

# The Ionic Hydrogen Bond and Ion Solvation. 2. Solvation of Onium Ions by One to Seven H<sub>2</sub>O Molecules. Relations between Monomolecular, Specific, and Bulk Hydration

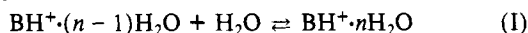
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**Abstract:** The relation between enthalpies of solvation of onium ions BH<sup>+</sup> by one water molecule,  $-\Delta H^\circ_{0,1}$ , and by four water molecules,  $-\Delta H^\circ_{0,4}$ , is constant for most onium ions:  $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$  is  $2.8 \pm 0.1$  for all oxonium ions and monoprotic ammonium and pyridinium ions, and  $3.1 \pm 0.1$  for polyprotic 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  $\pm 3$  kcal mol<sup>-1</sup>. 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.

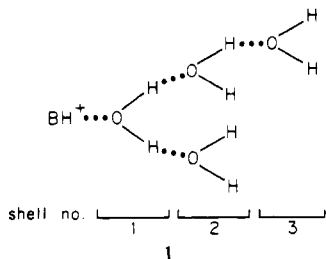
## Introduction

The hydration of the ions BH<sup>+</sup> has a strong influence on the basicities of organic compounds B in solution. Ionic hydrogen bonding between the protonated species BH<sup>+</sup> and water constitutes a major factor in the hydration of such ions.<sup>1,2</sup> The differential strength of hydrogen-bonding interactions of various BH<sup>+</sup> 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<sub>2</sub>O molecules. The thermochemistry of these inner-sphere specific ion-solvent interactions can be obtained from measurements of clustering equilibria (I) involving BH<sup>+</sup> and a few solvent molecules in the gas phase:



The strongest interaction of BH<sup>+</sup> is with the first solvent molecule. As was observed in the preceding paper,<sup>3</sup> 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  $\pm 1$  kcal mol<sup>-1</sup> 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<sup>+</sup> can affect the bonding energies of at least the first four H<sub>2</sub>O molecules. Thus, Kebarle and co-workers examined the hydration of the pyridinium ions 4-CNpyH<sup>+</sup> and of pyH<sup>+</sup> by three H<sub>2</sub>O molecules.<sup>4</sup> The proton affinity of 4-CNpy is lower than that of pyridine, and, correspondingly, the attachment energy of H<sub>2</sub>O to 4-CNpyH<sup>+</sup> is higher than to pyH<sup>+</sup>. With these monoprotic to ionic structure may be assumed as in ion 1. Even though here the first H<sub>2</sub>O molecule constitutes the entire first hydration shell (ion 1),



the attachment energies of the second and third H<sub>2</sub>O molecules to the 4-CNpyH<sup>+</sup>·nH<sub>2</sub>O cluster are also higher than the corresponding attachment energies in the pyH<sup>+</sup> cluster. Similar trends are also observed in the series CH<sub>2</sub>FCH<sub>2</sub>NH<sub>3</sub><sup>+</sup>·nH<sub>2</sub>O, CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>·nH<sub>2</sub>O, and C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>·nH<sub>2</sub>O.<sup>5</sup> With the addition of each H<sub>2</sub>O 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.<sup>5</sup>

The present work examines the hydration of a series of monoprotic oxonium ions by, depending on feasibility, four to seven H<sub>2</sub>O molecules. In these ions the differential hydration effects are generally significant up to the fourth H<sub>2</sub>O molecule. The total hydration enthalpy by the first four H<sub>2</sub>O molecules, i.e.,  $\Delta H^\circ_{0,4}$ , which depends significantly on the identity of the ion BH<sup>+</sup>, 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<sup>6,7</sup> and Castleman<sup>8</sup> 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  $\approx 8$ – $10$  kcal mol<sup>-1</sup>, which is usually reached at  $n = 4$ – $8$ . Small discontinuities (1–2 kcal mol<sup>-1</sup>) 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<sub>3</sub> molecules about Li<sup>+</sup> and Na<sup>+</sup>.<sup>8</sup> 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<sup>+</sup>, K<sup>+</sup>, Pb<sup>+</sup>, and Sr<sup>+</sup>.<sup>7,8</sup> 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<sub>2</sub>O molecule, i.e.,  $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$  is remarkably constant for all monoprotic oxonium and ammonium ions.

Kebarle,<sup>6</sup> Castleman,<sup>8</sup> and Klotz<sup>9</sup> 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  $\delta\Delta H^\circ_{g \rightarrow H_2O}(BH^+)$  which were obtained recently by Taft.<sup>10</sup> 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.<sup>6</sup> 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 Kebablar 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.<sup>12</sup> 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 ( $-\Delta H^\circ_{n-1,n}$  in neat  $H_2O$ ) – ( $-\Delta H^\circ_{n-1,n}$  in mixture) and corresponding  $\Delta S^\circ$  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;  $CH_3COOH^+ \cdot 4H_2O$ , –0.9, –2.7. On the average,  $\Delta H^\circ_D$  values obtained in neat  $H_2O$  were higher by 1.0 kcal mol<sup>–1</sup>, and  $\Delta S^\circ_D$  values by 2.1 cal mol<sup>–1</sup> K<sup>–1</sup>, 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 Kebablar.<sup>12</sup> 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 significantly 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  $\Delta S^\circ_D$ , with temperature, since the median temperatures of the mixture measurements were  $\approx 50-100^\circ$  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 Kebablar's experiments. Thus we work at  $H_2O$  pressures lower by an order of magnitude than neat  $H_2O$  in Kebablar'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  $\approx 1\%$   $H_2O/CH_4$  are used in Kebablar'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  $CH_3CHOH^+ \cdot H_2O$  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  $\pm 20\%$ . 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/cm 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  $\pm 1$  kcal mol<sup>–1</sup> and  $\approx 3$  cal mol<sup>–1</sup> K<sup>–1</sup> in  $\Delta H^\circ$  and  $\Delta S^\circ$ , 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  $\pm 0.5$  kcal mol<sup>–1</sup> in  $\Delta H^\circ$  and  $\pm 1$  cal mol<sup>–1</sup> K<sup>–1</sup> in  $\Delta S^\circ$ . However, replicate measurements lead to errors of  $\pm 1.5$  kcal mol<sup>–1</sup> in  $\Delta H^\circ$  and  $\pm 3$  cal mol<sup>–1</sup> K<sup>–1</sup> in  $\Delta S^\circ$ . Generally, our results agree with Kebablar'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  $\pm 1.5$  kcal mol<sup>–1</sup> error. To reduce the experimental scatter, we use in the Discussion adjusted values of  $\Delta H^\circ$ , obtained from  $\Delta G^\circ$  values measured at one temperature at the middle of the temperature range for each equilibrium, and using adjusted  $\Delta S^\circ$  as described below. The relative  $\Delta H^\circ$  values obtained in this manner are more precise, since  $\Delta G^\circ$  can be usually measured with a precision of  $\pm 0.3$  kcal mol<sup>–1</sup>, which is substantially better than the precision of  $\Delta H^\circ$  values obtained from the temperature dependence of  $\Delta G^\circ$ . A similar approach was used in Kebablar's treatment of the hydration of pyridinium ions.<sup>4</sup>

