Relations between Gas-Phase Stepwise and Bulk Solvation of Cl^- with Water and Aliphatic Alcohols

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Higher order clustering reactions of Cl^- with H_2O and ROH for ROH=CH_3OH, C_2H_5OH, and n-C_3H_7OH were measured in the gas phase with the pulsed electron-beam mass spectrometer. The general trend is found that the obtained $-\Delta H^\circ_{n-1,n}$ and $-\Delta S^\circ_{n-1,n}$ increase in the order $H_2O<CH_3OH<C_2H_5OH<n\text{-}C_3H_7OH$. This order is just the opposite to the free energies of solvation of Cl^-. This is due to the increasingly more unfavorable entropy changes for the solvation of Cl^- in the order $H_2O<CH_3OH<C_2H_5OH<n\text{-}C_3H_7OH$. This is clearly manifested on the increasing entropy changes $-\Delta S^\circ_{n-1,n}$ for the measured gas-phase clustering reactions for higher alcohols.

Cluster ions represent an aggregated state of matter, having properties midway between gaseous and condensed phase. Investigation into the formation and the properties of increasingly larger clusters offers a deep insight into the mode of the molecular interactions and a way of studying the molecular details of the course of change between gaseous and condensed phase.[1-4)]

Equilibria for the ion-solvent molecule clustering reactions involving positive or negative ions can be measured in the gas phase. The van't Hoff plots of the equilibrium constants lead to the determination of thermochemical data ΔG°, ΔH°, and ΔS° for the stepwise addition of solvent molecules to the ion. In our laboratory, we have been making an effort to obtain some information which may bridge between gas and condensed phase by measuring the higher-order solvation reactions of ions in the gas phase. In our previous work,[5)] we studied the stabilities and structures of cluster ions $X^-(M)_n$ for X^-=halide ions and M=protic solvents. In the present work, a study was made to extrapolate the thermochemical data obtained in the gas phase to those in the condensed phase. The obtained results give some insight for the elucidation of the ion solvation in the condensed phase.

Experimental

The measurements were made with a pulsed electron-beam mass spectrometer which has been described previously.[6,7)] About 20—100 mTorr[†] of H_2O or aliphatic alcohols and 1 mTorr of electron capture agent CCl_4 were introduced into 2—3 Torr of CH_4 major (buffer) gas through stainless steel capillaries. The equilibrium constants were found to be independent on the change of solvent vapor pressure in the range 20—100 mTorr.

The equilibrium constants for the clustering reactions were obtained from the expression

$$K_{n-1,n} = \frac{I_n}{I_{n-1}} \cdot \frac{1}{P},$$

where I_n/I_{n-1} is the ratio of ion intensities of the clusters $Cl^-(ROH)_n$ and $Cl^-(ROH)_{n-1}$ in equilibrium and P is the sample pressure. The measurements of I_n/I_{n-1} were made using a mass spectrometer (ULVAC, MSQ-400) with a pulsed electron beam. Pulsing permits one to follow the kinetics of the approach to equilibrium. The enthalpy and entropy changes for each clustering reactions (n−1, n) are determined from van't Hoff plots based on the equation

$$\ln K_{n-1,n} = -\frac{\Delta H^\circ_{n-1,n}}{RT} + \frac{\Delta S^\circ_{n-1,n}}{R},$$

where the standard state is 1 atm.

Results

The enthalpy and entropy changes for the clustering reactions

$$Cl^-(H_2O)_{n-1} + H_2O = Cl^-(H_2O)_n, \quad (1)$$

$$Cl^-(CH_3OH)_{n-1} + CH_3OH = Cl^-(CH_3OH)_n, \quad (2)$$

$$Cl^-(C_2H_5OH)_{n-1} + C_2H_5OH = Cl^-(C_2H_5OH)_n, \quad (3)$$

$$Cl^-(n\text{-}C_3H_7OH)_{n-1} + n\text{-}C_3H_7OH = Cl^-(n\text{-}C_3H_7OH)_n. \quad (4)$$

obtained from the van't Hoff plots are summarized in Tables 1 and 2. The experimental errors for the $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ values are about ±0.5 kcal mol^{-1}[††] and ±2 cal mol^{-1} K^{-1}, respectively. The obtained data are generally in good agreement with those obtained in other laboratories. The measurements for higher-order clustering reactions in the low temperature region were limited by the condensation of the sample vapor on the wall of the ion source. The values of $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ for Reactions 1—4 were measured down to temperatures just above the condensation of sample vapor.

