Excess Molar Enthalpies of Ternary Mixtures for Propanone or Benzene + Aniline + 2-Methyl-1-propanol and of Binary Mixtures for Propanone or Aniline + 2-Methyl-1-propanol at 298.15 K

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Experimental excess molar enthalpies for the ternary mixtures 2-methyl-1-propanol + aniline + propanone and 2-methyl-1-propanol + aniline + benzene and their constituent binary mixtures 2-methyl-1-propanol + aniline and 2-methyl-1-propanol + propanone at the temperature 298.15 K, measured by using an isothermal dilution calorimeter, are reported. The results have been analyzed using a polynomial equation and the UNIQUAC-associated solution model with binary and ternary parameters.

Introduction

We have conducted systematic studies on the thermodynamic properties of binary and ternary mixtures formed by aniline and butanols with propanone or benzene (Nagata, 1993, 1994a,b; Nagata and Książczak, 1995; Nagata et al., 1996). As a part of our program of measuring excess molar enthalpies of ternary liquid mixtures containing alcohol and aniline with a nonassociated component, we report the excess molar enthalpies at the temperature 298.15 K for ternary mixtures 2-methyl-1-propanol + aniline + propanone and 2-methyl-1-propanol + aniline + benzene and for their constituent binary mixtures 2-methyl-1-propanol + aniline or +propanone. Excess molar enthalpies of binary mixtures relevant to the ternary ones at 298.15 K had been published previously: aniline + propanone (Deshpande and Pandya, 1967; Nagata and Książczak, 1995); aniline + benzene (Deshpande and Pandya, 1965; Pannetier and Abello, 1965; Sosnkowska-Kehiaian and Kehiaian, 1966; Nigam et al., 1979; Nagata and Tamura, 1992); 2-methyl-1-propanol + aniline (Chao and Dai, 1989); 2-methyl-1-propanol + benzene (Brown et al., 1969; Vilcu and Cenuse, 1975; Nagata and Tamura, 1988).

Experimental Section

Materials. Guaranteed reagent grade 2-methyl-1-propanol (Wako Pure Chemical Co., purity >99.0 mass %) and aniline (Kanto Chemical Co., purity >99.0 mass %) were used without further purification. C.P. benzene was recrystallized three times. Analytical grade propanone (Wako Pure Chemical Co., purity >99.8 mass %) was fractionally distilled in a packed column (HP-9000B, Shibata Scientific Technology Ltd.) after drying over anhydrous copper sulfate. The purity was checked by gas chromatography, and no significant peaks of impurities in any of the components were detected. The densities of the chemicals used, measured with an Anton-Paar densimeter at 298.15 K, agreed with literature values (Riddick et al., 1986) within ±0.1 kg·m^3.

Procedure. Excess molar enthalpy H^E_m measurements at the temperature (298.15 ± 0.005) K were performed by using an isothermal dilution calorimeter described earlier (Nagata and Kazuma, 1977). Calibration of the calorimeter was carried out by comparing the excess molar enthalpies at 298.15 K of the mixture benzene + cyclohexane with literature values. The experimental errors were within ±0.5% of H^E_m in excess molar enthalpies and ±0.0001 in mole fraction. Ternary excess molar enthalpies $H^E_{m,123}$, obtained by adding a component 1 to binary mixtures composed of components 2 and 3, were given as

$$H^E_{m,123} = \Delta H^E_m + (1-x_1)H^E_{m,23} \quad (1)$$

where ΔH^E_m is the molar enthalpies measured for the pseudobinary mixture, $H^E_{m,23}$ is the molar enthalpy for the initial binary mixture, and x_1 is the mole fraction of component 1. Values of $H^E_{m,23}$ at three specified compositions x_2' were interpolated by means of a spline-fit.

