Solvation of Anions in Water-Acetonitrile Mixtures

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(Received December 26, 1985)

The enthalpies of transfer from water to mixtures with acetonitrile(ΔH°_t) for various anions reach maxima at a mole fraction of acetonitrile(x_{AN}) ca. 0.3, and decrease linearly and in parallel in the intermediate region. A linear relation is found between ΔH°_t at x_{AN} 0.3 and the hydration enthalpies for halide and symmetrical ions. This finding and the parallel x_{AN} dependence of ΔH°_t in the intermediate region are interpreted on the basis of the linear relation between the solvation enthalpies and the entropies for the halide ions. The reduction in the hydrogen-bonding interaction extending beyond the primary hydration sphere(ΔH_{INT}) for halide ions in the mixtures is estimated based on a modified Eley and Evans hydration model. At x_{AN} 0 to ca. 0.3, ΔH_{INT} compared with that in water agree well with the observed ΔH°_t, indicating that the increase in ΔH°_t is due to the reduction in the outer hydration sphere interaction. However, they split gradually at x_{AN} above 0.3. The adequacy of the modifications in the treatment of the solvation enthalpy cycle in the mixtures is re-evaluated from the structural viewpoint. The exothermic change in the intermediate region may be attributable to the reduction in the cavity formation energy.

Preferential solvation of ions has been studied in many kinds of mixed solvent systems by various methods.[1] Silver ion has been confirmed to be preferentially solvated by acetonitrile in water–acetonitrile mixtures by the measurements of the transference number,[2a] solubility,[2b] NMR,[2c] and the free energy of transfer.[2d] On the basis of this fact we have discussed the dependence of the ionic conductance[3] and ionic enthalpies of transfer (ΔH°_t)[4] on the solvent composition. Previously[4] the rapid changes of ΔH°_t for alkali and halide ions in the acetonitrile-rich region have been ascribed to the preferential hydration of smaller ions. The ΔH°_t maxima at a mole fraction of acetonitrile (x_{AN}) ca. 0.3 have been suggested to be due to the least favorable hydration for halide ions owing to the destruction of the water lattice caused by the addition of acetonitrile.

In this study we use a new approach to the discussion of the x_{AN} dependence of ΔH°_t for anions in the water-rich and in the intermediate regions from three viewpoints. The first viewpoint is ΔH°_t for anions in relation to the ionic enthalpy of hydration. Linear relations are found between ΔH°_t at x_{AN} 0.3 to 0.6 and the ionic hydration enthalpies, and the same relations are derived by using the entropies of transfer for halide ions. The second is an attempt to estimate the interaction in the outer hydration sphere for halide ions based on a modified Eley and Evans hydration model for the mixtures. It will be noted that the reduction in the interaction estimated from ionic solvation enthalpy cycle is found to be responsible for the endothermic process of ΔH°_t in the water-rich region. The third is ΔH°_t for anions in relation to the solvent structure of the mixtures. The adequacy of the correction for cavity formation energy in the mixtures arising from the change in the solvent structure is discussed. The change in ΔH°_t in the intermediate region is found to be due primarily to the reduction in the cavity formation energy.

Experimental

All chemicals used were of reagent grade. Sodium tetrafluoroborate was prepared from the acid and aqueous sodium carbonate solution, and recrystallized twice from water in a platinum dish. Other salts commercially available were once recrystallized from water. All salts were dried in vacuo, at 60 °C overnight and stored in a desiccator. Acetonitrile and water were distilled thrice and twice, respectively.[3] The enthalpy of solution was measured with a heat-exchange type calorimeter at 25±0.02 °C.[5] The reported standard enthalpy of solution (ΔH°_s) is the average of at least three determinations in a 10^{-3} to 10^{-2} mol dm^{-3} concentration range agreeing within ±0.4 kJ mol^{-1}.