Discussion

Referring to Table 1, the bond energies of ROH⋯Cl^-($-\Delta H^\circ_{0,1}$) increase in the order $H_2O<CH_3OH<C_2H_5OH<n\text{-}C_3H_7OH$. Interestingly, as shown in Table 3, the polarizabilities for H_2O, CH_3OH, C_2H_5OH, and n-C_3H_7OH follow the same order and the permanent dipole moments are just the opposite

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[†] 1 Torr=133.322 Pa.

[††] 1 cal=4.184 J.

Table 1. Experimentally Determined Enthalpy Changes $-\Delta H^{\circ}_{n-1,n}$ (kcal mol^{-1}) for Clustering Reactions $Cl^-(ROH)_{n-1}+ROH=Cl^-(ROH)_n$

n	1	2	3	4	5	6	7	8	9	10	11
H_2O	14.7	13.0	11.8	10.6	9.5	8.8	≈8.1$^{f)}$				
	13.1$^{a)}$	12.7$^{a)}$	11.7$^{a)}$	11.1$^{a)}$							
	14.9$^{b)}$	12.6$^{b)}$	11.5$^{b)}$	10.9$^{b)}$							
	14.4$^{d)}$										
	14.9$^{e)}$										
CH_3OH	17.4	14.1	11.8	10.5	9.2	8.9	8.0	7.6	7.6	7.4	≈7.3$^{f)}$
	14.2$^{c)}$	13.0$^{c)}$	12.3$^{c)}$	11.2$^{c)}$	10.5						
	16.8$^{d)}$										
	17.5$^{e)}$										
C_2H_5OH	17.6	16.1	12.8	12.0	11.5	11.1	9.8	9.2	≈9.0$^{f)}$	≈8.9$^{f)}$	
	17.3$^{d)}$										
n-C_3H_7OH	20.4	15.8	14.2	13.3	12.6	11.6	11.0	≈10.8$^{f)}$			
	17.7$^{d)}$										

a) Reference 10. b) Reference 11. c) Reference 12. d) Reference 9. Enthalpy value calculated from experimentally determined ΔG° and estimated ΔS° from statistical dynamics. e) Reference 13. f) Value obtained using the assumed entropy change. See Table 2.

Table 2. Experimentally Determined Entropy Changes $-\Delta S^{\circ}_{n-1,n}$ (cal mol^{-1} K^{-1}) for Clustering Reactions $Cl^-(ROH)_{n-1}+ROH=Cl^-(ROH)_n$. Standard State 1 atm

n	1	2	3	4	5	6	7	8	9	10	11
H_2O	19.7	21.4	22.3	22.7	21.7	21.2	(20)$^{f)}$				
	16.5$^{a)}$	20.8$^{a)}$	23.2$^{a)}$	25.8$^{a)}$							
	19.7$^{b)}$	20.5$^{b)}$	22.4$^{b)}$	24.8$^{b)}$							
	20.1$^{d)}$										
	19.7$^{e)}$										
CH_3OH	24.1	24.2	22.9	22.9	21.7	22.2	20.1	19.7	20.6	20.1	(20)$^{f)}$
	14.8$^{c)}$	19.4$^{c)}$	23.6$^{c)}$	26.4$^{c)}$	25.5$^{c)}$						
	22.9$^{d)}$										
	24.1$^{e)}$										
C_2H_5OH	23.7	25.9	25.8	29.5	30.6	31.0	26.9	25.2	(25)$^{f)}$	(25)$^{f)}$	
	23.1$^{d)}$										
n-C_3H_7OH	29.0	25.4	31.2	32.1	32.9	31.0	30.2	(30)$^{f)}$			
	23.2$^{d)}$										

a) Reference 10. b) Reference 11. c) Reference 12. d) Reference 9. Entropy value estimated from statistical dynamics. e) Reference 13. f) Entropy value assumed.

