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The Ionic Hydrogen Bond and Ion Solvation. 2. Solvation of Onium Ions by One to Seven H_2O Molecules. Relations between Monomolecular, Specific, and Bulk Hydration

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Abstract: The relation between enthalpies of solvation of onium ions BH^+ by one water molecule, $-\Delta H^\circ_{0,1}$, and by four water molecules, $-\Delta H^\circ_{0,4}$, is constant for most onium ions: $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$ is 2.8 ± 0.1 for all oxonium ions and monoprotonic ammonium and pyridinium ions, and 3.1 ± 0.1 for polyprotonic ammonium ions. These relations, in conjunction with the correlation between $\Delta H^\circ_{0,1}$ and the proton affinity difference $\Delta PA = PA(B) - PA(H_2O)$, allow the prediction of the total four-molecule specific hydration energy $-\Delta H^\circ_{0,4}$ for all onium ions within the experimental accuracy of ±3 kcal mol^{-1}. The observed (or predicted) fourfold specific relative hydration energies simulate closely the relative bulk hydration enthalpies for most ions. In other words, for most onium ions differential hydration effects are determined by the specific hydrogen-bonding interactions. Deviations are useful to identify bulk solvation effects. For example, such deviations indicate attenuated bulk solvation of ions with phenyl substituents.

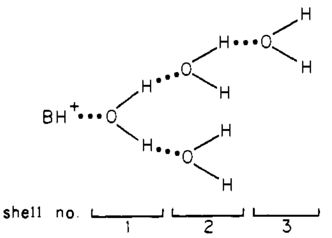
Introduction

The hydration of the ions BH^+ has a strong influence on the basicities of organic compounds B in solution. Ionic hydrogen bonding between the protonated species BH^+ and water constitutes a major factor in the hydration of such ions.[1,2] The differential strength of hydrogen-bonding interactions of various BH^+ ions with water is most pronounced in the inner solvent spheres, i.e., in the interactions of the ions with the first one to four H_2O molecules. The thermochemistry of these inner-sphere specific ion–solvent interactions can be obtained from measurements of clustering equilibria (I) involving BH^+ and a few solvent molecules in the gas phase:

$$BH^+\cdot(n-1)H_2O + H_2O \rightleftarrows BH^+\cdot nH_2O \qquad \text{(I)}$$

The strongest interaction of BH^+ is with the first solvent molecule. As was observed in the preceding paper,[3] the enthalpy of this hydrogen-bonding interaction, i.e., $\Delta H^\circ_D(BH^+\cdots OH_2) \equiv -\Delta H^\circ_{0,1}$, can be estimated to within about ±1 kcal mol^{-1} from a linear correlation with the proton affinity difference, $\Delta PA = PA(B) - PA(H_2O)$.

Specific ion–solvent interactions extend beyond the first solvent molecule. In other words, the properties of the ion BH^+ can affect the bonding energies of at least the first four H_2O molecules. Thus, Kebarle and co-workers examined the hydration of the pyridinium ions 4-CNpyH^+ and of pyH^+ by three H_2O molecules.[4] The proton affinity of 4-CNpy is lower than that of pyridine, and, correspondingly, the attachment energy of H_2O to 4-CNpyH^+ is higher than to pyH^+. With these monoprotonic ions the shell structure may be assumed as in ion **1**. Even though here the first H_2O molecule constitutes the entire first hydration shell (ion **1**), the attachment energies of the second and third H_2O molecules to the 4-CNpy$H^+\cdot nH_2O$ cluster are also higher than the corresponding attachment energies in the pyH^+ cluster. Similar trends are also observed in the series $CH_2FCH_2NH_3^+\cdot nH_2O$, $CH_3NH_3^+\cdot nH_2O$, and $C_2H_5NH_3^+\cdot nH_2O$.[5] With the addition of each H_2O molecule in these series the cumulative gas-phase solvation energies approach, but do not quite reach, the differential hydration enthalpies of the ions by bulk water.[5]



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The present work examines the hydration of a series of monoprotonic oxonium ions by, depending on feasibility, four to seven H_2O molecules. In these ions the differential hydration effects are generally significant up to the fourth H_2O molecule. The total hydration enthalpy by the first four H_2O molecules, i.e., $\Delta H^\circ_{0,4}$, which depends significantly on the identity of the ion BH^+, may be termed the specific hydration enthalpy. The present work, in conjunction with data from Kebarle's work, extends to onium ions the comprehensive studies of Kebarle[6,7] and Castleman[8] on the specific solvation of metal ions and anions. As usual, the attachment energies $-\Delta H^\circ_{n-1,n}$ in those clusters decrease monotonically and asymptotically toward a lower limit of ≈8–10 kcal mol^{-1}, which is usually reached at $n = 4$–8. Small discontinuities (1–2 kcal mol^{-1}) in the plots of $\Delta H^\circ_{n-1,n}$ vs. n are discernible when a stable solvent shell is filled, such as four NH_3 molecules about Li^+ and Na^+.[8] The rate of decrease of solvation energies with n can depend strongly on the identity of the metal ion, or on special bonding effects: for example, $\Delta H^\circ_{1,2}/\Delta H^\circ_{0,1}$ = 0.76, 0.95, 0.75, and 0.88 for the hydration of Li^+, K^+, Pb^+, and Sr^+.[7,8] In this respect, as we shall see, the onium ions show a more uniform behavior. Thus, we shall observe that the relation of the cumulative fourfold hydration enthalpy to the attachment enthalpy of the first H_2O molecule, i.e., $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$ is remarkably constant for all monoprotonic oxonium and ammonium ions.

Kebarle,[6] Castleman,[8] and Klotz[8] discussed the relation between specific ion solvation in clusters and single ion solvation energies in bulk solvent, for metal ions and some anions. The important conclusion is that, since specific ion–solvent interactions are significant only in the first few solvation steps, the differences between the cumulative clustering enthalpies $-\Delta H^\circ_{0,n}$, even in small clusters (n = 6–8), approach the differential bulk solvation enthalpies. In a similar manner, we shall compare the fourfold enthalpies of hydration $\Delta H^\circ_{0,4}$ of onium ions with bulk water solvation en-

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thalpies $\delta\Delta H°_{g\rightarrow H_2O}(BH^+)$ which were obtained recently by Taft.[10] We shall note that the differential enthalpies of bulk solvation and specific solvation are comparable for many ions.

Experimental Section

The measurements were conducted using the NBS pulsed high-pressure mass spectrometer.[6] Reaction mixtures containing neat H_2O or 5–25% H_2O in a carrier gas (CH_4 or i-C_4H_{10}), and a trace (about 0.001–0.01%) of the base B at total pressures of 0.2–1.0 torr, were irradiated by 1-1.5-ms, 500–1000-V pulses of electrons. Signal intensities corresponding to the reactant and product ions were followed to reaction times of 1–3 ms. Equilibrium constants K for clustering reactions were obtained by the usual methods. van't Hoff plots were constructed using the temperature dependence of K. Some van't Hoff plots were taken over a narrow temperature range, avoiding points where the concentration of the higher cluster is very small (<5%) or large (>50%). Such points can be inaccurate due to sensitivity problems or cluster dissociation, respectively.

