

## EXCESS ENTHALPIES OF BINARY MIXTURES OF PROPANEDIAMINE+PROPANEDIOL AT 298.15 K

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### Abstract

The molar excess enthalpies of 1,2- and 1,3-propanediamine+1,2- and 1,3-propanediol have been determined at 298.15 K by using a twin-microcalorimeter which requires each component liquid 1 to 1.5 cm<sup>3</sup> for a series of runs over the whole range of mole fraction. All excess enthalpies are exothermic and large. An equilibrium constant  $K_1$  expressed in terms of mole fractions and standard enthalpy of formation of 1:1 complex have been evaluated by ideal mixtures of monomeric molecules and their associated complexes.

**Keywords:** 1,2- and 1,3-propanediamine, 1,2- and 1,3-propanediol, excess enthalpies, ideal association treatment

### Introduction

A series of thermodynamic measurements of vapour pressures, excess enthalpies and excess volumes for the aqueous binary mixtures containing four butanediol isomers have been measured by the present authors, to understand the behaviour of amphiphilic molecules which have hydroxyl groups and methyl or methylene groups in aqueous and non aqueous solutions. Excess thermodynamic properties of those mixtures showed a strong effect on hydrogen-bonding between water and butanediols. Recently, one of the present author reported that the mixtures of alcohol+amine showed a characteristic concentration-dependence of glass transition temperatures [1].

There are several thermodynamic studies of calorimetric [2, 3], volumetric [4, 5] and vapour-liquid equilibrium measurements [6] for monoamines+monoalcohols. The steric effect and the influences of hydrophobic groups on hydrogen-bonding were discussed. In order to clarify the reason of those characteristic concentration-dependencies of glass transition temperatures, excess enthalpies of propanediamines(PDA)+propanediols(PDO) have been measured at 298.15 K as the functions of concentrations.

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## Experimental

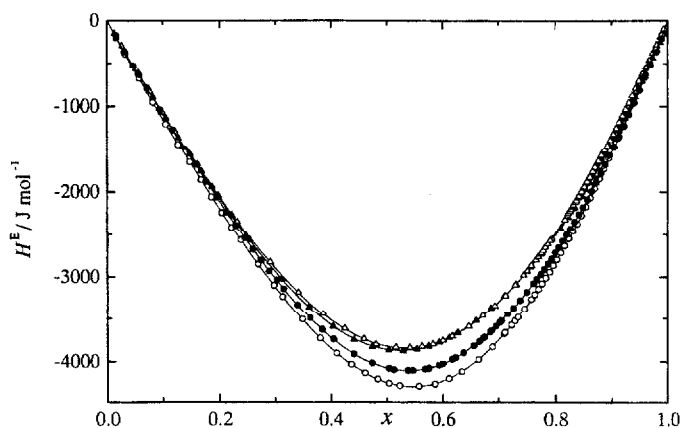
1,2- and 1,3-PDA, and 1,2- and 1,3-PDO (Kishida Chemical, GR) were fractionally distilled over freshly activated molecular sieves 4A which had been evacuated at 453 K for 12 h under  $10^{-2}$  to  $10^{-3}$  Pa. GLC results showed merely some trace-impurity peaks. Coulometric Karl-Fischer's method on a moisture-meter (Mitsubishi Chemical Ind., CA-02) gave the water content of each sample to be 0.01 mole per cent or less.

Partial molar excess enthalpies over the whole range of mole fraction were measured using a 0.8 ml vessel [7] on a Thermal Activity Monitor (Thermometric AB). The total amount of the sample used for each system was less than 0.8 g for PDAs and 1.5 g for PDO.

**Table 1** Densities of propanediamines and propanediols at 298.15 K

Propanediamine	$\rho/\text{g cm}^{-3}$	Propanediol	$\rho/\text{g cm}^{-3}$
1,2-Propanediamine	0.85707	1,2-Propanediol	1.0336
1,3-Propanediamine	0.87975	1,3-Propanediol	1.04985

The densities of pure PDAs and PDOs were measured with a vibrating-tube densimeter (Anton Paar DMA55) at  $(298.15 \pm 0.001)$  K and are shown in Table 1. An apparatus constant of the densimeter was determined before and after the measurements with carbon tetrachloride, cyclohexane, water and pure nitrogen. The details of densimetric procedures and reproducibility tests of this densimeter system are described elsewhere by Kimura *et al.* [8].