The adjusted values  $\Delta H^\circ_D$  were obtained as follows. For the addition of the  $m$ th  $H_2O$  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  $\Delta S^\circ$ . The major differential effect should be in  $\Delta S^\circ_{translational}$ . The largest difference between  $\Delta S^\circ_{translational}$  for a given  $n$  in the present set is between  $H_2COH^+ + H_2O$  and  $(c-C_3H_5)_2COH^+ + H_2O$ , where  $\Delta\Delta S^\circ_{translational} = 0.8$  cal mol<sup>–1</sup> K<sup>–1</sup>. Differences between  $\Delta S^\circ$  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  $\Delta S^\circ$  are similar and range between 24 and 28 cal mol<sup>–1</sup> K<sup>–1</sup>, 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  $\Delta S^\circ$  should be even smaller, although the exact effects of the multiple loose vibrations are not known. We assume that the differences between measured  $\Delta S^\circ$  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  $\Delta H^\circ$  values, we therefore use the average value of  $\Delta S^\circ$  for a given  $n$ , i.e.,  $(\Delta S^\circ_{av})_{n-1,n}$  values in conjunction with  $\Delta G^\circ = RT_m \ln K$  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  $\Delta H^\circ_a = (\Delta G^\circ)_{T_m} + T_m(\Delta S^\circ_{av})_{n-1,n}$ .

It should be emphasized that in 30 of the 32 measurements the original  $\Delta H^\circ_{exptl}$  and adjusted  $\Delta H^\circ_a$  values agree within 1.5 kcal mol<sup>–1</sup>. 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  $\Delta H^\circ$  values are obtained from  $\Delta G^\circ$  measured (see footnote, d, Table I) at one temperature, using  $(\Delta S^\circ_{av})_{n-1,n}$ . The next sections will examine multiple vs. monomolecular solvation, i.e.,  $\Delta H^\circ_{0,n}$  vs.  $\Delta H^\circ_{0,1}$ , 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  $-\Delta H^\circ_{n-1,n}$  decrease with increasing  $n$  as the ionic charge becomes delocalized in the larger clusters. At the same time, the differential attachment energies  $-(\Delta H^\circ_{n-1,n}(B_1H^+) - \Delta H^\circ_{n-1,n}(B_2H^+))$  for any pairs of ions  $B_1$  and  $B_2$  decrease with increasing  $n$  (Figure 2).

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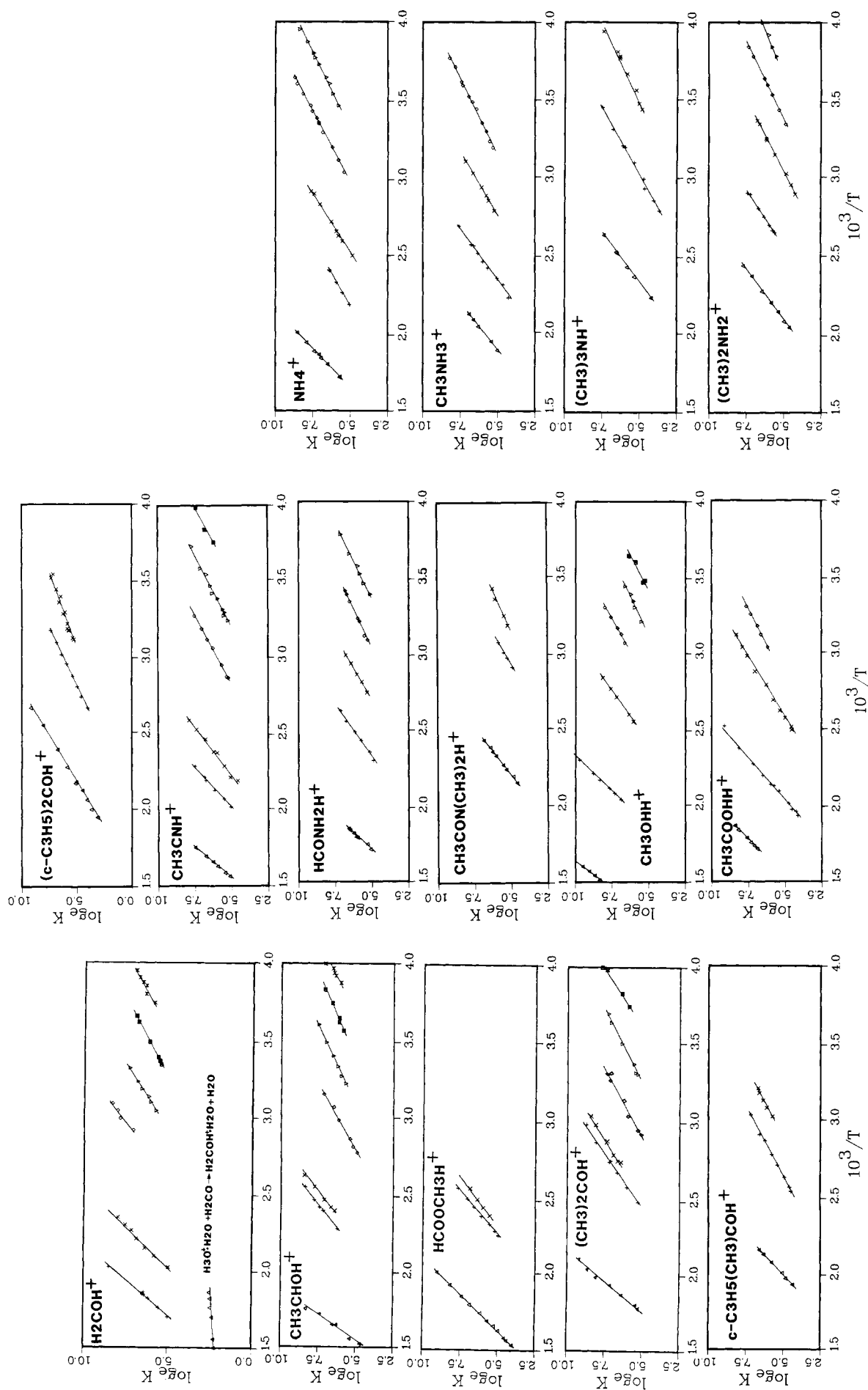
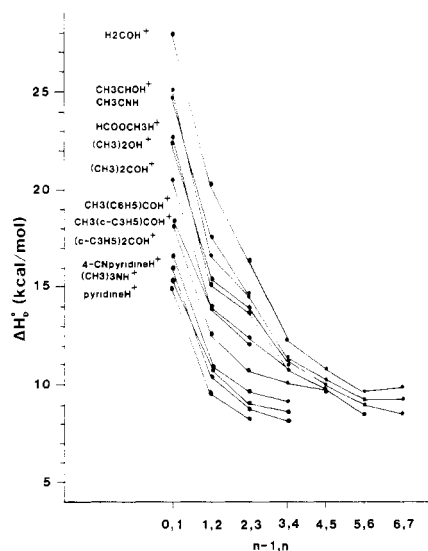


Figure 1. van't Hoff plots for cluster dissociation equilibria  $\text{BH}^+ \cdot (n-1)\text{H}_2\text{O} \rightleftharpoons \text{BH}^+ \cdot n\text{H}_2\text{O}$  as follows: 0,1 ( $\Delta$ ); 1,2 ( $+$ ); 2,3 ( $\times$ ); 3,4 ( $\diamond$ ); 4,5 ( $\nabla$ ); 5,6 ( $\square$ ); 6,7 ( $*$ ).

