Hydrate Cluster Formation of Diol Compounds in Aqueous Solution

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Dilute aqueous solutions of seven diols (1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2-pentanediol, 2,4-pentanediol, 1,4-pentanediol, and 1,5-pentanediol) were examined by mass spectrometric analysis of the clusters isolated through adiabatic expansion of liquid droplets in vacuum. Stability constants of the solute m-mer hydrate clusters κ_m ($m=1$, 2) were estimated by analyzing the obtained mass spectra. All the stability constants for the diols were found to be approximately equal to or less than 1.0, suggesting that the hydrate clusters of the solute species are as strong as or weaker than those of *pure water* clusters. Stabilities of the diol hydrate clusters are also dependent on the distance between the two OH groups and/or the number of methylene groups between the two OH groups. From the temperature dependence of the population ratio of the diol-hydrate clusters to pure water ones, we evaluated thermochemical values for the elemental association-dissociation processes.

Frank and Evans pointed out that the presence of the hydration processes of nonpolar (hydrophobic) gases was accompanied by entropy reduction.[1] They suggested that such solutes promote the structuring of the neighboring water molecules, producing an ice-like structure. Now, such a hydration process is called "hydrophobic hydration". Later, the concept of "hydrophobic interaction" was introduced by Franks and Ives, and Ben-Naim.[2—4] The two concepts are used very widely for explaining thermochemical properties of aqueous solutions.

The methods of mass spectrometric analyses of the clusters generated through adiabatic expansion of liquid droplets in vacuum have been reported for the study of the molecular association in 1-alkanol– and carboxylic acid–water systems.[5,6] According to the previous results, the longer alkyl groups showed larger stability constants for hydrate cluster formation in accord with the concept of "hydrate shell formation" around the alkyl group due to hydrophobic hydration.[7—11]

From an energetical point of view that is applicable to the cluster formation in gas collision processes, the introduction of one more OH group into a 1-alkanol is expected to produce diol-hydrates with more water molecules. What we observed in this study is just the the opposite: The hydration process is highly affected by the dominated entropy contribution to the free energy change. This is characteristic of solution systems. Hydration of poly-hydroxylated compounds in aqueous solution have been studied comprehensively.[12—16] It seems very important to clarify the feature of hydration behavior of such solutes for the understanding of some interesting phenomena in biological systems. The systems studied here are the seven dilute aqueous solutions of diols (1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2-pentanediol, 2,4-pentanediol, 1,4-pentanediol and 1,5-pentanediol). The method of the mass spectrometric analysis of the solutions fragmented as clusters is essentially the molecular composition analysis of the fragments. It can afford insight into the compositional distribution of the clustering species in solution. In this study, we present the experimental data for the enthalpy and entropy changes in molecular exchange or association-dissociation processes in the aqueous environment.

Experimental

The essential part of the apparatus is composed of four beam chambers coupled with a coaxial quadrupole mass spectrometer (Extrel 270-9/150QC). A liquid chromatograph pumping unit (Shimadzu LC-5A) was used to introduce the liquid into vacuum. The optimum flow rate of aqueous solution was fixed at 0.08 mL min^{-1}. The pressure of the flowing liquid in the stainless pipe was measured by a Bourdon type pressure gauge (Shinagawa Sokki, Model LCG50D) directly connected to the pipe at the entrance to the vacuum chamber. Conversion of liquid jets to cluster beams was carried out by using a modified injector needle (Hamilton type N731) which has an exit zig-zag hole of 40 (±15) μm. The aqueous solution was converted to mist particles in the first chamber with a backing pressure maintained below 0.3 Torr (1 Torr=133.322 Pa). The jet is skimmed by the first 2 mm skimmer and the second 1 mm skimmer, and finally passed into the third high vacuum chamber maintained below 10^{-5} Torr. After passing the second skimmer, the mist particles were converted to clusters. In the third chamber, the clusters (generated by adiabatic expansion of the droplets) were ionized by electron impact ionization at 40 eV, and analyzed with a quadrupole mass spectrometer. Ion energy was adjusted as low as 0.2 eV for unit-mass resolution measurement. Correction of the mass dependence of the ion intensity distribution for the ion focusing condition was calibrated by measuring both spectral patterns of perfluorohexane and the water clusters isolated from pure water droplets at 60 °C. The signals from a ceramic electron multiplier (Murata EMS-6081B) were amplified by an electrometer and averaged over 120 times by using a Nicolet 1170 signal averager with 4088 data points. The temperature of the liquid nozzle was monitored at 4 mm behind the nozzle-head by a thermocouple. The final liquid droplet temperature was calibrated by observing the lower critical solution temperature 49 °C and the upper temperature 128 °C of an aqueous solution (with molar fraction of 2-butoxyethanol=0.05). This solution shows a mass spectral intensity anomaly due to the phase-separation in the range between the two critical temperatures.[5)]

1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2-pentanediol, and 1,5-pentanediol (Tokyo Kasei Kogyo Co., Ltd.); 2,4-pentanediol, and 1,4-pentanediol (Aldrich) were used as solutes without further purification. High purity water obtained through a water purifier (Puric Z, Organo Co., Ltd.) was used as solvent. Each aqueous solution was prepared by mixing each solute with water in the molar ratios of solute to solvent: $x_1/x_2=1/800$—$1/50$. Temperature dependence of the cluster distribution was measured at liquid-droplet temperatures in the range of 30—90 °C.