**Fig. 1** Excess enthalpies of  $(1-x)$ PDAs+ $x$ PDOs at 298.15 K:  $\blacktriangle$  – 1,2-PDA+1,2-PDO;  $\triangle$  – 1,2-PDA+1,3-PDOs;  $\bullet$  – 1,3-PDA+1,2-PDO;  $\circ$  – 1,3-PDA+1,3-PDO

**Table 2** Excess enthalpies  $H^E$  of propanediamines+propanediols at 298.15 K

$x$	$H^E/$ J mol <sup>-1</sup>	$x$	$H^E/$ J mol <sup>-1</sup>	$x$	$H^E/$ J mol <sup>-1</sup>
(1-x)1,2-propanediamine+x1,2-propanediol					
0.01651	-184.65	0.5742	-3819.3	0.8754	-1732.9
0.03248	-361.79	0.5935	-3775.1	0.8827	-1645.2
0.05797	-638.37	0.6112	3721.6	0.8902	-1563.5
0.08216	-897.92	0.6267	-3665.7	0.8978	-1470.9
0.1051	-1139.0	0.6274	-3664.2	0.9055	-1370.9
0.1270	-1360.7	0.6594	-3520.1	0.9133	-1279.0
0.1478	-1569.3	0.6869	-3369.1	0.9190	-1206.0
0.1676	-1763.5	0.7102	-3224.1	0.9248	-1130.6
0.1866	-1942.5	0.7304	-3085.5	0.9306	-1055.7
0.2220	-2266.3	0.7558	-2886.8	0.9365	-971.06
0.2544	-2566.4	0.7768	-2714.7	0.9425	-888.51
0.3118	-3027.3	0.7945	-2556.2	0.9486	-799.86
0.3610	-3359.5	0.8096	-2418.5	0.9547	-713.58
0.4037	-3596.5	0.8227	-2289.6	0.9609	-622.33
0.4410	-3746.3	0.8340	-2183.5	0.9672	-529.98
0.4739	-3830.3	0.8473	-2045.3	0.9736	-434.56
0.5031	-3865.6	0.8541	-1973.8	0.9801	-343.15
0.5293	-3876.4	0.8611	-1897.8	0.9866	-250.10
0.5528	-3855.8	0.8682	-1818.2	0.9933	-155.81
(1-x)1,3-propanediamine+x1,2-propanediol					
0.01607	-181.59	0.1763	-1880.2	0.3634	-3496.3
0.01620	-172.99	0.1945	-2060.9	0.3848	-3629.3
0.03163	-361.49	0.2119	-2231.1	0.4049	-3740.5
0.03188	-361.23	0.2286	-2386.5	0.4414	-3912.1
0.04707	-528.90	0.2446	-2539.4	0.4737	-4016.8
0.05649	-634.81	0.2599	-2676.4	0.5036	-4078.2
0.07135	-792.46	0.2747	-2803.4	0.5124	-4093.2
0.09442	-1039.3	0.2888	-2928.9	0.5378	-4102.2
0.1164	-1269.2	0.3024	-3038.1	0.5458	-4102.2
0.1373	-1484.9	0.3155	-3147.2	0.5676	-4086.2
0.1572	-1686.3	0.3403	-3332.4	0.5750	-4076.4