Table I. Thermochemistry<sup>a</sup> of Clustering Reactions  $\text{BH}^+ \cdot (n-1)\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{BH}^+ \cdot n\text{H}_2\text{O}$ 

	$-\Delta H^\circ_{n-1,n}$													
	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
$\text{H}_3\text{O}^+{}^b$	31.5		20		17		15		13		12			
$\text{H}_2\text{COH}^+$	28.5 <sup>c</sup>		21.5	20.4	17.6	16.4	12.9	12.3	11.1	10.8	9.5	9.7	10.0	9.0
$\text{CH}_3\text{CHOH}^+$	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
$\text{CH}_3\text{OH}_2^+$	25	26.5	21.0		14.8		11.6		9.1		9.4		8.9 <sup>d</sup>	
$\text{C}_2\text{H}_5\text{OH}_2^+{}^b$	24		19.2		14.2		12.5							
$\text{CH}_3\text{C}(\text{OH})_2^+$	20.1	22.1	17.8		12.9		10.8		10.3 <sup>d</sup>					
$\text{H}(\text{OCH}_3)\text{COH}^+$	21.5	22.0	16.2	15.4	13.6	14.0	11.0 <sup>d</sup>							
$(\text{CH}_3)_2\text{OH}^+{}^e$	22.6		15.3		13.8		10.2 <sup>e</sup>							
$(\text{CH}_3)_2\text{OH}^+$	24.0													
$(\text{CH}_3)_2\text{COH}^+$	20.5	21.0	13.6	14.0	12.7	12.4	10.3	10.8	10.3	9.8				
$\text{c-C}_3\text{H}_7(\text{CH}_3)\text{COH}^+$	18.2	18.2	11.8	12.5	10.2	10.7	10.0 <sup>d</sup>		9.7 <sup>d</sup>					
$\text{C}_6\text{H}_5(\text{CH}_3)\text{COH}^+$	19.5	18.3	12.7	14.1	12.1 <sup>d</sup>		9.1 <sup>d</sup>							
$(\text{c-C}_3\text{H}_7)_2\text{COH}^+$	16.5	16.6	11.2	12.3	8.9	9.8	9.1 <sup>d</sup>							
$\text{H}(\text{NH}_2)\text{COH}^+$	21.2	21.2	14.0	14.7	11.8	11.6	9.7	10.0	9.9	8.7				
$\text{CH}_3(\text{N}(\text{CH}_3)_2)\text{COH}^+$	16.5	16.5	12.3	11.4	9.3	9.6	9.2 <sup>d</sup>							
$\text{CH}_3\text{CNH}^+$	24.8	24.4	17.5	17.5	15.6	14.6	11.2	11.2	10.4	10.0	10.1	9.0		
$\text{NH}_4^+{}^b$	19.9	20.6	12.4	14.8	12.2	12.4	10.8	10.6	10.6	9.2	9.1		8.4	
$\text{NH}_4^+{}^b$	17.2		14.7		13.4		12.2		9.7					
$\text{CF}_3\text{CH}_2\text{NH}_3^+{}^f$	21.1		17.3		14.2		(11) <sup>h</sup>							
$\text{CH}_3\text{NH}_3^+{}^f$	16.8	18.4	14.6	14.8	12.3	11.6	10.3	10.1	9.0 <sup>d</sup>		8.5 <sup>d</sup>			
$\text{CH}_3\text{NH}_3^+{}^f$	18.8		14.6		12.4									
$\text{C}_2\text{H}_5\text{NH}_3^+{}^f$	17.5		14.7		13.2		(11) <sup>h</sup>							
$n\text{-C}_3\text{H}_7\text{NH}_3^+{}^f$	15.1		11.6		10.3		9.9							
$(\text{CH}_3)_2\text{NH}_2^+$	15.0	16.2	13.5	13.4	11.3	10.1	10.5	9.7	9.4	8.5	8.4 <sup>d</sup>			
$(\text{CH}_3)_3\text{NH}^+$	14.5	15.2	11.4	10.8	10.0	9.0	8.4 <sup>d</sup>							
$4\text{-CNpyH}^+{}^g$	16.0		10.4		8.9		8.2							
$\text{pyrH}^+{}^g$	15.0		9.6		8.3		(8) <sup>h</sup>							
$\text{CH}_3\text{OH}_2^+ \cdot n\text{CH}_3\text{OH}^h$	33.1		21.3		16.1		13.5		12.5		11.9			
$\text{NH}_4^+ \cdot n\text{NH}_3^i$	24.8		17.5		13.8		12.5		9.5 <sup>h</sup>					
$\text{H}_2\text{SH}^+ \cdot n\text{H}_2\text{S}^j$	15.4		9.1		8.4		6.7							
$(\text{CH}_3)_2\text{OH}^+ \cdot \text{CH}_3\text{OH}^e$	26.3		18.8		15.9		13.7							
$\text{CH}_3\text{NH}_3^+ \cdot n\text{CH}_3\text{CH}$	24.5		17.9		13.4									
$-\Delta S^\circ_{n-1,n}$														
$\text{H}_3\text{O}^+{}^b$	24.4		22		27		32		30		20			
$\text{H}_2\text{COH}^+$			27.0		25.5		23.2		22.6		20.8		25.7	
$\text{CH}_3\text{CHOH}^+$	27.6		25.2		27.9		21.4		18.8		21.7		25.8	
$\text{CH}_3\text{OH}_2^+$	23		28.9		25.9		22.1		18.5		22.2			
$\text{C}_2\text{H}_5\text{OH}_2^+{}^b$	26		28		26		26							
$\text{CH}_3\text{C}(\text{OH})_2^+$	21.0		26.4		23.2		20.4							
$\text{H}(\text{OCH}_3)\text{COH}^+$	25.0		26.5		21.4									
$(\text{CH}_3)_2\text{OH}^+{}^e$	26.5		26.3		25.4		19.0							
$(\text{CH}_3)_2\text{OH}^+$	29.0													
$(\text{CH}_3)_2\text{COH}^+$	26.0		23.2		21.9		20.2		23.5					
$\text{CH}_3(\text{c-C}_3\text{H}_7)\text{COH}^+$	26.8		20.8		19.3									
$\text{CH}_3(\text{C}_6\text{H}_5)\text{COH}^+$	29.1		21.1											
$(\text{c-C}_3\text{H}_7)_2\text{COH}^+$	26.0		22.3		17.1									
$\text{H}(\text{NH}_2)\text{COH}^+$	27.2		22.8		21.0		20.2		25.6					
$\text{CH}_3(\text{N}(\text{CH}_3)_2)\text{COH}^+$	26.3		26.4		19.2									
$\text{CH}_3\text{CNH}^+$	28.4		25.1		24.8		21.8		23.4		25.5			
$\text{NH}_4^+{}^b$	23.1				21.2		23.0		27.0					
$\text{NH}_4^+{}^b$	20		22		25		27		22					
$\text{CF}_3\text{CH}_2\text{NH}_3^+{}^f$	30.0		29.9		29.2									
$\text{CH}_3\text{NH}_3^+{}^f$	21.8		24.2		24.1		22.0							
$\text{CH}_3\text{NH}_3^+{}^f$	26.3		26.7		26.4									
$\text{C}_2\text{H}_5\text{NH}_3^+{}^f$	25.9		29.7		30.8									
$n\text{-C}_3\text{H}_7\text{NH}_3^+{}^f$	21.5		21.3		23.1		24.9							
$(\text{CH}_3)_2\text{NH}_2^+$	22.9		24.7		24.4		25.2		24.4					
$(\text{CH}_3)_3\text{NH}^+$	24.1		24.8		24.9									
$4\text{-CNpyH}^+{}^g$	25.7		20.2		20.2		19.7							
$\text{pyrH}^+{}^g$	25.5		19.6		19.6									
$\text{CH}_3\text{OH}_2^+ \cdot n\text{CH}_3\text{OH}^h$	30.5		28.2		28.9		28.7		31.1		32.9			
$\text{NH}_4^+ \cdot n\text{NH}_3^i$	26		23		26		30							
$\text{H}_2\text{S}^+ \cdot n\text{H}_2\text{S}^j$	24.4		20.9		24.5		24.7							
$(\text{CH}_3)_2\text{OH}^+ \cdot n\text{CH}_3\text{OH}^h$	27.1		28.9		31.2		30.8							
$\text{CH}_3\text{NH}_3^+ \cdot n\text{CH}_3\text{CN}$	25.8		21.8		21.0									