For experimental reasons, it was convenient to use neat H_2O, rather than a mixture of H_2O in a carrier gas, as the main gas component. In particular, the use of neat H_2O was required for the observation of weakly bonded large clusters (n = 4–7). However, Sunner and Kebarle showed that it is preferable to observe clustering equilibria using low partial pressures of H_2O, as this permits the measurement of K at low temperatures.[12] In contrast, measurements at high temperatures may lead to errors due to thermal decomposition of the cluster ions outside the ion source. To examine whether this problem affects our results, we measured several equilibria both using neat H_2O and 5–20% H_2O in a carrier gas (CH_4, i-C_4H_{10}, cyclohexane). The difference ($-\Delta H°_{n-1,n}$ in neat H_2O) – ($-\Delta H°_{n-1,n}$ in mixture) and corresponding $\Delta S°$ values, about the average values given in Table I, were: $CH_3OH_2^+ \cdot H_2O$, 1.0, 1.9; $(CH_3)_2COH^+ \cdot H_2O$, 1.1, 3.4; $(CH_3)_2COH^+ \cdot 2H_2O$, 1.6, 4.9; c-$C_3H_5COCH_3H^+ \cdot H_2O$, 2.1, 3.5; $H(NH_2)COH^+ \cdot H_2O$, 1.0, 3.2; $H(NH_2)COH^+ \cdot 2H_2O$, 1.4, 2.5; $CH_3NH_3^+ \cdot H_2O$, 0.5, 0.7; $CH_3COOHH^+ \cdot 4H_2O$, –0.9, –2.7. On the average, $\Delta H°_D$ values obtained in neat H_2O were higher by 1.0 kcal mol^{-1}, and $\Delta S°_D$ values by 2.1 cal mol^{-1}K^{-1}, than the results in carrier gas/H_2O mixtures. The differences are within the combined errors of the two measurements. However, the difference is systematic and in the direction and of the general magnitude predicted by the decomposition effects of Sunner and Kebarle.[12] On the other hand, the difference is not more severe, but indeed reversed in the large cluster $CH_3COOH_2^+ \cdot 4H_2O$, and does not increase signficantly with ion flight-time (see below). These observations suggest that the differences may be due to other factors. In part, they may reflect the true variation, especially of $\Delta S°_D$, with temperature, since the median temperatures of the mixture measurements were ≈ 50–100° lower than those in neat H_2O.

With respect to this problem we also note that our source pressures were usually 0.2–0.4 torr, vs. usual pressures of 2–4 torr in Kebarle's experiments. Thus we work at H_2O pressures lower by an order of magnitude than neat H_2O in Kebarle's experiments, and we observe a given equilibrium at temperatures intermediate between the high temperatures required for measurements using neat H_2O and the low temperatures required when mixtures of ≈1% H_2O/CH_4 are used in Kebarle's work. Therefore, in any given equilibrium we avoid the highest temperatures where thermal decomposition is expected to be most serious. Indeed, we did not observe the curvature that would result from this effect in any of our van't Hoff plots.

In addition to thermal decomposition, collisional dissociation of clusters may also occur outside the ion source. The absence of significant dissociation due to either effect can be checked by varying the electric field strength in the ion acceleration region (see preceding paper). This affects the translational energy of the ions, which would result in increased collisional dissociation with increased E. Also, the total transit time of ions between the source exit and the detector varies, for example, for $(CH_3)_2COH^+ \cdot 4H_2O$ (m/z 131) from 0.032 s for V_{source} = 15 V to 0.10 s for V_{source} = 1.5 V. The effect was tested in two model systems: the dimer $CH_3CHOHH^+ \cdot H_2O$ at 610 K, $P(H_2O)$ = 0.90 torr, and the large cluster $(CH_3)_2OH^+ \cdot 4H_2O$ at 300 K, $P(H_2O)$ = 0.7 torr. In both cases, K was independent of E within the usual limits of ±20%. A small decrease of 10% in K was observed at the lowest field (E = 1.25 V/cm), suggesting some thermal decomposition at the longest ion transit times (0.10 s). With our usual value of E = 8.3 V/cn the effect is negligible.

The absence of collisional dissociation was also verified by checking that K was independent of P(source) between 0.2 and 1.0 torr in these model systems. Pressure checks, usually between 0.4 and 0.8 torr, were also performed in other reactions. In summary, the observed consistency of results under varied conditions suggests that systematic errors due to instrumentation are not larger than ±1 kcal mol^{-1} and ≈3 cal mol^{-1} K^{-1} in $\Delta H°$ and $\Delta S°$, respectively.

Results

van't Hoff plots for clustering equilibria are presented in Figure 1. The resultant thermochemical values are summarized in Table I. Standard deviations of slopes and intercepts in the van't Hoff plots lead on the average to error estimates of ±0.5 kcal mol^{-1} in $\Delta H°$ and ±1 cal mol^{-1} K^{-1} in $\Delta S°$. However, replicate measurements lead to errors of ±1.5 kcal mol^{-1} in $\Delta H°$ and ±3 cal mol^{-1} K^{-1} in $\Delta S°$. Generally, our results agree with Kebarle's results within the combined error limits, when comparable data are available ($NH_4^+ \cdot nH_2O$, $CH_3NH_3^+ \cdot nH_2O$; see Table I).

Some features of interest such as the distinction between successive solvation shells are within the limits of ±1.5 kcal mol^{-1} error. To reduce the experimental scatter, we use in the Discussion adjusted values of $\Delta H°$, obtained from $\Delta G°$ values measured at one temperature at the middle of the temperature range for each equilibrium, and using adjusted $\Delta S°$ as described below. The relative $\Delta H°$ values obtained in this matter are more precise, since $\Delta G°$ can be usually measured with a precision of ±0.3 kcal mol^{-1}, which is substantially better than the precision of $\Delta H°$ values obtained from the temperature dependence of $\Delta G°$. A similar approach was used in Kebarle's treatment of the hydration of pyridinium ions.[4]

The adjusted values $\Delta H°_D$ were obtained as follows. For the addition of the nth H_2O molecule to a cluster ion $BH^+ \cdot (n-1)H_2O$, it may be assumed that the nature of BH^+ will have only minor effects of $\Delta S°$. The major differential effect should be in $\Delta S°_{translational}$. The largest difference between $\Delta S°_{translational}$ for a given n in the present set is between $H_2COH^+ + H_2O$ and $(c\text{-}C_3H_5)_2COH^+ + H_2O$, where $\Delta\Delta S°_{translational}$ = 0.8 cal mol^{-1} K^{-1}. Differences between $\Delta S°$ terms due to molecular rotations and internal rotations, and librations about the loose hydrogen bonds, should be comparably small. Indeed for complexes of monoprotonic oxonium ions with the first H_2O molecule, where data are most accurate, the values of $\Delta S°$ are similar and range between 24 and 28 cal mol^{-1} K^{-1}, which is a spread comparable to the experimental error. For the addition of H_2O molecules beyond the first shell, the effects of the nature of the ion on $\Delta S°$ should be even smaller, although the exact effects of the multiple loose vibrations are not known. We assume that the differences between measured $\Delta S°$ values for various BH^+ and a given n should therefore result from experimental scatter and from the difference in the temperature at which the equilibria are observed. To obtain adjusted $\Delta H°$ values, we therefore use the average value of $\Delta S°$ for a given n, i.e., $(\Delta S°_{av})_{n-1,n}$ values in conjunction with $\Delta G° = RT_m \ln K$ taken from an equilibrium measurement at the middle of the temperature range (T_m) for each van't Hoff plot. We obtain the adjusted values $\Delta H°_a = (\Delta G°)_{T_m} + T_m(\Delta S°_{av})_{n-1,n}$.

It should be emphasized that in 30 of the 32 measurements the original $\Delta H°_{exptl}$ and adjusted $\Delta H°_a$ values agree within 1.5 kcal mol^{-1}. It should also be noted that for some clusters the highest clustering equilibria could be observed only at a limited temperature range which precluded reliable van't Hoff plots. In these cases $\Delta H°$ values are obtained from $\Delta G°$ measured (see footnote, d, Table I) at one temperature, using $(\Delta S°_{av})_{n-1,n}$. The next sections will examine multiple vs. monomolecular solvation, i.e., $\Delta H°_{0,n}$ vs. $\Delta H°_{0,1}$, for all 28 onium ion–solvent systems (17 from the present work) for which data are available.

Discussion

1. Hydration of Monoprotonic Ions by One to Seven H_2O Molecules. For all ions, the attachment energies $-\Delta H°_{n-1,n}$ decrease with increasing n as the ionic charge becomes delocalized in the larger clusters. At the same time, the differential attachment energies $-(\Delta H°_{n-1,n}(B_1H^+) - \Delta H_{n-1,n}(B_2H^+))$ for any pairs of ions B_1 and B_2 decrease with increasing n (Figure 2).

