were analyzed using the UNIQUAC-associated solution model proposed by Nagata and co-workers (Nagata, 1993, 1994a−c; Nagata and Ksiażczak, 1995). The expression of excess molar enthalpies is given by the sum of chemical and physical contributions. The chemical term of the excess molar enthalpies is derived on the basis of following chemical equilibria. In a ternary mixture of alcohol (A), aniline (B), and propanone (C), the model includes the self-association of alcohol and aniline molecules and the cross-association between unlike molecules. The association of alcohol and aniline is characterized by forming open linear chains of any length as follows:

$$K_{\mathrm{A}} = \Phi_{\mathrm{A}_{i+1}}/\Phi_{\mathrm{A}_i}\Phi_{\mathrm{A}_1}(i/i+1) \qquad \text{for} \qquad \mathrm{A}_1 + \mathrm{A}_i = \mathrm{A}_{i+1}$$

$$K_{\mathrm{B}} = \Phi_{\mathrm{B}_{i+1}}/\Phi_{\mathrm{B}_i}\Phi_{\mathrm{B}_1}(i/i+1) \qquad \text{for} \qquad \mathrm{B}_1 + \mathrm{B}_i = \mathrm{B}_{i+1}$$

where i ranges from 1 to ∞ and the equilibrium constants of alcohol and aniline are not concerned with the degree of association. The open linear chains solvate to produce open cross-chains according to

Table 4. Calculated Results for Binary H^E_m at 298.15 K

system ($i + j$)	no. of data points	$-h_{ij}$/kJ·mol^{-1}	$K_{ij}(T)$	C_{ji}/K	C_{ij}/K	D_{ji}	D_{ij}	$\delta(H^E_m)$/J·mol^{-1}	ref
$x_A$butan-1-ol + $x_B$aniline	16	14.5	17	7.95	445.58	0.6056	2.0530	2.0	Nagata (1993)
$x_A$butan-2-ol + $x_B$aniline	15	14.5	11	36.18	361.02	0.7728	0.7123	17.1	Nagata (1994a)
$x_A$butan-1-ol + $x_C$propanone	20	14.0	13[a]	1973.54	452.40	8.5870	−0.2255	15.8	this work
$x_A$butan-2-ol + $x_C$propanone	17	14.0	10[a]	−74.48	369.95	0.8174	−2.3267	13.0	this work
$x_B$aniline + $x_C$propanone	19	14.2	6[a]	−319.34	−1.68	−1.7935	1.6273	13.7	Nagata and Ksiażczak (1995)

[a] $T = 323.15$ K.

Table 5. Calculated Results for Ternary $H^E_{m,123}$ at 298.15 K

system (A + B + C)	no. of data points	ternary parameters	$\delta(H^E_m)^a$/J·mol^{-1}	$\delta(H^E_m)^b$/J·mol^{-1}
$x_A$butan-1-ol + x_B aniline + $x_C$propanone	62	$\tau_{BCA} = 0.8864$, $\tau'_{BCA} = 73.7434$ $\tau_{ACB} = 4.6841$, $\tau'_{ACB} = 511.9143$ $\tau_{ABC} = 0.6415$, $\tau'_{ABC} = -323.3160$	33.7	10.7
$x_A$butan-2-ol + $x_B$aniline + $x_C$propanone	66	$\tau_{BCA} = -0.4131$, $\tau'_{BCA} = 328.7109$ $\tau_{ACB} = 1.3401$, $\tau'_{ACB} = 8.4452$ $\tau_{ABC} = 0.3467$, $\tau'_{ABC} = -469.0520$	26.8	6.1

[a] Calculated using only binary parameters. [b] Calculated with binary and ternary parameters.