Results and Discussion

The standard enthalpies of solution for electroly-

Table 1. The Enthalpies of Solution for Electrolytes in Water and Water–Acetonitrile Mixtures, ΔH°_s/kJ mol^{-1}

	x_{AN}							
	0	0.1	0.2	0.4	0.6	0.8	0.9	1.0
$NaNO_2$	$+13._9$	$+9._8$	$+8._0$	$+3._3$	-0.9			
$NaClO_3$	$+21._5$	$+19._0$	$+15._7$	$+10._1$	$+7._1$			
$NaBrO_3$	$+26._8$	$+24._3$	$+21._7$	$+17._0$				
NaN_3	$+12._5$	$+6._7$	$+4._4$	-0.7	$-5._2$			
$NaBF_4$	$+27._4$	$+21._9$	$+14._4$	$+7._3$	$+2._4$	$-3._6$		
$NaHCO_2$	$+0.7$	0	$-1._7$	$-7._0$	$-11._4$			
$NaCH_3CO_2$	$-16._5$	$-14._4$	$-14._8$	$-18._9$				
$NaCF_3CO_2$	$-8._7$	$-6._4$	$-7._5$	$-10._9$	$-14._2$	$-16._5$	$-15._0$	$-6._3$

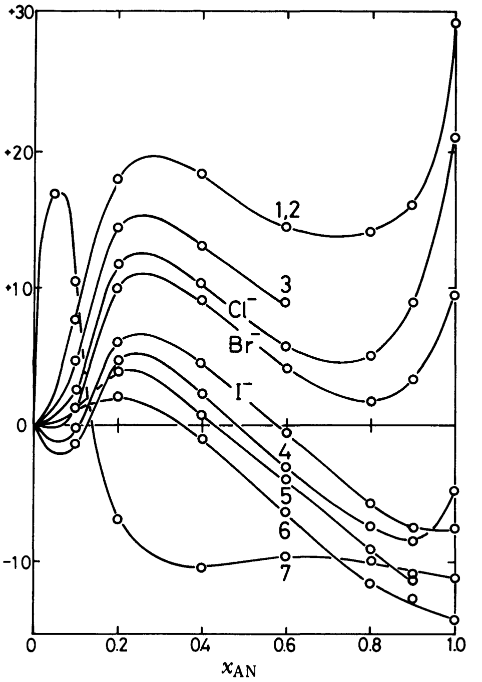

Fig. 1. The enthalpies of transfer from water to water-acetonitrile mixtures (ΔH°_t), for anions plotted against the mole fraction of acetonitrile, x_{AN}. 1,2: $CF_3CO_2^-$, $CH_3CO_2^-$, ($x_{AN}\leq 0.4$), 3: HCO_2^-, 4: NCS^-, 5: BF_4^-, 6: ClO_4^-, 7: Ph_4B^-.

tes are listed in Table 1. The ΔH°_s values for sodium bromate, chlorate and nitrite obtained in water agreed with the literature[6] values within ±0.2 kJ mol^{-1} and ΔH°_s for sodium acetate within ±0.8 kJ mol^{-1}.

The enthalpies of transfer from water to water-acetonitrile mixtures (ΔH°_t) for anions were calculated by using ΔH°_t value for Na^+ estimated previously[4] based on the TATB assumption ($\Delta H^\circ_t[Ph_4As^+]=\Delta H^\circ_t[Ph_4B^-]$).[7] Figure 1 shows the x_{AN} dependence of ΔH°_t for typical anions, although ΔH°_t for seventeen anions have been estimated in our laboratory.

The ΔH°_t values for anions reach maxima at x_{AN} ca. 0.3 except for some large anions containing phenyl groups. They decrease linearly and in parallel in the intermediate region, and reach minima at x_{AN} ca. 0.8. Those for small anions increase rapidly in the acetonitrile-rich region. From the extent of these rapid changes the order of the preference to water for anions has been determined.[4] The following order can be determined: $CF_3CO_2^- > Cl^- > Br^- > NCS^- > I^- > Pi^-$ (picrate)$> ClO_4^- \simeq BF_4^-$.