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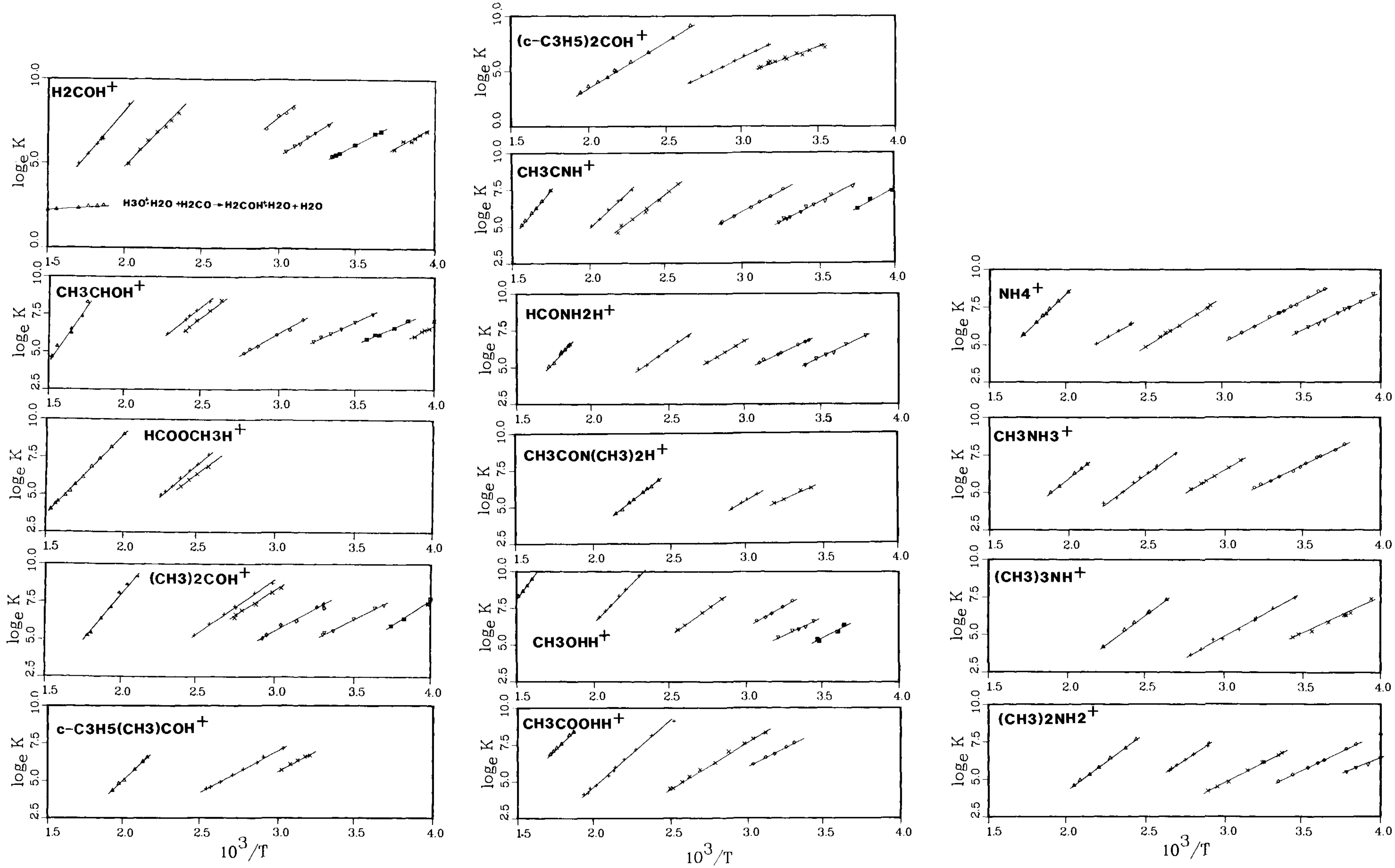

Figure 1. van't Hoff plots for cluster dissociation equilibria $BH^+ \cdot nH_2O \rightleftarrows BH^+ \cdot (n-1)H_2O + H_2O$. BH^+ as indicated. Symbols for $(n-1,n)$ as follows: 0,1 (Δ); 1,2 (+); 2,3 (x); 3,4 (◇); 4,5 (∇); 5,6 (□); 6,7 (*).

Table I. Thermochemistry[a] of Clustering Reactions $BH^{+}\cdot(n-1)H_2O + H_2O \rightarrow BH^{+}\cdot nH_2O$

	$-\Delta H°_{n-1,n}$													
	0,1		1,2		2,3		3,4		4,5		5,6		6,7	
	exptl	adj	exptl	adj	exptl	adj	exptl	adj	exptl	adj	exptl	adj	exptl	adj
H_3O^{+}[b]	31.5		20		17		15		13		12			
H_2COH^{+}	28.5[c]		21.5	20.4	17.6	16.4	12.9	12.3	11.1	10.8	9.5	9.7	10.0	9.0
CH_3CHOH^{+}	25.0	25.2	16.8	16.6	17.0	15.6	11.3	11.3	9.4	10.3	9.3	9.2	9.8	8.8
$CH_3OH_2^{+}$	25	26.5	21.0		14.8		11.6		9.1		9.4		8.9[d]	
$C_2H_5OH_2^{+}$[b]	24		19.2		14.2		12.5							
$CH_3C(OH)_2^{+}$	20.1	22.1	17.8		12.9		10.8		10.3[d]					
$H(OCH_3)COH^{+}$	21.5	22.0	16.2	15.4	13.6	14.0	11.0[d]							
$(CH_3)_2OH^{+}$[e]	22.6		15.3		13.8		10.2							
$(CH_3)_2OH^{+}$	24.0													
$(CH_3)_2COH^{+}$	20.5	21.0	13.6	14.0	12.7	12.4	10.3	10.8	10.3	9.8				
$c\text{-}C_3H_5(CH_3)COH^{+}$	18.2	18.2	11.8	12.5	10.2	10.7	10.0[d]		9.7[d]					
$C_6H_5(CH_3)COH^{+}$	19.5	18.3	12.7	14.1	12.1[d]		9.1[d]							
$(c\text{-}C_3H_5)_2COH^{+}$	16.5	16.6	11.2	12.3	8.9	9.8	9.1[d]							
$H(NH_2)COH^{+}$	21.2	21.2	14.0	14.7	11.8	11.6	9.7	10.0	9.9	8.7				
$CH_3(N(CH_3)_2)COH^{+}$	16.5	16.5	12.3	11.4	9.3	9.6	9.2[d]							
CH_3CNH^{+}	24.8	24.4	17.5	17.5	15.6	14.6	11.2	11.2	10.4	10.0	10.1	9.0		
NH_4^{+}	19.9	20.6	12.4	14.8	12.2	12.4	10.8	10.6	10.6	9.2	9.1		8.4	
NH_4^{+}[b]	17.2		14.7		13.4		12.2		9.7					
$CF_3CH_2NH_3^{+}$[f]	21.1		17.3		14.2		(11)[h]							
$CH_3NH_3^{+}$	16.8	18.4	14.6	14.8	12.3	11.6	10.3	10.1	9.0[d]		8.5[d]			
$CH_3NH_3^{+}$[f]	18.8		14.6		12.4									
$C_2H_5NH_3^{+}$[f]	17.5		14.7		13.2		(11)[h]							
$n\text{-}C_3H_7NH_3^{+}$	15.1		11.6		10.3		9.9							
$(CH_3)_2NH_2^{+}$	15.0	16.2	13.5	13.4	11.3	10.1	10.5	9.7	9.4	8.5	8.4[d]			
$(CH_3)_3NH^{+}$	14.5	15.2	11.4	10.8	10.0	9.0	8.4[d]							
4-CNpyH^{+}[g]	16.0		10.4		8.9		8.2							
pyrH^{+}[g]	15.0		9.6		8.3		(8)[h]							
$CH_3OH_2^{+}\cdot nCH_3OH$[k]	33.1		21.3		16.1		13.5		12.5		11.9			
$NH_4^{+}\cdot nNH_3$[i]	24.8		17.5		13.8		12.5		9.5[h]					
$H_2SH^{+}\cdot nH_2S$[j]	15.4		9.1		8.4		6.7							
$(CH_3)_2OH^{+}\cdot CH_3OH$[e]	26.3		18.8		15.9		13.7							
$CH_3NH_3^{+}\cdot nCH_3CH$	24.5		17.9		13.4									
						$-\Delta S°_{n-1,n}$								
H_3O^{+}[b]	24.4		22		27		32		30		20			
H_2COH^{+}			27.0		25.5		23.2		22.6		20.8		25.7	
CH_3CHOH^{+}	27.6		25.2		27.9		21.4		18.8		21.7		25.8	
$CH_3OH_2^{+}$	23		28.9		25.9		22.1		18.5		22.2			
$C_2H_5OH_2^{+}$[b]	26		28		26		26							
$CH_3C(OH)_2^{+}$	21.0		26.4		23.2		20.4							
$H(OCH_3)COH^{+}$	25.0		26.5		21.4									
$(CH_3)_2OH^{+}$[e]	26.5		26.3		25.4		19.0							
$(CH_3)_2OH^{+}$	29.0													
$(CH_3)_2COH^{+}$	26.0		23.2		21.9		20.2		23.5					
$CH_3(c\text{-}C_3H_5)COH^{+}$	26.8		20.8		19.3									
$CH_3(C_6H_5)COH^{+}$	29.1		21.1											
$(c\text{-}C_3H_5)_2COH^{+}$	26.0		22.3		17.1									
$H(NH_2)COH^{+}$	27.2		22.8		21.0		20.2		25.6					
$CH_3(N(CH_3)_2)COH^{+}$	26.3		26.4		19.2									
CH_3CNH^{+}	28.4		25.1		24.8		21.8		23.4		25.5			
NH_4^{+}	23.1				21.2		23.0		27.0					
NH_4^{+}[b]	20		22		25		27		22					
$CF_3CH_2NH_2^{+}$[f]	30.0		29.9		29.2									
$CH_3NH_3^{+}$	21.8		24.2		24.1		22.0							
$CH_3NH_3^{+}$[f]	26.3		26.7		26.4									
$C_2H_5NH_3^{+}$[f]	25.9		29.7		30.8									
$n\text{-}C_3H_7NH_3^{+}$	21.5		21.3		23.1		24.9							
$(CH_3)_2NH_2^{+}$	22.9		24.7		24.4		25.2		24.4					
$(CH_3)_3NH^{+}$	24.1		24.8		24.9									
4-CNpyH^{+}[g]	25.7		20.2		20.2		19.7							
pyH^{+}[g]	25.5		19.6		19.6									
$CH_3OH_2^{+}\cdot nCH_3OH$	30.5		28.2		28.9		28.7		31.1		32.9			
$NH_4^{+}\cdot nNH_3$[i]	26		23		26		30							
$H_3S^{+}\cdot nH_2S$[i]	24.4		20.9		24.5		24.7							
$(CH_3)_2OH^{+}\cdot nCH_3OH$[k]	27.1		28.9		31.2		30.8							
$CH_3NH_3^{+}\cdot nCH_3CN$	25.8		21.8		21.0									