Results and Discussion

Mass Spectra. Mass spectra of the solutions of the three isomers, 1,2-pentanediol, 2,4-pentanediol, and 1,5-pentanediol ($x_1/x_2=1/300$), measured at a liquid-droplet temperature of 60 °C are shown in Fig. 1. In the three spectra, one can see clear differences in the signal intensities of the monomer-hydrate clusters ($[H^+A(H_2O)_{n-1}]$) relative to those of the pure water clusters ($[H^+(H_2O)_n]$). The monomer-hydrate signals of 1,2-pentanediol are slightly stronger than those of 2,4-pentanediol, and those of 1,4-pentanediol are very weak. The spectra of the three times more concentrated aqueous solutions of 1,4-pentanediol and 1,5-pentanediol ($x_1/x_2=1/100$) are shown in Fig. 2. The monomer-hydrate signals of 1,5-pentanediol are much weaker than those of 1,4-pentanediol. Thus the solute-hydrate signals of these diol-compounds are found to be highly dependent on the mutual positions of the two OH groups. The concentrations required for the observation of the diol-hydrates are 10—40 times higher than those for the alkyl alcohols with similar molecular sizes.

Evaluation of Stability Constant. On the basis of the previous systematic study on the carboxylic acids,[6)] the following assumption can be reasonably proposed: the observed population of the clusters reflects the association–dissociation equilibrium in the liquid state just before the instantaneous expansion-cooling, although the evaporation of 4—8 water molecules from the original neutral clusters should be considered for the detection process. Association–dissociation equilibrium of hydrate clusters in aqueous solution can be generally expressed by the following equation:[5,6)]

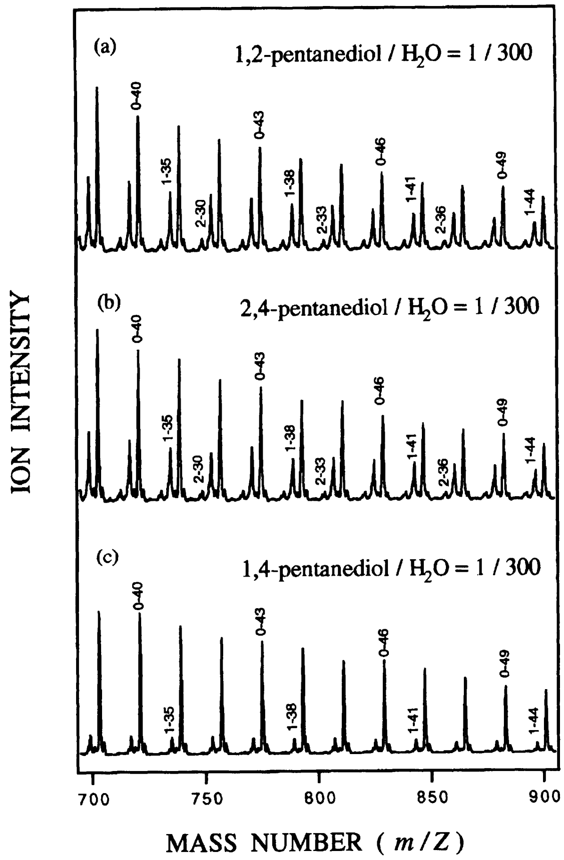

Fig. 1. Mass spectra of cluster beams generated from three diol aqueous solutions ($x_1/x_2=1/300$) at 60 °C. (a) 1,2-pentanediol, (b) 2,4-pentanediol, and (c) 1,4-pentanediol. m–n stands for $H^+A_m(H_2O)_n$.

$$A_{m-1}(H_2O)_n + A \overset{K_m^n}{\rightleftharpoons} A_m(H_2O)_{n-1} + H_2O, \qquad (1)$$

where m is the number of solute molecules A, n the number of water molecules, and K_m^n the equilibrium constant. Here, the stability constant of m-mer hydrates, κ_m, is expressed as follows based on the original definition from the stochastic consideration:[5)]

$$\kappa_m = (m/n)K_m^n. \qquad (2)$$

κ_m can provide an equilibrium constant independent of the association number n. For the hydrate clusters with a large value of n ($n>30\gg m$), the average number of evaporated water molecules from $A_m(H_2O)_{n-1}$ in the detection process could be regarded as nearly the same as that from $A_{m-1}(H_2O)_n$, so that the following relation could be assumed:[5,6)]

$$[A_m(H_2O)_{n-1}]/[A_{m-1}(H_2O)_n] = [H^+A_m(H_2O)_{n'-1}]/[H^+A_{m-1}(H_2O)_{n'}]. \qquad (3)$$