A Linear Relation between Enthalpies of Transfer at x_{AN} 0.3 and Enthalpies of Hydration for Anions. The enthalpies of transfer for anions from water to the mixtures at x_{AN} 0.3 ($\Delta H^\circ_t(x_{AN}=0\rightarrow 0.3)$) are plotted against the ionic enthalpies of hydration (ΔH_W) in Fig. 2. The ΔH_W values for anions except BF_4^- were cited from the literature.[8] The ΔH°_t value for BF_4^- was estimated from a linear relation between ΔH_W and the reciprocal of the thermochemical radii of polyatomic anions.[9] Noticeably, the values for the halide and symmetrical anions lie on a straight line. This finding means that the more strongly hydrated is an anion, the more unfavorable will be its solvation in the mixtures.

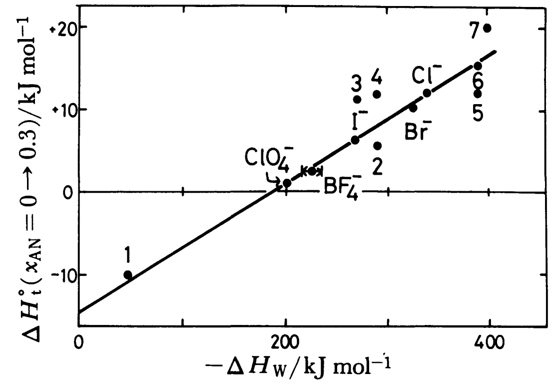

Fig. 2. The enthalpies of transfer from water to water-acetonitrile mixtures at the mole fraction of acetonitrile (x_{AN}) 0.3, ΔH°_t ($x_{AN}=0\rightarrow 0.3$), plotted against the enthalpies of hydration, ΔH_W, for anions.

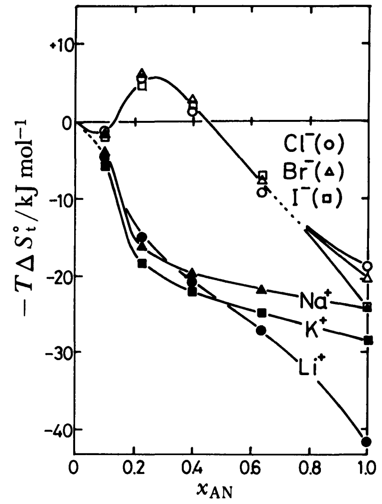

Fig. 3. The entropies of transfer from water to water-acetonitrile mixtures ($T\Delta S^\circ_t$) for alkali and halide ions plotted against the mole fraction of acetonitrile (x_{AN}).
○: Cl^-, △: Br^-, □: I^-, ●: Li^+, ▲: Na^+, ■: K^+.

The same relation will be derived by using the ionic solvation entropy as follows. Fortunately, the free energies of transfer (ΔG°_t) for alkali metal and halide ions in these mixtures have been published on TATB assumption.[10] The entropies of transfer (ΔS°_t) for these ions can be estimated ($-T\Delta S^\circ_t=\Delta G^\circ_t-\Delta H^\circ_t$) and are plotted against x_{AN} in Fig. 3. The ΔS°_t values for anions are considered to be nearly equal to each other in the range of x_{AN} 0 to ca. 0.6, while those for cations are differentiated in this range.

As suggested by Eley and Evans,[11] the more negative the ionic hydration enthalpy, the more negative the corresponding entropy. The same relation would be expected to hold in the mixtures. Figure 4 shows the analysis of the thermodynamic functions in water and in the mixtures. The values of the thermodynamic

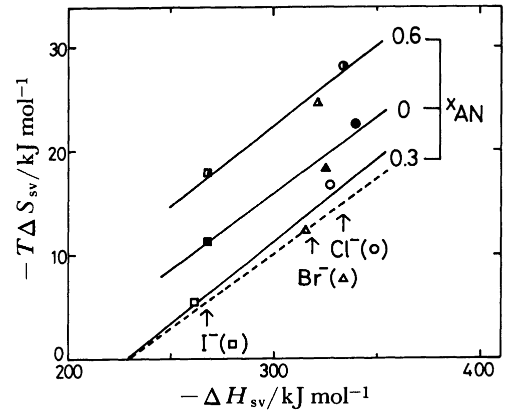

Fig. 4. The entropies of solvation, $-T\Delta S_{SV}$, plotted against the enthalpies of solvation, $-\Delta H_{SV}$, for halide ions in water and water-acetonitrile mixtures. Broken line indicates the plot of $-T\Delta S_{0.3}$ vs. $-\Delta H_W$.

