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Excess enthalpies of binary mixtures of some propylamines + some propanols at 298.15 K

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Abstract

The molar excess enthalpies of 1,2- and 1,3-propanediamine + 1- or 2-propanol and 1,2- and 1,3-propanediol + 1- or 2-propaneamine have been determined at 298.15 K using a twin-microcalorimeter for a series of runs over the whole range of mole fractions. All excess enthalpies were large exothermic, in particular, the systems of amines + propanediols were more than $-5\,\mathrm{kJ\,mol^{-1}}$ at the minimum. Primary or secondary alcohols and amines showed systematically different enthalpic behaviors. Equilibrium constant K1 expressed in terms of mole fractions and standard enthalpy of the formation of a 1:1 complex have been evaluated by ideal mixtures of momomeric molecules and their associated complexes.

Keywords: Excess enthalpies; 1,2- and 1,3-propanediamine; 1,2- and 1,3-propanediol; 1- and 2-propanol; 1- and 2-propaneamine; Ideal association treatment

1. Introduction

A series of thermodynamic measurements of vapour pressure, excess enthalpy and excess volume for aqueous binary mixtures containing four butanediol isomers and dioxane have been measured by the present authors to understand the behaviour of amphiphilic molecules that have hydroxyl groups and methyl or methylene groups in aqueous and non-aqueous solutions [1,2]. The excess thermodynamic properties of these mixtures showed a strong effect on hydrogen bonding between water and butanediols [2]. The mixtures of alcohol + amine also showed a characteristic concentration-dependence of glass transition temperatures [3] and transportation phenomena [4]. There are several thermodynamic studies on calorimetric [5,6], volumetric [7,8], vapour–liquid equilibrium measurements [9], solid–liquid equilibrium [10] and theoretical studies on ERAS [11–14] for monoamines + monoalcohols. The steric effect and the influences of hydrophobic groups on hydrogen bonding have been discussed in previous works. In a previous paper [15], excess enthalpies of propanediols(PDOs) + propanediamines (PDAs) were reported to reveal the hydrogen-bonding properties of the positional effect on the hydrogen bond in those molecules having two hydroxyl groups or amine groups in propane. In particular, the excess partial molar enthalpies of PDAs in PODs and PDOs in PDAs linearly decreased with a decreasing molar ratio of PDA/PDO and PDO/PDA, respectively, except of the mixtures of 1,3-PDA(1) + 1,2-PDO(2) and of 1,2-PDA(1) + 1,3-PDO(2). The excess partial molar enthalpies of 1,3-PDA, for the mixtures of 1,3-PDA + 1,2-PDO showed different concentration dependencies at the boundary of 0.05 in the molar ratio of *n*(1,3-PDA)/*n*(1,2-PDO). In order to clarify the reason for the large stabilization on mixing and the steric effect, and the influences of hydrophobic groups on hydrogen bonding, excess enthalpies of diamines + monoalcohols or monoamines + diols were measured at 298.15 K as the functions of concentrations.

2. Experimental

1,2- and 1,3-PDA, and 1,2-, 1,3-PDO, 1- and 2-propanol (PrOH), 1- and 2-propylamine (PrA, Kishida Chemical, CGR) were fractionally distilled over freshly activated molecular sieves 4A that had been evacuated at 453 K for 12 h under 10^{-2} to 10^{-3} Pa. Their chemical purities determined by gas chromatography each using a 2 m column of 10% SE-30 on chromosorb and 20% PEG-1000 on celite 545 with FID on Yanagimoto G180FP were more than 99.99%. The water contents of samples obtained by the Coulometric Karl–Fischer method on a Moisturemeter (Mitsubishi Chemical Ind., CA-02) were less than 0.001 mol%.