Thus the observed intensity ratios are expressed as fol-

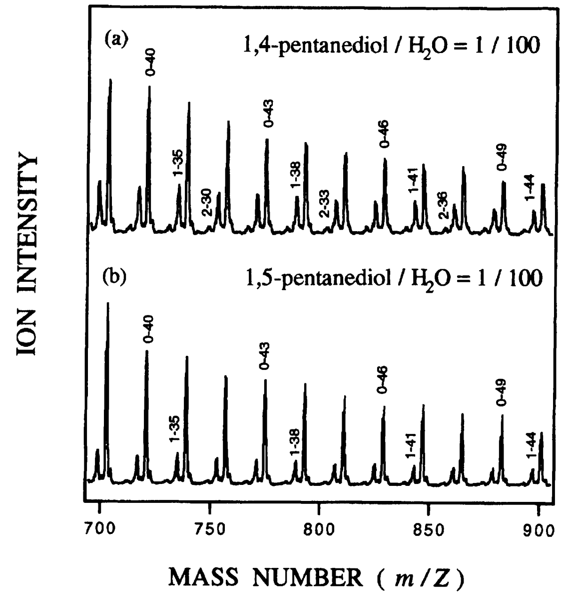

Fig. 2. Mass spectra of cluster beams generated from two diol aqueous solutions ($x_1/x_2=1/100$) at 60 °C. (a) 1,4-pentanediol and (b) 1,5-pentanediol. m–n stands for $H^+A_m(H_2O)_n$.

lows:

$$\frac{[H^+A_m(H_2O)_{n'-1}]}{[H^+A_{m-1}(H_2O)_{n'}]}=\frac{\kappa_m}{m}\frac{x_1}{x_2}n, \tag{4}$$

where, x_1/x_2 denotes the molar ratio of solute to solvent. Here it is assumed that the population ratio of free water to free solute is proportional to the total molar ratio of solvent to solute x_2/x_1 in a dilute solution. The validity of this assumption was confirmed by observing the invariability of the κ_m values with the change of solute concentration. Such stability constants independent of hydration numbers are only quantitatively meaningful in this kind of study because it does not provide any quantitative information for a specific hydrate species.

The observed intensity ratios of $[H^+A_m(H_2O)_{n-1}]/[H^+A_{m-1}(H_2O)_n]$ of 1,2-pentanediol, 2,4-pentanediol, 1,4-pentanediol, and 1,5-pentanediol are plotted as functions of the number of water molecules n as shown in Fig. 3. All the intensity ratios of the diols linearly increased with increasing number of hydration number n, suggesting that Eq. 4 is applicable to these diol–water systems. The decreasing order of the slopes of the plots is 1,2-pentanediol>2,4-pentanediol>1,4-pentanediol>1,5-pentanediol. The stability constants of the monomer-hydrate clusters (κ_1) and the dimer-hydrate clusters (κ_2) of the seven diols at a liquid-droplet temperature of 60 °C are listed in Table 1.

Effect of Two OH Groups of a Solute on Hydrate Cluster Formation. The stability constants of the three 1-alkanols with the same numbers of carbon atoms of the diols (e.g., ethanol versus 1,2-ethanediol) are also listed in Table 1. In contrast to the large κ_1 and κ_2 of the 1-alkanols (indicating that the process of Eq. 1 largely shifts to the right direction forming stable hydrate clusters), those of the diols with the same numbers of carbon atoms are very small. For example, κ_1 of 1,5-pentanediol is approximately 1/50 of that of 1-pentanol. All the κ_1 and κ_2 values of the diols are approximately equal to or less than 1.0, meaning that the process of Eq. 1 for the diols tends to shift to the left direction. This suggests that the introduction of one more OH group to a 1-alkanol leads to the marked reduction of the stability of hydrate clusters.

Table 1. Stability Constants for Diols and 1-Alkanols at 60 °C

Solute species	κ_1	κ_2
Ethanol	7.6	8.8
1,2-Ethanediol	0.6	0.8
1-Propanol	9.5	10.9
1,2-Propanediol	1.3	1.6
1,3-Propanediol	0.4	0.5
1-Pentanol	15	18
1,2-Pentanediol	2.7	3.4
2,4-Pentanediol	2.2	2.7
1,4-Pentanediol	0.7	0.8
1,5-Pentanediol	0.3	0.4

As shown in Table 1, the stability constants of the diol hydrate clusters vary with the number of methylene groups between the two OH groups. Both κ_1 and κ_2 of the diols decrease with increasing number of methylene groups in the order of 1,2-ethanediol, 1,3-propanediol, and 1,5-pentanediol: the stability of the hydrate clusters of the diols decreases with increasing number of the methylene groups between the two OH groups. This trend is opposite to that in 1-alkanols and carboxylic acids,[6] where stability of the hydrate clusters increases with increasing length of alkyl groups, owing to hydrophobic hydration. In addition to this, the κ_1 and κ_2 of the isomer species also vary with changing the relative position of the two OH groups: the decreasing order of both κ_1 and κ_2 of the propanediols is 1,2-propanediol>1,3-propanediol, and that of the pentanediols is 1,2-pentanediol>2,4-pentanediol>1,4-pentanediol>1,5-pentanediol, respectively.