Table 3. Dipole Moments (debye) and Polarizabilities (Å^3) of H_2O, CH_3OH, C_2H_5OH, n-C_3H_7OH, and Cl^-

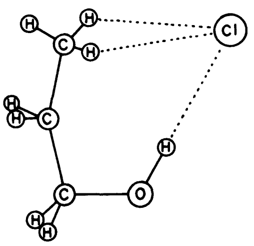
Compound	Dipole moment$^{a)}$	Polarizability$^{b)}$
H_2O	1.84	1.45
CH_3OH	1.75	3.25
C_2H_5OH	1.69	5.01
n-C_3H_7OH	1.68	6.81
Cl^-	0	3.5

a) Reference 14. b) Reference 15.

to the observed bond energies. Polarization must be one of the crucial factors in the determination of the bond energy of the cluster $ROH\cdots Cl^-$. This may be due to the ability of the ligand to approach close to the ion, and thereby become more influenced by the ionic electric field with the attendant result of a larger induced dipole. Qualitatively, consideration of the polarizabilities partially explains the increased bonding strength of CH_3OH, C_2H_5OH, and n-C_3H_7OH over that of H_2O in clustering to the Cl^- ion.

It has been already pointed out that there is a good correlation between the gas-phase acidity and the bond energy $ROH\cdots Cl^-$.[8,9] With increase of the polarizability, the acidity of oxygen acid ROH increases, i.e., the decrease of the heterogeneous bond energy $ROH \rightarrow RO^- + H^+$. The binding energy in $ROH \cdots Cl^-$ can be considered as a partial proton transfer, $[RO \cdots H \cdots Cl]^-$, in which the strength of the interaction increases with the acidity of ROH. This is an alternative explanation for the order of the bond strengths of $ROH \cdots Cl^-$.

The bond energy of n-$C_3H_7OH \cdots Cl^-$ is larger than expected from its polarizability since it is appreciably larger than those of $CH_3OH \cdots Cl^-$ and $C_2H_5OH \cdots Cl^-$. The strong bond may be explained by the head-and-tail interaction in n-$C_3H_7OH \cdots Cl^-$ as shown below.



Structure I

In such a configuration, acidic hydrogen atoms of -OH and $-CH_3$ can realize the most favorable interaction with Cl^- by adjusting the rotations around the C–O and two C–C bond axes. In the structure I, the C_3H_7OH ligand suffers a considerable restriction of internal rotations. This may explain the exceptionally large negative entropy change for Reaction 4 with $n=1$ (Table 2).

Castleman et al. measured the clustering reactions of Cl^- with H_2O and SO_2 in the gas phase. They found that the bond energy ($-\Delta H^\circ_{0,1}$) of $Cl^- \cdots SO_2$ (21.8 kcal mol^{-1}) is much larger than that of $Cl^- \cdots H_2O$ (14.9 kcal mol^{-1}). However, the $-\Delta H^\circ_{n-1,n}$ values for SO_2 show a much a faster fall-off than those for H_2O with n and the cross-over of the values $-\Delta H^\circ_{n-1,n}$ was observed between $n=3$ and 4. A similar trend was also observed for the clustering reactions of alkali positive ions with H_2O and CH_3CN.[17] The bond energies $-\Delta H^\circ_{n-1,n}$ of $M^+(CH_3CN)_n$ for M=Na and Cs are considerably higher than those of $M^+(H_2O)_n$ for small n. However, much faster decrease of $\Delta H^\circ_{n-1,n}$ for the formers than those for the latters with n leads to the cross-over of $-\Delta H^\circ_{n-1,n}$ between $n=4$ and 5. Generally, the bond energies of the ionic clusters of aprotic solvents show faster decrease than those of protic solvents and the crossover of the bond energies are observed at relatively small n. Such a trend is not observed for the clusters $Cl^-(ROH)_n$ between ROH= H_2O and aliphatic alcohols (see Table 1). The ionic clusters of higher alcohols have increasingly stronger bonds compared to $Cl^-(H_2O)_n$ up to the largest n measured. This indicates that in the cluster $Cl^-(ROH)_n$, aliphatic alcohols in the inner shell maintain the stronger bonds with the core ion Cl^- at the expense of the more unfavorable entropy changes (see Table 2) than in the cluster $Cl^-(H_2O)_n$.

