Table VIII. Comparison of Experimental and Calculated $^3J_{HH}$ Coupling Constants (Hz) in 8(a),10(a)-Dihydroxy-2,4,6-trioxaadamantane (See Figure 9)

coupling	J_{exptl}[a]	J_{calcd}
1-8	1.4	2.0
1-9	4.8	3.7
1-9'	1.5	1.4
3-10	1.9	2.5
5-9	2.7	2.2
5-9'	2.4	2.3
7-8	4.0	4.2
7-10	3.9	3.7

[a] Experimental couplings taken from ref 73.

As a final test of the predictive power of the present EHMO parameters, coupling constant calculations on 8(a),10(a)-dihydroxy-2,4,6-trioxaadamantane were carried out (Figure 9, Table VIII). This compound is well suited for this purpose, because it has a rigid geometry and contains a number of suitably placed electronegative oxygen atoms. Thus, the combined effect of anti, gauche, and geminal oxygens upon various couplings can be studied. Table VIII shows excellent agreement between observed[73] and calculated couplings. The rms deviation is nearly equal to the final rms deviation obtained for the data set used in the derivation of the EHMO parameters.

Conclusion

In this paper new parameter sets for the EHMO model are given, optimizing the agreement between calculated and observed $^1J_{CH}$ and $^3J_{HH}$ couplings. With the use of these parameter sets, a host of experimental trends due to substituent or stereochemical effects are reproduced by the calculations. In combination with the relatively small amount of computer time and storage needed for the EHMO calculations, this approach allows accurate theoretical studies concerning the various factors that influence the magnitude of coupling constants with the aim of incorporating these factors in practically useful relationships between coupling constants and geometrical factors such as the generalized Karplus equation.[69]

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Preferential Solvation of Hydrogen Ions in Mixed Water-Amine Ion Clusters

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Abstract: A combined molecular beam-mass spectrometer apparatus has been used to generate mixed water-amine ion clusters of the general form $\{(A)_n{\cdot}(H_2O)_m\}H^+$ for $n + m \leq 18$ and for A equal to one of the following: NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $CH_3CH_2NH_2$, $(CH_3CH_2)_2NH$, $(CH_3CH_2)_3N$, $CH_3CH_2CH_2NH_2$, or C_5H_5N (pyridine). By monitoring the competitive decomposition processes via metastable peak intensities, it has been possible to produce a qualitative picture of the primary, secondary, and tertiary solvation shells surrounding the proton. Despite the nonequilibrium nature of the experiment, the proposed solvent structure surrounding a proton in mixed water-ammonia ion clusters is in qualitative agreement with equilibrium thermodynamic results from the high-pressure mass spectrometry experiments of Kebarle et al. and Castleman et al. In mixed ion clusters containing either a primary or a secondary amine, the hydrogen ion is attached to a primary solvation shell composed of amine molecules. We have called these proton solvation units. In the secondary solvation shells surrounding these units it is found that both water and amine molecules compete for the available hydrogen-bonding sites. In the tertiary solvation shell water alone is the preferred solvent. This transition in solvent preference is rationalized in terms of a gradual decline in the ability of the proton to contribute to the formation of charge-enhanced hydrogen bonds as the size of the cluster increases. In order to account for the observed behavior of the tertiary alkylamine and pyridine mixed ion clusters, a series of structures with protonated water molecules contained within an amine shell are proposed. The possible significance of these structures in selective ion sequestering is discussed. In almost every example studied the number of available hydrogen-bonding sites appears to play a major role in determining the size, shape, and constitution of the solvation shells. The relationship between basicity of the amine and the proposed solvent structures is also discussed.

The protonation of amines in dilute aqueous acid has been the subject of numerous experimental[1-7] and theoretical[8-17] papers. Of particular interest in many of these studies has been the effect alkyl substitution has on the irregular ordering of the basicities (pK_a's). By combining quantitative results on gas-phase basicities with accurate solution thermochemical measurements, it has been possible to separate the bulk protonation data for a number of amines into molecule-dependent and solvent-dependent terms.[18-26] Because gas-phase measurements of both the proton affinities and the basicities[27] have established the order $NH_3 < CH_3NH_2 < \{CH_3\}_2NH < \{CH_3\}_3N$ for the proton-acceptor abilities, it has generally been concluded that anomalies in the pK_a's arise from

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solvation effects. As the aqueous enthalpies of protonation are proportional to the gas-phase proton affinities, it has been suggested that it is an entropy term which is largely responsible. However, exacty which entropy term makes the major contribution appears to be a matter of some discussion.[2,20,24] Everett and Wynne-Jones[1] also measured the heat capacity change associated with the protonation of amines in solution. Electrostatic theory suggests that this should closely follow the entropy change;[1] the fact that it does not has yet to receive a satisfactory explanation. It has been suggested that hydrophobic interactions are responsible for the unexpected heat capacity results.[1,28,29]