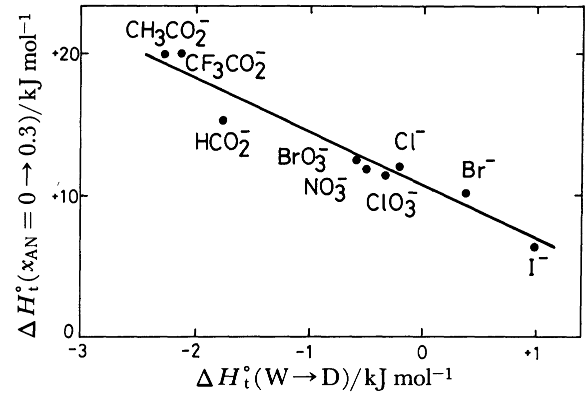

Fig. 5. The enthalpies of transfer from water to water-acetonitrile mixtures at the mole fraction of acetonitrile (x_{AN}) 0.3, $\Delta H_t^\circ(x_{AN}=0\rightarrow0.3)$, plotted against the enthalpies of transfer from normal water to heavy water, $\Delta H_t^\circ(W\rightarrow D)$ for anions.

functions in water (ΔS_W and ΔH_W) are cited from the literature,[8] and those in the mixtures are calculated from values of the transfer functions. The broken line represents $-T\Delta S_{0.3}$ plotted against $-\Delta H_W$ and intersects the line of $-T\Delta S_{0.3}$ plotted against $-\Delta H_{0.3}$ close to the same position on the abscissa.

Equations 1, 2, and 4 are derived from the plots of $-T\Delta S_{SV}$ vs. ΔH_{SV} in water and the mixtures of x_{AN} 0.3 and 0.5, respectively. Equation 3 is derived from the broken line. In those equations, the subscripts denote the solvent compositions.

$$-T\Delta S_w = -28._0 + 0.14_6(-\Delta H_w) \quad (1)$$

$$-T\Delta S_{0.3} = -36._3 + 0.15_8(-\Delta H_{0.3}) \quad (2)$$

$$-T\Delta S_{0.3} = -33._9 + 0.14_6(-\Delta H_w) \quad (3)$$

$$-T\Delta S_{0.5} = -29._0 + 0.15_9(-\Delta H_{0.5}) \quad (4)$$

$$\Delta H_t^\circ(x_{AN} = 0 \rightarrow 0.3) = -15._2 + 0.076(-\Delta H_w) \quad (5)$$

By subtracting Eq. 1 from Eq. 2, the relation between ΔH_t° and ΔH_W is obtained. When the experimental value for $-T\Delta S_t^\circ$ (5.9 kJ mol^{-1}) is substituted in this relation, we obtain Eq. 5. The values of the slope and intercept of Eq. 5 are in good agreement with the experimental ones (slope 0.078, intercept 14.8).

In x_{AN} over the range 0.3 to 0.6, linear relations with the same slope as Eq. 5 can be derived in a similar manner as above, since the plots of $-T\Delta S_{SV}$ vs. $-\Delta H_{SV}$ have the same slope as that of Eq. 2. Therefore, the x_{AN} dependence of ΔH_t° is parallel in this range. Thus, we have been able to derive the linear relations between ΔH_t° at x_{AN} 0.3 to 0.6 and ΔH_W for halide ions by using ΔG_t° data.