Results

The excess molar enthalpies of binary mixtures 2-methyl-1-propanol + propanone or +aniline at the temperature 298.15 K and atmospheric conditions are listed in Table 1, along with the deviations $\delta H^E_m = H^E_m - H^E_{(cal)}$ of the experimental results minus values calculated from a polynomial equation of the form

$$H^E_{m,ij}/\mathrm{J\cdot mol^{-1}} = x_i x_j \sum_{n=1}^{p} a_{n,ji}(x_i - x_j)^{n-1}/\{1 - k(x_i - x_j)\} \quad (2)$$

where $a_{n,ji}$ and k are the coefficients obtained by the unweighted least-squares method. Table 2 presents the coefficients of eq 2 and the absolute arithmetic mean deviations and standard deviations, calculated from $\delta(H^E_m) = \sum_{i=1}^{m}|H^E_m - H^E_{(cal)}|/m$ and $\sigma(H^E_m) = \{\sum_{i=1}^{m}(H^E_m - H^E_{(cal)})^2/(m-p)\}^{0.5}$, where m is the number of experimental data points and p is the number of parameters. Figure 1 compares our experimental H^E_m on the binary mixture 2-methyl-1-propanol + aniline or +propanone at 298.15 K with the literature. Figure 2 shows the deviations δH^E_m of H^E_m for 2-methyl-1-propanol + aniline measured by Chao and Dai (1989) from the values calculated by eq 2 with the coefficients given in Table 2, and the results of Chao and Dai deviate noticeably from ours over the concentrated mole fraction range of 2-methyl-1-propanol. Similar differences between the measurements of Chao and Dai (1989) and ours (Nagata, 1993; Nagata, 1994b) were observed in excess molar enthalpies of the mixtures aniline + 1-butanol

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Table 1. Experimental Binary Excess Molar Enthalpies at 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}
2-Methyl-1-propanol (1) + Propanone (2)								
0.0537	351.6	−0.4	0.3776	1613.6	−0.3	0.6948	1522.2	−0.2
0.1073	662.4	0.3	0.4307	1686.7	−1.4	0.7625	1326.8	0.1
0.1612	932.2	0.7	0.4828	1723.2	−3.2	0.8286	1065.6	−0.2
0.2154	1162.6	1.3	0.5000	1728.0	−3.4	0.8917	743.6	−0.2
0.2697	1352.4	1.0	0.5578	1725.2	4.0	0.9519	362.7	−0.1
0.3240	1502.1	−0.5	0.6266	1654.9	2.0			
2-Methyl-1-propanol (1) + Aniline (2)								
0.0690	361.1	−0.2	0.4242	1313.1	−1.2	0.6334	1250.0	−0.2
0.1386	663.9	−0.2	0.4806	1341.1	1.3	0.7092	1119.2	0.1
0.2076	908.4	3.7	0.4995	1339.8	−1.8	0.7847	930.0	1.6
0.2797	1097.6	−1.1	0.5298	1339.0	2.8	0.8579	680.0	−1.3
0.3521	1232.7	−1.6	0.5582	1321.6	−1.5	0.9304	370.0	0.2

Table 2. Coefficients of Eq 2 and Absolute Arithmetic Mean Deviations $\delta(H_m^E)$ and Standard Deviations $\sigma(H_m^E)$

system ($i + j$)	$a_{1,ij}$	$a_{2,ij}$	$a_{3,ij}$	$a_{4,ij}$	$a_{5,ij}$	k	$\delta(H_m^E)$/J·mol^{-1}	$\sigma(H_m^E)$/J·mol^{-1}	ref
2-methyl-1-propanol (1) + aniline (2)	5364.78	−46.08	408.89	129.77			1.1	1.7	this work
2-methyl-1-propanol (1) + propanone (3)	6925.63	378.39	619.24	209.81			1.1	1.9	this work
2-methyl-1-propanol (1) + benzene (3)	5269.9	2496.1	−938.3	521.3		0.8663	1.7	2.7	Nagata and Tamura (1988)
aniline (2) + benzene (3)	3003.51	−721.57	447.94	−333.36			0.9	1.3	Nagata and Tamura (1992)
aniline (2) + propanone (3)	−4895.20	1098.30	811.95	−428.67	−932.02		4.9	8.1	Nagata and Książczak (1995)