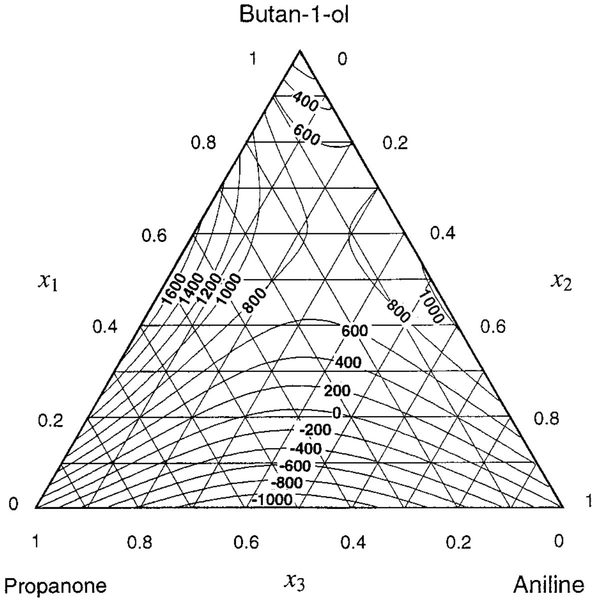

Figure 2. Contours of ternary excess molar enthalpy $H^E_{m,123}$ at 298.15 K for the butan-1-ol (1) + aniline (2) + propanone (3) system. (—): calculated from eqs 1, 3, and 4.

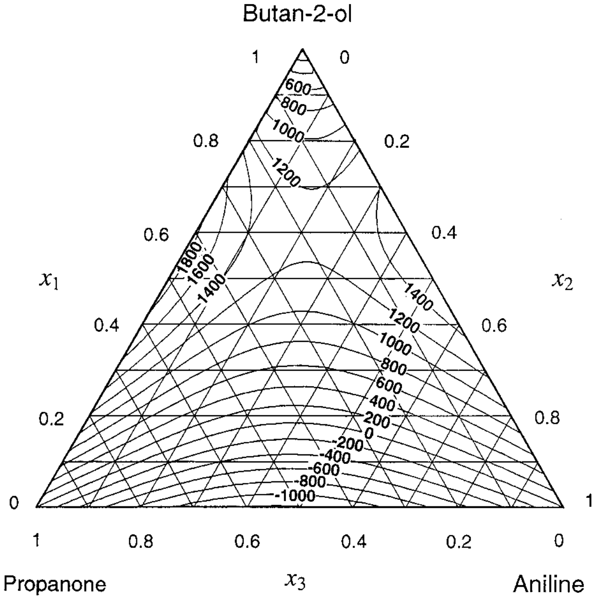

Figure 3. Contours of ternary excess molar enthalpy $H^E_{m,123}$ at 298.15 K for the butan-2-ol (1) + aniline (2) + propanone (3) system. Curves (—): calculated from eqs 1, 3, and 4.

$$K_{AB} = \Phi_{A_iB_j}/\Phi_{A_i}\Phi_{B_j}\{ij/(ir_A + jr_B)\} \quad \text{for} \quad A_i + B_j = A_iB_j$$

$$K_{AB} = \Phi_{A_iB_jA_k}/\Phi_{A_iB_j}\Phi_{A_j}\{r_{A_iB_j}/(r_{A_iB_jA_k}r_Ar_B)\} \quad \text{for} \quad A_iB_j + A_k = A_iB_jA_k$$

$$K_{AB} = \Phi_{B_iA_jB_k}/\Phi_{B_iA_j}\Phi_{B_j}\{r_{B_iA_j}/(r_{B_iA_jB_k}r_Ar_B)\} \quad \text{for} \quad B_iA_j + B_k = B_iA_jB_k, \text{ etc.}$$