Estimation of the Hydrogen-Bonding Interaction Extending beyond the Primary Hydration Sphere based on Modified Eley and Evans Hydration Model. The relation between $\Delta H_t^\circ(x_{AN}=0\rightarrow0.3)$ and the enthalpies of transfer from normal water to heavy water ($\Delta H_t^\circ(W\rightarrow D)$) is shown in Fig. 5. The $\Delta H_t^\circ(W\rightarrow D)$ values were cited from the literature.[12] Thus $\Delta H_t^\circ(x_{AN}=0\rightarrow0.3)$ was related closely to $\Delta H_t^\circ(W\rightarrow D)$. Anions which are more strongly hydrated by hydrogen-bonding interaction should have the more negative $\Delta H_t^\circ(W\rightarrow D)$ value, because heavy water has been shown to be more strongly hydrogen bonded than normal water.[12] Noticeably, those anions have the more positive $\Delta H_t^\circ(x_{AN}=0\rightarrow0.3)$ values. This finding suggests that the endothermicity in the mixtures results from an unfavorable interaction between the primary hydration sphere and the surroundings, since anions should be preferentially hydrated in the water-rich region. Accordingly we have developed the Eley and Evans treatment of the ionic hydration enthalpy cycle to estimate the outer sphere hydrogen-bonding interaction in the mixtures.

Several molecular models of the ionic hydration of the water structure, the orientation of the water dipole, various ion-water interactions and the water structure of the outer hydration sphere have been proposed,[13a-d] since Bernal and Fowler published their pioneer work in 1933. Eley and Evans have proposed a thought experiment involving the following steps to estimate theoretically the ionic hydration enthalpy for a tetrahydrated ion. (1) A cluster of five water molecules corresponding to the volume of the primary hydrated ion is removed from the liquid phase to the gas phase leaving a cavity in the liquid, $\Delta H_{CF}(>0)$. (2) The tetrahedral water cluster is dissociated into water monomers in the gas phase, $\Delta H_D(>0)$. (3) Four water molecules are coordinated to an ion in the gas phase, $\Delta H_{I\text{-}S(g)}(<0)$. (4) The hydrated ion is returned to the cavity, $\Delta H_{BC}(<0)$. (5) The water molecules of the returned hydrated ion interact with their neighbor, $\Delta H_{INT}(<0)$. In other words, ΔH_{INT} represents hydrogen-bonding interaction extending beyond the primary hydration sphere, namely the outer hydration sphere of anions. (6) Finally, one water molecule left in the gas phase is returned to the liquid phase, $\Delta H_C(<0)$.

Table 2. The Enthalpies of Solvation, ΔH_{SV}, the Enthalpies of Born Charging, ΔH_{BC}, the Enthalpies of Hydration in Gas Phase, $\Delta H_{\mathrm{I-S(g)}}$, for Halide Ions and the Relative Partial Molar Enthalpies of Water in Water-Accetonitrile Mixtures, L_{W}/kJ mol^{-1}

		x_{AN}						
		0	0.1	0.2	0.3	0.4	0.5	0.6
Cl$^-$	$-\Delta H_{\mathrm{SV}}$	340$^{a)}$	337.5	328.2	328.0	329.7	332.2	334.3
	$-\Delta H_{\mathrm{BC}}$	153.2	153.0	153.5	153.6	152.9	152.9	152.4
	$-\Delta H_{\mathrm{I-S(g)}}$$^{b)}$				203.3			
Br$^-$	$-\Delta H_{\mathrm{SV}}$	320$^{a)}$	324.7	315.9	315.7	316.7	319.1	321.9
	$-\Delta H_{\mathrm{BC}}$	148.3	148.0	148.3	148.3	147.8	147.7	147.2
	$-\Delta H_{\mathrm{I-S(g)}}$$^{b)}$				197.9			
I$^-$	$-\Delta H_{\mathrm{SV}}$	268$^{a)}$	268.3	262.0	261.7	263.5	266.0	268.6
	$-\Delta H_{\mathrm{BC}}$	141.1	140.9	141.2	141.2	140.6	140.5	140.1
	$-\Delta H_{\mathrm{I-S(g)}}$$^{b)}$				161.5			
	$-4L_{\mathrm{W}}$$^{c)}$	0	+0.6	+0.2	−0.2	−1.2	−2.4	−3.6

a) From Ref. 8. b) From Ref. 4 (for tetrahedral hydration). c) From Ref. 24.