Table 2 Continued

$x$	$H^E/\text{J mol}^{-1}$	$x$	$H^E/\text{J mol}^{-1}$	$x$	$H^E/\text{J mol}^{-1}$
0.5938	-4039.3	0.7378	-3277.8	0.8567	-2038.8
0.6006	-4021.9	0.7494	-3182.3	0.8645	-1989.2
0.6170	3973.2	0.7613	3078.5	0.8724	-1891.3
0.6233	-3951.1	0.7674	-3025.3	0.8804	-1790.7
0.6377	-3895.6	0.7736	-2967.3	0.8886	-1685.5
0.6563	-3814.2	0.7799	-2910.1	0.8969	-1575.6
0.6659	-3763.1	0.7863	-2846.3	0.9054	-1460.7
0.6731	-3722.1	0.7928	-2783.1	0.9140	-1344.2
0.6753	-3712.2	0.7995	-2715.2	0.9228	-1223.2
0.6850	-3654.5	0.8062	-2646.6	0.9318	-1091.2
0.6883	-3634.2	0.8131	-2574.8	0.9410	-956.53
0.6949	-3592.2	0.8200	-2500.2	0.9503	-816.34
0.7021	-3543.3	0.8271	-2422.5	0.9599	-666.62
0.7052	-3522.9	0.8343	-2342.3	0.9696	-519.06
0.7157	-3446.3	0.8417	-2257.7	0.9795	-365.98
0.7266	-3368.0	0.8491	-2174.3	0.9897	-206.04
(1-x)1,2-propanediamine+x1,3-propanediol					
0.01349	-151.23	0.4806	-3800.9	0.7581	-2867.7
0.02662	-297.04	0.5161	-3832.9	0.7660	-2799.9
0.05186	-570.86	0.5404	-3838.1	0.7700	-2762.6
0.07582	-828.27	0.5624	-3823.0	0.7741	-2726.9
0.09861	-1066.3	0.5824	-3794.3	0.7755	-2713.3
0.1203	-1281.9	0.6007	-3751.8	0.7782	-2688.7
0.1410	-1492.8	0.6174	-3702.3	0.7823	-2651.9
0.1607	-1685.9	0.6467	-3588.2	0.7865	-2611.9
0.1975	-2040.0	0.6718	-3463.8	0.7907	-2572.1
0.2313	-2345.4	0.6936	-3344.3	0.8713	-1704.9
0.2909	-2825.2	0.7126	-3222.2	0.8170	-2317.7
0.3419	-3184.5	0.7295	-3097.9	0.8215	-2269.4
0.3861	-3441.2	0.7444	-2981.2	0.8231	-2245.1
0.4248	-3618.1	0.7504	-2932.9	0.8262	-2219.9
0.4588	-3732.8	0.7578	-2870.3	0.8277	-2197.0

Table 2 Continued

$x$	$H^E/\text{J mol}^{-1}$	$x$	$H^E/\text{J mol}^{-1}$	$x$	$H^E/\text{J mol}^{-1}$
0.8308	-2167.7	0.8752	-1654.5	0.9490	-713.42
0.8323	-2147.1	0.8764	-1643.5	0.9546	-636.65
0.8355	-2215.7	0.8805	-1590.5	0.9551	-632.31
0.8370	-2097.6	0.8816	-1581.0	0.9551	-632.31
0.8403	-2062.3	0.8858	-1525.6	0.9609	-552.29
0.8417	-2046.0	0.8868	-1517.0	0.9613	-549.98
0.8451	-2006.6	0.8922	-1453.9	0.9672	-465.19
0.8465	-1992.6	0.8975	-1387.7	0.9675	-463.71
0.8500	-1950.8	0.9030	-1319.4	0.9736	-378.09
0.8514	-1937.4	0.9085	-1249.8	0.9738	-376.14
0.8549	-1895.2	0.9141	-1179.5	0.9800	-289.13
0.8562	-1882.0	0.9197	-1106.3	0.9803	-285.76
0.8599	-1836.7	0.9254	-1031.3	0.9866	-195.25
0.8612	-1826.0	0.9312	955.14	0.9867	-194.26
0.8650	-1776.6	0.9371	-875.79	0.9933	-102.56
0.8662	-1765.0	0.9430	-794.55	0.9930	-99.962
0.8701	-1716.3	0.9485	-719.55		
(1-x)1,3-propanediamine+x1,3-propanediol					
0.01645	-199.48	0.3134	-3233.8	0.6889	-3824.8
0.03236	-391.31	0.3491	-3508.9	0.7104	-3673.8
0.05777	-681.17	0.3812	-3728.3	0.7119	-3660.2
0.08188	-952.11	0.4104	-3901.1	0.7229	-3576.1
0.1048	-1203.8	0.4369	-4032.5	0.7292	-3524.2
0.1266	-1440.5	0.4611	-4131.1	0.7342	-3482.8
0.1473	-1660.3	0.4834	-4201.1	0.7457	-3382.2
0.1671	-1861.2	0.5039	-4248.2	0.7458	-3377.9
0.1860	-2058.5	0.5228	-4276.5	0.7579	-3265.2
0.2041	-2240.6	0.5566	-4285.1	0.7641	-3205.0
0.2213	-2408.3	0.5859	-4257.2	0.7703	-3143.9
0.2379	-2564.3	0.6116	-4194.8	0.7767	-3078.9
0.2689	-2851.1	0.6343	-4115.3	0.7832	-3011.4
0.2979	-3102.2	0.6638	-3974.9	0.7898	-2943.9