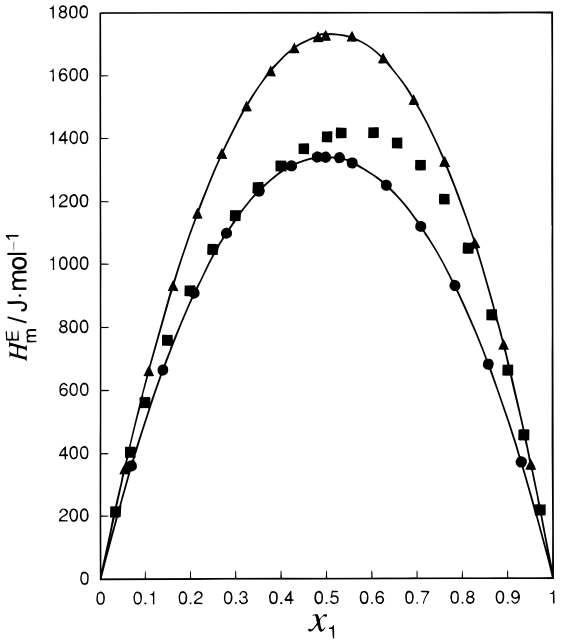

Figure 1. Experimental excess molar enthalpies for binary mixtures at 298.15 K: (●) this work; (■) Chao and Dai (1989) for 2-methyl-1-propanol (1) + aniline (2); (▲) this work for 2-methyl-1-propanol (1) + propanone (2); (—) calculated from eq 2 with the coefficients given in Table 2.

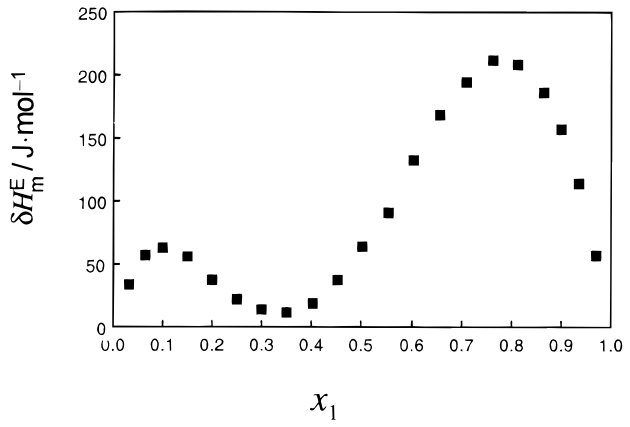

Figure 2. Deviation of excess molar enthalpies for the binary mixture of 2-methyl-1-propanol (1) + aniline (2) at 298.15 K. Data points show the deviations of excess molar enthalpies of Chao and Dai (1989) from those calculated by eq 2 with the coefficients given in Table 2.

(Nagata, 1993) or +2-butanol (Nagata, 1994b). These discrepancies seem to be mainly due to the calorimeters used in the measurements. Our results for these viscous mixtures measured by the isothermal dilution calorimeter can give precise and reliable values compared to the flow measurement of Chao and Dai (1989).

The ternary excess molar enthalpies for the mixtures 2-methyl-1-propanol (1) + aniline (2) + propanone (3) and 2-methyl-1-propanol (1) + aniline (2) + benzene (3) at 298.15 K are given 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 $H_{m,23}^E$ is calculated from eq 2 with the coefficients in Table 2 and Δ_{123} is expressed by

$$\Delta_{123}/RT = b_0 - b_1x_1 - b_2x_2 - b_3x_1^2 - b_4x_2^2 - b_5x_1x_2 - b_6x^3 \qquad (4)$$

The values of coefficients, absolute arithmetic mean deviations, and standard deviations fitting eqs 3 and 4 to the experimental ternary H_m^E are $b_0 = 1.8603$, $b_1 = 13.3853$, $b_2 = 14.9764$, $b_3 = -10.9510$, $b_4 = -13.9971$, $b_5 = -21.0153$, $b_6 = 10.1526$, $\delta(H_m^E) = 10.3$ J·mol^{-1}, and $\sigma(H_m^E) = 12.8$ J·mol^{-1} for the mixture 2-methyl-1-propanol (1) + aniline (2) + propanone (3), and $b_0 = 9.4267$, $b_1 = 35.6899$, $b_2 = 20.4072$, $b_3 = -66.5433$, $b_4 = -15.9218$, $b_5 = -23.9614$, $b_6 = 45.7647$, $\delta(H_m^E) = 11.4$ J·mol^{-1}, and $\sigma(H_m^E) = 16.2$ J·mol^{-1} for the mixture 2-methyl-1-propanol (1) + aniline (2) + benzene (3). Figures 3 and 4 shows lines of constant excess molar enthalpies for the ternary mixtures 2-methyl-