Table 3. The Sum of the Enthalpies of Cavity Formation and Outer Hydration Sphere Interaction, $\Delta H_{\mathrm{CF(W)}}+\Delta H_{\mathrm{INT}}$, for Halide Ions in Water and Water-Acetonitrile Mixtures/kJ mol^{-1}

	x_{AN}						
	0	0.1	0.2	0.3	0.4	0.5	0.6
Cl$^-$	−37.5	−35.8	−25.6	−25.1	−26.3	−27.5	−29.0
Br$^-$	−34.5	−33.4	−23.9	−23.1	−23.8	−25.1	−27.2
I$^-$	−19.4	−20.5	−13.5	−12.6	−14.2	−15.6	−17.4

We propose a novel method to estimate the ΔH_{INT} term for the mixtures based on a modified hydration model.

Table 2 shows values of some terms used to estimate the sum of $\Delta H_{\mathrm{CF(W)}}$ and ΔH_{INT} terms ($\Delta H_{\mathrm{CF(W)}}+\Delta H_{\mathrm{INT}}$) in aqueous solution according to the following equation:

$$\Delta H_{\mathrm{CF(W)}} + \Delta H_{\mathrm{INT}} = \Delta H_{\mathrm{W}} - (\Delta H_{\mathrm{I-S(g)}} + \Delta H_{\mathrm{BC}} + \Delta H_{\mathrm{D}} + \Delta H_{\mathrm{C}}), \quad (6)$$

where $\Delta H_{\mathrm{I-S(g)}}$ is the ionic hydration enthalpy in the gas phase measured with a mass spectrometer.[14] Stepwise enthalpies of hydration ($\Delta H_{3,4}$) for I$^-$ are obtained by extrapolation of the $\Delta H_{n-1,n}$ vs. n plot. The ΔH_{BC} values are calculated by the Born equation in kJ mol^{-1}:

$$\Delta H_{\mathrm{BC}} = 1398/2R_{\mathrm{i}} \times (1-1/\varepsilon-1/\varepsilon \times \mathrm{d}\varepsilon/\mathrm{d}T), \quad (7)$$

where $R_{\mathrm{i}}(=r_{\mathrm{c}}+2r_{\mathrm{w}})$ is the radius of the hydrated ion, r_{c} the crystal radius of the ion,[16] r_{w} the radius of the water molecule (1.38 Å),[17] and $\mathrm{d}\varepsilon/\mathrm{d}T$ is the temperature coefficient of the dielectric constant of water (0.355/°C).[18] In this calculation the effect of dielectric saturation can reasonably be neglected, since the radius of the hydrated in is larger than 4 Å in every case.[13b] The ΔH_{D} value is the enthalpy of breaking four hydrogen bonds in water (83.7 kJ mol^{-1})[15,17] and ΔH_{C} is the enthalpy of condensation of water (29.7 kJ mol^{-1}).[19]

Next we attempt to consider the solvation enthalpy cycle in the mixtures up to x_{AN} 0.6. We assume that an anion is preferentially hydrated in the primary hydration sphere in the mixtures. This assumption seems to be reasonable for the following reasons. An anion is more strongly solvated in water than in a dipolar aprotic solvent, since the positive charge end of the acetonitrile dipole is distributed over a large part of the molecule.[21] Furthermore, the activity of water in the intermediate region remains nearly constant as deduced from the marked positive deviation of the partial vapor pressure of water.[22] In fact, halide ions have been pointed out to be preferentially hydrated in those mixtures by the measurement of NMR on halide ion nucleus.[23]

The ΔH_{CF} term in the mixtures is assumed to differ from that in water by $-5L_{\mathrm{W}}$, the enthalpy of demixing five water molecules from the mixtures, and ΔH_{C} term by $+L_{\mathrm{W}}$, the enthalpy of mixing one water molecule with the mixtures. Therefore, ($\Delta H_{\mathrm{CF}}+\Delta H_{\mathrm{C}}$) in the mixtures differ by $-4L_{\mathrm{W}}$ from that in water, where L_{W} denotes the relative partial molar enthalpy for water in the mixtures and can be calculated from the excess enthalpy of mixing data[24,25] by an intercept method.[26] The ΔH_{BC} values in the mixtures are calculated in the same way as that in aqueous solution by using ε and $\mathrm{d}\varepsilon/\mathrm{d}T$ data.[18]