For interpreting these results, the total contribution to hydrate cluster formation of the diols is divided into two parts: an alkyl group as a side chain, $CH_3(CH_2)_n$–, and methylene groups between the two OH groups, $-HOCH(CH_2)_nCHOH-$. Here, the former group plays a role in promoting hydrate cluster formation due to hydrophobic hydration and the latter may play a role in decoupling the water clusters from the solute. For example, 1,2-pentanediol and 2,4-pentanediol can be expressed as follows:

$$CH_3CH_2CH_2CH(OH)CH_2OH \rightarrow CH_3CH_2CH_2\text{– and –}CH(OH)CH_2OH, \tag{5}$$

and

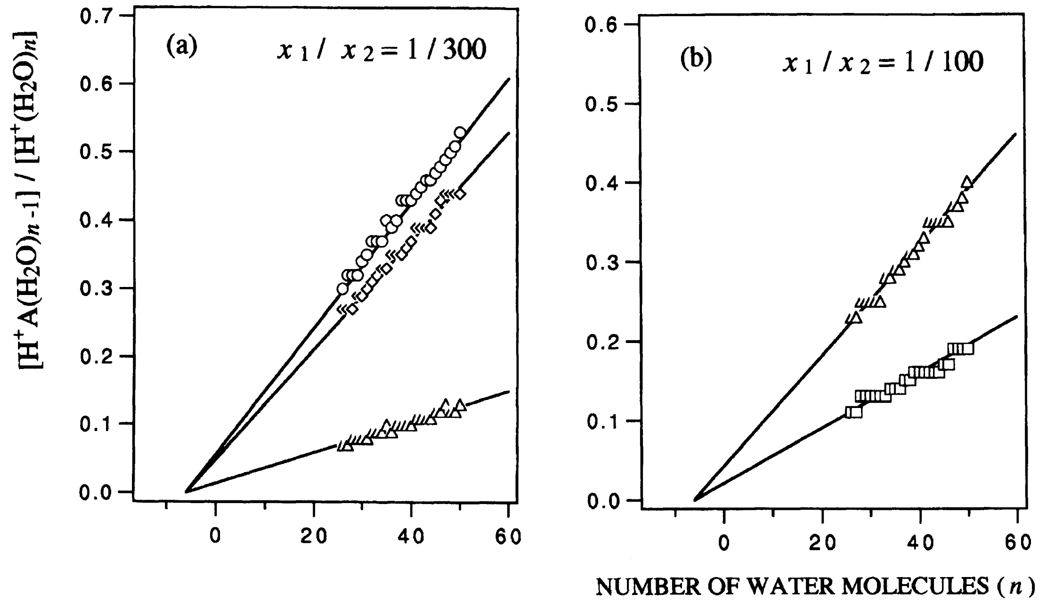

Fig. 3. Plots of population ratio ($[H^+A(H_2O)_{n-1}]/[H^+(H_2O)_n]$) vs. number of water molecules (n) at 60 °C. (a) ○, 1,2-pentanediol; ◇, 2,4-pentanediol; △, 1,4-pentanediol ($x_1/x_2=1/300$). (b) △, 1,4-pentanediol; □, 1,5-pentanediol ($x_1/x_2=1/100$).

$$CH_3CH(OH)CH_2CH(OH)CH_3 \rightarrow$$
$$2{\cdot}CH_3\text{– and –}CH(OH)CH_2CH(OH)\text{–}. \quad (6)$$

The alkyl group of 1,2-pentanediol, $CH_3CH_2CH_2$–, is longer than the two CH_3– groups of 2,4-pentanediol, and the alkyl group between the two OH groups of 1,2-pentanediol, –$CH(OH)CH_2OH$, is shorter than that of 2,4-pentanediol, –$CH(OH)CH_2CH(OH)$–. The lengths of the alkyl groups and of the methylene chain indicate that 1,2-pentanediol is more advantageous for forming hydrate clusters than 2,4-pentanediol. The same elucidation is applicable to the difference of the stability constants between 1,4-pentanediol and 1,5-pentanediol. Thus the hydrate cluster formation of diols may be determined by the contribution from hydration promoting alkyl groups, $CH_3(CH_2)_n$–, and hydration destroying methylene groups between the two OH groups, –$HOCH(CH_2)_nCHOH$–.