<sup>a</sup>  $\Delta H^\circ$  in kcal mol<sup>-1</sup> (=4.18 kJ mol<sup>-1</sup>);  $\Delta S^\circ$  in cal mol<sup>-1</sup> K<sup>-1</sup> (=4.18 J mol<sup>-1</sup> K<sup>-1</sup>). Results from this work unless noted otherwise. Corrected  $\Delta H^\circ$ 's; (see text), using the following average  $\Delta S^\circ_{\text{D}}$  values and average observational temperatures ( $n$ ,  $\Delta S^\circ_{\text{D}}$ ,  $T$ (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). <sup>b</sup> Reference 7. <sup>c</sup> From ligand-exchange equilibrium  $(\text{H}_2\text{O})_2\text{H}^+ + \text{H}_2\text{CO} \rightleftharpoons \text{H}_2\text{COH}^+ \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$ ,  $\Delta H^\circ_{\text{ex}} = -1.3$  kcal mol<sup>-1</sup>,  $\Delta S^\circ_{\text{ex}} = 2.7$  cal mol<sup>-1</sup> K<sup>-1</sup>. Calculated from  $\Delta H^\circ_{\text{D}}(\text{H}_2\text{COH}^+ \cdot \text{H}_2\text{O}) = \Delta H^\circ_{\text{D}}(\text{H}_2\text{O})_2\text{H}^+ - (\text{PA}(\text{CH}_2\text{O}) - \text{PA}(\text{H}_2\text{O})) - \Delta H^\circ_{\text{ex}}$ , where  $\Delta H^\circ_{\text{D}}(\text{H}_2\text{O})_2\text{H}^+ = 31.5$  kcal mol<sup>-1</sup> (ref 4) and  $\text{PA}(\text{CH}_2\text{O}) - \text{PA}(\text{H}_2\text{O}) = 4.3$  kcal mol<sup>-1</sup>. <sup>d</sup> From equilibrium measurements at one temperature, using  $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$  and  $\Delta S^\circ$  values as in footnote a. Experimental values are:  $(\text{BH}^+ \cdot n\text{H}_2\text{O}, -\Delta G^\circ(\text{kcal mol}^{-1}), T(\text{K}))$ :  $(\text{CH}_3)_2\text{COH}^+ \cdot 6\text{H}_2\text{O}$ , 6.3, 251;  $\text{c-C}_3\text{H}_7(\text{CH}_3)\text{COH}^+ \cdot 4\text{H}_2\text{O}$ , 4.0, 284;  $\text{c-C}_3\text{H}_7(\text{CH}_3)\text{COH}^+ \cdot 5\text{H}_2\text{O}$ , 3.5, 281;  $(\text{c-C}_3\text{H}_7)_2\text{COH}^+ \cdot 4\text{H}_2\text{O}$ , 3.5, 269;  $\text{H}(\text{OCH}_3)\text{COH}^+ \cdot 4\text{H}_2\text{O}$ , 3.8, 334;  $\text{CH}_3\text{C}(\text{OH})_2^+ \cdot 4\text{H}_2\text{O}$ , 8.9, 350;  $\text{CH}_3\text{C}(\text{OH})_2^+ \cdot 5\text{H}_2\text{O}$ , 4.1, 280;  $\text{CH}_3\text{OH}_2^+ \cdot 7\text{H}_2\text{O}$ , 3.0, 269;  $\text{CH}_3\text{NH}_3^+ \cdot 5\text{H}_2\text{O}$ , 3.5, 269;  $\text{CH}_3\text{NH}_3^+ \cdot 6\text{H}_2\text{O}$ , 3.1, 259;  $(\text{CH}_3)_2\text{NH}_2^+ \cdot 6\text{H}_2\text{O}$ , 3.0, 255;  $\text{CH}_3\text{NH}_3^+ \cdot 4\text{H}_2\text{O}$ , 3.0, 254;  $\text{NH}_4^+ \cdot 2\text{H}_2\text{O}$ , 4.6, 414;  $\text{NH}_4^+ \cdot 6\text{H}_2\text{O}$ , 3.2, 266;  $\text{NH}_4^+ \cdot 7\text{H}_2\text{O}$ , 2.8, 254;  $\text{C}_6\text{H}_5(\text{CH}_3)\text{COH}^+ \cdot 3\text{H}_2\text{O}$ , 3.9, 375;  $\text{CH}_3(\text{C}_6\text{H}_5)\text{COH}^+ \cdot 4\text{H}_2\text{O}$ , 3.8, 284;  $\text{CH}_3(\text{N}(\text{CH}_3)_2)\text{COH}^+ \cdot 4\text{H}_2\text{O}$ , 3.4, 268. <sup>e</sup> Hiraoka, K.; Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* 1974, 96, 3359. <sup>f</sup> Lau, Y. K.; Kebarle, P. *Can. J. Chem.* 1981, 59, 151. <sup>g</sup> Davidson, W. R.; Sunner, J.; Kebarle, P. *J. Am. Chem. Soc.* 1979, 101, 1675. <sup>h</sup> Estimated. <sup>i</sup> Payzant, J. D.; Cunningham, A. J.; Kebarle, P. *Can. J. Chem.* 1973, 51, 3252. <sup>j</sup> Hiraoka, K.; Kebarle, P. *Ibid.* 1977, 55, 24. <sup>k</sup> 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  $n$ .