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[a] $\Delta H°$ in kcal mol^{-1} (=4.18 kJ mol^{-1}); $\Delta S°$ in cal mol^{-1} K^{-1} (=4.18 J mol^{-1} K^{-1}). Results from this work unless noted otherwise. Corrected $\Delta H°_c$; (see text), using the following average $\Delta S°_D$ values and average observational temperatures (n, $\Delta S°_D$, T(K)): 1, 26.7, 500; 2, 24.5, 400; 3, 22.0, 400; 4, 21.6, 350; 5, 22.1, 300; 6, 21.2, 280; 7, 22, 270). [b] Reference 7. [c] From ligand-exchange equilibrium $(H_2O)_2H^{+} + H_2CO \rightleftarrows H_2COH^{+}\cdot H_2O + H_2O$, $\Delta H°_{ex} = -1.3$ kcal mol, $\Delta S°_{ex} = 2.7$ cal mol^{-1} K^{-1}. Calculated from $\Delta H°_D(H_2COH^{+}\cdot H_2O) = \Delta H°_D(H_2O)_2H^{+} - (PA(CH_2O) - PA(H_2O)) - \Delta H°_{ex}$, where $\Delta H°_D(H_2O)_2H^{+} = 31.5$ kcal mol^{-1} (ref 4) and $PA(CH_2O) - PA(H_2O) = 4.3$ kcal mol^{-1}. [d] From equilibrium measurements at one temperature, using $\Delta H° = \Delta G° + T\Delta S°$ and $\Delta S°$ values as in footnote *a*. Experimental values are: ($BH^{+}\cdot nH_2O$, $-\Delta G°$(kcal mol^{-1}), T(K)): $(CH_3)_2COH^{+}\cdot 6H_2O$, 6.3, 251; $c\text{-}C_3H_5(CH_3)COH^{+}\cdot 4H_2O$, 4.0, 284; $c\text{-}C_3H_5(CH_3)COH^{+}\cdot 5H_2O$, 3.5, 281; $(c\text{-}C_3H_5)_2COH^{+}\cdot 4H_2O$, 3.5, 269; $H(OCH_3)COH^{+}\cdot 4H_2O$, 3.8, 334; $CH_3C(OH_2)^{+}\cdot 4H_2O$, 8.9, 350; $CH_3C(OH_2)^{+}\cdot 5H_2O$, 4.1, 280; $CH_3OH_2^{+}\cdot 7H_2O$, 3.0, 269; $CH_3NH_3^{+}\cdot 5H_2O$, 3.5, 269; $CH_3NH_3^{+}\cdot 6H_2O$, 3.1, 259; $(CH_3)_2NH_2^{+}\cdot 6H_2O$, 3.0, 255; $CH_3NH_3^{+}\cdot 4H_2O$, 3.0, 254; $NH_4^{+}\cdot 2H_2O$, 4.6, 414; $NH_4^{+}\cdot 6H_2O$, 3.2, 266; $NH_4^{+}\cdot 7H_2O$, 2,8, 254; $C_6H_5(CH_3)COH^{+}\cdot 3H_2O$, 3.9, 375; $CH_3(C_6H_5)COH^{+}\cdot 4H_2O$, 3.8, 284; $CH_3(N(CH_3)_2)COH^{+}\cdot 4H_2O$, 3.4, 268. [e] Hiraoka, K.; Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* 1974, *96*, 3359. [f] Lau, Y. K.; Kebarle, P. *Can. J. Chem.* 1981, *59*, 151. [g] Davidson, W. R.; Sunner, J.; Kebarle, P. *J. Am. Chem. Soc.* 1979, *101*, 1675. [h] Estimated. [i] Payzant, J. D.; Cunningham, A. J.; Kebarle, P. *Can. J. Chem.* 1973, *51*, 3252. [j] Hiraoka, K.; Kebarle, P. *Ibid.* 1977, *55*, 24. [k] Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* 1973, *95*, 7939.

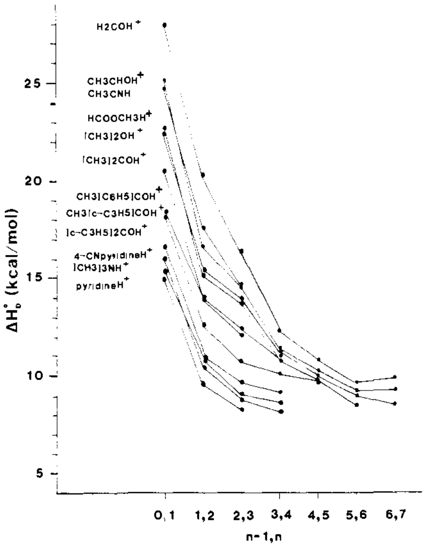


Figure 2. Enthalpies of specific hydration of monoprotonic onium ions BH^+ by the *n*th H_2O molecule, i.e., $\Delta H^\circ_D(n,n-1)$, as a function of *n*.