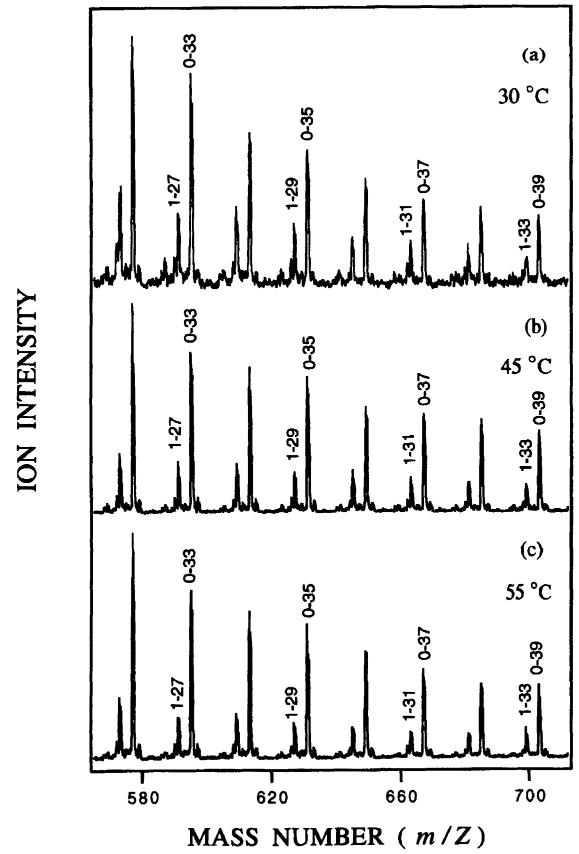

Fig. 4. Temperature change of mass spectral pattern of 1,4-pentanediol ($x_1/x_2=1/100$) at the temperatures. (a) 30 °C, (b) 45 °C, and (c) 55 °C. m–n stands for $H^+A_m(H_2O)_n$.

Temperature Dependence of Stability Constants and Its Relation to Association–Dissociation Equilibria. Temperature dependence of the stability constants of the diol-hydrate clusters was examined in the liquid-droplet temperature range of 30—90 °C. Mass spectra obtained at 30, 45, and 55 °C from an aqueous solution of 1,4-pentanediol ($x_1/x_2=1/100$) are shown in Fig. 4. One can see that the signal intensity ratios of the monomer-hydrates to the pure-water clusters decrease with increasing temperature, indicating that the stability of the hydrate clusters relative to the pure-water clusters becomes lower and lower with increasing temperature in the low temperature region (30—55 °C). This tendency is similar to 1-alkanols and carboxylic acids;[6] their stability constants decrease with increasing temperature. These observations are in accord with the well-known characteristics of hydrophobic hydration. Thus, the temperature dependence of the stability constants of the diol-hydrate clusters seen at the low temperature region is peculiar to the hydrophobic nature of the solute species.

Figure 5 shows mass spectra of 1,4-pentanediol ($x_1/x_2=1/100$) at 55, 70, and 80 °C. In contrast to the low temperature behavior, the signal intensity ratios of the monomer-hydrates to the pure-water clusters increased with increasing temperature. This means that the relative stability of the hydrate clusters increases with increasing temperature at the high temperature region (55—90 °C). The temperature dependence of process 1 could be analyzed with the following relation of κ_m to temperature:[6)]

$$\ln \kappa_m = -\frac{\Delta \overline{H}_m}{R}\frac{1}{T} + \frac{\Delta \overline{S}_m}{R}, \tag{7}$$

where $\Delta \overline{H}_m$ and $\Delta \overline{S}_m$ are the enthalpy and the entropy changes in process 1, respectively. From the van't Hoff plot of κ_m, one can obtain the enthalpy change $\Delta \overline{H}_m$ and the entropy change $\Delta \overline{S}_m$.

The logarithms of the stability constants κ_1 and κ_2 are plotted against T^{-1}, as shown in Fig. 6. In the range of $T^{-1}=2.75\times10^{-3}$—3.30×10^{-3} K^{-1} (30—90 °C), 1-hexanol showed a monotonous increase of the plots in the same way as other 1-alkanols and carboxylic acids.[5,6)] On the other hand, all the diol compounds exhibited the respective minima of the plots at $T^{-1}=3.05\times10^{-3}$ K^{-1} (55 °C)[17)] with negative slopes in the high temperature region (55—90 °C) and positive slopes in the low temperature region (30—55 °C). This behavior is quite different from that of 1-alkanols. Based on Eq. 7, we estimated the enthalpy and the entropy changes ($\Delta \overline{H}_m$ and $\Delta \overline{S}_m$) for the diols. The obtained values in the low temperature and the high temperature regions are listed in Tables 2 and 3, respectively.