Table 3. Experimental Ternary Excess Molar Enthalpies at 298.15 K

x_1	x_2	$\Delta H^E_{m,123}$/J·mol^{-1}	$H^E_{m,123}$/J·mol^{-1}	x_1	x_2	ΔH^E_m/J·mol^{-1}	$H^E_{m,123}$/J·mol^{-1}	x_1	x_2	ΔH^E_m/J·mol^{-1}	$H^E_{m,123}$/J·mol^{-1}
2-Methyl-1-propanol (1) + Aniline (2) + Propanone (3)[a]											
$x_2' = 0.2494$, $H^E_{m,23} = -984.02$ J·mol^{-1}				$x_2' = 0.5007$, $H^E_{m,23} = -1224.64$ J·mol^{-1}				$x_2' = 0.7490$, $H^E_{m,23} = -809.60$ J·mol^{-1}			
0.0435	0.2386	285.0	−656.2	0.0499	0.4757	297.5	−866.0	0.0555	0.7074	311.8	−452.8
0.0870	0.2277	542.3	−356.1	0.1003	0.4505	562.6	−539.3	0.1112	0.6657	586.2	−133.4
0.1313	0.2167	775.1	−79.7	0.1516	0.4248	796.8	−242.3	0.1679	0.6232	822.8	149.1
0.1758	0.2056	979.5	168.5	0.2026	0.3993	998.3	21.8	0.2257	0.5799	1022.2	395.3
0.2205	0.1944	1158.3	391.2	0.2536	0.3737	1168.3	254.3	0.2836	0.5366	1182.4	602.4
0.2650	0.1834	1309.5	586.2	0.3047	0.3481	1306.6	455.1	0.3418	0.4929	1306.4	773.6
0.3092	0.1723	1434.3	754.5	0.3545	0.3232	1413.4	622.9	0.3983	0.4507	1391.6	904.5
0.3531	0.1614	1534.4	897.9	0.4039	0.2985	1491.5	761.6	0.4536	0.4093	1443.9	1001.5
0.3964	0.1506	1610.5	1016.6	0.4521	0.2743	1541.5	870.5	0.4968	0.3769	1462.6	1055.2
0.4389	0.1399	1663.0	1110.9	0.4901	0.2553	1563.5	939.0	0.5357	0.3479	1459.9	1084.0
0.4714	0.1319	1685.5	1165.3	0.4938	0.2535	1556.3	936.4	0.5979	0.3013	1425.2	1099.4
0.5253	0.1184	1698.5	1231.4	0.5428	0.2289	1559.0	999.1	0.6525	0.2603	1361.7	1080.4
0.5904	0.1022	1666.1	1263.0	0.5899	0.2054	1535.9	1033.7	0.6895	0.2326	1299.4	1048.1
0.6359	0.0908	1612.7	1254.4	0.6350	0.1828	1488.8	1041.8	0.7241	0.2067	1227.3	1003.9
0.6717	0.0819	1552.5	1229.5	0.6705	0.1650	1435.3	1031.9	0.7452	0.1909	1175.3	969.0
0.6995	0.0750	1494.4	1198.6	0.6982	0.1511	1382.9	1013.3	0.7708	0.1717	1104.3	918.8
0.7196	0.0699	1445.5	1169.6	0.7041	0.1482	1370.3	1007.9	0.8021	0.1482	1005.0	844.8
0.7360	0.0659	1398.8	1139.0	0.7345	0.1330	1291.0	966.1	0.8243	0.1316	926.5	784.2
0.7785	0.0553	1265.2	1047.2	0.7710	0.1147	1188.6	908.1	0.8450	0.1161	847.5	722.0
0.8067	0.0482	1159.5	969.4	0.8004	0.0999	1092.5	848.0	0.8611	0.1041	780.7	668.3
0.8301	0.0424	1062.3	895.0	0.8223	0.0890	1011.7	794.2				
0.8453	0.0386	993.6	841.3	0.8377	0.0813	950.4	751.6				
				0.8506	0.0748	895.7	712.7				
2-Methyl-1-propanol (1) + Aniline (2) + Benzene (3)[b]											
$x_2' = 0.2510$, $H^E_{m,23} = 1029.35$ J·mol^{-1}				$x_2' = 0$ 4994, $H^E_{m,23} = 1339.82$ J·mol^{-1}				$x_2' = 0.7502$, $H^E_{m,23} = 1024.20$ J·mol^{-1}			
0.2341	0.6988	166.4	1126.7	0.4703	0.4691	167.8	1426.4	0.7075	0.2355	178.2	1144.1
0.2169	0.6475	309.8	1199.6	0.4416	0.4405	312.6	1494.4	0.6685	0.2226	335.1	1247.4
0.2014	0.6012	432.5	1258.8	0.4138	0.4129	438.3	1545.9	0.6317	0.2103	473.3	1335.7
0.1863	0.5560	532.9	1297.0	0.3881	0.3871	549.8	1588.5	0.5962	0.1985	596.1	1410.0
0.1728	0.5157	617.5	1326.2	0.3630	0.3621	641.8	1613.3	0.5621	0.1871	702.9	1470.3
0.1599	0.4773	685.7	1341.6	0.3394	0.3386	720.4	1628.8	0.5297	0.1763	795.7	1517.7
0.1482	0.4423	741.6	1349.4	0.3186	0.3178	787.5	1640.2	0.4993	0.1662	873.8	1555.5
0.1369	0.4086	783.6	1345.1	0.2978	0.2971	840.9	1638.0	0.4702	0.1565	940.3	1599.2
0.1263	0.3770	813.7	1331.8	0.2598	0.2591	916.3	1611.5	0.4168	0.1388	1039.9	1608.8
0.1127	0.3366	838.7	1301.2	0.2491	0.2485	929.7	1569.5	0.4072	0.1356	1053.0	1608.9
0.0982	0.2931	845.9	1248.7	0.2220	0.2214	959.9	1554.0	0.3691	0.1229	1099.9	1603.8
0.0858	0.2560	839.3	1191.1	0.1978	0.1973	972.8	1502.2	0.3341	0.1112	1128.1	1584.2
0.0746	0.2228	818.3	1124.4	0.1753	0.1749	966.8	1436.1	0.3030	0.1009	1141.5	1555.2
0.0685	0.2043	798.6	1079.4	0.1641	0.1637	963.1	1402.3	0.2748	0.0915	1142.1	1517.3
0.0680	0.2031	799.9	1078.9	0.1528	0.1525	952.1	1361.1	0.2543	0.0847	1136.2	1483.4
0.0593	0.1771	764.6	1008.0	0.1426	0.1423	939.5	1321.3	0.2353	0.0783	1124.7	1445.9
0.0513	0.1531	719.9	930.2	0.1259	0.1256	910.3	1247.1	0.2199	0.0732	1111.3	1411.5
0.0458	0.1366	683.7	871.4	0.1103	0.1099	873.4	1168.4	0.2151	0.0716	1105.7	1399.4
0.0406	0.1213	644.0	810.7	0.0962	0.0959	829.6	1086.9	0.1931	0.0643	1077.3	1341.0
0.0359	0.1073	602.1	749.5	0.0861	0.0859	792.3	1022.6	0.1736	0.0578	1044.3	1281.3
				0.0786	0.0755	768.1	969.3	0.1562	0.0520	1008.7	1222.0
				0.0702	0.0700	720.6	908.5	0.1433	0.0477	977.7	1173.3
								0.1314	0.0437	945.7	1125.1
								0.1205	0.0401	913.1	1077.7