A twin-microcalorimeter of the heat-conduction type, the thermal activity monitor (Thermometric AB, Järfälla, Sweden) with a volume of $0.8\,\mathrm{cm^3}$ for each mixing vessel, which had been

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Table 1
Densities and phesicochemical properties of amines and alcohols at 298.15 K

Sample	ρ(obs.) (g cm^{-3})	$10^5 s_f$ (g cm^{-3})	ρ(ref.) (g cm^{-3})	$\Delta_v H^a$ (kJ mol^{-1})	$\Delta_v S^b$ (J K^{-1} mol^{-1})
1-Propanol	0.79910	1.3	0.79960[a]	47.32	127.8
2-Propanol	0.78035	2.1	0.78126[a]	45.52	112.2
1-Propylamine	0.71276	5.6	0.7121[a]	31.26	92.98
2-Propylamine	0.68394	2.4	0.6821[a]	28.36	90.98
1,2-Propanediol	1.0336	6.8	1.0328[a]	64.4	113.6
1,3-Propanediol	1.0499	5.4	1.050[a]	72.8	118.7
1,2-Propanediamine	0.85709	7.2	0.85707[c], 0.8583[d]	39.04	130.9
1,3-Propanediamine	0.87981	1.1	0.87975[c]	50.21	168.4

[a] Ref. [18].
[b] Calculated values of $\Delta_v S = \Delta_v H/T$ ($T = 298.15$ K).
[c] Ref. [15].
[d] Ref. [14].

modified by a previous work [16], was used for the measurement of excess enthalpies at 298.15 K over the entire range of mole fractions.

The densities of the pure samples were measured by a vibrating-tube densimeter (Anton Paar DMA55) at (298.15 ± 0.001 K) and are shown in Table 1. The densities of the samples agreed with the reference value as shown in Table 1. The apparatus constant of the densimeter was determined before and after the measurements with carbon tetrachloride, cyclohexane, water and pure nitrogen. The details of the densimetric procedures and reproducibility tests of this densimeter system are described by Kimura et al. [17]. Raman spectrums were measured by Nicolet 870 (Thermo Electron).

3. Results and discussion

The experimental results of the excess enthalpies obtained are summarized in the table [19] and plotted in Figs. 1 and 2. All the excess enthalpies of the amines + alcohols observed were negative over the whole range of mole fractions at this temperature and showed enormous values at their minimum around the equimolar mixtures. The excess enthalpies of amines + alcohols were fitted with Eq. (1) by the least squares method. The smoothed values are shown as solid lines in Figs. 1 and 2:

$$H^E\,(\mathrm{J\,mol^{-1}}) = (1-x)x\sum_{i=1}^{k} A_i(1-2x)^{i-1} \tag{1}$$

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

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

are listed in Table 2.

The mixtures of amines + alcohols showed enormous enthalpic stabilization, and the mixtures of $(1-x)$2-PrA + x1,3-PDO showed the largest stabilization among the mixtures of amines + alcohols measured. The excess enthalpies of the mixtures containing primary alcohols showed larger enthalpic stabilization than those containing secondary alcohols. However, the excess enthalpies of the mixtures containing primary amines showed less enthalpic stabilization than those containing secondary amines. The minimum excess enthalpies of the system,

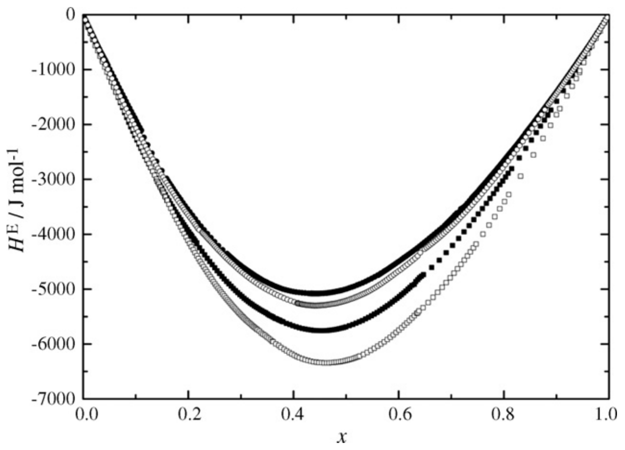

Fig. 1. Excess enthalpies of $(1-x)$propaneamines (PrA) + $x$propanediols (PDO) at 298.15 K—●: 1-PrA + 1,2-PDO; ○: 1-PrA + 1,3-PDOs; ■: 2-PrA + 1,2-PDO; □: 2-PrA + 1,3-PDO.