Although the amine-aqueous acid proton-transfer process is possibly one of the most thoroughly characterized condensed-phase reactions, it still serves to illustrate how a quantitative interpretation of ion solvation is made difficult through an absence of any detailed understanding of the complex interactions which exist between an ion and the host solvent. One of the most obvious difficulties is that bulk thermodynamic measurements often reveal nothing of the microscopic environment experienced by a solvated ion. So that even when the various contributions to the solvation process are factored out,[18-26] there is still no clear picture of the local ion-solvent configuration.

In order to develop accurate models of the ion solvation process[17] it is particularly important to have some knowledge of the degree of local ordering which arises from the presence of an ion. As an example, the Born equation[30,31] can be used in a continuum model to calculate $\Delta G_s°$, the free energy of solvation

$$\Delta G_s° = (z_i^2 e^2/2r_i)(1 - 1/\epsilon) \tag{1}$$

where z_i is the charge on the ion, e is the charge on the electron, r_i is the ionic radius, and ϵ is the dielectric constant. When it comes to determining the magnitude of ϵ, dielectric saturation as the result of local ordering induced by the presence of the ion can have important consequences. For example, the dielectric constant for water could vary between 80 and 2 depending on the degree of dielectric saturation.[29] To a limited extent it may be possible to compensate for any decrease in ϵ by assuming that local ordering is equivalent to charge delocalization into the surrounding solvent; thus r_i could be increased to include the primary solvation shell.[32] Alternatively, a larger effective ionic radius could also be justified by assuming the positive charge is delocalized within the protonated molecule.[24] Differentiation of eq 1 with respect to temperature, T, yields an expression for the entropy of solvation, and by combining eq 1 and 2 an expression for the enthalpy of solvation

$$\Delta S_s° = \frac{z_i^2 e^2}{2r_i\epsilon^2}\left(\frac{\delta\epsilon}{\delta T}\right)_p \tag{2}$$

can also be derived. It can clearly be seen from these equations

$$\Delta H_s° = \frac{z_i^2 e^2}{2r_i}\left[\frac{1}{\epsilon} - 1 + \frac{T}{\epsilon^2}\left(\frac{\delta\epsilon}{\delta T}\right)_p\right] \tag{3}$$

that, although r_i and ϵ operate in the same direction when $\Delta G_s°$ is calculated, any attempt to compensate for dielectric saturation by increasing r_i will result in a substantial underestimation of both $\Delta S_s°$ and $\Delta H_s°$. It therefore becomes apparent that a discrete or discrete-continuum model[16] offers a better prospect with regard to calculating ion solvation effects. However, in order to develop and test such models it is necessary to have experimental information about the microscopic environment surrounding the solvated ion.

With the development of high-pressure mass spectrometric techniques for studying ion clusters,[33-36] it has become possible to combine the attraction of gas-phase isolation with the desire to study the thermodynamic properties of partially solvated ions. Although quantitative studies of this type are often restricted to systems containing fewer than six solvent molecules, it has been shown that solvation energy differences ($\delta\Delta G_{0,n}°$ and $\delta\Delta H_{0,n}°$ in the notation of ref. 37 and 38) can approach the liquid solvent values for clusters containing as few as five solvent molecules. Not all systems behave this well.[39] High-pressure mass spectrometry appears to be able to provide the necessary microscopic picture of the first or primary solvation shell without interference from the bulk solvent. However, because the technique relies on the generation of an equilibrium concentration of the species of interest, it is often not possible to study clusters containing more than six solvent molecules. In a recent series of papers we have sought to study hydrogen ion solvation in much larger clusters by using adiabatic expansion to generate large neutral clusters prior to ionization. In this way it has been possible to study the behavior of ion clusters containing up to 25 solvent molecules. However, because the clusters are generated in a nonequilibrium manner, the experiments do not yield information of a thermodynamic nature; but they do provide details of the relative strengths of the various interactions which exist between an ion and the different components of a mixed solvent cluster.