In Table 4, free energies (ΔG°_s), enthalpies (ΔH°_s), and entropies (ΔS°_s) of transfer of Cl^- from the gas phase into ROH solvents are summarized. These values are calculated from the free energies, enthalpies, and entropies of transfer of Cl^- from the gas phase into the aqueous solution[18] and those from the aqueous solution to CH_3OH, C_2H_5OH, and n-C_3H_7OH solvents.[19] The free energies of solution of Cl^- ($-\Delta G^\circ_s$) decrease in the order $H_2O > CH_3OH > C_2H_5OH > n\text{-}C_3H_7OH$, i.e., the solvating power of ROH solvents for Cl^- decreases in that order. Since the values of enthalpies of solution ($-\Delta H^\circ_s$) are more or less the same, the observed weaker solvating power for higher alcohols are mainly due to the increase of entropies of solution ($-\Delta S^\circ_s$). Interestingly, there is a similar trend in the gas phase clustering reactions as the case of entropies of solution, i.e., the greater $-\Delta S^\circ_{n-1,n}$ values for higher alcohols (see Table 2). It is evident that ligands of higher alcohols are highly immobilized in the inner shell of the clusters $Cl^-(ROH)_n$. The observed greater entropy changes $-\Delta S^\circ_{n-1,n}$ for the gas-phase clustering reactions may partly explain the more unfavorable entropies of solution for higher alcohols.

Recently Swain et al. have evaluated the anion and cation solvation components based on rate constants, product ratios, equilibrium constants, and electronic, IR, ESR, and NMR spectra.[25] They found that the solvating power for ion can be represented by the two factors, the acity (anion-solvating tendency) and the basity (cation-solvating tendency). It would be informative to compare the bond energy of single-molecule solvated Cl^-, $D(ROH \cdots Cl^-)$, with the acity which represents the solvating power of the bulk ROH solvent toward anions. Figure 1 shows the correlation between the bond energies $D(ROH \cdots Cl^-)$ and the solvent acity for H_2O, CH_3OH, C_2H_5OH, and n-C_3H_5OH. The solvent with larger value of acity is a better solvent for anion. As shown in Fig. 1, H_2O which is the best solvent for anion has the smallest bond energy $D(HOH \cdots Cl^-)$, and $D(ROH \cdots Cl^-)$ increases with decrease of solvent acity for higher

Table 4. Free Energies (ΔG°_s), Enthalpies (ΔH°_s), and Entropies (ΔS°_s) of Transfer of Cl^- from Gas Phase into Solvents

	$-\Delta G^\circ_s$ kcal mol^{-1}	$-\Delta H^\circ_s$ kcal mol^{-1}	$-\Delta S^\circ_s$ cal mol^{-1} K^{-1}
H_2O	75.8	81.3	18.2
CH_3OH	72.6	79.3	22.3
C_2H_5OH	70.9	78.8	26.1
n-C_3H_7OH	69.6	79.2	32.1

alcohols. Since the enthalpies of solution of Cl^- are about the same for the four solvents (Table 4), the reverse order observed in Fig. 1 suggests that for solvents with larger acities, greater number of solvent molecules participate in the ion solvation and contribute to stabilize the anion in solution.

Some more detailed discussion on the stepwise solvation into the ultimate solvation may be given as follows.

In the interaction of ROH with Cl^-, the ROH molecule is polarized, $RO^{\delta-}$-$H^{\delta+}\cdots Cl^-$. For hard Brönsted acids, like H_2O and CH_3OH, the negative charge in the polarized ROH is mainly localized on the oxygen atom. The negatively polarized oxygen atom in ROH would enhance further hydrogen bonding with the ROH molecules in the outer solvation shell. This effect would extend from inner ligands to outer ligands in the shells surrounding the core ion and thus make the solvation energy ultimately large (enhancement effect).[4,20] When the size of alkyl group R gets larger, the ROH ligands in the inner shell of the cluster $Cl^-(ROH)_n$ bind more strongly due to their larger polarizabilities. However, the negative charge will be more delocalized in the rest parts of the acidic hydrogen atom, and the enhancement effect will become less effective than the case of harder ROH solvents. Such a cancellation may explain about the same enthalpies of solvation of Cl^- for H_2O, CH_3OH, C_2H_5OH, and n-C_3H_7OH.