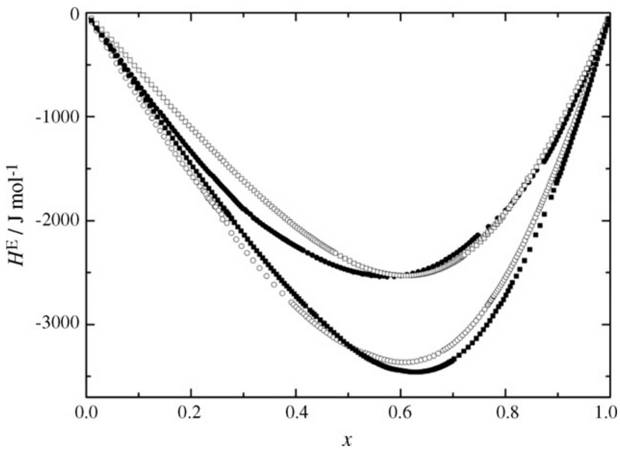

Fig. 2. Excess enthalpies of $(1-x)$propanediamines(PDA) + $x$propanols(PrOH) at 298.15 K—●: 1,2-PDA + 1-PrOH; ○: 1,2-PDA + 2-PrOH; ■: 1,3-PDA + 1-PrOH; □: 1,3-PDA + 2-PrOH.

Table 2
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^{-1})
$(1-x)$1,2-Propanediamine + x1-propanol	−12877.3	5878.7	−174.7	−2121.4	662.3	4.8
$(1-x)$1,2-Propanediamine + x2-propanol	−9925.1	2563.1	−530.5	1263.2	−306.8	4.8
$(1-x)$1,3-Propanediamine + x1-propanol	−12808.1	7573.2	−1336.3	−2432.6	1384.0	2.9
$(1-x)$1,3-Propanediamine + x2-propanol	−9548.3	4932.2	−161.3	−1746.0	1040.1	4.1
$(1-x)$1-Propylamine + x1,2-propandiol	−19949.7	−5658.7	818.2	3020.9	1992.3	4.7
$(1-x)$1-Propylamine + x1,3-propandiol	−20782.4	−5371.7	2721.5	1970.1	−998.6	5.4
$(1-x)$2-Propylamine + x1,2-propandiol	−22670.4	−5520.9	2788.9	1653.6	−593.0	4.9
$(1-x)$2-Propylamine + x1,3-propandiol	−25135.8	−4906.9	5113.2	4310.5	−2514.1	5.1

Table 3
Excess enthalpies of amines + alcohols at minimum values

System	x	ϕ	H^E (kJ mol^{-1})
$(1-x)$1,2-PDA + x2-PrOH	0.5759	0.5952	−2.409
$(1-x)$1,3-PDA + x2-PrOH	0.6123	0.5473	−2.478
$(1-x)$1,3-PDA + x1-PrOH	0.6074	0.5800	−3.355
$(1-x)$1,2-PDA + x1-PrOH	0.6284	0.5952	−3.457
$(1-x)$1-PrA + x1,2-PDO	0.4458	0.4166	−4.930
$(1-x)$1-PrA + x1,3-PDO	0.4371	0.4043	−5.175
$(1-x)$2-PrA + x1,2-PDO	0.4540	0.4147	−5.758
$(1-x)$2-PrA + x1,3-PDO	0.4676	0.4242	−6.343

ϕ: volume fraction of alcohols calculated from ideal mixing.

mole fraction and volume fraction calculated from the ideal mixing volume are listed in Table 3. The mole fractions at the minimum excess enthalpy of the system of amine + alcohol had nearly equal molar ratios between the amines and alcohols, but those of the propanediamine(PDA) + propanol(PrOH) systems and the propaneamine(PrA) + propanediol(PDO) systems were (0.606 ± 0.022) and (0.451 ± 0.013), respectively.