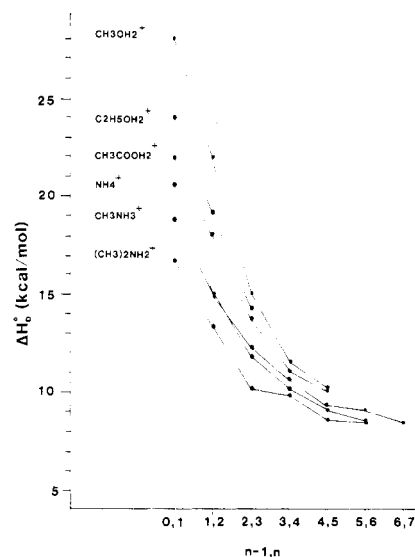
Beyond the fifth  $H_2O$  molecule, i.e., for  $n \geq 5$ , the attachment energies span only a range of 9–12 kcal mol<sup>-1</sup>, a spread which is comparable to the magnitude of the experimental error,  $\pm 1.5$  kcal mol<sup>-1</sup>. The limiting values of  $\Delta H^\circ$  for large  $n$  seem to approach asymptotically  $\approx 8$  kcal mol<sup>-1</sup>.

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 structure 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  $HCNH^+ \cdot 2HCN$ .<sup>13,14</sup>

The hydration profile also becomes different for the large, weakly solvated ions (Figure 2). Here a large drop in  $\Delta H^\circ$  from the first and second shell is still observed. However, a large drop from the third to fourth  $H_2O$  molecule is prevented since  $\Delta H^\circ$  for the fourth  $H_2O$  molecule already approaches the low limit of  $\approx 8$  kcal mol<sup>-1</sup>.

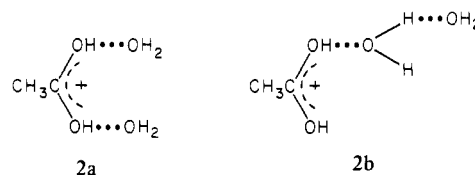
Concerning the structure observed between the first, second, and third shells in Figure 2, it must also be recognized, however, that these features are within experimental error. Thus, for example, raising  $-\Delta H^\circ$  by 1 kcal mol<sup>-1</sup> for  $n = 2$  and decreasing it by 1 kcal mol<sup>-1</sup> 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 polyprotionic 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  $\Delta H^\circ$  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 polyprotionic 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



**Figure 3.** Enthalpies of specific hydration of polyprotionic onium ions  $BH^+$  by the  $n$ th  $H_2O$  molecule, i.e.,  $\Delta H^\circ_D(n,n-1)$ , as a function of  $n$ .

polyprotionic rather than monoprotionic type suggests that the first two  $H_2O$  molecules attach as in **2a** rather than **2b**.



**2. Relation between Attachment of One Solvent Molecule and Higher Solvation.** The attachment energies of  $H_2O$  to the monoprotionic ions in Table I range, in agreement with  $\Delta H^\circ$  vs. PA correlation, from 29 to 15 kcal mol<sup>-1</sup>. For consecutive hydration steps the attachment energies to the various ions decrease in parallel toward the asymptotic limit. For all monoprotionic ions,  $-\Delta H^\circ_{1,2}$  is smaller by a factor of  $0.70 \pm 0.05$  than  $-\Delta H^\circ_{0,1}$  and  $-\Delta H^\circ_{2,3}$  is smaller by a factor of  $0.85 \pm 0.05$  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.,  $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$  (where  $\Delta H^\circ_{0,n} = \sum_1^n \Delta H^\circ_{n-1,n}$ ). The ratios are remarkably constant and show that for all monoprotionic ions the exothermicity of hydration by a total of two, three, or four  $H_2O$  molecules is larger by factors of  $1.8 \pm 0.1$ ,  $2.3 \pm 0.1$ , and  $2.8 \pm 0.1$ , respectively, than hydration by a single  $H_2O$  molecule (Table II). With an average of 70 kcal mol<sup>-1</sup> for  $\Delta H^\circ_{0,4}$  the scatter of  $\pm 0.1$  in  $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$  can result from a scatter of  $\pm 2$  kcal mol<sup>-1</sup> in  $\Delta H^\circ_{0,1}$  or in  $\Delta H^\circ_{0,4}$ . In comparison, the error of  $\pm 1$  kcal mol<sup>-1</sup> in each solvation step causes an uncertainty of  $\pm 4$  kcal mol<sup>-1</sup> 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  $\pm 4$  kcal mol<sup>-1</sup> 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  $\Delta H^\circ$  vs.  $\Delta PA$  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 polyprotionic 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<sup>-1</sup> is substituted in  $\Delta PA = PA(B) - PA(H_2O)$ .

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

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

(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

$$-\text{OH}^+\cdots 4\text{H}_2\text{O} \text{ clusters: } -\Delta H^\circ_{0,4} = 85 - 0.84\Delta\text{PA} \quad (2a)$$

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

tertiary amines, pyridines

$$-\text{NH}^+\cdots 4\text{H}_2\text{O} \text{ clusters: } -\Delta H^\circ_{0,4} = 79.2 - 0.64\Delta\text{PA} \quad (3a)$$

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

primary, secondary amines

$$-\text{NH}^+\cdots 4\text{H}_2\text{O} \text{ clusters: } -H^\circ_{0,4} = 87.7 - 0.71\Delta\text{PA} \quad (4a)$$

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

These empirical equations predict the fourfold differential hydration enthalpies of most of the ions within better than  $\pm 3.5$  kcal mol<sup>-1</sup>. (Compare columns 4 and 5, Table II). Of the 24 onium ions where gas-phase hydration data are available, only three ( $\text{CH}_3\text{OH}_2^+$ ,  $\text{C}_2\text{H}_5\text{OH}_2^+$ , and  $\text{C}_2\text{H}_5\text{NH}_3^+$ ) show deviations of 4–5 kcal mol<sup>-1</sup>. One large deviation occurs in  $4\text{-CNpyH}^+$ , probably reflecting large experimental error. Thus, in general, eq 1–4 predict  $\Delta H_{0,4}$  to within the experimental cumulative error of  $\pm 4$  kcal mol<sup>-1</sup>.

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 polyprotic ions where several  $\text{H}_2\text{O}$  molecules can attach directly to the ion. Nevertheless, the ratios  $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$ , for the hydration of triprotic and diprotic oxonium ions  $\text{H}_3\text{O}^+$ ,  $\text{CH}_3\text{OH}_2^+$ , and  $\text{CH}_3\text{COOH}_2^+$ , fall within the same range as the monoprotic ions. However, in polyprotic ammonium ions, the average value of  $\Delta H^\circ_{0,4}/\Delta H^\circ_{0,1}$  is somewhat higher, as may be expected in polyprotic species, i.e.,  $3.1 \pm 0.1$ .