In our previous paper,[3] gas-phase stepwise hydration and single-ion enthalpies and free energies of solution in water were studied. Here, the similar but some more detailed examination will be given. The stepwise solvation free energies $\Delta G^\circ_{n-1,n}$ and the free energies of solution ΔG°_s or the stepwise solvation enthalpies $\Delta H^\circ_{n-1,n}$ and the enthalpies of solution ΔH°_s, or the stepwise solvation entropies $\Delta S^\circ_{n-1,n}$ and the entropies of solution ΔS°_s are related as[3,21,22]

$$\Delta G^\circ_s = \sum_{n=1}^{n=N} \Delta G^\circ_{n-1,n}(\text{ion}(\text{solvent})_n) - \sum_{n=2}^{n=N} \Delta G^\circ_{n-1,n}(\text{solvent})_n \tag{5}$$

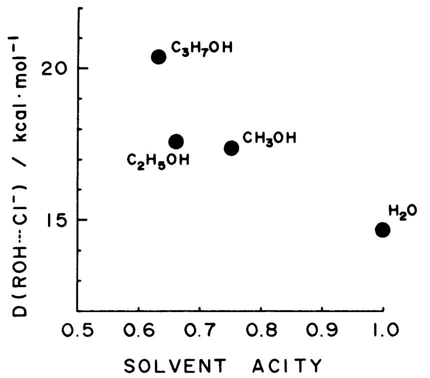


Fig. 1. Correlation between the bond energy D-(ROH···Cl^-) and the solvent acity.

$$\Delta H^\circ_s = \sum_{n=1}^{n=N} \Delta H^\circ_{n-1,n}(\text{ion}(\text{solvent})_n) - \sum_{n=2}^{n=N} \Delta H^\circ_{n-1,n}(\text{solvent})_n, \tag{6}$$

$$\Delta S^\circ_s = \sum_{n=1}^{n=N} \Delta S^\circ_{n-1,n}(\text{ion}(\text{solvent})_n) - \sum_{n=2}^{n=N} \Delta S^\circ_{n-1,n}(\text{solvent})_n. \tag{7}$$

The values of $\Delta G^\circ_{n-1,n}(\text{ion}(\text{solvent})_n)$ and $\Delta G^\circ_{n-1,n}(\text{solvent})_n$, or $\Delta H^\circ_{n-1,n}(\text{ion}(\text{solvent})_n)$ and $\Delta H^\circ_{n-1,n}(\text{solvent})_n$, or $\Delta S^\circ_{n-1,n}(\text{ion}(\text{solvent})_n)$ and $\Delta S^\circ_{n-1,n}(\text{solvent})_n$ converge at $n=N$. In this section, relationships between $\Delta G^\circ_{0,n}$ and ΔG°_s, or $\Delta H^\circ_{0,n}$ and ΔH°_s, or $\Delta S^\circ_{0,n}$ and ΔS°_s are studied on the ground of Eqs. 5—7 with use of the presently available experimental $\Delta G^\circ_{n-1,n}$, $\Delta H^\circ_{n-1,n}$, and $\Delta S^\circ_{n-1,n}$ values.

Unfortunately not much thermochemical data are available for neutral solvent clusters. As a crude approximation, we assume that the enthalpy and entropy changes of stepwise Reaction 8

$$(H_2O)_{n-1} + H_2O = (H_2O)_n \tag{8}$$

are the same as that for $n=2$ for small n, $\Delta H^\circ_{1,2}(H_2O)_2$. In water, an H_2O molecule has four hydrogen bonds with neighboring H_2O molecules. Upon vaporization, each H_2O molecule dissociates these four hydrogen bonds. If one assumes that the strength of each hydrogen bond in water is the same as $-\Delta H^\circ_{1,2}(H_2O)_2$, the relation, $4\times\Delta H^\circ_{1,2}(H_2O)_2\times1/2=-\Delta H^\circ_{\text{evap}}$, holds. The factor 1/2 comes from the fact that two H_2O molecules participate in each hydrogen bond. Thus $\Delta H^\circ_{1,2}(H_2O)_2$ may be approximated to be $-1/2\Delta H^\circ_{\text{evap}}$. Similarly, the entropy change $\Delta S^\circ_{1,2}(H_2O)_2$ may also be approximated to be $-1/2\ \Delta S^\circ_{\text{evap}}$. The values of $\Delta H^\circ_{\text{evap}}=10.5$ kcal mol^{-1} and $\Delta S^\circ_{\text{evap}}=35.2$ cal mol^{-1} K^{-1} for water at the standard state lead to the approximated values $\Delta H^\circ_{1,2}(H_2O)_2=-5.3$ kcal mol^{-1} and $\Delta S^\circ_{1,2}(H_2O)_2=-18$ cal mol^{-1}K^{-1}.