For an elementary consideration of pair interaction, limiting excess partial molar enthalpies determined from Eq. (1) and coefficients in Table 2 are summarized in Table 4. The limiting excess partial molar enthalpies of amines $H_1^{E,\infty}$ of all the mixtures studied were stabilized in the range from −12 kJ mol^{-1} to −17 kJ mol^{-1}. The averages of $H_1^{E,\infty}$ were −15.1 kJ mol^{-1} and −17.2 kJ mol^{-1} for PDAs + PrOHs and PrAs + PDOs, respectively. $H_1^{E,\infty}$ of these two systems agreed within the standard deviations of each system. On the other hand, the limiting excess partial molar enthalpies of alcohols $H_2^{E,\infty}$ were stabilized in the range from −5 kJ mol^{-1} to −24 kJ mol^{-1}. The averages of $H_2^{E,\infty}$ were −7.2 kJ mol^{-1} and −22.4 kJ mol^{-1} for PDAs + PrOHs and PrAs + PDOs, respectively. $H_2^{E,\infty}$ of the system of PDAs + PDOs were 3.1 times larger than those of PDAs + PrOHs. Four limiting excess partial molar enthalpies of PDAs + PDOs were reported in a previous paper [15], where PDAs showed more large enthalpic stabilization than that of PDOs. The limiting excess partial molar enthalpies of alcohols showed a large structural effect of stabilization on mixing. The limiting excess partial molar enthalpies of the PDAs of all the mixtures studied were less stabilized than those of PrOHs. However, the limiting excess partial molar enthalpies of the PrAs of all the mixtures of PrAs + PDOs studied were more stabilized than those of PDOs. $H_1^{E,\infty}$ of 2-PrA for the mixture of 2-PrA + 1,3-PDO showed the largest enthalpic stabilization, and that of 1,3-PDA for the mixture of 1,3-PDA + 2-PrOH showed the least enthalpic stabilization among the mixtures measured. On the other hand, $H_2^{E,\infty}$ of 1,2-PDO for the mixture of 2-PrA + 1,2-PDO showed the largest enthalpic stabilization and that of 2-PrOH for the mixture of 1,3-PDA + 2-PrOH showed the least enthalpic stabilization among the mixtures measured. Pair interaction of 2-PrA with 1,2-PDO showed the highest enthalpic stabilization compared to the others. The molecular structures of amines and alcohols may significantly affect hydrogen bonding between amines and alcohols.

Table 4
Limiting excess partial molar enthalpies of amine(1) + alcohol(2) at 298.15 K

System	H_1^∞ (kJ mol^{-1})	H_2^∞ (kJ mol^{-1})
1,2-Propanediamine + 1-propanol	−16.15	−8.63
1,2-Propanediamine + 2-propanol	−17.90	−7.62
1,3-Propanediamine + 1-propanol	−14.59	−6.94
1,3-Propanediamine + 2-propanol	−11.86	−5.48
1-Propylamine + 1,2-propandiol	−14.50	−19.78
1-Propylamine + 1,3-propandiol	−15.66	−22.46
2-Propylamine + 1,2-propandiol	−16.61	−24.34
2-Propylamine + 1,3-propandiol	−21.94	−23.13

Enthalpies of the vaporization of amines and alcohols are summarized in the third column of Table 1. Entropies of vaporization are calculated and listed in the fifth column of Table 1. All amines and alcohols used were much larger than Trouton's rule except for 2-propylamine. Then, these might be strongly associated in each liquid state. The results showed that the hydrogen bonding of amine–alcohol was extremely stable compared to those of amine–amine and alcohol–alcohol. The excess enthalpies of methanol + ethanol + triethylamine [5], 1-propanol + triethylamine [6] were −1.9 kJ mol^{-1}, −1.3 kJ mol^{-1}, and −1.4 kJ mol^{-1} at minimum, respectively, showing large enthalpic stabilization on mixing.

The steric effect of amines between hydroxyl and amino radicals are discussed [3]. An example of the Raman spectrum of the mixtures of 1,2-propandiamine + 1-propanol are shown in Fig. 3. These showed an increasing amount and power of hydrogen bonding between the hydroxyl groups and amine groups. Moreover, the concentration dependence of the intensities show

Table 5
Thermodynamic quantities for 1:1 complex formation of amines and propanols

System	K_1	$\Delta_f G$ (kJ mol^{-1})	$\Delta_f H$ (kJ mol^{-1})	$\Delta_f S$ (J K^{-1} mol^{-1})
1,3-Propanediamine + 1-propanol	9.15	−5.49	−8.32	−9.52
1,3-Propanediamine + 2-propanol	13.4	−6.43	−5.78	2.17
1,2-Propanediamine + 1-propanol	1.83	−1.50	−13.3	−39.5
1,2-Propanediamine + 2-propanol	6.60	−4.68	−8.05	−11.3
1-Propylamine + 1,2-propanediol	2.58	−2.35	−20.1	−59.4
1-Propylamine + 1,3-propanediol	2.05	−1.77	−24.9	−77.5
2-Propylamine + 1,2-propanediol	1.18	−0.41	−30.7	−101.6
2-Propylamine + 1,3-propanediol	1.26	−0.58	−34.4	−113.5

minimum around the equlimolar concentration. This might be consistent with the 1:1 association between amines and alcohols. Spectroscopic considerations based on this will be discussed precisely [2].