Ratios  $\Delta H^\circ_{0,n}/\Delta H^\circ_{0,1}$  in some clusters with nonaqueous solvents are shown in Table II. The solvents  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{S}$  can, like  $\text{H}_2\text{O}$ , form unlimited hydrogen-bonded structures, and, in the case of  $\text{CH}_3\text{NH}_3^+\cdots n\text{CH}_3\text{CN}$ , 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  $\text{Li}^+\cdots n\text{H}_2\text{O}$ .<sup>7</sup> Only with some large metal ions where four or more  $\text{H}_2\text{O}$  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<sup>1,2,10</sup> obtained the differential bulk hydration enthalpies  $\delta\Delta H^\circ(\text{BH}^+)_{\text{g}\rightarrow\text{H}_2\text{O}}$ , referred to  $\text{NH}_4^+$  (e.g., 1), for the transfer of onium ions from the gas phase to bulk water.

$$\delta\Delta H^\circ_{\text{g}\rightarrow\text{H}_2\text{O}}(\text{BH}^+) = \Delta H^\circ_{\text{g}\rightarrow\text{H}_2\text{O}}(\text{BH}^+) - \Delta H^\circ_{\text{g}\rightarrow\text{H}_2\text{O}}(\text{NH}_4^+) \quad (5)$$

$$\delta\Delta H^\circ_{0,4}(\text{BH}^+) = \Delta H^\circ_{0,4}(\text{BH}^+) - \Delta H^\circ_{0,4}(\text{NH}_4^+) \quad (6)$$

Between the hydration of weakly solvated ions such as pyridineH<sup>+</sup> or  $(\text{CH}_3)_3\text{NH}^+$  and strongly hydrated ions such as  $\text{H}_3\text{O}^+$ , the bulk hydration enthalpies vary by over 60 kcal mol<sup>-1</sup>.

As consecutive  $\text{H}_2\text{O}$  molecules are added to the clusters  $\text{BH}^+\cdots n\text{H}_2\text{O}$ , the differential integrated enthalpies of hydration  $\Delta H^\circ_{0,n}$  (referred to  $\text{NH}_4^+$ , eq 6) should approach the relative bulk hydration enthalpies  $\Delta H^\circ_{\text{g}\rightarrow\text{H}_2\text{O}}(\text{BH}^+)$ . Such trends were observed by Kebabian et al. for the solvation of  $\text{XpyH}^+$  and  $\text{RNH}_3^+$  ions.<sup>4,5</sup> However, in those studies the range of proton affinities of the

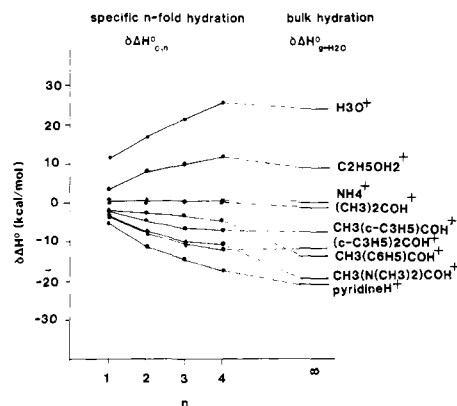


Figure 4. Integrated enthalpies of hydration  $\Delta H^\circ_{0,n}$  and bulk hydration enthalpies  $\Delta H^\circ_{\text{g}\rightarrow\text{H}_2\text{O}}(\text{BH}^+)$ , both vs.  $\text{NH}_4^+$  as reference.

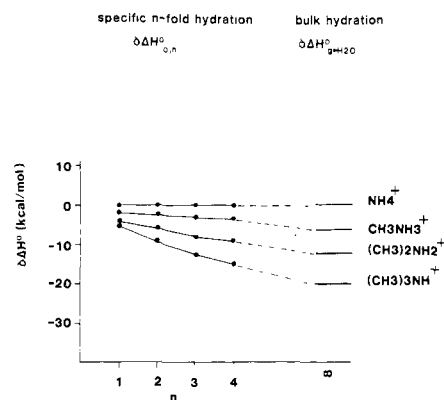


Figure 5. Integrated enthalpies of hydration  $\Delta H^\circ_{0,n}$  of ammonium ions by one to four  $\text{H}_2\text{O}$  molecules,  $\Delta H^\circ_{0,n}$ , and bulk hydration enthalpies,  $\Delta H^\circ_{\text{g}\rightarrow\text{H}_2\text{O}}(\text{BH}^+)$ , both vs.  $\text{NH}_4^+$  as reference.

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.

The most significant differences in  $\Delta H^\circ$  values for the various ions  $\text{BH}^+$  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  $\text{H}_2\text{O}$  molecules are sufficient to approach differential bulk hydration enthalpies to within 5 kcal mol<sup>-1</sup>. The integrated effects of the next few  $\text{H}_2\text{O}$  molecules may bring the agreement even closer by a few kcal mol<sup>-1</sup>; 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  $\text{NH}_4^+$ , with increasing elimination of acidic protons by methyl substitution from  $\text{NH}_4^+$  to  $(\text{CH}_3)_3\text{NH}^+$ . It should be noted that the number of  $\text{H}_2\text{O}$  molecules that can bond directly to the ion varies in the clusters as well as in bulk  $\text{H}_2\text{O}$ . Therefore, the increased attenuation of bulk solvation vs. clustering enthalpies must reflect increased stabilities of outer solvation shells in bulk water about the  $\text{H}_2\text{O}$  molecules bonded directly to the ammonium ion.

The solvation of two oxonium ions  $\text{CH}_3(\text{N}(\text{CH}_3)_2)\text{COH}^+$  and  $\text{CH}_3(\text{C}_6\text{H}_5)\text{COH}^+$  shows behavior different from the other ions (Figure 4). For these ions the specific hydration enthalpies (relative to  $\text{NH}_4^+$ ) are larger by 7–10 kcal mol<sup>-1</sup> than the relative bulk hydration enthalpies. This could result either from excessively strong interactions in the hydrogen-bonded clusters or from excessive attenuation of solvation in bulk  $\text{H}_2\text{O}$ . As to the hydro-