For the clustering reactions of alcohols,

$$(ROH)_{n-1} + ROH = (ROH)_n, \tag{9}$$

$\Delta H^\circ_{n-1,n}(ROH)_n$ values are also assumed to be equal to $-1/2\Delta H_{\text{evap}}$. Since the standard state $\Delta S^\circ_{\text{evap}}$ values are not available for alcohols, the $\Delta S^\circ_{n-1,n}(ROH)_n$ values are assumed to be the same as that of Reaction 8, i.e., -18 cal mol^{-1} K^{-1}.

Figures 2—5 show the n dependences of the right-hand side of Eqs. 5—7, $-[\Delta G^\circ_{0,n}(Cl^-(ROH)_n)-\Delta G^\circ_{0,n}(ROH)_n]$, (denoted as $-\Delta\Delta G^\circ_n$), $-[\Delta H^\circ_{0,n}(Cl^-(ROH)_n)-\Delta H^\circ_{0,n}(ROH)_n]$, (denoted as $-\Delta\Delta H^\circ_n$), and $-T[\Delta S^\circ_{0,n}(Cl^-(ROH)_n)-\Delta S^\circ_{0,n}(ROH)_n]$, (denoted as $-T\Delta\Delta S^\circ_{0,n}$) at $T=298$ K for ROH=H_2O, CH_3OH, C_2H_5OH, and n-C_3H_7OH. In these figures, the values of $-\Delta\Delta G^\circ_n$, $-\Delta\Delta H^\circ_n$, and $-T\Delta\Delta S^\circ_n$ with $n=0$ are taken as values of ΔG°_s, ΔH°_s, and $T\Delta S^\circ_s$, respectively. Since the values of the right-hand side of Eqs. 5—7 converge to ΔG°_s, ΔH°_s, and $T\Delta S^\circ_s$ with $n\rightarrow N$, all curves which start from the values ΔG°_s, ΔH°_s, and $T\Delta S^\circ_s$ at $n=0$

converge to the value 0 with an increase of n. Such a representation is useful because one can see how the stepwise solvation thermochemical data approach the ultimate values with an increase of n.

In Fig. 2, $-\Delta\Delta G_n^\circ$ and $-\Delta\Delta H_n^\circ$ converge to zero only very gradually. This suggests that a greater number of H_2O solvent molecules take part in the hydration of Cl^- in aqueous solution (enhancement effect). The small positive values of $-T\Delta\Delta S_n^\circ$ with n=1—7 suggest that H_2O ligands in the inner shell of $Cl^-(H_2O)_n$ are only slightly more immobilized than that of $(H_2O)_n$. The interaction of H_2O ligands with Cl^- does not

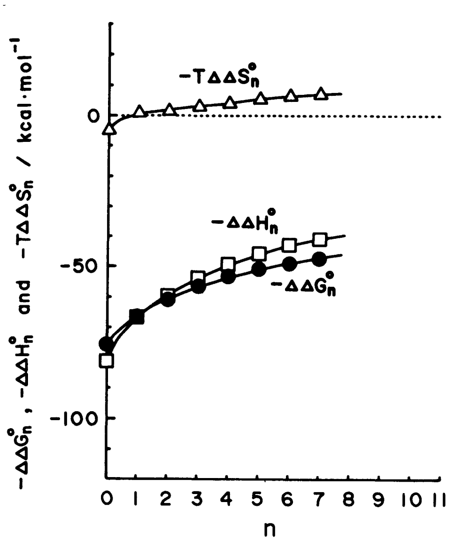


Fig. 2. The n dependence of the values of $-\Delta\Delta G_n^\circ$, $-\Delta\Delta H_n^\circ$, and $-T\Delta\Delta S_n^\circ$ (T=298 K) for reaction $Cl^-(H_2O)_{n-1}+H_2O=Cl^-(H_2O)_n$. The values of $-\Delta\Delta G_n^\circ$, $-\Delta\Delta H_n^\circ$, and $-\Delta\Delta S_n^\circ$, with n=0 are taken as those for the free energy of hydration, the enthalpy of hydration, and the entropy of hydration for Cl^-, respectively.