[a] Ternary mixtures were prepared by mixing pure 2-methyl-1-propanol with {x_2' aniline + x_3' propanone}. [b] Ternary mixtures were prepared by mixing pure benzene with {x_2' 2-methyl-1-propanol + x_3' aniline}.

Table 4. Calculated Results of Excess Molar Enthalpies for the Binary Systems 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_1$2-methyl-1-propanol + $x_2$aniline	15	14.5	13.0	−22.89	−17.54	−1.5716	2.1292	15.9	this work
$x_1$2-methyl-1-propanol + $x_2$propanone	17	14.0	13.0[a]	−276.71	468.78	2.7462	−7.9737	16.6	this work
$x_1$2-methyl-1-propanol + $x_2$benzene	16	8.3	2.0[a]	15.27	−0.5256	−1.6555	1.6440	12.1	Nagata and Tamura (1988)
$x_2$aniline + $x_3$propanone	19	14.2	6.0[a]	−319.39	−1.6839	−1.7935	1.6273	13.7	Nagata and Tamura (1992)
$x_2$aniline + $x_3$benzene	15	10.8	1.0[a]	−188.06	519.51	−1.0731	2.111	4.5	Nagata and Książczak (1995)

[a] T = 323.15 K.

1-propanol + aniline + propanone and 2-methyl-1-propanol + aniline + benzene.