Beyond the fifth H_2O molecule, i.e., for $n \geq 5$, the attachment energies span only a range of 9–12 kcal mol^{-1}, a spread which is comparable to the magnitude of the experimental error, ±1.5 kcal mol^{-1}. The limiting values of ΔH° for large *n* seem to approach asymptotically ≈ 8 kcal mol^{-1}.

For monoprotonic onium ions the first H_2O molecule constitutes the first hydration shell, and the second to third and the fourth to seventh molecules constitute the second and third shells, respectively (ion **1**). The shell structre is observed distinctly in the positions of the van't Hoff plots as well as the enthalpy profiles of hydration of ions from $CH_3CHOH^+{\cdot}nH_2O$ to $(CH_3)_2COH^+{\cdot}nH_2O$ (Figure 2). The somewhat different profile for $H_2COH^+{\cdot}nH_2O$ may result from strong binding of the second H_2O molecule because of the highly localized charge on this small ion. Alternatively, in this case the second H_2O molecule could be bonded directly to H_2COH^+ to form a $H_2O{\cdots}HCHOH^+{\cdots}OH_2$ structure analogous to the $HCN{\cdots}{}^+HNCH{\cdots}NCH$ structure in $HCNH^+{\cdot}2HCN$.[13,14]

The hydration profile also becomes different for the large, weakly solvated ions (Figure 2). Here a large drop in ΔH° from the first and second shell is still observed, However, a large drop from the third to fourth H_2O molecule is prevented since ΔH° for the fourth H_2O molecule already approaches the low limit of ≈ 8 kcal mol^{-1}.

Concerning the structure observed between the first, second, and third shells in Figure 2, it must also be recognized, however, that these features are within experimental error. Thus, for example, raising $-\Delta H^\circ$ by 1 kcal mol^{-1} for $n = 2$ and decreasing it by 1 kcal mol^{-1} for $n = 3$ would eliminate the shell structure for most ions. The grouping of the lines on the van't Hoff plots constitutes a more reliable evidence for the existence of the shells.

Beyond monoprotonic species, data are also available for ions where more than one hydrogen atom is available for attachment of H_2O molecules, e.g., ROH_2^+, RNH_3^+, etc. Such singly protonated but multiply hydrogen-bonding species will be termed polyprotonic ions. For such ions the second H_2O molecule can attach directly to the protonated species and thus belongs to the first shell. In these ions the decrease of ΔH° with *n* is smooth (Figure 3), and effects of shell structure at higher *n*, if any, are not resolvable. It is interesting to note that $CH_3COOH{\cdot}H^+$ shows a profile similar to that of other polyprotonic ions. This ion is a special case in that the two hydrogen bonding sites are on two separate oxygen atoms, i.e., the structure is $CH_3C(OH)_2^+$, while in the other ions the acidic protons are attached to one heavy atom. The fact that the hydration profile of $CH_3COOH{\cdot}H^+$ is of the polyprotonic rather than monoprotonic type suggests that the first two H_2O molecules attach as in **2a** rather than **2b**.

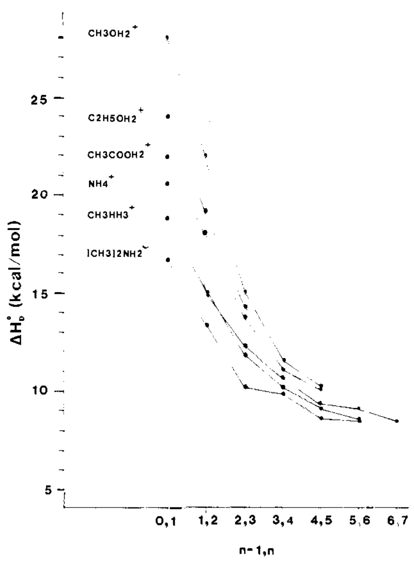
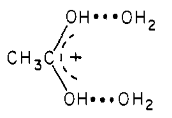
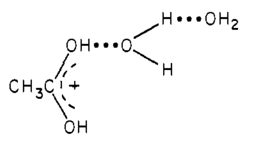


Figure 3. Enthalpies of specific hydration of polyprotonic onium ions BH^+ by the *n*th H_2O molecule, i.e., ΔH°_D $(n,n-1)$, as a function of *n*.



2a



2b

2. Relation between Attachment of One Solvent Molecule and Higher Solvation. The attachment energies of H_2O to the monoprotonic ions in Table I range, in agreement with ΔH^a vs. PA correlation, from 29 to 15 kcal mol^{-1}. For consecutive hydration steps the attachment energies to the various ions decrease in parallel toward the asymptotic limit. For all monoprotonic ions, $-\Delta H^\circ_{1,2}$ is smaller by a factor of 0.70 ± 0.05 than $-\Delta H^\circ_{0,1}$ and $-\Delta H^\circ_{2,3}$ is smaller by a factor of 0.85 ± 0.05 than $-\Delta H^\circ_{1,2}$.

As an alternative treatment of the same data we may examine the ratio of the total solvation enthalpy by *n* solvent molecules to that of solvation by the first solvent molecule alone, i.e., $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$ (where $\Delta H^\circ_{0,4} = \Sigma_1{}^4\Delta H^\circ_{n-1,n}$). The ratios are remarkably constant and show that for all monoprotonic ions the exothermicity of hydration by a total of two, three, or four H_2O molecules is larger by factors of 1,8 ± 0.1, 2.3 ± 0.1, and 2.8 ± 0.1, respectively, than hydration by a single H_2O molecule (Table II). With an average of 70 kcal mol^{-1} for $\Delta H^\circ_{0,4}$ the scatter of ±0,1 in $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$ can result from a scatter of ±2 kcal mol^{-1} in $\Delta H^\circ_{0,1}$ or in $\Delta H^\circ_{0,4}$. In comparison, the error of ±1 kcal mol^{-1} in each solvation step causes an uncertainty of ±4 kcal mol^{-1} in $\Delta H^\circ_{0,n}$. Thus all the scatter in the ratio $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$ may be due to experimental error. On the other hand, systematic trends leading to differences less than ±4 kcal mol^{-1} in the values of $\Delta H^\circ_{0,4}$ would not be discernible by this analysis.

The trends found in the specific hydration of onium ions are formulated quantitatively in eq 1–4. Here, the ΔH° vs. ΔPA correlations (eq 1) can be used to predict the attachment energy of the first H_2O molecule, $\Delta H^\circ_{0,1}$. These values can be multiplied by the constant values of $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$ to predict the total specific solvation enthalpy (eq 2a, 3a,4a). The latter ratio is 2.8 for all compounds, except for polyprotonic ammonium ions where its average value, 3,1 (Table I), is used. Equations 2a–4a yield eq 2b–4b when $PA(H_2O) = 166.5$ kcal mol^{-1} is substituted in $\Delta PA = PA(B) - PA(H_2O)$.

$$-OH^+{\cdots}OH_2 \text{ bonds: } -\Delta H^\circ_{0,1} = 30.4 - 0.30\Delta PA \quad (1a)$$

$$-NH^+{\cdots}OH_2 \text{ bonds: } -\Delta H^\circ_{0,1} = 28.3 - 0.23\Delta PA \quad (1b)$$

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(13) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1978**, *100*, 4694.