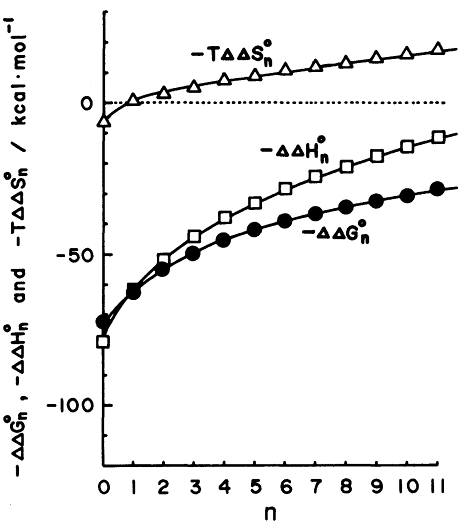


Fig. 3. The n dependence of the values of $-\Delta\Delta G_n^\circ$, $-\Delta\Delta H_n^\circ$, and $-T\Delta\Delta S_n^\circ$ (T=298 K) for reaction $Cl^-(CH_3OH)_{n-1}+CH_3OH=Cl^-(CH_3OH)_n$. The values of $-\Delta\Delta G_n^\circ$, $-\Delta\Delta H_n^\circ$, and $-\Delta\Delta S_n^\circ$ with n=0 are taken as those for the free energy of solution, the enthalpy of solution, and the entropy of solution for Cl^-, respectively.

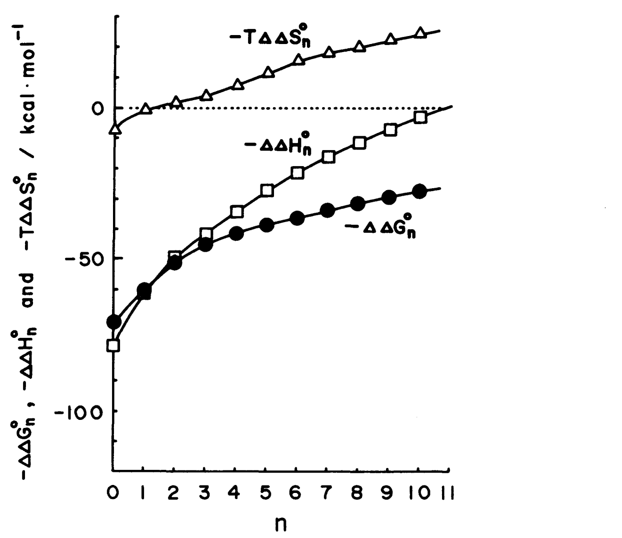


Fig. 4. The n dependence of the values of $-\Delta\Delta G_n^\circ$, $-\Delta\Delta H_n^\circ$, and $-T\Delta\Delta S_n^\circ$ (T=298 K) for reaction $Cl^-(C_2H_5OH)_{n-1}+C_2H_5OH=Cl^-(C_2H_5OH)_n$. The values of $-\Delta\Delta G_n^\circ$, $-\Delta\Delta H_n^\circ$, and $-\Delta\Delta S_n^\circ$ with n=0 are taken as those for the free energy of solution, the enthalpy of solution, and the entropy of solution for Cl^-, respectively.

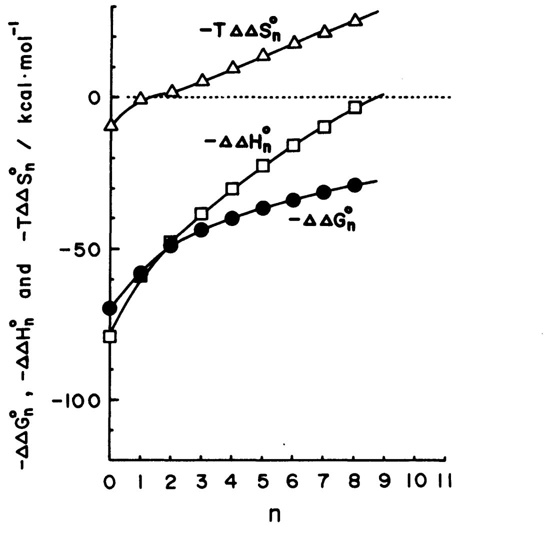


Fig. 5. The n dependence of the values of $-\Delta\Delta G_n^\circ$, $-\Delta\Delta H_n^\circ$, and $-T\Delta\Delta S_n^\circ$ (T=298 K) for reaction $Cl^-(C_3H_7OH)_{n-1}+C_3H_7OH=Cl^-(C_3H_7OH)_n$. The values of $-\Delta\Delta G_n^\circ$, $-\Delta\Delta H_n^\circ$, and $-\Delta\Delta S_n^\circ$ with n=0 are taken as those for the free energy of solution, the enthalpy of solution, and the entropy of solution for Cl^-, respectively.