The general formulas of the chemical complexes between A_i and B_j are expressed as $(A_iB_j)_k$, $(B_iA_j)_k$, $B_i(A_jB_k)_l$, and $A_i(B_jA_k)_l$, where i, j, k, and l range from 1 to ∞. Further, these open homo- and heterochains solvate with C to form the chemical complexes A_iC, B_iC, $(A_iB_j)_kC$, $(B_iA_j)_kC$, $B_i(A_jB_k)_lC$, and $A_i(B_jA_k)_lC$ as follows:

$$K_{AC} = \Phi_{A_iC}/\Phi_{A_i}\Phi_{C1}\{i/(ir_A + r_C)\} \quad \text{for} \quad A_i + C_1 = A_iC$$

$$K_{BC} = \Phi_{B_iC}/\Phi_{B_i}\Phi_{C1}\{i/(ir_B + r_C)\} \quad \text{for} \quad B_i + C_1 = B_iC, \text{ etc.}$$

The chemical term of excess molar enthalpies and the mass balance equations, described in detail previously (Nagata, 1994b,c), are not repeated here. The equilibrium constant and enthalpy of hydrogen-bond formation for alcohols (A) and aniline (B) were taken from the literature (Brandani, 1983; Stokes and Burfitt, 1973; Nagata, 1993, 1994b): $K_A = 69.5$ at 323.15 K and $h_A = -23.2$ kJ·mol^{-1} for butan-1-ol, $K_A = 31.1$ at 323.15 K and $h_A = -23.2$ kJ·mol^{-1} for butan-2-ol, and $K_B = 15$ and $h_B = -15.4$ kJ·mol^{-1}. The solvation constants and enthalpy of complex formation between unlike molecules are given in Table 4. The enthalpy was assumed to be independent of temperature and the temperature dependence of the equilibrium constants was fixed by the van't Hoff equation. The pure structural parameters r_i and q_i were estimated from the method of Vera et al. (1977), and the geometric size parameters of the chemical species were expressed in terms of those of pure monomeric properties.

The physical term of H^E_m, obtained by applying the residual term of the Gibbs free energy of the UNIQUAC equation to the Gibbs−Helmholtz equation, is presented by eq 12 in the reference of Nagata (1994b). The binary parameter τ_{ij} is expressed by $\tau_{ij} = \exp(-a_{ij}/T)$ and the energy parameter a_{ij} is assumed to be a function of temperature: $a_{ij} = C_{ij} + D_{ij}\,(T - 273.15)$. The binary parameters were obtained by minimizing the sum-of-squares between the experimental binary H_m^E and values calculated from the model using the association parameters by means of the simplex method (Nelder and Mead, 1965). Table 5 gives the binary parameters and the absolute arithmetic mean deviations $\delta(H_m^E)$ between the binary results and those calculated from the association model.

The ternary parameters τ_{ijk} and $\tau'_{ijk} = \partial\tau_{ijk}/\partial(1/T)$ are determined by fitting the model to the ternary experimental $H_{m,123}^E$ using the association parameters and binary parameters obtained above. Table 5 lists the ternary parameters and compares the ternary experimental results with the values calculated using the binary parameters alone and with those calculated using the binary and additional ternary parameters.

Conclusion

The UNIQUAC-associated solution model with the binary and ternary parameters gives better representation for the ternary $H_{m,123}^E$ curves in comparison with this model having only binary parameters, and that is comparable to the polynomial equation studied here.

Acknowledgment

The authors are grateful to Mr. K. Miyai for experimental work.

Glossary

$\delta(H_m^E)$	absolute arithmetic mean deviation, $\sum_{i=1}^{m}\lvert H_{m(exp)}^E - H_{m(cal)}^E\rvert/m$, where m is the number of data points
$\sigma(H_m^E)$	standard deviation, $[\sum_{i=1}^{m}(H_{m(exp)}^E - H_{m(cal)}^E)^2/(m - p)]^{1/2}$, where m is the number of data points and p the number of parameters

Literature Cited

Battler, J. R.; Rowley, R. L. Excess Enthalpies between 293 and 323 K for Constituent Binaries of Ternary Mixtures Exhibiting Partial Miscibility. *J. Chem. Thermodyn.* **1985**, *17*, 719−732.

Brandani, V. A Continuous Linear Association Model for Determining the Enthalpy of Hydrogen-Bond Formation and the Equilibrium Association Constant for pure Hydrogen-Bond Liquids. *Fluid Phase Equilib.* **1983**, *12*, 87−104.