In a study of hydrogen ion solvation in mixed water-alcohol clusters[40,41] it was observed that in all cases the alcohol molecules were preferentially bound to the proton in small clusters. However, as the size of the cluster increased so the preference changed in favor of water. It was concluded that the hydrogen ion was solvated with a shell of between 8 and 13 alcohol molecules (the exact number appeared to depend upon the nature of the alcohol concerned; a crude correlation with polarizability was noted[41]). Beyond this shell water rather than alcohol became the preferred solvent. It was not possible to identify any experimental features associated with the formation of discrete solvation shells,[42-44] nor

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Table I. Molecular Dipole Moments, Polarizabilities, and Proton Affinities

molecule	μ,[a] D	α_p,[b] Å^3	PA,[c] kJ mol^{-1}
NH_3	1.48	2.26	861
CH_3NH_2	1.30		899
$(CH_3)_2NH$	0.93	5.55	935
$(CH_3)_3N$	0.71	7.76	942
$CH_3CH_2NH_2$	0.99	5.86	912
$(CH_3CH_2)_2NH$	0.92	9.66	945
$(CH_3CH_2)_3N$	0.82	13.39	971
$CH_3CH_2CH_2NH_2$	1.35	7.68	918
C_5H_5N	2.20	9.53	924
H_2O	1.85	1.48	727

[a] Dipole moment, taken from: Harrison, R. D., Ed. "Book of Data"; Nuffield Advance Science Series, Penguin Books: England, 1972. [b] Polarizability, calculated from eq 4. [c] Proton affinity, taken from ref 27.

was it possible to positively identify the type of bonding responsible for retention of water in the larger clusters. This paper presents the results of a detailed study of hydrogen ion solvation in mixed water–amine clusters. As we shall show below, the experiment derives its most interesting results from those ion clusters which are capable of displaying two competing decomposition processes. Hence, it is not always possible to gain useful information from the behavior of those mixed clusters with a composition close to that expected in a very dilute aqueous solution. The ion clusters generated by electron impact are of the general form $\{(A)_n\cdot(H_2O)_m\}H^+$, and most of the significant results come from those species where $n \simeq m$. Results will be presented to show the various stages in the development of the first, second, and third solvation shell surrounding a hydrogen ion in a mixed water–amine solution. In the light of some of the observations presented in this paper it may be possible to provide a more accurate interpretation of our previous water–alcohol results.[40,41]

In aqueous solution a number of factors can be identified as contributing to the magnitude of the free energy of solvation.[29,45–56] For a cation these are as follows: (a) the formation of a cavity to accommodate the ion; (b) hydrogen bond formation between the ion and the solvent; (c) electrostatic interactions, either in the form represented by eq 1–3 or in terms of a discrete model where individual ion–induced dipole and ion–dipole interactions are taken into consideration; and (d) van der Waals dispersion force interactions. Of these, cluster studies are more likely to make a significant contribution to our understanding of b and c rather than a and d. Obviously, difficulties associated with determining the dimensions of an ion cluster make it almost impossible to comment on a. We have already discussed the fact that the experiment provides a mechanism for generating large water–amine ion clusters. While it is highly probable that the molecules in these clusters will be subjected to van der Waals type forces, it is unlikely that we can detect events which arise in response to a subtle interaction of this nature.

The interpretation of the water–alcohol results[40,41] took into account those ion–induced dipole ($\alpha_p e^2/2r^4$) and ion–dipole ($\mu e/r^2$) interactions that it might be reasonable to assume are present in an ion cluster. Using values of α_p and μ for the various cluster components it was possible to rationalize the results in a semiquantitative manner. In order that we may be able to apply the same technique to the water–amine clusters the values for the appropriate constants have been assembled in Table I. For reference purposes some additional data on the gas-phase properties of water and the amines is also provided. The polarizabilities were calculated from the equation[57]

$$\alpha_p = \frac{3(n_D^2 - 1)M}{4\pi(n_D^2 + 2)\rho N_A} \tag{4}$$

where n_D is the refractive index measured by using the sodium D line, M is the mass, ρ is the density, and N_A is Avogadro's number. While it is recognized that this approach is very much an oversimplification, it does serve the purpose of providing a crude classification of the relative strengths of the major electrostatic interactions present in these systems.

Experimental Section

Neutral clusters of the general form $(A)_n\cdot(H_2O)_m$ are generated by the adiabatic expansion of a gaseous mixture through a pulsed nozzle operating at approximately 100 Hz.[58] In a typical experiment a mixture of the appropriate amine and water is placed in an unheated reservoir and carried through to the nozzle in a stream of argon. All the results reported here were obtained by using a 100-μm-diameter nozzle held at a temperature of 40 °C and a reservoir stagnation pressure of 3000 torr. Following collimation the modulated cluster beam is ionized by electron impact and mass analyzed on a modified A.E.I. MS 12 mass spectrometer. During an experiment the pressure in the ion source of the mass spectrometer remains below 1×10^{-6} torr. In view of this low value we are able to disregard the possibility that ion–molecule reactions may be responsible for some of our observations. Because the signal-to-noise ratio of the peaks we are particularly interested in is quite low (see below), all the experiments have been performed under those conditions which give the highest cluster intensities. For the mass spectrometer this means setting the source and collector slits to their maximum values and using an electron impact energy of 70 eV. It has been observed that the absolute intensities of ion cluster peaks increase quite rapidly as a function of electron impact voltage up to approximately 40 eV; between 40 and 70 eV the intensities continue to increase but very much more slowly.[59]