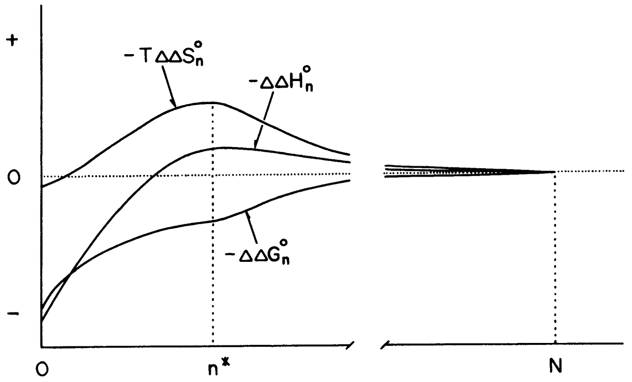


Fig. 6. Schematic representation of n-dependence of $-\Delta\Delta G^\circ_n$, $-\Delta\Delta H^\circ_n$, and $-T\Delta\Delta S^\circ_n$ for $n=0 \rightarrow N$.

seem to induce a serious restriction of freedoms of motion. In fact, the libration motion of the H_2O molecule with a large amplitude in the cluster is suggested by a theoretical molecular orbital calculation.[23)]

In Fig. 3, $-\Delta\Delta H^\circ_n$ and $-\Delta\Delta G^\circ_n$ deviate from each other progressively with an increase of n, and the deviation of $-T\Delta\Delta S^\circ_n$ from zero is larger than the case of H_2O. Such a tendency gets more prominent in the order $CH_3OH < C_2H_5OH < n\text{-}C_3H_7OH$ as shown in Figs. 3—5. For n-C_3H_7OH, $-\Delta\Delta H^\circ_n$ seems to cross the ultimate value zero and become positive after $n=8$. The rapid increase of both of $-\Delta\Delta H^\circ_n$ and $-T\Delta\Delta S^\circ_n$ up to $n=8$ clearly indicates that strong bonds are formed between the Cl^- ion and the ligand molecules at the expense of the unfavorable entropy changes in the inner shell of the cluster ion $Cl^-(n\text{-}C_3H_7OH)_n$. Since all the values of $-\Delta\Delta G^\circ_n$, $-\Delta\Delta H^\circ_n$, and $-T\Delta\Delta S^\circ_n$ converge to zero at $n=N$, the latter two must decrease at certain value of $n=n^*$. With this n^*, $\Delta H^\circ_{n-1,n}(\text{ion-}(ROH)_n) \approx \Delta H^\circ_{n-1,n}(ROH)_n$ and $\Delta S^\circ_{n-1,n}(\text{ion}(ROH)_n) \approx \Delta S^\circ_{n-1,n}(ROH)_n$. The decrease in $-\Delta\Delta H^\circ_n$ and $-T\Delta\Delta S^\circ_n$ may begin at the same time when the tight inner shells are completed and the loose outer shells start to be formed. Figure 6 shows the predicted conceptional idea of n-dependence of $-\Delta\Delta G^\circ_n$, $-\Delta\Delta H^\circ_n$, and $-T\Delta\Delta S^\circ_n$ for $n=0 \rightarrow N$. After the completion of the tight inner shells at $n=n^*$, the $-\Delta\Delta H^\circ_n$ and $-T\Delta\Delta S^\circ_n$ value start to decrease and the $-\Delta\Delta G^\circ_n$ value to increase more steeply at n^* where the outher shell formation begins. The values of n^* and N may increase in the order $n\text{-}C_3H_7OH < C_2H_5OH < CH_3OH < H_2O$ since the enhancement effect becomes more effective in that order. On the version of Frank and Wen,[24)] the ligands with $n < n^*$ and $n > n^*$ may be regarded as those belonging to the structure making and structure breaking region, respectively.

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