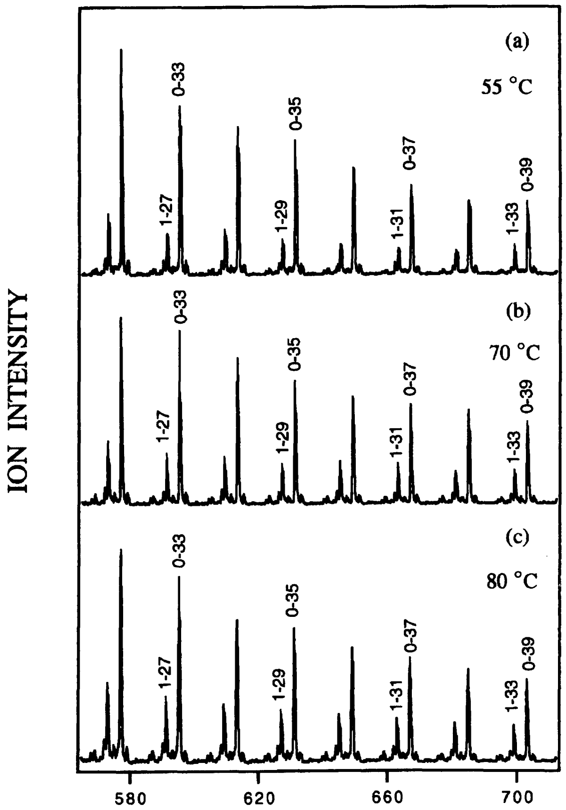

Fig. 5. Temperature change of mass spectral pattern of 1,4-pentanediol ($x_1/x_2=1/100$) at the temperatures. (a) 55 °C, (b) 70 °C, and (c) 80 °C. m–n stands for $H^+A_m(H_2O)_n$.

At the low temperatures, all the values of $\Delta \overline{H}_m$ and $\Delta \overline{S}_m$ ($m=1,2$) showed negative values, like those for ethanol and 1-hexanol. This indicates that process 1 for the diol-compounds is dominated by hydrophobic hydration to the alkyl groups. In contrast to the low temperature region, all the values of $\Delta \overline{H}_m$ and $\Delta \overline{S}_m$ ($m=1,2$) for the diols showed positive values at high temperatures (as seen in Table 3). The positive enthalpy changes (endothermic processes) were also observed in formic acid, formamide and formaldehyde with no alkyl chains in common.[6)] Such endothermic changes may be due to "hydrophilic hydration". The hydration processes of the diols at the high temperatures may be due to such hydrophilic hydration behavior of the two OH groups. Since all the diol compounds showed the minima at the same temperature, so the change of "hydrophilic hydration" to "hydrophobic hydration" may be related to the temperature change of water structure.

Solute–Solute Interaction in Dimer Hydrate Clusters. Here, we tried to estimate the "solute–solute interaction" which is produced when a dimer-hydrate cluster formed due to pairing of two solute molecules. As two special cases of Eq. 1, the monomer- and the dimer-hydrate formation processes are expressed:

$$(H_2O)_n + A \rightleftarrows A(H_2O)_{n-1} + H_2O, \tag{8}$$

and

$$A(H_2O)_nA \rightleftarrows A_2(H_2O)_{n-1} + H_2O. \tag{9}$$

Combination of Eqs. 8 and 9 yields the dimer-hydrate formation process from the two monomer-hydrate species.

$$A(H_2O)_n + A(H_2O)_{n'-1} \rightleftarrows A_2(H_2O)_{n-1} + (H_2O)_{n'}. \tag{10}$$

Equation 10 may describe a dimerization process in aqueous solution properly since all the hydrate clusters in the equation are dominant species in the solution.

In process 9, the enthalpy change ($\Delta \overline{H}_2$) and the entropy change ($\Delta \overline{S}_2$) can be divided into solute–water (S–W) and solute–solute (S–S) parts:

$$\Delta \overline{H}_2 = \Delta \overline{H}_2^{\mathrm{S-W}} + \Delta \overline{H}_2^{\mathrm{S-S}},$$