In addition to providing relative intensities the mass spectrometer has also been used to monitor the intensities of metastable peaks. If an ion has a lifetime in the range 10^{-5}–10^{-6} s, there is a high probability that it will decompose in the field-free region between the ion source and the magnet. Under such circumstances the ion is not properly focused by the instrument and is recorded at a noninteger position on the mass scale. Such peaks are normally referred to as metastable peaks.[60] Because of the simple relationship that exists between the expected position of a metastable peak on the mass scale, m^*, and the masses of the parent and product ions, m_1 and m_2, respectively ($m^* = m_2^2/m_1$), the identification of ion cluster decomposition routes is relatively straightforward. Typically, metastable peaks are between 1 and 2 orders of magnitude less intense than the precursor ions. In most cases, however, the peaks are sufficiently intense that it is possible to make an unambiguous identification of the decomposition route. This is not always the situation in mass spectrometry, particularly on a single focusing instrument such as the MS 12. However, we shall show that in mixed ion clusters of the type studied in this paper there are only two possible decomposition routes leading to metastable peak formation, and in almost all cases only one of those routes appears to be open to an ion cluster of given composition.

Relative metastable peak intensities have been measured for a number of decomposition processes involving mixed ion clusters composed of water in conjunction with the following amines: NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $CH_3CH_2NH_2$, $(CH_3CH_2)_2NH$, $(CH_3CH_2)_3N$, $CH_3CH_2CH_2NH_2$, and C_5H_5N (pyridine). Most of the systems were found to produce very clean ion cluster mass spectra, with little or no evidence of monomer unit fragmentation. Some loss of CH_3 and CH_3CH_2 does occur in the tertiary amines, but this results in only a few instances of interference between the normal ion peaks and the metastable peaks. Our objective for each mixed ion cluster has been to

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generate and study the decomposition routes of ions with the general formula $\{(A)_n{\cdot}(H_2O)_m\}H^+$. In a typical mass spectrum the ranges of n and m appear to depend primarily on the water–amine ratio in the reservoir. High values of n result when the amine is in excess and high values of m when the water is in excess. One aspect of the experiment which can make the interpretation of mass spectra difficult is when two different combinations of n and m have the same nominal mass (the wide slit settings necessary for maximum sensitivity have a dramatic effect on the mass resolving power of the instrument). For example, the clusters $\{((CH_3)_2NH)_4{\cdot}(H_2O)_3\}H^+$ and $\{((CH_3)_2NH)_2{\cdot}(H_2O)_8\}H^+$ fall into this category. Normally it is possible to reduce, and in some cases eliminate, this type of interference by carefully adjusting the proportions of water and amine in the reservoir.

Results and Discussion

The nonequilibrium nature of the experiment means that it is not possible to relate relative ion intensities directly to thermodynamic quantities of interest.[33-36] However, because it is this nonequilibrium aspect that is responsible for the large ion clusters observed, it is desirable to try and identify some feature of the experiment which can be associated with ion cluster stability. Therefore use has been made of the fact that for two competing unimolecular decompositions in a mass spectrometer, the respective metastable peak intensities reflect any difference between the critical energies for the two reactions. The most facile reaction will produce a metastable peak, while the decomposition step involving the loss of that species which is more strongly bound to the ion cluster will not produce a peak of significant intensity. The assumption that critical energy differences alone are responsible for variations in metastable peak intensities is not strictly correct. A combination of both enthalpy and entropy of activation can determine peak intensity. However, the fact that we are dealing with competing fission reactions and that processes of this type very often have little or no reverse critical energy leads us to believe that our observations are determined primarily by critical energy considerations. A series of RRKM calculations on competing reactions in water–alcohol ion clusters has helped to confirm this assumption.[41] This ability the lowest energy decomposition process has to influence metastable peak intensities is often referred to as the competitive shift.[61,62] A similar argument to that given above has been used to rationalize the determination of proton affinities from relative metastable peak intensities.[63]

In the previous study on aliphatic alcohols the two competing reactions found to be most suitable for studying the solvation process were[40,41]

$$\{(ROH)_n{\cdot}H_2O\}H^+ \rightarrow (ROH)_nH^+ + H_2O \qquad (5)$$

$$\{(ROH)_n{\cdot}H_2O\}H^+ \rightarrow \{(ROH)_{n-1}{\cdot}H_2O\}H^+ + ROH \qquad (6)$$