Chao, J. P.; Dai, M. Studies of Thermodynamic Properties of Binary Mixtures Containing an Alcohol XI. Excess Enthalpies of Each of (One of the Four Butanols + Chlorobenzene or Aniline). *J. Chem. Thermodyn.* **1989**, *21*, 337−342.

Coomber, B. A.; Wormald, C. J. A Stirred Flow Calorimeter. The excess Enthalpies of Acetone + Water and Acetone + Some Normal Alcohols. *J. Chem. Thermodyn.* **1976**, *8*, 793−799.

Murakami, S.; Fujishiro, R. The Heats of Mixing for Binary Mixtures III. The Intermolecular Energy of Hydrogen Bonding Between Alcohol and Several Other Molecules. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 720−725.

Nagata, I. Excess Enthalpies of (Aniline + Butan-1-ol) and of (Aniline + Butan-1-ol + Benzene) at the Temperature 298.15 K *J. Chem. Thermodyn.* **1993**, *25*, 1281−1285.

Nagata, I. Excess Molar Enthalpies of (Methanol + Aniline + Propanone) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1994a**, *26*, 1015−1018.

Nagata, I. Thermodynamics of Associated Solutions. Correlation of Ternary Excess Molar Enthalpies for Aniline + Alkanol + Benzene or Acetone Mixtures Using the UNIQUAC Associated-Solution Model. *Thermochim. Acta* **1994b**, *244*, 21−32.

Nagata, I. Excess Molar Enthalpies of Binary and Ternary Mixtures Containing Aniline and 2-Butanol. *Thermochim. Acta* **1994c**, *232*, 19−28.

Nagata, I.; Kazuma, K. Heats of Mixing for the Ternary System Ethanol−1-Propanol−Cyclohexane at 25 °C. *J. Chem. Eng. Data* **1977**, *22*, 79−84.

Nagata, I.; Tamura, K. Excess Enthalpies of Binary and Ternary Mixtures of Methanol with Acetone, Chloroform, Benzene and Tetrachloromethane. *Fluid Phase Equilib.* **1983**, *15*, 67−79.

Nagata, I.; Tamura, K. Excess Molar Enthalpies of (Butan-1-ol or 2-Methylpropan-1-ol + Acetonitrile), (2-methylpropan-1-ol + Benzene), and (Butan-1-ol or 2-Methylpropan-1-ol + Acetonitrile + Benzene) at 298.15 K. *J. Chem. Thermodyn.* **1988**, *20*, 1101−1107.

Nagata, I.; Książczak, A. Excess Enthalpies of (Ethanol or Propan-2-ol + Aniline + Propanone) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1995**, *27*, 1235−1240.

Nelder, J. A.; Mead, R. A Simplex Method for Minimization. *Comput. J.* **1965**, *7*, 308−313.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

Stokes, R. H.; Burfitt, C. Enthalpies of Dilution and Transfer of Ethanol in Non-Polar Solvents. *J. Chem. Thermodyn.* **1973**, *5*, 623−631.

Tanaka, R.; Murakami, S.; Fujishiro, R. An Isothermal Displacement Calorimeter for Measuring Enthalpies of Mixing. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2107−2110.

Tanaka, R.; D'arcy; Benson, G. C. Application of a Flow Microcalorimeter to Determine the Excess Enthalpies of Binary Mixtures of Non-electrolytes. *Thermochim. Acta* **1975**, *11*, 163−175.

Vera, J. H.; Sayegh, S. G.; Ratcliff, G. A. A Quasi-Lattice-Local Composition Model for the Excess Gibbs Free Energy of Liquid Mixtures. *Fluid Phase Equilib.* **1977**, *1*, 113−135.

Received for review January 12, 1996. Accepted February 26, 1996.⊗

JE960013L

⊗ Abstract published in *Advance ACS Abstracts*, April 15, 1996.