Table II. Relations between Enthalpies of Ion Solvation

	$\frac{\Delta H^\circ_{0,2}}{\Delta H^\circ_{0,1}}$ <sup>b</sup>	$\frac{\Delta H^\circ_{0,3}}{\Delta H^\circ_{0,1}}$ <sup>b</sup>	$\frac{\Delta H^\circ_{0,4}}{\Delta H^\circ_{0,1}}$ <sup>b</sup>	$\delta \Delta H^\circ_{0,4}$		$\delta \Delta H^\circ_{g \rightarrow H_2O}$	$\Delta_{s,cr1}$
				exptl <sup>c</sup>	correl. <sup>d</sup>		
Monoprotonic Ions							
Ethers							
(CH <sub>3</sub> ) <sub>2</sub> OH <sup>+</sup>	1.7	2.3	2.8	3.3	3.6	1.9	-1.7
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> OH <sup>+</sup>					-2.2	-4.1	-1.9
Aldehydes, Ketones							
H <sub>2</sub> COH <sup>+</sup>	1.7	2.3	2.7	19.0	20.7		
CH <sub>3</sub> CHOH <sup>+</sup>	1.7	2.3	2.7	10.1	12.2		
C <sub>6</sub> H <sub>5</sub> CHOH <sup>+</sup>					-3.2	-7.0	-3.8
(CH <sub>3</sub> ) <sub>2</sub> COH <sup>+</sup>	1.7	2.3	2.8	-0.4	0.2	-1.7	-1.9
CH <sub>3</sub> ( <i>c</i> -C <sub>3</sub> H <sub>5</sub> )COH <sup>+</sup>	1.7	2.3	2.8	-7.2	-6.3	-7.5	-1.2
CH <sub>3</sub> ( <i>tert</i> -C <sub>4</sub> H <sub>9</sub> )COH <sup>+</sup>					-5.0	-7.8	-2.8
CH <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> )COH <sup>+</sup>	1.8	2.4	2.9	-5.0	-7.6	-13.6	-6.0
( <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> COH <sup>+</sup>					-5.7	-9.2	-3.5
( <i>c</i> -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> COH <sup>+</sup>	1.7	2.2	2.8	-12.3	-11.4	-11.8	-0.4
Esters							
H(OCH <sub>3</sub> )COH <sup>+</sup>	1.7	2.3	2.8	3.8	6.3		
CH <sub>3</sub> (OCH <sub>3</sub> )COH <sup>+</sup>					-1.2	-3.3	-2.1
<i>i</i> -C <sub>3</sub> H <sub>7</sub> (OCH <sub>3</sub> )COH <sup>+</sup>					-4.4	-10.1	-5.7
<i>c</i> -C <sub>3</sub> H <sub>5</sub> (OCH <sub>3</sub> )COH <sup>+</sup>					-5.5	-8.6	-3.1
C <sub>6</sub> H <sub>5</sub> (OCH <sub>3</sub> )COH <sup>+</sup>					-6.1	-20.6	-14.5
Amides, Sulfoxide							
H(NH <sub>2</sub> )COH <sup>+</sup>	1.7	2.2	2.7	-1.1	-1.8		
CH <sub>3</sub> (NCH <sub>3</sub> ) <sub>2</sub> COH <sup>+</sup>	1.7	2.3	2.9	-10.7	-7.3	-19.3	-12.0
(CH <sub>3</sub> ) <sub>2</sub> SOH <sup>+</sup>					-12.6	-13.1	-0.5
Nitriles, Amines, Pyridines							
CH <sub>3</sub> CNH <sup>+</sup>	1.7	2.3	2.8	9.1	5.7		
(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup>	1.7	2.3	2.8	-15.1	-17.3	-20.2	-2.9
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NH <sup>+</sup>					-22.3	-22.6	-0.3
4-CNpyH <sup>+</sup>	1.7	2.2	2.7	-15.1	-7.3		
4-CF <sub>3</sub> pyH <sup>+</sup>					-9.2	-17.8	-8.6
pyH <sup>+</sup>	1.6	2.2	2.7	-17.7	-14.6	-21.1	-6.5
4-CH <sub>3</sub> pyH <sup>+</sup>					-17.7	-22.0	-4.3
Polyprotic Ions							
Water, Alcohols, Acids							
H <sub>3</sub> O <sup>+</sup>	1.6	2.2	2.7	24.9	25.0	23.5	
CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	1.8	2.3	2.7	16.1	12.1	10.4	
C <sub>2</sub> H <sub>5</sub> OH <sub>2</sub> <sup>+</sup>	1.0	2.4	2.9	11.3	6.7	8.6	
CH <sub>3</sub> C(OH) <sub>2</sub> <sup>+</sup>	1.8	2.4	2.9	5.0	5.1		
Amines							
NH <sub>4</sub> <sup>+</sup>	1.7	2.3	2.8	(0)	(0)	(0)	(0)
CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	1.8	2.4	3.0	-3.7	-5.1	-6.3	-1.2
CF <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	1.8	2.5	3.0	5.0	3.5	-0.3	-3.5
C <sub>2</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>	1.5	2.6	3.2	-2.2	-7.2	-6.8	0.4
<i>n</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>3</sub> <sup>+</sup>					-8.1	-7.3	0.5
<i>tert</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>3</sub> <sup>+</sup>					-10.1	-10.1	0.0
<i>c</i> -C <sub>6</sub> H <sub>11</sub> NH <sub>3</sub> <sup>+</sup>					-10.1	-9.0	1.1
C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>					-1.9	-7.4	5.6
(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	1.8	2.5	3.1	-9.2	-9.7	-12.5	-2.8
piperidine H <sup>+</sup>					-13.8	-14.5	-0.7
Nonaqueous Solvents							
CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup> · <i>n</i> CH <sub>3</sub> OH	1.6	2.1	2.5				
(CH <sub>3</sub> ) <sub>2</sub> OH <sup>+</sup> · <i>n</i> CH <sub>3</sub> OH	1.7	2.3	2.8				
NH <sub>4</sub> <sup>+</sup> · <i>n</i> NH <sub>3</sub>	1.7	2.2	2.6				
H <sub>3</sub> S <sup>+</sup> · <i>n</i> H <sub>2</sub> S	1.6	2.1	2.6				
CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> · <i>n</i> CH <sub>3</sub> CN	1.7	2.3					
Hydration of Metal Ions <sup>f</sup>							
Li <sup>+</sup>	1.8	2.4	2.9				
Na <sup>+</sup>	1.8	2.5	3.1				
K <sup>+</sup>	2.0	2.7	3.4				
Sr <sup>+</sup>	1.9	2.6	3.3				

<sup>a</sup> Using data in Table I, unless otherwise noted.  $\Delta H^\circ_D$  (adjusted) is used if given in Table I.  $\Delta H^\circ$  in kcal mol<sup>-1</sup>. <sup>b</sup>  $\Delta H^\circ_{0,n} \equiv \sum_1^n \Delta H^\circ_{D-}(n, n-1)$ ;  $\Delta H^\circ_1 \equiv \Delta H^\circ_D(1, 0)$ . <sup>c</sup>  $\delta \Delta H^\circ_{0,4} = \Delta H^\circ_{0,4}(\text{BH}^+) - \Delta H^\circ_{0,4}(\text{NH}_4^+)$ . Experimental values for  $\Delta H^\circ_{0,4} = \sum_1^4 \Delta H^\circ_{D-}(n, n-1)$  from Table I. Correlation values from eq 2a-c; for the reference ion the value  $\Delta H^\circ_{0,4}(\text{NH}_4^+) = 59 \text{ kcal mol}^{-1}$  is used. <sup>d</sup> Taft, R. W. *Prog. Phys. Org. Chem.* 1983, 14, 248. <sup>e</sup>  $\Delta_{s,cr1} = \delta \Delta H^\circ_{g \rightarrow H_2O} - \delta \Delta H^\circ_{0,4}(\text{correlation})$ . <sup>f</sup> References 6-9.

gen-bonded clusters, the first hydration step of these ions agrees with the  $\Delta H^\circ$  vs.  $\Delta \text{PA}$  correlation,<sup>15</sup> 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<sub>3</sub>(N(CH<sub>3</sub>)<sub>2</sub>)COH<sup>+</sup> and CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)COH<sup>+</sup> in Figure 4 must be due to anomalous solvation effects—or inaccurate data—in bulk H<sub>2</sub>O.

The difference  $\Delta_{s,cr1}$  between differential bulk solvation, and the specific fourfold solvation enthalpies as calculated from the

correlation eq 1-4, i.e.,  $\Delta H^\circ_{0.4 \text{ crl}}$ , is shown in Table II, column 7.

$$\Delta_{s, \text{crl}} = \delta \Delta H^\circ_{g \rightarrow \text{H}_2\text{O}} - \delta \Delta H^\circ_{0.4} = [\Delta H^\circ_{g \rightarrow \text{H}_2\text{O}}(\text{BH}^+) - \Delta H^\circ_{0.4 \text{ crl}}(\text{BH}^+)] - [\Delta H^\circ_{g \rightarrow \text{H}_2\text{O}}(\text{NH}_4^+) - \Delta H^\circ_{0.4 \text{ crl}}(\text{NH}_4^+)] \quad (7)$$

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  $\Delta_{s, \text{crl}}$  should be constant (with an absolute value determined by the right-hand term, eq 7, for the reference ion,  $\text{NH}_4^+$ ). Conversely, widely scattered values of  $\Delta_{s, \text{crl}}$  would mean little correlation between specific and bulk hydration.