For small values of n reaction 5 was found to be the principal decomposition route in all the samples studied; but as the size of the ion cluster increased so the reaction path was observed to change in favor of reaction 6. The transition in solvent preference was rationalized in terms of the ion–induced dipole and ion–permanent dipole interactions present in the clusters. In particular, it was noted that the value for n at which the transition occurred displayed a crude correlation with alcohol polarizability. Values of n at the transition ranged from 7 to 8 for those alcohols with small polarizabilities and to 13 for 1-butanol, which had the largest polarizability of the alcohols studied.[41]

During a preliminary analysis of the water–amine ion cluster data, it became apparent that a more detailed picture of the hydrogen ion solvation process could be obtained by studying the reactions of mixed ion cluster containing more than just a single water molecule. Hence the results presented in this paper will correspond to two competing reactions of the general form

$$\{(A)_n{\cdot}(H_2O)_m\}H^+ \rightarrow \{(A)_n{\cdot}(H_2O)_{m-1}\}H^+ + H_2O \qquad (7)$$

$$\{(A)_n{\cdot}(H_2O)_m\}H^+ \rightarrow \{(A)_{n-1}{\cdot}(H_2O)_m\}H^+ + A \qquad (8)$$

for $n + m \leq 18$. Here A is used to signify any of the amines including NH_3. It is acknowledged that because the proton affinities of the amines are all larger than that of water (see Table I), the cluster structures should strictly be written as $AH^+{\cdot}\{(A)_{n-1}{\cdot}(H_2O)_m\}$. However, at this stage we find it more convenient to express the configurations in the form given in (7) and (8) above.

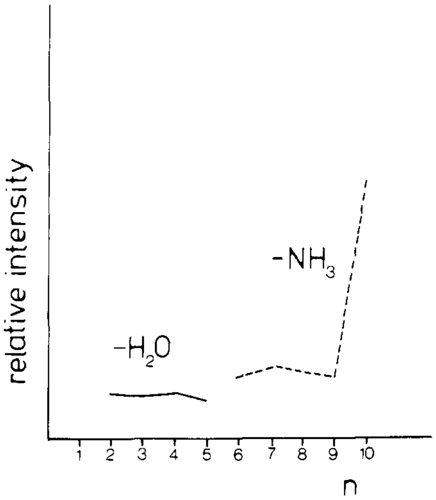

Figure 1. Relative metastable peak intensities for the unimolecular decomposition of $\{(NH_3)_n{\cdot}H_2O\}H^+$ clusters as a function of n. For each value of n the metastable peak intensity has been divided by the intensity of the respective parent peak. The solid line is for the reaction step involving loss of the water molecule (reaction 7), and the dashed line is for the reaction step involving loss of an ammonia molecule (reaction 8). These results correspond to the first column of Table II; i.e., no metastable peaks are observed for loss of NH_3 below $n = 6$ and there are none above $n = 5$ for loss of H_2O.

Figure 1 shows a plot of the relative metastable peak intensities for the unimolecular decomposition of $\{(NH_3)_n{\cdot}H_2O\}H^+$ as a function of n. These results exhibit behavior not observed previously,[40,41] in that there is a very sharp transition in decomposition route as n increases. For $n \leq 5$, only metastable peaks corresponding to reaction 7 are observed; but for $n > 5$ the decomposition path, as indicated by the appearance of new metastable peaks, changes in favor of reaction 8. As we have stated above, our objective in these experiments is to try and provide useful information on the relative strengths of the various electrostatic and hydrogen-bonding interactions that exist between the component molecules of these larger mixed ion clusters. From that viewpoint Figure 1 represents an important result because it provides an opportunity for making a direct comparison with the high-pressure mass spectrometry measurements of Kebarle et al.[64] and Castleman et al.[65] In a detailed study of the $\{(NH_3)_n{\cdot}(H_2O)_m\}H^+$ system for $n + m \leq 6$, Kebarle et al.[64] observed that when n was greater than 5 the ion cluster interacted more strongly with a water molecule than it did with an additional ammonia molecule. If, as we have discussed previously,[40,41] the most intense metastable peak in our experiment is produced by that reaction involving the loss of the least strongly bound molecule, then our observations agree exactly with those from the high-pressure study.[64] The fact these equilibrium measurements show that when $n > 5$ the $\Delta H°$ values for the addition of either a water or ammonia molecule differ by $\simeq 2$ kcal[64,65] would suggest that relative metastable peak intensities are quite sensitive as a probe to the relative interaction energies present in an ion cluster.[63]