Data Analysis

The experimental results were analyzed with the UNIQUAC-associated solution model proposed by Nagata et al. (Nagata, 1993, 1994a,b; Nagata and Książczak, 1995; Nagata et al., 1996). The model includes chemical and physical contributions to the excess molar enthalpies. We consider a ternary mixture of 2-methyl-1-propanol (A), aniline (B), and propanone or benzene (C). The chemical term of the excess molar enthalpies is based on the self-association of alcohol and aniline molecules and the cross-

Table 5. Calculated Results of Excess Molar Enthalpies for the Ternary Systems at 298.15 K

system	no. of data points	ternary parameters		$\delta(H_m^E)^a$/J·mol^{-1}	$\delta(H_m^E)^b$/J·mol^{-1}
$x_1$2-methyl-1-propanol + $x_2$aniline + $x_3$propanone	65	$\tau_{231} = -1.3786$	$\tau'_{231} = 1046.8360$	19.7	7.3
		$\tau_{132} = 4.2074$	$\tau'_{132} = 2722.1352$		
		$\tau_{123} = 0.7337$	$\tau'_{123} = -2299.8415$		
$x_1$2-methyl-1-propanol + $x_2$aniline + $x_3$benzene	69	$\tau_{231} = -0.7790$	$\tau'_{231} = 15.0039$	18.9	12.3
		$\tau_{132} = -0.8358$	$\tau'_{132} = -23.9548$		
		$\tau_{123} = 1.0334$	$\tau'_{123} = 320.4259$		

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

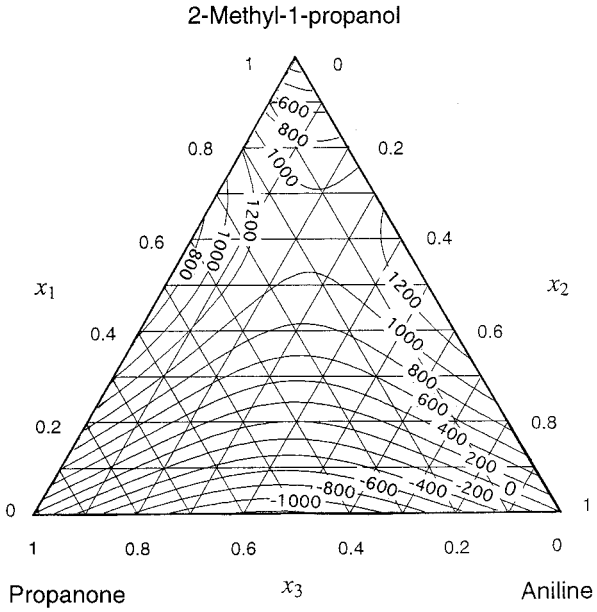

Figure 3. Curves of constant excess molar enthalpies for the ternary mixtures of 2-methyl-1-propanol (1) + aniline (2) + propanone (3) at 298.15 K: (—) calculated from eqs 3 and 4.

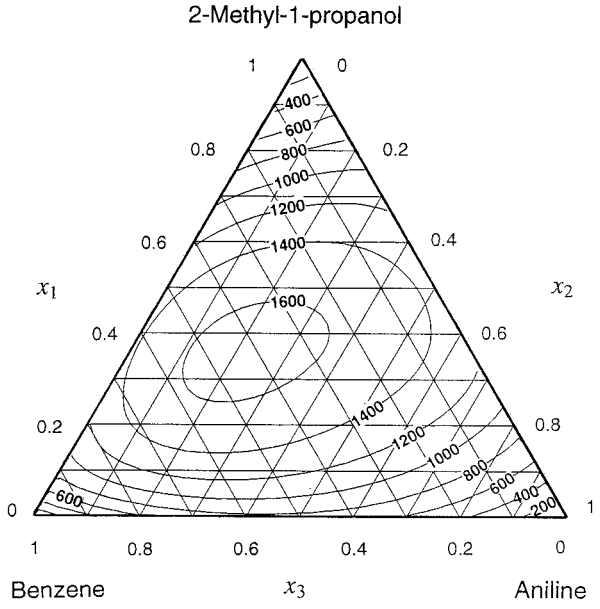

Figure 4. Curves of constant excess molar enthalpies for the ternary mixtures of 2-methyl-1-propanol (1) + aniline (2) + benzene (3) at 298.15 K: (—) calculated from eqs 3 and 4.