(14) Hirao, K.; Yamabe, S.; Sano, M. *J. Phys. Chem.* **1983**, *85*, 2626.

oxonium ions

$$-\mathrm{OH^+\cdots 4H_2O\ clusters:}\ -\Delta H^\circ_{0,4} = 85 - 0.84\Delta\mathrm{PA} \quad (2a)$$

$$-\Delta H^\circ_{0,4} = 224 - 0.84\mathrm{PA(B)} \quad (2b)$$

tertiary amines, pyridines

$$-\mathrm{NH^+\cdots 4H_2O\ clusters:}\ -\Delta H^\circ_{0,4} = 79.2 - 0.64\Delta\mathrm{PA} \quad (3a)$$

$$-\Delta H^\circ_{0,4} = 186 - 0.64\mathrm{PA(B)} \quad (3b)$$

primary, secondary amines

$$-\mathrm{NH^+\cdots 4H_2O\ clusters;}\ -H^\circ_{0,4} = 87.7 - 0.71\Delta\mathrm{PA} \quad (4a)$$

$$-\Delta H^\circ_{0,4} = 206 - 0.71\mathrm{PA(B)} \quad (4b)$$

These empirical equations predict the fourfold differential hydration enthalpies of most of the ions within better than ±3.5 kcal mol^{-1}. (Compare columns 4 and 5, Table II). Of the 24 onium ions where gas-phase hydration data are available, only three ($CH_3OH_2^+$, $C_2H_2OH_2^+$, and $C_2H_5NH_3^+$) show deviations of 4–5 kcal mol^{-1}. One large deviation occurs in 4-CNpyH$^+$, probably reflecting large experimental error. Thus, in general, eq 1–4 predict $\Delta H_{0,4}$ to within the experimental cumulative error of ±4 kcal mol^{-1}.

The ratios $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$ are available for solvation systems other than the hydration of monoprotonic oxonium ions. Thus, Table II shows data for some polyprotonic ions where several H_2O molecules can attach directly to the ion. Nevertheless, the ratios $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$, for the hydration of triprotonic and diprotonic oxonium ions H_3O^+, $CH_3OH_2^+$, and $CH_3COOH_2^+$, fall within the same range as the monoprotonic ions. However, in polyprotonic ammonium ions, the average value of $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$ is somewhat higher, as may be expected in polyprotonic species, i.e., 3.1 ± 0.1.

Ratios $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$ in some clusters with nonaqueous solvents are shown in Table II. The solvents CH_3OH, NH_3, and H_2S can, like H_2O, form unlimited hydrogen-bonded structures, and, in the case of $CH_3NH_3^+\cdot nCH_3CN$, three solvent molecules can attach directly to the ion. Despite the difference in the polarizabilities and dipole moments of these solvents, the attenuation of attachment energies with increasing n, and thus the ratios $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$, are comparable to the hydrated clusters. Finally, similar ratios are found even in the hydration of the small alkali metal ion $Li^+\cdot nH_2O$.[7] Only with some large metal ions where four or more H_2O molecules attach directly to the metal ion is the falloff of attachment energies less pronounced, and thus large values of $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$ are found.

3. Specific vs. Bulk Hydration. In this section we shall compare the fourfold vs. bulk hydration of onium ions and illustrate the use of eq 1–4 to identify bulk solvation effects. For this purpose we shall use $\Delta H^\circ_{0,4}$ as predicted by eq 2–4, since these values are easily obtained even where clustering data are missing.

Using Born cycles, Taft and co-workers[1,2,10] obtained the differential bulk hydration enthalpies $\delta\Delta H^\circ(BH^+)_{g\rightarrow H_2O}$, referred to NH_4^+ (e.g., 1), for the transfer of onium ions from the gas phase to bulk water.

$$\delta\Delta H^\circ_{g\rightarrow H_2O}(BH^+) = \Delta H^\circ_{g\rightarrow H_2O}(BH^+) - \Delta H^\circ_{g\rightarrow H_2O}(NH_4^+) \quad (5)$$

$$\delta\Delta H^\circ_{0,4}(BH^+) = \Delta H^\circ_{0,4}(BH^+) - \Delta H^\circ_{0,4}(NH_4^+) \quad (6)$$

Between the hydration of weakly solvated ions such as pyridineH$^+$ or $(CH_3)_3NH^+$ and strongly hydrated ions such as H_3O^+, the bulk hydration enthalpies vary by over 60 kcal mol^{-1}.

As consecutive H_2O molecules are added to the clusters $BH^+\cdot nH_2O$, the differential integrated enthalpies of hydration $\Delta H^\circ_{0,n}$ (referred to NH_4^+, eq 6) should approach the relative bulk hydration enthalpies $\Delta H^\circ_{g\rightarrow H_2O}(BH^+)$. Such trends were observed by Kebarle et al. for the solvation of XpyH$^+$ and RNH_3^+ ions.[4,5] However, in those studies the range of proton affinities of the reactants was small and thus the differential solvation enthalpies were within the range of experimental error. The present data allow the comparison of specific vs. bulk hydration over a more extended range of ions.

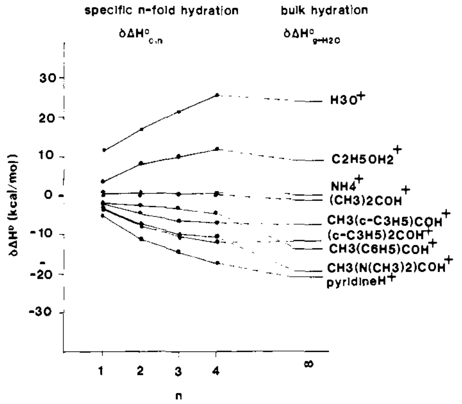

Figure 4. Integrated enthalpies of hydration $\Delta H^\circ_{0,n}$ and bulk hydration enthalpies $\Delta H^\circ_{g\rightarrow H_2O}(BH^+)$, both vs. NH_4^+ as reference.

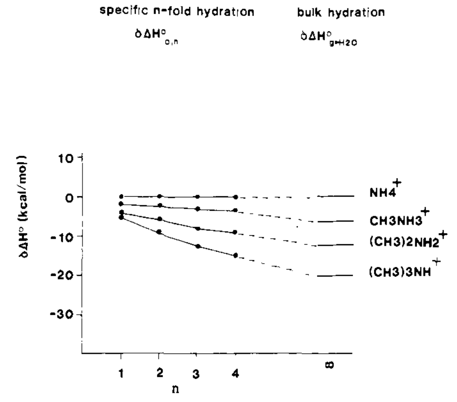

Figure 5. Integrated enthalpies of hydration $\Delta H^\circ_{0,n}$ of ammonium ions by one to four H_2O molecules, $\Delta H^\circ_{0,n}$, and bulk hydration enthalpies, $\Delta H^\circ_{g\rightarrow H_2O}(BH^+)$, both vs. NH_4^+ as reference.

The most significant differences in ΔH° values for the various ions BH^+ occur in the first four hydration steps. Although small differences may persist in higher hydration steps, data for the more weakly solvated ions are not accessible beyond $n = 4$. We therefore observe the cumulative hydration enthalpies for $n = 1$ to 4 and compare those with differential bulk hydration enthalpies (Figures 4 and 5).

Over the fairly wide range of hydration enthalpies of the ions in Figure 4, four H_2O molecules are sufficient to approach differential bulk hydration enthalpies to within 5 kcal mol^{-1}. The integrated effects of the next few H_2O molecules may bring the agreement even closer by a few kcal mol^{-1}; however, such small effects for large clusters cannot be measured reliably. Qualitatively similar trends are observed also in the hydration of ammonium ions (Figure 5). A trend evident in Figure 5 is the increased attenuation of bulk hydration of ammonium ions, relative to NH_4^+, with increasing elimination of acidic protons by methyl substitution from NH_4^+ to $(CH_3)_3NH^+$. It should be noted that the number of H_2O molecules that can bond directly to the ion varies in the clusters as well as in bulk H_2O. Therefore, the increased attenuation of bulk solvation vs. clustering enthalpies must reflect increased stabilities of outer solvation shells in bulk water about the H_2O molecules bonded directly to the ammonium ion.