Because of the very large number of reactions studied it was not considered practicable to present all the data in graph form. Therefore, the results are presented in tables, with the dominant reaction being indicated by the presence of the neutral product, i.e., $-H_2O$ for reaction 7 and $-NH_3$ and $-A$ for reaction 8. In

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Table II. Unimolecular Decomposition Routes of $\{(NH_3)_n\cdot(H_2O)_m\}H^+$ Clusters As Determined from the Presence of Metastable Peaks[a]

	m						
n	1	2	3	4	5	6	7
1							
2	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	
3	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$		
4	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$			
5	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$
6	$-NH_3$	$-NH_3$[b]	$-NH_3$[b]	$-NH_3$[b]	$-NH_3$[b]	$-NH_3$	$-NH_3$
7	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$
8	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$	
9	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$	
10	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$		
11	$-NH_3$	$-NH_3$	$-NH_3$	$-NH_3$			

[a] $-NH_3$ denotes loss of ammonia and $-H_2O$ loss of water.
[b] Not possible to confirm that the alternative decomposition route is absent.

a few instances metastable peaks for both reactions from the same ion cluster were observed. Under those circumstances the most intense peak was assumed to be generated by the dominant reaction, and that is the one which is indicated in the table. Table II present results for the reactions observed from $\{(NH_3)_n\cdot(H_2O)_m\}H^+$ clusters with $n + m \leq 15$. The results show these clusters to have a very distinct pattern of behavior, with species containing less than or equal to five NH_3 molecules always losing water and species containing greater than five NH_3 molecules always losing ammonia. Such behavior is consistent with the picture of the $\{(NH_3)_n\cdot(H_2O)_m\}H^+$ cluster described by Kebarle et al.[64] The central core of the cluster consists of an NH_4^+ unit surrounded by four NH_3 molecules. The cationic nature of the protons on NH_4^+[66] will ensure that the ammonia molecules with their higher polarizabilities (see Table I) will form stronger hydrogen bonds than those between NH_4^+ and water, This accounts for the observation that up to $n = 5$ the ion clusters always prefer to lose an H_2O rather than an NH_3 molecule. Beyond the first solvation shell of NH_3 molecules the positive charge is sufficiently dispersed that it can no longer influence bonding, At this stage the water molecules, which are capable of forming stronger hydrogen bonds than NH_3 in the absence of a positive charge, form the next solvation shell. This would account for the fact that beyond $n = 5$ the only metastable peaks observed are those corresponding to the loss of NH_3. From Table II it can be seen that for $n = 6$, even when there are up to seven water molecules in the outer shell, it is still the single NH_3 molecule which is lost. This observation confirms our view that the results are determined primarily by energetic considerations rather than by reaction path degeneracy or some other statistical factor.[40] Transitions in solvent preference of the type described above have also been observed in ion clusters of water and ammonia with metal ions.[43,44,67,68]

The preferential solvation of the $NH_4^+(NH_3)_4$ unit by water could also be rationalized on the grounds that water has a larger dipole moment than ammonia (see Table I). This would suggest that it is the long-ranged ion–permanent dipole interaction which is important in the larger ion clusters. It is unlikely that the hydrogen atoms on the inner NH_3 solvation shell would be sufficiently cationic that they could interact effectively with the water dipole. What is perhaps more likely is that the water molecules would be influenced directly by the protons on the NH_4^+ unit. Clearly there is a need for further detailed theoretical work.[66]

To examine the influence which alkyl groups have on proton solvation, reactions 7 and 8 were also studied for a number of alkylamines. Table III presents results for the series CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$; Table IV presents results for the series $CH_3CH_2NH_2$, $(CH_3CH_2)_2NH$, and $(CH_3CH_2)_3N$; Table V presents results for $CH_3CH_2CH_2NH_2$; and Table VI presents results for pyridine, C_5H_5N. We shall discuss in some depth the results for methylamine and then consider how the solvation process is modified through the addition of further alkyl groups, either CH_3 or CH_3CH_2. Over those values of n and m where a direct comparison is possible, the fragmentation patterns for the water–methylamine and water–ethylamine ion clusters are identical. Hence, the discussion on methylamine will also be relevant to ethylamine. The trimethylamine, triethylamine, and pyridine results will be discussed together in a separate section.

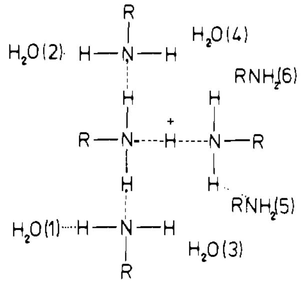

Figure 2. Schematic structure of the methylamine proton solvation unit together with the secondary solvation shell as derived from the fragmentation pattern. $R \equiv CH_3$; chemical bonding within the solvation unit is denoted by solid lines and hydrogen bonding by dashed lines. Hydrogen bonding between sites on the unit and the secondary solvation shell is denoted by dotted lines.