Values of ($\Delta H_{\mathrm{CF(W)}}+\Delta H_{\mathrm{INT}}$) estimated for the mixtures according to the following equation are shown in Tab. 3 together with those in water for comparison;

$$\Delta H_{\mathrm{CF(W)}} + \Delta H_{\mathrm{INT(mix)}} = -\Delta H_{\mathrm{SV(mix)}} - (\Delta H_{\mathrm{I-S(g)}} + \Delta H_{\mathrm{BC(mix)}} + \Delta H_{\mathrm{D}} + \Delta H_{\mathrm{C}}) + 4L_{\mathrm{W}}. \quad (8)$$

So, ΔH_{t}° is represented as follows:

$$\Delta H_{t}^{\circ} = -4L_{\mathrm{W}} + \Delta\Delta H_{\mathrm{BC}} + \Delta\Delta H_{\mathrm{INT}}. \quad (9)$$

The smaller an anion, the more negative ($\Delta H_{\mathrm{CF(W)}}+\Delta H_{\mathrm{INT}}$) will be in water. If $\Delta H_{\mathrm{CF(W)}}$ is assumed to be the latent heat of vaporization for water according to the suggestion of Buckingham,[13b] ΔH_{INT} for the chloride ion in water is approximately −60 kJ mol^{-1}.

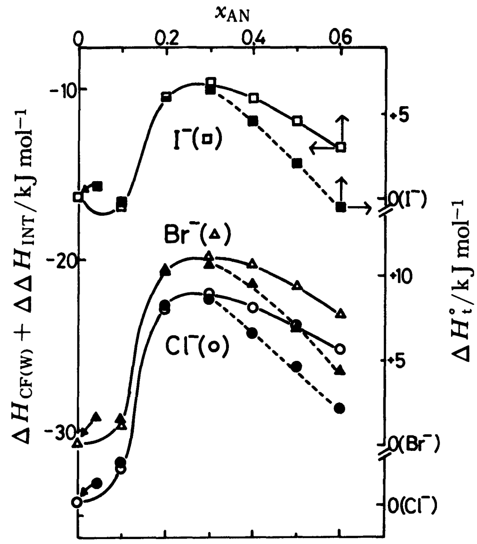

Fig. 6. The sum of the enthalpies of cavity formation and outer hydration sphere interaction, $\Delta H_{CF(W)}+\Delta H_{INT}$, and the enthalpies of transfer, ΔH°_t, for halide ions plotted against the mole fraction of acetonitrile (x_{AN}).

This means that several hydrogen bonds are formed in the outer hydration sphere for a halide ion through these cooperative effects.[20]

Figure 6 shows the comparison of $\Delta\Delta H_{INT}$ with ΔH°_t for halide ions. In this figure the broken curves represent the x_{AN} dependence of ΔH°_t, and the ordinate is adjusted so that the origin for each anion corresponds to $\Delta H_{CF(W)}+\Delta H_{INT}$ value in water. As shown in Tab. 2, the possibility of a ΔH_{BC} contribution to ΔH°_t is safely excluded, because the x_{AN} dependence of this term is negligible. If the ΔH_{CF} value in the mixtures can be correctly estimated by subtracting $5L_W$ from that in water, the left-hand ordinate will represent the $\Delta\Delta H_{INT}$. The two curves for each anion appear to show a similar trend in x_{AN} dependence. It can be said that the x_{AN} dependence of ΔH°_t at x_{AN} 0 to 0.6 may be explained semiquantitatively as the x_{AN} dependence of $\Delta\Delta H_{INT}$ based on the modified Eley and Evans hydration model. Noticeably, at x_{AN} 0 to ca. 0.3 the two curves agree well, while they split gradually with increasing x_{AN} beyond 0.3.