Table 2 Continued

$x$	$H^E/\text{J mol}^{-1}$	$x$	$H^E/\text{J mol}^{-1}$	$x$	$H^E/\text{J mol}^{-1}$
0.7965	-2868.1	0.8544	-2170.4	0.9215	-1226.1
0.8033	-2792.1	0.8623	-2065.9	0.9306	-1090.2
0.8102	-2713.3	0.8703	-1957.4	0.9399	-951.46
0.8172	-2631.6	0.8784	-1846.4	0.9494	-805.39
0.8244	-2549.9	0.8867	-1730.5	0.9591	-654.17
0.8317	-2456.9	0.8951	-1610.8	0.9690	-498.74
0.8392	-2363.7	0.9038	-1487.1	0.9791	-337.66
0.8467	-2268.6	0.9125	-1358.8	0.9895	-172.37

## Results and discussion

The experimental results of excess enthalpies obtained are summarized in Table 2 and plotted in Fig. 1. All the excess enthalpies of PDAs+PDOs observed were negative over the whole range of mole fractions at this temperature and showed enormous values at their maxima around 0.55 in mole fractions. Excess enthalpies of PDAs+PDOs were fitted with Eq. (1) by the method of least squares in the range from 0.03 to 0.97 in mole fractions. The smoothed values are described as solid lines in Fig. 1.

$$H^E/\text{J mol}^{-1} = (1-x)x \sum_{i=1}^k A_i (1-2x)^{i-1} \quad (1)$$

where  $x$  denotes the mole fraction of PDOs in the mixtures. The coefficients  $A_i$ 's in Eq. (1), and standard deviations of the fits  $s_f$ :

$$s_f = \left[ \sum_{i=1}^n [H^E(\text{obs.}) - H^E(\text{calc.})]^2 / (n-k) \right]^{1/2} \quad (2)$$

are given in Table 3.

The mixtures of 1,3-PDA+1,3-PDO and 1,2-PDA+1,3-PDO showed the largest enthalpic stabilization and the least one respectively, among the mixtures of PDAs+PDOs. Excess enthalpies of the mixtures containing 1,3-PDA showed larger enthalpic stabilization than those containing 1,2-PDA. The mixtures of 1,2-PDO with 1,3-PDA showed smaller enthalpic stabilization than those of 1,3-PDO.

**Table 3** Best-fit values for the coefficients  $A_i$  of Eq. (1) and the calculated standard deviations of the fit  $s_f$ 

System	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$S_f$ J mol <sup>-1</sup>
(1-x)1,3-Propanediamine+x1,3-propanediol	-16971.5	4030.6	4036.7	-2045.7	-1423.7	2.0
(1-x)1,3-Propanediamine+x1,2-propanediol	-16304.2	3191.1	4463.6	-199.9	-2872.6	2.5
(1-x)1,2-Propanediamine+x1,3-propanediol	-15285.1	2539.4	3483.6	-934.5	-1143.8	3.3
(1-x)1,2-Propanediamine+x1,2-propanediol	-15437.1	1930.8	4187.3	903.4	-3103.2	3.9