and

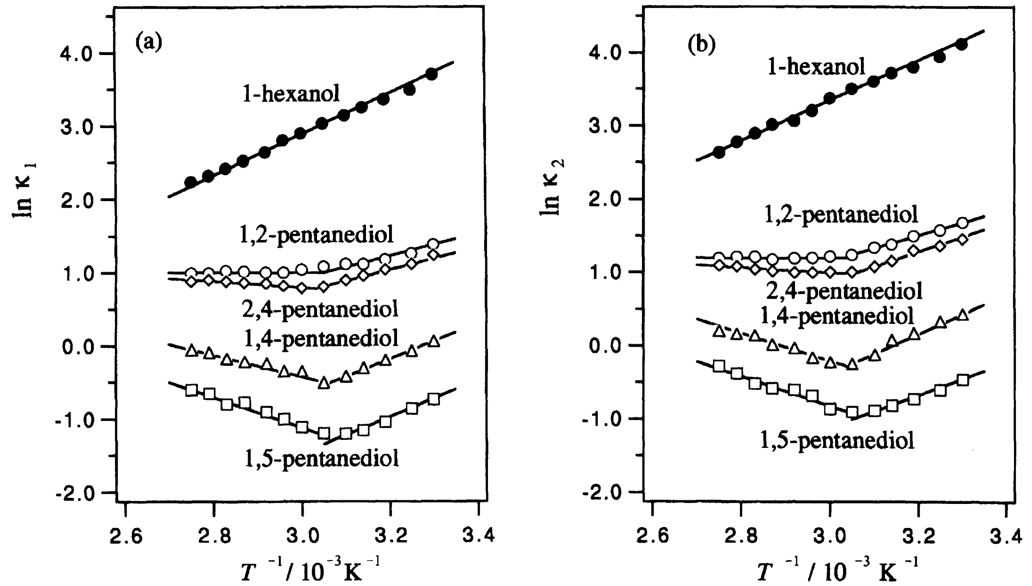

Fig. 6. van't Hoff plots for four diols and 1-hexanol. (a) logarithmic plots of κ_1 (stability constants for monomer-hydrates) as functions of T^{-1}. (b) logarithmic plots of κ_2 (stability constants for dimer-hydrates) as functions of T^{-1}.

Table 2. Enthalpy Changes and Entropy Changes of Diols for Molecular Exchange Processes (Eq. 1) at 30—55 °C (1 cal=4.184 J)

Solute species	$\Delta\overline{H}_1$	$\Delta\overline{H}_2$	$\Delta\overline{S}_1$	$\Delta\overline{S}_2$
	kcal mol^{-1}	kcal mol^{-1}	cal mol^{-1} K^{-1}	cal mol^{-1} K^{-1}
1,2-Ethanediol	−3.0	−3.0	−10.2	−9.6
1,2-Propanediol	−2.8	−2.6	−8.0	−7.0
1,3-Propanediol	−3.2	−3.2	−11.4	−10.8
1,2-Pentanediol	−3.4	−2.9	−8.4	−6.6
2,4-Pentanediol	−4.0	−4.0	−10.7	−10.2
1,4-Pentanediol	−4.8	−4.8	−15.6	−14.9
1,5-Pentanediol	−5.0	−4.4	−17.8	−16.3
Ethanol	−4.1	−4.1	−8.1	−7.9
1-Hexanol	−5.5	−5.4	−13.0	−9.7

Table 3. Enthalpy Changes and Entropy Changes of Diols for Molecular Exchange Processes (Eq. 1) at 55—90 °C (1 cal=4.184 J)

Solute species	$\Delta\overline{H}_1$	$\Delta\overline{H}_2$	$\Delta\overline{S}_1$	$\Delta\overline{S}_2$
	kcal mol^{-1}	kcal mol^{-1}	cal mol^{-1} K^{-1}	cal mol^{-1} K^{-1}
1,2-Ethanediol	2.3	2.4	5.6	6.5
1,2-Propanediol	2.1	2.0	6.8	6.8
1,3-Propanediol	2.9	2.9	7.0	7.3
1,2-Pentanediol	0.0	0.0	2.0	2.4
2,4-Pentanediol	0.8	0.7	4.0	4.0
1,4-Pentanediol	2.9	4.0	7.9	9.4
1,5-Pentanediol	4.0	4.2	9.7	10.9
Ethanol	−4.1	−4.1	−8.1	−7.9
1-Hexanol	−5.5	−5.4	−13.0	−9.7

$$\Delta\overline{S}_2 = \Delta\overline{S}_2^{\text{S-W}} + \Delta\overline{S}_2^{\text{S-S}}. \tag{11}$$

For large clusters, the solute-water interaction terms ($\Delta\overline{H}_2^{\text{S-W}}$ and $\Delta\overline{S}_2^{\text{S-W}}$) may be assumed to be equivalent to the quantities ($\Delta\overline{H}_1$ and $\Delta\overline{S}_1$) in the monomer-hydrate formation process 8. Thus we obtain:

$$\Delta\overline{H}_2^{\text{S-S}} = \Delta\overline{H}_2 - \Delta\overline{H}_1,$$

Table 4. Enthalpy Changes and Entropy Changes of Diols Dimerization Processes (Eq. 10) at 30—55 °C (1 cal=4.184 J)

Solute species	$\Delta\overline{H}_D$	$\Delta\overline{S}_D$	$-T\Delta\overline{S}_D$ a)	$\Delta\overline{G}_D^{298}$ b)
	kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}	kcal mol^{-1}
1,2-Ethanediol	0.0	0.6	−0.2	−0.2
1,2-Propanediol	0.2	1.0	−0.3	−0.1
1,3-Propanediol	0.0	0.6	−0.2	−0.2
1,2-Pentanediol	0.5	1.8	−0.5	0.0
2,4-Pentanediol	0.0	0.6	−0.2	−0.2
1,4-Pentanediol	0.0	0.7	−0.2	−0.2
1,5-Pentanediol	0.6	1.5	−0.4	0.2
Ethanol	0.0	0.2	−0.1	−0.1
1-Hexanol	0.1	3.3	−1.0	−0.9

a) $T=298$ K. b) Calculated from the relation $\Delta\overline{G}_D=\Delta\overline{H}_D-T\Delta\overline{S}_D$.