In the treatment of the solvation enthalpy cycle described above, hydration numbers for the halide ions were assumed to be four, although hydration numbers other than four have been reported.[27] The enthalpies of hydration in the gas phase have been reported up to the fourth water molecule for Cl^- and Br^-, and up to the third molecule for I^-, respectively.[14] It is possible to estimate approximately the hydration enthalpies in the gas phase up to the sixth water molecule by extrapolation. We have carried out a similar calculation to estimate ($\Delta H_{CF(W)}+\Delta\Delta H_{INT}$) for a hexahydrated ion by using such extrapolated values. The x_{AN} dependence of those values is very close to that for a tetrahydrated ion. So the same conclusion as before can be reached.

Solvation of Anions and Solvent Structure of Water–Acetonitrile Mixtures. In the previous section it has been clarified that the increase in ΔH°_t for halide ions in the range of x_{AN} 0 to ca. 0.3 was ascribed to the change in the ΔH_{INT} term. Accordingly the validity of the modified hydration model will now be discussed in relation to the solvent structure of the mixtures.

Three structurally different regions have been suggested to exist in those mixtures according to studies on the volumetric, viscosity and dielectric properties[18] and vapor pressure[22] measurements; (1) water-rich, (2) intermediate and (3) acetonitrile-rich regions. In the region (1) the voids inside the aqueous framework of the water lattice are considered to be progressively filled with acetonitrile. That is, no significant enhancement of the water lattice is caused by the addition of cosolvent in contrast to the other aqueous mixtures (water-*t*-butyl alcohol).[28a] This region, therefore, is stated as "essentially aqueous."[30] In the region (2), on the other hand, the large aggregates formed in the former region are considered to be progressively broken to smaller ones after the filling of the voids. The mixtures of x_{AN} ca. 0.3 seems to have the most compact solvent structure, since some physicochemical properties of the mixtures show extrema at this composition, such as excess volume[28a,b] and excess entropy[29] of mixing, energy-volume coefficient and isothermal compressibility.[30] Thus, this mixed solvent system can be classified as one of the simplest aqueous mixtures in which the added acetonitrile acts as a slightly weak structure maker of the water lattice in the water-rich region and a strong structure breaker in the intermediate region.

There is no doubt that the ΔH°_t maxima at x_{AN} ca. 0.3 may be closely associated with the most compact solvent structure at nearly the same solvent composition. As shown in Fig. 6, the estimated $\Delta\Delta H_{INT}(=\Delta H^\circ_t+4L_W-\Delta\Delta H_{BC})$ in x_{AN} range 0 to ca. 0.3 agree with the observed ΔH°_t better than expected. The proposed model may be applicable in this range, because the mixtures of x_{AN} 0 to ca. 0.3 can be regarded as the essentially aqueous solvent. Also from the above structural viewpoint, it is reasonable to interpret the increase in ΔH°_t with increasing x_{AN} in this region in terms of the reduction in the hydrogen-bonding interaction extending beyond the primary hydration sphere for smaller anions.

Since the observed ΔH°_t is clearly less than the estimated ΔH_{INT} in the intermediated region, the modified hydration model does not appear to work so well as in the water-rich region. As can be seen in Fig. 6, the x_{AN} dependence of $\Delta\Delta H_{INT}$ is reversed in going from the water-rich region to the intermediate region. If the correction for the ΔH_{CF} term has been made in the intermediate region as adequately as in the water-rich region, this reversal means the recovery of the outer hydration sphere disrupted somewhat in the water-rich region. The possibility of this recovery, however, may be very low in consideration of the decrease in the water content. Reasonably, the outer hydration sphere which has been incompletely disrupted at x_{AN} ca. 0.3 is considered to reduce with increasing x_{AN} in this region though to a smaller extent. The interaction between the water cluster demixed from the mixtures and the surroundings was assumed to be equal to that in water in the above treatment of the solvation enthalpy cycle. This assumption, however, seems unreasonable in the intermediate region in which the water cluster has been broken to a certain extent. This interaction in the intermediate region should be weaker than that in water and should decrease with increasing x_{AN}. A consideration of this effect will lead to the reduction in the ΔH_{CF} value in this region. That is to say, the additional correction term besides $5L_W$ employed in this study seems to be needed for cavity formation in the intermediate region from the viewpoint of the solvent structure. Eventually, the exothermic change in ΔH_t° in the intermediate region may be considered to be due primarily to the decrease in ΔH_{CF} energy.

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