The solvation of two oxonium ions $CH_3(N(CH_3)_2)COH^+$ and $CH_3(C_6H_5)COH^+$ shows behavior different from the other ions (Figure 4). For these ions the specific hydration enthalpies (relative to NH_4^+) are larger by 7–10 kcal mol^{-1} than the relative bulk hydration enthalpies. This could result either from excessively strong interactions in the hydrogen-bonded clusters or from excessive attentuation of solvation in bulk H_2O. As to the hydro-

Table II. Relations between Enthalpies of Ion Solvation

	$\Delta H^\circ_{0,2}/\Delta H^\circ_{0,1}$ [b]	$\Delta H^\circ_{0,3}/\Delta H^\circ_{0,1}$ [b]	$\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$ [b]	$\delta\Delta H^\circ_{0,4}$		$\delta\Delta H^\circ_{g\rightarrow H_2O}$	$\Delta_{s,crl}$
				exptl[c]	correl.[d]		
Monoprotonic Ions							
Ethers							
$(CH_3)_2OH^+$	1.7	2.3	2.8	3.3	3.6	1.9	−1.7
$(C_2H_5)_2OH^+$					−2.2	−4.1	−1.9
Aldehydes, Ketones							
H_2COH^+	1.7	2.3	2.7	19.0	20.7		
CH_3CHOH^+	1.7	2.3	2.7	10.1	12.2		
$C_6H_5CHOH^+$					−3.2	−7.0	−3.8
$(CH_3)_2COH^+$	1.7	2.3	2.8	−0.4	0.2	−1.7	−1.9
$CH_3(c\text{-}C_3H_5)COH^+$	1.7	2.3	2.8	−7.2	−6.3	−7.5	−1.2
$CH_3(tert\text{-}C_4H_9)COH^+$					−5.0	−7.8	−2.8
$CH_3(C_6H_5)COH^+$	1.8	2.4	2.9	−5.0	−7.6	−13.6	−6.0
$(i\text{-}C_3H_7)_2COH^+$					−5.7	−9.2	−3.5
$(c\text{-}C_3H_5)_2COH^+$	1.7	2.2	2.8	−12.3	−11.4	−11.8	−0.4
Esters							
$H(OCH_3)COH^+$	1.7	2.3	2.8	3.8	6.3		
$CH_3(OCH_3)COH^+$					−1.2	−3.3	−2.1
$i\text{-}C_3H_7(OCH_3)COH^+$					−4.4	−10.1	−5.7
$c\text{-}C_3H_5(OCH_3)COH^+$					−5.5	−8.6	−3.1
$C_6H_5(OCH_3)COH^+$					−6.1	−20.6	−14.5
Amides, Sulfoxide							
$H(NH_2)COH^+$	1.7	2.2	2.7	−1.1	−1.8		
$CH_3(NCH_3)_2COH^+$	1.7	2.3	2.9	−10.7	−7.3	−19.3	−12.0
$(CH_3)_2SOH^+$					−12.6	−13.1	−0.5
Nitriles, Amines, Pyridines							
CH_3CNH^+	1.7	2.3	2.8	9.1	5.7		
$(CH_3)_3NH^+$	1.7	2.3	2.8	−15.1	−17.3	−20.2	−2.9
$(C_2H_5)_3NH^+$					−22.3	−22.6	−0.3
4-CNpyH$^+$	1.7	2.2	2.7	−15.1	−7.3		
4-CF$_3$pyH$^+$					−9.2	−17.8	−8.6
pyH$^+$	1.6	2.2	2.7	−17.7	−14.6	−21.1	−6.5
4-CH$_4$pyH$^+$					−17.7	−22.0	−4.3
Polyprotonic Ions							
Water, Alcohols, Acids							
H_3O^+	1.6	2.2	2.7	24.9	25.0	23.5	
$CH_3OH_2^+$	1.8	2.3	2.7	16.1	12.1	10.4	
$C_2H_5OH_2^+$	1.0	2.4	2.9	11.3	6.7	8.6	
$CH_3C(OH)_2^+$	1.8	2.4	2.9	5.0	5.1		
Amines							
NH_4^+	1.7	2.3	2.8	(0)	(0)	(0)	(0)
$CH_3NH_3^+$	1.8	2.4	3.0	−3.7	−5.1	−6.3	−1.2
$CF_3CH_2NH_3^+$	1.8	2.5	3.0	5.0	3.5	−0.3	−3.5
$C_2H_5NH_3^+$	1.5	2.6	3.2	−2.2	−7.2	−6.8	0.4
$n\text{-}C_4H_9NH_3^+$					−8.1	−7.3	0.5
$tert\text{-}C_4H_4NH_3^+$					−10.1	−10.1	0.0
$c\text{-}C_6H_{11}NH_3^+$					−10.1	−9.0	1.1
$C_6H_5NH_3^+$					−1.9	−7.4	5.6
$(CH_3)_2NH_2^+$	1.8	2.5	3.1	−9.2	−9.7	−12.5	−2.8
piperidine H$^+$					−13.8	−14.5	−0.7
Nonaqueous Solvents							
$CH_3OH_2^+\cdot nCH_3OH$	1.6	2.1	2.5				
$(CH_3)_2OH^+\cdot nCH_3OH$	1.7	2.3	2.8				
$NH_4^+\cdot nNH_3$	1.7	2.2	2.6				
$H_3S^+\cdot nH_2S$	1.6	2.1	2.6				
$CH_3NH_3^+\cdot nCH_3CN$	1.7	2.3					
Hydration of Metal Ions[f]							
Li^+	1.8	2.4	2.9				
Na^+	1.8	2.5	3.1				
K^+	2.0	2.7	3.4				
Sr^+	1.9	2.6	3.3				

[a] Using data in Table I, unless otherwise noted. ΔH°_D(adjusted) is used if given in Table I, ΔH° in kcal mol^{-1}. [b] $\Delta H^\circ_{0,n} \equiv \Sigma_1{}^4\Delta H^\circ_D(n, n\text{-}1)$; $\Delta H^\circ_1 \equiv \Delta H^\circ_D(1, 0)$. [c] $\delta\Delta H^\circ_{0,4} = \Delta H^\circ_{0,4}(BH^+) - \Delta H^\circ_{0,4}(NH_4^+)$. Experimental values for $\Delta H^\circ_{0,4} = \Sigma_1{}^4\Delta H^\circ(n,n\text{-}1)$ from Table I. Correlation values from eq 2a–c; for the reference ion the value $\Delta H^\circ_{0,4}(NH^+) = 59$ kcal mol^{-1} is used. [d] Taft, R. W. *Prog. Phys. Org. Chem.* 1983, *14*, 248. [e] $\Delta_{s,crl} = \delta\Delta H^\circ_{g\rightarrow H_2O} - \delta\Delta H^\circ_{0,4(correlation)}$. [f] References 6–9.

gen-bonded clusters, the first hydration step of these ions agrees with the ΔH° vs. ΔPA correlation,[15] and the subsequent steps show $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$ ratios similar to the other ions. Therefore, the anomalies exhibited by $CH_3(N(CH_3)_2)COH^+$ and $CH_3(C_6H_5)COH^+$ in Figure 4 must be due to anomalous solvation effects—or inaccurate data—in bulk H_2O.

The difference $\Delta_{s,crl}$ between differential bulk solvation, and the specific fourfold solvation enthalpies as calculated from the

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[15] Meot-Ner (Mautner), M., preceding paper in this issue.

correlation eq 1–4, i.e., $\Delta H^\circ_{0,4\ \mathrm{crl}}$, is shown in Table II, column 7.

$$\Delta_{\mathrm{s,crl}} = \delta\Delta H^\circ_{\mathrm{g}\rightarrow\mathrm{H_2O}} - \delta\Delta H^\circ_{0,4} = [\Delta H^\circ_{\mathrm{g}\rightarrow\mathrm{H_2O}}(\mathrm{BH^+}) - \Delta H^\circ_{0,4\mathrm{crl}}(\mathrm{BH^+})] - [\Delta H^\circ_{\mathrm{g}\rightarrow\mathrm{H_2O}}(\mathrm{NH_4^+}) - \Delta H^\circ_{0,4\mathrm{crl}}(\mathrm{NH_4^+})] \quad (7)$$

If for a series of ions the differential bulk solvation enthalpies are affected mostly by specific interactions in the inner shells, then for these ions $\Delta_{\mathrm{s,crl}}$ should be constant (with an absolute value determined by the right-hand term, eq 7, for the reference ion, NH_4^+). Conversely, widely scattered values of $\Delta_{\mathrm{s,crl}}$ would mean little correlation between specific and bulk hydration.