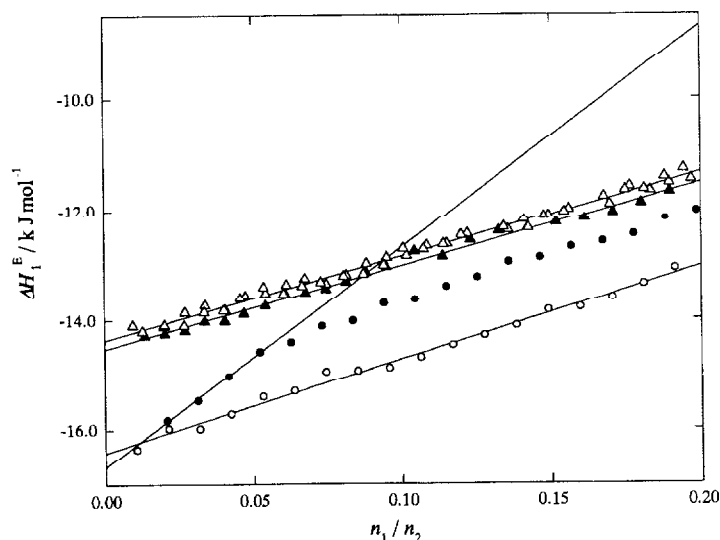
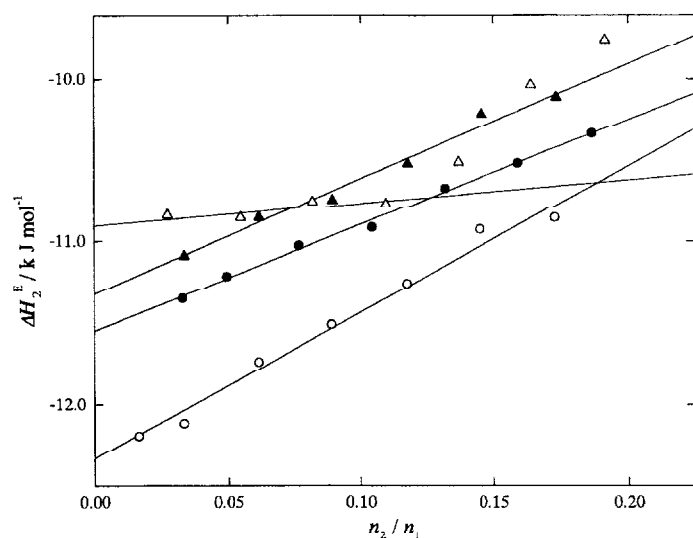


Fig. 2 Excess partial molar enthalpies of PDAs for mixtures of PDAs(1)+PDOs(2) at 298.15 K:  $\blacktriangle$  - 1,2-PDA(1)+1,2-PDO(2);  $\triangle$  - 1,2-PDA(1)+1,3-PDO(2);  $\bullet$  - 1,3-PDA(1)+1,2-PDO(2);  $\circ$  - 1,3-PDA(1)+1,3-PDO(2)

For the sake of elementary consideration of pair interaction, excess partial molar enthalpies,  $H_1^E$  and  $H_2^E$  in the range of high ratio of  $n_1/n_2$  and  $n_2/n_1$  were plotted in Figs 2 and 3, respectively. Excess partial molar enthalpies of PDAs in PDOs and PDOs in PDAs were linearly decreased with decreasing molar ratio of PDA/PDO and PDO/PDA, respectively, except  $H_1^E$  of the mixtures of 1,3-PDA(1)+1,2-PDO(2) and  $H_2^{E,\infty}$  of 1,2-PDA(1)+1,3-PDO(2). Excess partial molar enthalpies of 1,3-PDA,  $H_1^E$ , for the mixtures of 1,3-PDA+1,2-PDO showed different concentration dependence at boundary of 0.05 in molar ratio of  $n(1,3\text{-PDA})/n(1,2\text{-PDO})$ . Excess partial molar enthalpies of 1,3-PDO,  $H_2^E$ , for the mixtures of 1,2-PDA(1)+1,3-PDO(2) also showed a boundary of 0.11 in molar ratio of  $n(1,3\text{-PDO})/n(1,2\text{-PDA})$ . Excess partial molar enthalpies were fitted with Eq. (3) over the most dilute concentration range for each component. Limiting excess partial molar enthalpies determined from intercepts of Eq. (3) are summarized in Table 4. Limiting excess partial molar enthalpies were also determined from Eq. (1) and the coefficients listed in Table 2. The extrapolated values from Eq. (1) with the coefficients listed in Table 2 and direct determined values from Eq. (3) were agreed with experimental error except the mixtures of 1,3-PDA+1,2-PDO and 1,2-PDA+1,3-PDO.