association between unlike molecules according to the following chemical equilibria. The association of alcohol and aniline is defined by segment fractions Φ_{Ai}, Φ_{Bi}, and Φ_{C1} of forming open linear chains of any length as follows:

$$K_A = \frac{\Phi_{Ai+1}}{\Phi_{Ai}\Phi_{A1}}\frac{i}{i+1} \quad \text{for} \quad A_1 + A_i = A_{i+1}$$

$$K_B = \frac{\Phi_{Bi+1}}{\Phi_{Bi}\Phi_{B1}}\frac{i}{i+1} \quad \text{for} \quad B_1 + B_i = B_{i+1}$$

where i ranges from 1 to ∞ and the equilibrium constants of alcohol and aniline are independent of the degree of association. The open linear chains A_i and B_j solvate to produce open cross-chains according to

$$K_{AB} = \frac{\Phi_{AiBj}}{\Phi_{Ai}\Phi_{Bj}}\frac{ij}{ir_A + jr_B} \quad \text{for} \quad A_i + B_j = A_iB_j,$$

$$K_{AB} = \frac{\Phi_{AiBjAk}}{\Phi_{AiBj}\Phi_{Ak}}\frac{r_{AiBj}}{r_{AiBjAr}r_Ar_B} \quad \text{for} \quad A_iB_j + A_k = A_iB_jA_k,$$

$$K_{AB} = \frac{\Phi_{BiAjBk}}{\Phi_{BiAj}\Phi_{Bk}}\frac{r_{BiAj}}{r_{BiAjBk}r_Ar_B} \quad \text{for} \quad B_iA_j + B_k = B_jA_jB_k, \quad \text{etc.}$$

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:

$$K_{AC} = \frac{\Phi_{AiC1}}{\Phi_{Ai}\Phi_{C1}}\frac{i}{ir_A + r_C} \quad \text{for} \quad A_i + C_1 = A_iC,$$

$$K_{BC} = \frac{\Phi_{BiC1}}{\Phi_{Bi}\Phi_{C1}}\frac{i}{ir_B + r_C} \quad \text{for} \quad B_i + C_1 = B_iC, \text{ etc.}$$

Detailed expressions for the chemical term of excess molar enthalpies and the mass balance equations to solve the monomer segment fractions Φ_{A1}, Φ_{B1}, and Φ_{C1} have been described previously (Nagata, 1994a,b). The equilibrium constant and enthalpy of hydrogen-bond formation for 2-methyl-1-propanol (A) and aniline (B) were taken from previous papers: $K_A = 50.6$ (Brandani, 1983) at 323.15 K and $h_A = -23.2$ kJ·mol^{-1} (Stokes and Burfitt, 1973) for 2-methyl-1-propanol, and $K_B = 15$ and $h_B = -15.4$ kJ·mol^{-1} for aniline (Nagata, 1993, 1994a,b). Table 4 gives the solvation constant and enthalpy of complex formation between unlike molecules taken from Nagata (1993, 1994a—c) and those of 2-methyl-1-propanol + aniline or +propanone estimated by fitting the model to excess molar enthalpies. These enthalpies of formation were assumed to be independent of temperature and the temperature-dependence of the equilibrium constants is fixed by the van't Hoff equation. The pure structural parameters r_i and q_j were estimated by the method of Vera et al. (1977) and the geometric size parameters of the chemical species are expressed in terms of those of pure monomeric properties.

The physical term of H_m^E is obtained from the residual term of the Gibbs free energy of the UNIQUAC equation through the Gibbs−Helmholtz relation. The energy parameter a_{ij} is assumed to be a function temperature: $a_{ij} = C_{ij} + D_{ij}\{(T/\mathrm{K}) - 273.15\}$ and the binary parameter τ_{ij} is expressed by $\tau_{ij} = \exp(-a_{ij}/T)$. The binary parameters were obtained by minimizing the sum-of-squares between the experimental binary H_m^E and values calculated from the model with the association and solvation parameters by means of Nelder and Mead (1965). Table 4 gives the binary parameters and the absolute arithmetic mean deviations $\delta(H_m^E)$ between the binary experimental and calculated values.

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

Conclusions

Ternary excess molar enthalpies have been measured for the mixtures 2-methyl-1-propanol + aniline + propanone and 2-methyl-1-propanol + aniline + benzene at 298.15 K, and the results were compared with the polynomial equation and UNIQUAC-associated solution model. Good agreements are obtained between the experimental results and values calculated by the polynomial equation and UNIQUAC-associated solution model having the binary and additional ternary parameters.

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