From the general pattern displayed by all the results it is evident that reaction 7 dominates in the smaler ion clusters and, therefore, the proton is preferentially solvated by the amines. Such a result could possibly have been predicted from the relative water–amine proton affinities given in Table I. What is perhaps less predictable is the switch in reaction path as the ion clusters increase in size. In all the examples there is a transition from reaction 7 to reaction 8, indicating that at some stage in the development of the ion clusters the solvent preference changes in favor of water. The cluster size at which this transition occurs does appear to depend in some cases on the size and in all cases on the number of substituted alkyl groups.

Knowledge of the size of the proton solvation unit (the alkylamine equivalent of $NH_4^+(NH_3)_4$) can be gained from a consideration of the reactions of ion clusters of the type $\{(A)_n\cdot H_2O\}H^+$. In a sense the single water molecule acts as a probe as to the nature of the dominant bonding interaction present as the size of the ion cluster varies, If the hydrogen-bonding sites are sufficiently cationic that polarization effects are important, then reaction 7 will be expected to dominate the decomposition process. However, as in the case of $\{(NH_3)_n\cdot(H_2O)_m\}H^+$ clusters, at some critical size the positive charge should become sufficiently dispersed that the superior ability of water molecules to form hydrogen bonds (in the absence of a positive charge) will become more important. At that critical size the metastable peak intensities should register a switch from reaction 7 to reaction 8. Obviously if steric factors are also important then a water molecule presents the smallest molecular volume. An examination of Table IIIa reveals that a transition in decomposition route for $\{(CH_3NH_2)_n\cdot H_2O\}H^+$ occurs at $n = 4$, indicating that the methylamine–proton solvation unit is $(CH_3NH_2)_4H^+$. When the behavior of ion clusters containing more than one water molecule is considered, it can be seen from Table IIIa that the reaction path transition point is offset by one with the addition of each water molecule up to $m = 3$. In order to understand this effect it is necessary to appreciate that the experiment monitors the presence of metastable peaks arising from competitive decomposition within different combinations of n and m. The molecule lost, either CH_3NH_2 or H_2O, is going to be that one which occupies the least favorable site in the particular n and m configuration under consideration. Increasing either n or m by one may lead to the generation of a hydrogen bonding site which is even more unfavorable than the site taken up through the addition of a molecule to the original cluster. As a consequence it is most probable that the species lost occupies a different hy-

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Table III. Unimolecular Decomposition Routes of Mixed Amine-Water Ion Clusters, $\{(A)_n \cdot (H_2O)_m\}H^+$, As Determined from the Presence of Metastable Peaks[a]

	m									
n	1	2	3	4	5	6	7	8	9	10
				a. A = Methylamine (CH_3NH_2)						
1		$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$				
2	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$			
3	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$			
4	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$			
5	−A	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$			
6	−A	−A	$-H_2O$*	$-H_2O$	$-H_2O$	$-H_2O$				
7		−A	−A	−A	−A	−A	−A	−A	−A	
8				−A	−A	−A	−A	−A	−A	−A
9					−A	−A	−A	−A	−A	
10						−A	−A			
				b. A = Dimethylamine ($(CH_3)_2NH$)						
1		$-H_2O$								
2	$-H_2O$	$-H_2O$								
3	$-H_2O$	$-H_2O$	$-H_2O$							
4	$-H_2O$	$-H_2O$	$-H_2O$							
5	−A	$-H_2O$	$-H_2O$	$-H_2O$						
6	−A	−A	−A	−A[b]						
7			−A							
				c. A = Trimethylamine ($(CH_3)_3N$)						
1										
2	$-H_2O$									
3	$-H_2O$	$-H_2O$								
4		−A	$-H_2O$	$-H_2O$						
5			−A	$-H_2O$	$-H_2O$					
6				−A	−A[b]	$-H_2O$				
7					−A	−A				

[a] −A denotes loss of amine and $-H_2O$ loss of water. [b] Not possible to confirm that the alternative decomposition route is absent.