$$H_1^{E,\infty} = a + bn_1/n_1 \quad (3)$$





**Fig. 3** Excess partial molar enthalpies of PDOs for mixtures of PDAs(1)+PDOs(2) at 298.15 K: ▲ – 1,2-PDA(1)+1,2-PDO(2); △ – 1,2-PDA(1)+1,3-PDO(2); ● – 1,3-PDA(1)+1,2-PDO(2); ○ – 1,3-PDA(1)+1,3-PDO(2)

Here  $i$ 's and  $j$ 's are PDAs or PDOs. The limiting excess partial molar enthalpies or the PDAs,  $H_1^{E,\infty}$ , of all the mixtures of PDAs+PDOs studied were smaller than those of PDOs,  $H_2^{E,\infty}$ , for each system.  $H_1^{E,\infty}$  of 1,3-PDA for the mixture of 1,3-PDA+1,2-PDO showed the largest enthalpic stabilization and that of 1,2-PDA for the mixture of 1,2-PDA+1,3-PDO the least one among the mixtures of PDOs+PDAs. On the other hand,  $H_2^{E,\infty}$  of 1,3-PDO for the mixture of 1,3-PDA+1,3-PDO showed the largest enthalpic stabilization and that of 1,3-PDO for the mixture of 1,2-PDA+1,3-PDO the least one among the mixtures of PDOs+PDAs. Pair interaction of 1,3-PDA with 1,2-PDO showed the largest enthalpic stabilization than others. The molecular structures of PDA and PDO may effect hydrogen bonding between PDA and PDO largely.

The results showed that the hydrogen-bonding of amine-alcohol were extremely stable than those of amine-amine and alcohol-alcohols. Excess enthalpies of methanol+diethylamine [3] and ethanol+triethylamine [2] were also  $-3.5$  to  $-4$  kJ mol $^{-1}$  at minimum showing large enthalpic stabilization on mixing. The steric effect of amines between hydroxyl and amino radicals were discussed [3].

The concentrations where the excess enthalpies are minimum correspond to the concentrations where the temperatures of glass transition of PDAs+PDOs mixtures are maximum [1]. This result might show a strong interaction between PDAs and PDOs. Association constants and enthalpies between amine and hydroxyl groups tried to determine by the use of ideal association treatment [9–11].

**Table 4** The limiting excess partial molar enthalpies of the mixtures of propanediamine+propanediol at 298.15 K

System	$H_1^{E,\infty}$ kJ mol <sup>-1</sup>	$H_2^{E,\infty}$ kJ mol <sup>-1</sup>
1,3-Propanediamine(1)+1,3-propanediol(2)	-16.42±0.04	-12.34±0.05
1,3-Propanediamine(1)+1,2-propanediol(2)	-16.69±0.06	-11.55±0.02
1,2-Propanediamine(1)+1,3-propanediol(2)	-14.37±0.04	-10.31±0.03
1,2-Propanediamine(1)+1,2-propanediol(2)	-14.53±0.03	-11.32±0.04

**Table 5** Comparison of the thermodynamic quantities for 1:1 complex formation of propanediamines and propanediols

System	$K_1$	$\Delta_f G_i$ kJ mol <sup>-1</sup>	$\Delta_f H_i$ kJ mol <sup>-1</sup>	$\Delta_f S_i$ J K <sup>-1</sup> mol <sup>-1</sup>
(1-x)1,3-Propanediamine+x1,3-propanediol	2.53	2.30	-18.6	-70.1
(1-x)1,3-Propanediamine+x1,2-propanediol	2.22	1.98	-18.8	-69.7
(1-x)1,2-Propanediamine+x1,3-propanediol	1.84	1.51	-19.1	-69.1
(1-x)1,2-Propanediamine+x1,2-propanediol	1.40	0.85	-22.0	-76.6

Three associated species of different molar ratios AB, AB<sub>2</sub> and A<sub>2</sub>B were treated. Only the result of 1:1 association is described here.



Here A and B show molecules of PDA and PDO, respectively. Results of excess enthalpies of mixing were applied by least squares curve fitting treatment. Equilibrium constant and thermodynamic properties from Eq. (4) were listed in Table 5.

Raman spectrum of the mixtures of PDAs+PDOs also showed an increasing amount and power of hydrogen-bonding between hydroxyl groups and amine groups [12].

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