Table II shows  $\Delta_{s, \text{crl}}$  values for 30 representative ions from the 58 for which bulk solvation data are available.<sup>10</sup> Of the 30 ions in Table II, the value of  $\Delta_{s, \text{crl}}$  is constant at  $-2 \pm 2$  kcal mol<sup>-1</sup> 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  $\text{H}_2\text{O}$  molecules. As noted above, similar conclusions were reached for metal ions and small anions.<sup>6-9</sup>

Of the nine ions that substantially deviate from this constant value of  $\Delta_{s, \text{crl}}$ , 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  $\text{C}_6\text{H}_5\text{CHOH}^+$ ) in Table II. Two of the nonaromatic ions that show negative  $\Delta_{s, \text{crl}}$  values also contain bulky, i.e., *i*- $\text{C}_3\text{H}_7$ , groups. The other ion that shows large negative deviation is  $\text{CH}_3(\text{N}(\text{CH}_3)_2)\text{COH}^+$ .

For three of the nine ions with unusually negative  $\Delta_{s, \text{crl}}$ ,  $\text{CH}_3(\text{C}_6\text{H}_5)\text{COH}^+$ ,  $\text{CH}_3(\text{N}(\text{CH}_3)_2)\text{COH}^+$ , and  $\text{pyH}^+$ , experimental clustering data are available. Table II shows that for all three ions,  $\Delta H^\circ_{0.4}(\text{exptl})$  and  $\Delta H^\circ_{0.4}(\text{correlation})$  agree within the usual limits. Thus, the gas-phase specific inner-shell hydrations of these ions is not anomalous, and the low values of  $\Delta_{s, \text{crl}}$  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  $\Delta_{s, \text{crl}}$  for the aliphatic analogues of aniline $\text{H}^+$  and pyridine $\text{H}^+$ , i.e.,  $\text{c-C}_6\text{H}_{11}\text{NH}_3^+$  and piperidine $\text{H}^+$ , is not anomalous. Similar effects by aromatic substituents were also observed in polycyclic nitrogen heterocycles.<sup>16</sup> 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  $\text{CH}^{\delta+} \cdots \text{O}$  interactions of the aromatic vs. aliphatic substituents with the solvent, due to the smaller number of hydrogens in the former. Such  $\text{CH}^{\delta+} \cdots \text{O}$  interactions may be as strong as 7-9 kcal mol<sup>-1</sup>, as is seen in the hydration of quaternary ammonium ions.<sup>3</sup>

### 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  $\text{-XH}^+ \cdots \text{Y-}$  correlates with  $\Delta\text{PA} = \text{PA}(\text{X}) - \text{PA}(\text{Y})$ . Linear correlations  $\Delta H^\circ_{\text{D}} = \Delta H^\circ_{\text{D}}(0) - b\Delta\text{PA}$  are observed over a wide range of  $\Delta\text{PA}$ .  $\Delta H^\circ_{\text{D}}(0)$ , i.e., the dissociation energies for dimers with  $\Delta\text{PA} = 0$ , 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  $\text{XH}^+$  becomes a less efficient proton donor and Y a less efficient proton acceptor.

2. In symmetric dimers  $\text{BH}^+\text{B}$  with  $\text{-OH}^+ \cdots \text{O-}$  and  $\text{-NH}^+ \cdots \text{N-}$  bonds,  $\Delta H^\circ_{\text{D}}$  is constant at  $31 \pm 2$  and  $23 \pm 2$  kcal mol<sup>-1</sup>, 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  $\text{BH}^+$ , toward the asymptotic lower limit of  $\approx 8$  kcal mol<sup>-1</sup>. Effects of shell structure are resolvable within the error limits only for the second and third hydration steps (second shell) of some monoprotic 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  $3.1 \pm 0.1$  for the hydration of polyprotic 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  $\text{BH}^+$  ions by four  $\text{H}_2\text{O}$  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  $\Delta H^\circ_{\text{D}}$  vs.  $\Delta\text{PA}$  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  $\delta \Delta H^\circ_{g \rightarrow \text{H}_2\text{O}}$ . Deviations are useful to identify bulk solvation effects.

7. Deviations from  $\Delta H^\circ_{\text{D}}$  vs.  $\Delta\text{PA}$  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<sup>-1</sup>, and lead to negative entropies of protonation, 4-20 cal mol<sup>-1</sup> K<sup>-1</sup>. The intramolecular hydrogen bonds weaken solvation by external solvent molecules.<sup>17</sup>

8. In complexes with polyfunctional ligands, multiple hydrogen bonding leads to exceptionally stable complexes.  $\Delta H^\circ_{\text{D}}$  of a second and third  $\text{-NH}^+ \cdots \text{X-}$  bond in a dimer ions is generally  $8 \pm 1$  and  $4 \pm 1$  kcal mol<sup>-1</sup>, respectively. Polydentate complexes with total  $\Delta H^\circ_{\text{D}}$  up to 45 kcal mol<sup>-1</sup> are observed.  $\text{-CH}^{\delta+} \cdots \text{X-}$  interactions up to 10 kcal mol<sup>-1</sup> are also indicated.<sup>18</sup> Interactions of this type, with strength of 7-15 kcal mol<sup>-1</sup>, are observed directly in the clustering of  $(\text{CH}_3)_3\text{NCH}_3^+$  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.<sup>11</sup>

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**Registry No.**  $\text{H}_2\text{COH}^+$ , 18682-95-6;  $\text{CH}_3\text{CHOH}^+$ , 18682-96-7;  $\text{CH}_3\text{OH}_2^+$ , 17836-08-7;  $\text{CH}_3\text{C}(\text{OH})_2^+$ , 18639-92-4;  $\text{H}(\text{OCH}_3)\text{COH}^+$ , 39014-35-2;  $(\text{CH}_3)_2\text{COH}^+$ , 43022-03-3; *c*- $\text{C}_6\text{H}_5(\text{CH}_3)\text{COH}^+$ , 70058-20-7;  $\text{C}_6\text{H}_5(\text{CH}_3)\text{COH}^+$ , 39922-13-9; *(c*- $\text{C}_6\text{H}_5)_2\text{COH}^+$ , 70058-21-8;  $\text{H}(\text{NH}_2)\text{COH}^+$ , 50785-80-3;  $\text{CH}_3(\text{N}(\text{CH}_3)_2)\text{COH}^+$ , 52754-55-9;  $\text{CH}_3\text{CNH}^+$ , 20813-12-1;  $\text{NH}_4^+$ , 14798-03-9;  $\text{CH}_3\text{NH}_3^+$ , 17000-00-9; *n*- $\text{C}_3\text{H}_7\text{NH}_3^+$ , 17033-39-5;  $(\text{CH}_3)_2\text{NH}_2^+$ , 17000-01-0;  $(\text{CH}_3)_3\text{NH}^+$ , 16962-53-1.

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