It was attempted to determine the association of constants and enthalpies between amines and hydroxyl groups by the use of ideal association treatment [21–23]. Three associated species of different molar ratios, AB, AB_2 and AB_3, were treated. Only the result of 1:1 association is described here:

$$A + B = AB,\ \Delta H_1,\ K_1 \tag{3}$$

here, A and B show the molecules of amines and alcohols, respectively. The least squares curve-fitting treatment was applied to the results of the excess enthalpies of mixing in the low concentration range where a 1:1 association might be possible. The equilibrium constant and thermodynamic properties from Eq. (3) are listed in Table 5. The enthalpies of the formation of association complexes of propylamine and propanediol were larger than those of propyldiamine and propanol. The enthalpy of the formation of the association complex between 2-propylamine and 1,3-propanediol showed the largest stabilization. That between 1,3-propanediamine and 2-propanol showed the least stabilization.

The correlations of the thermodynamic properties of the association between amines and alcohols are plotted in Fig. 4 with previously reported values [15]. The so-called compensation rule of enthalpies and entropies on association properties between amines and alcohols was established as in Fig. 4. The open circles in Fig. 4 show the relation between propanediamines + propanediols. The relations of entropy–enthalpy of propanediamines + propanols, propaneamines + propanediols, and propanediols + propanediamines show different behaviours as indicated in Fig. 4. The relations are summarized as Eq. (4) for propylamines + propanediols and propanediamines + propanols:

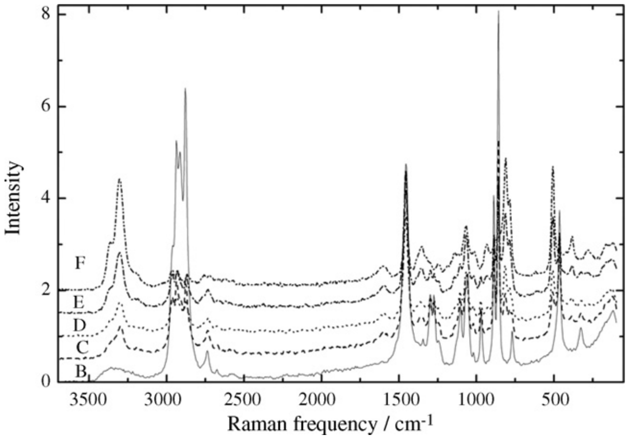

Fig. 3. Raman spectrum of $(1-x)$1,2-propanediamine + x1-propanol—B: $x = 0$; C: $x = 0.7075$; D: $x = 0.5434$; E: $x = 0.3628$; F: $x = 1$.

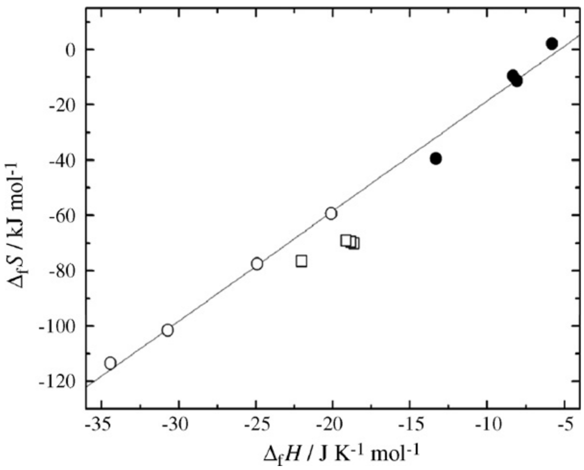

Fig. 4. Correlation between entropies and enthalpies of complex formation for propylamines + propanols—●: propylamines + propanediols; ○: propanediamines + propanols; □: propanediamine + propanediols.

$$\Delta_f H\ (\text{kJ mol}^{-1}) = -5.4 + 0.250\Delta_f S, \qquad s_f = 0.9\ \text{kJ mol}^{-1} \tag{4}$$

The results indicate an association scheme between the amines and alcohols measured, showing similar mechanisms in each linear relation. A more precise scheme of the interactions between alcohols and amines in a solution state will be discussed in detail by combining thermodynamic and Raman spectroscopic results [20].

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.08.006.

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