and

$$\Delta\overline{S}_2^{S-S}=\Delta\overline{S}_2-\Delta\overline{S}_1. \qquad (12)$$

The above assumption leads to an estimation of the contribution of solute-solute interaction. Here, we defined the thermodynamic properties, $\Delta\overline{H}_D$ and $\Delta\overline{S}_D$ in process 10 as follows:

$$\Delta\overline{H}_D=\Delta\overline{H}_2-\Delta\overline{H}_1,$$

and

$$\Delta\overline{S}_D=\Delta\overline{S}_2-\Delta\overline{S}_1. \qquad (13)$$

We calculated the enthalpy changes ($\Delta\overline{H}_D$) and the entropy changes ($\Delta\overline{S}_D$) concerned with solute-solute interaction by using Eq. 13. The obtained values are listed in Table 4.

As seen in Table 4, all the enthalpy changes of the diols, as well as those of ethanol and 1-hexanol, are very small and/or approximately zero. A similar trend was seen in carboxylic acids.[6] This means that the contribution of the enthalpy change ($\Delta\overline{H}_D$) is not effective in the dimerization process (Eq. 10) of the diols or of the 1-alkanols. The entropy changes ($\Delta\overline{S}_D$) for the diols are positive, like those of ethanol and 1-hexanol. We also calculated the values of the Gibbs free energy change in process 10, $\Delta\overline{G}_D$, by extrapolating the van't Hoff plots to $T=25$°C based on the relation of $\Delta\overline{G}_D=\Delta\overline{H}_D-T\Delta\overline{S}_D$. The obtained values are shown in Table 4. It should be noted that the experimental errors in $\Delta\overline{G}_D^{298}$ are in the range of 0.1—0.2 kcal mol^{-1} (1 kcal mol^{-1}=4.184 kJ mol^{-1}). The negative value of $\Delta\overline{G}_D^{298}$ for 1-hexanol (−0.9 kcal mol^{-1}) implies that the association of the two solute molecules in aqueous environment is favorable. On the other hand, all the values of $\Delta\overline{G}_D^{298}$ for the diols are approximately equal to zero. It means that the association of two diol molecules is not so favorable in the aqueous environment at 25 °C. Therefore, the diol molecules in aqueous environment are expected to be well-mixed with water molecules, resulting in large solubilities of these compounds in water at room temperature.

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References

1) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

2) F. Franks and D. J. G. Ives, *Q. Rev. Chem. Soc.*, **20**, 1 (1966).

3) F. Franks and D. S. Reid, in "Water, A Comprehensive Treaties," ed by F. Franks, Plenum, New York (1973), Vol. 2, Chap. 5.

4) a) A. Ben-Naim, "Hydrophobic Interaction," Plenum Press, New York (1980); b) A. Ben-Naim, "Statistical Thermodynamics for Chemists and Biochemists," Plenum Press, New York (1992).

5) N. Nishi and K. Yamamoto, *J. Am. Chem. Soc.*, **109**, 7353 (1987).

6) K. Yamamoto and N. Nishi, *J. Am. Chem. Soc.*, **112**, 549 (1990).

7) G. Barone, B. Bove, G. Castronuovo, and V. Elia, *J. Solution Chem.*, **10**, 803 (1981).

8) I. R. Tasker and R. H. Wood, *J. Solution Chem.*, **11**, 469 (1982).

9) F. Franks, M. Pedley, and S. Reid, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1359 (1976).

10) F. Franks and D. M. Reid, *J. Chem. Soc., Faraday Trans. 1*, **79**, 2249 (1983).

11) H. L. Friedman and C. V. Krishnan, *J. Solution Chem.*, **2**, 119 (1973).

12) T. E. Leslie and T. H. Lilley, *Biopolymers*, **24**, 695 (1985).

13) C. Jolicoeur and G. Lacroix, *Can. J. Chem.*, **54**, 629 (1976).

14) S. Andini, G. Castronuovo, V. Elia, and L. Fasano, *J. Chem. Soc., Faraday Trans.*, **86**, 3567 (1990).

15) C. Cascella, G. Castronuovo, V. Elia, R. Sartorio, and S. Wurzburger, *J. Chem. Soc., Faraday Trans.*, **86**, 85 (1992).

16) G. Castronuovo, C. D. Volpe, V. Elia, and G. Scire, *J. Chem. Soc., Faraday Trans.*, **88**, 2667 (1992).

17) The estimation of the droplet average temperature may include a systematic error within ±10 °C.