Table II shows $\Delta_{\mathrm{s,crl}}$ values for 30 representative ions from the 58 for which bulk solvation data are available.[10] Of the 30 ions in Table II, the value of $\Delta_{\mathrm{s,crl}}$ is constant at -2 ± 2 kcal mol^{-1} for 21 ions. Therefore, for the majority of ions the difference between bulk hydration enthalpies seems to be determined by specific interactions with the first four H_2O molecules. As noted above, similar conclusions were reached for metal ions and small anions.[6-9]

Of the nine ions that substantially deviate from this constant value of $\Delta_{\mathrm{s,crl}}$, six contain a specific structural feature: the presence of an aromatic nucleus, i.e., a phenyl or pyridine function. Indeed, these six ions constitute all the aromatic ions (except $C_6H_5CHOH^+$) in Table II. Two of the nonaromatic ions that show negative $\Delta_{\mathrm{s,crl}}$ values also contain bulky, i.e., *i*-C_3H_7, groups. The other ion that shows large negative deviation is $CH_3(N(CH_3)_2)COH^+$.

For three of the nine ions with unusually negative $\Delta_{\mathrm{s,crl}}$, $CH_3(C_6H_5)COH^+$, $CH_3(N(CH_3)_2)COH^+$, and pyH$^+$, experimental clustering data are available. Table II shows that for all three ions, $\Delta H^\circ_{0,4}$(exptl) and $\Delta H^\circ_{0,4}$(correlation) agree within the usual limits. Thus, the gas-phase specific inner-shell hydrations of these ions is not anomalous, and the low values of $\Delta_{\mathrm{s,crl}}$ must reflect inefficient bulk hydration.

The inefficient bulk hydration of phenyl- and pyridine-containing ions seems to be associated specifically with the aromatic nucleus, since $\Delta_{\mathrm{s,crl}}$ for the aliphatic analogues of anilineH$^+$ and pyridineH$^+$, i.e., c-$C_6H_{11}NH_3^+$ and piperidineH$^+$, is not anomalous. Similar effects by aromatic substituents were also observed in polycyclic nitrogen heterocyclics.[16] Evidently, the effect does not result from charge delocalization in the aromatic ions, since this would also weaken hydrogen bonding in the gas-phase clusters; however, the clustering data agree with the general correlations of eq 1–4. The weak solvation may be due to decreased $CH^{\delta+}\cdots O$ interactions of the aromatic vs. aliphatic substituents with the solvent, due to the smaller number of hydrogens in the former. Such $CH^{\delta+}\cdots O$ interactions may be as strong as 7–9 kcal mol^{-1}, as is seen in the hydration of quaternary ammonium ions.[3]

Conclusions: General Properties of Ionic Hydrogen Bonds

The present results, in conjunction with several preceding papers, allow some generalizations concerning the ionic hydrogen bond and ion solvation.

1. The strength of the ionic hydrogen bond $-XH^+\cdots Y-$ correlates with $\Delta PA = PA(X) - PA(Y)$. Linear correlations $\Delta H^\circ_D = \Delta H^\circ_D(0) - b\Delta PA$ are observed over a wide range of ΔPA. $\Delta H^\circ_D(0)$, i.e., the dissociation energies for dimers with $\Delta PA = 0$, depends on the identity of X and Y, but the slopes of all the correlation lines are similar, i.e., $b = 0.23 - 0.30$. These correlations reflect the decreasing strength of the hydrogen bond as XH^+ becomes a less efficient proton donor and Y a less efficient proton acceptor.

2. In symmetric dimers BH^+B with $-OH^+\cdots O-$ and $-NH^+\cdots N-$ bonds, ΔH°_D is constant at 31 ± 2 and 23 ± 2 kcal mol^{-1}, respectively, over a wide range of oxygen and nitrogen bases.

3. Hydrogen-bond energies $-\Delta H^\circ_{n-1,n}$ decrease with increasing n as the charge is increasingly delocalized in the growing cluster. $-\Delta H^\circ_{n-1,n}$ decreases in parallel in the hydration of the various onium ions BH^+, toward the asymptotic lower limit of ≈ 8 kcal mol^{-1}. Effects of shell structure are resolvable within the error limits only for the second and third hydration steps (second shell) of some monoprotonic oxonium ions.

4. The ratios of enthalpies of higher to monomolecular solvation $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$, are constant for a wide range of onium ions. $\Delta H^\circ_{0,4}/\Delta H^\circ 0_1 = 2.8 \pm 0.1$ for the hydration wide range of ions including oxonium and pyridinium ions; the ratio is 3.1 ± 0.1 for the hydration of polyprotonic ammonium ions. Similar ratios are found even in solvation by nonaqueous hydrogen-bonding solvents and in the hydration of small metal ions.

5. For the majority of onium ions, the variation in enthalpies of specific hydration of various BH^+ ions by four H_2O molecules is equal to the variation in bulk hydration enthalpies. In other words, for these ions the variation in bulk solvation enthalpies is determined completely by the variation in the specific hydrogen bonding interactions.

6. The correlation of ΔH°_D vs. ΔPA in conjunction with the constant $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$ ratios predicts $\Delta H^\circ_{0,4}$ for all onium ions within experimental error. The calculated $\Delta H^\circ_{0,4}$ values can be in turn used to predict differential bulk solvation enthalpies $\delta\Delta H^\circ_{\mathrm{g}\rightarrow\mathrm{H_2O}}$. Deviations are useful to identify bulk solvation effects.

7. Deviations from ΔH°_D vs. ΔPA correlations identify and quantify structural effects on the ionic hydrogen bond. Such analysis shows that in polyfunctional ions (polyethers, crown ethers, polyamines, peptide analogues) the enthalpies of intramolecular hydrogen bonds range from 4 to 30 kcal mol^{-1}, and lead to negative entropies of protonation, 4–20 cal mol^{-1} K^{-1}. The intramolecular hydrogen bonds weaken solvation by external solvent molecules.[17]

8. In complexes with polyfunctional ligands, multiple hydrogen bonding leads to exceptionally stable complexes. ΔH°_D of a second and third $-NH^+\cdots X-$ bond in a dimer ions is generally 8 ± 1 and 4 ± 1 kcal mol^{-1}, respectively. Polydentate complexes with total ΔH°_D up to 45 kcal mol^{-1} are observed. $-CH^{\delta+}\cdots X-$ interactions up to 10 kcal mol^{-1} are also indicated.[18] Interactions of this type, with strength of 7–15 kcal mol^{-1}, are observed directly in the clustering of $(CH_3)_3NCH_3^+$ with oxygen and nitrogen bases.

9. Steric crowding does not weaken the ionic hydrogen bond, as long as optimal hydrogen bonding is possible in some conformation of the bulky substituents. However, steric crowding results in substantial entropy effects.[11]

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Registry No. H_2COH^+, 18682-95-6; CH_3CHOH^+, 18682-96-7; $CH_3OH_2^+$, 17836-08-7; $CH_3C(OH)_2^+$, 18639-92-4; $H(OCH_3)COH^+$, 39014-35-2; $(CH_3)_2COH^+$, 43022-03-3; c-$C_3H_5(CH_3)COH^+$, 70058-20-7; $C_6H_5(CH_3)COH^+$, 39922-13-9; (c-$C_3H_5)_2COH^+$, 70058-21-8; $H(NH_2)COH^+$, 50785-80-3; $CH_3(N(CH_3)_2)COH^+$, 52754-55-9; CH_3CNH^+, 20813-12-1; NH_4^+, 14798-03-9; $CH_3NH_3^+$, 17000-00-9; *n*-$C_3H_7NH_3^+$, 17033-39-5; $(CH_3)_2NH_2^+$, 17000-01-0; $(CH_3)_3NH^+$, 16962-53-1.

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