Table IV. Unimolecular Decomposition Routes of Mixed Amine-Water Ion Clusters, $\{(A)_n \cdot (H_2O)_m\}H^+$, As Determined from the Presence of Metastable Peaks[a]

	m						
n	1	2	3	4	5	6	7
			a. A = Ethylamine ($CH_3CH_2NH_2$)				
1							
2	$-H_2O$	$-H_2O$	$-H_2O$				
3	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$			
4	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$		
5	−A	$-H_2O$	$-H_2O$	$-H_2O$[b]			
6	−A	−A	$-H_2O$	$-H_2O$	$-H_2O$		
7	−A	−A	−A	−A[b]	−A[b]		
			b. A = Diethylamine ($(CH_3CH_2)_2NH$)				
1	$-H_2O$						
2	$-H_2O$	$-H_2O$					
3	$-H_2O$	$-H_2O$	$-H_2O$				
4	−A	$-H_2O$	$-H_2O$				
5	−A	−A	$-H_2O$				
6	−A	−A	−A	$-H_2O$			
7		−A	−A	−A	$-H_2O$	$-H_2O$	
8				−A	−A	$-H_2O$[b]	
9				−A	−A	−A	−A[b]
			c. A = Triethylamine ($(CH_3CH_2)_3N$)				
1	$-H_2O$						
2	$-H_2O$	$-H_2O$	$-H_2O$				
3	−A	$-H_2O$	$-H_2O$	$-H_2O$			
4		−A	$-H_2O$	$-H_2O$	$-H_2O$		
5			−A	$-H_2O$	$-H_2O$	$-H_2O$	
6				−A	$-H_2O$		
7					−A		

[a] −A denotes loss of amine and $-H_2O$ loss of water. [b] Not possible to confirm that the alternative decomposition route is absent.

drogen-bonding site in each *n* and *m* combination. Figure 2 presents a schematic structure for the $(CH_3NH_2)_4H^+$ solvation unit together with the sites occupied by the potential decomposition products from higher order ion clusters. The solvation unit follows the pattern found for ammonia in that it has a structure corresponding to $CH_3NH_3^+(CH_3NH_2)_3$, with each proton on the $CH_3NH_3^+$ moiety being bonded to a methylamine molecule.

The interesting decomposition pattern in Table IIIa arises when the ion cluster proceeds to develop the secondary solvation shell or, to be more precise, when additional molecules begin to compete for hydrogen-bonding sites on the $CH_3NH_3^+(CH_3NH_2)_3$ unit. In the cluster $\{(CH_3NH_2)_5 \cdot H_2O\}H^+$ the competition is probably between the molecules labeled $H_2O(1)$ and $CH_3NH_2(5)$ (the sites chosen are quite arbitrary; however, CH_3NH_2 will prefer a site close to where the positive charge is concentrated if it is to remain preferentially bound to the ion cluster). From the results in Table IIIa it can be assumed that of these two molecules $H_2O(1)$ is the more strongly bound. With the addition of a second water molecule, $H_2O(2)$, it is observed that this is lost from the cluster $\{(CH_3NH_2)_5 \cdot (H_2O)_2\}H^+$ but retained in the cluster $\{(CH_3NH_2)_6 \cdot (H_2O)_2\}H^+$. This we have taken as an indication that $H_2O(2)$ is less strongly bound than $CH_3NH_2(5)$ but more strongly bound than $CH_3NH_2(6)$. Similarly, $\{(CH_3NH_2)_6 \cdot (H_2O)_3\}H^+$ loses water, but $\{(CH_3NH_2)_7 \cdot (H_2O)_3\}H^+$ loses CH_3NH_2. In the cluster $\{(CH_3NH_2)_6 \cdot (H_2O)_4\}H^+$ all the available hydrogen-bonding sites on the $CH_3NH_3^+(CH_3NH_2)_3$ unit are occupied, and we suggest that this is the most stable configuration for the secondary solvation shell. All the sites are also occupied in the structure $\{(CH_3NH_2)_7 \cdot (H_2O)_3\}H^+$; however, the fact that this unit loses CH_3NH_2 when a further water molecule is added would suggest that one of the methylamine molecules is in an unfavorable position. In Figure 2 the secondary solvation shell has been presented as a symmetric structure; it is, however, recognized that there is a large number of possible permutations when it comes to assigning the H_2O and CH_3NH_2 molecules to hydrogen-bonding sites on the proton solvation unit. Obviously, the most favorable sites are going to be occupied first, and for the amine molecules they are going to be those sites closest to the proton. Because the water–methylamine and the water–ethylamine results are identical, it is unlikely that steric factors play a significant role in determining the constitution of the solvation shells. Perhaps the most interesting feature of these results is the conclusion that alkyl substitution leads to the formation of a mixed secondary

Table V. Unimolecular Decomposition Routes of Mixed Amine–Water Ion Clusters, $\{(A)_n \cdot (H_2O)_m\}H^+$, As Determined from the Presence of Metastable Peaks for Propylamine ($CH_3CH_2CH_2NH_2$)[a]

	m								
n	1	2	3	4	5	6	7	8	9
1	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$
2	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$
3	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$					
4	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$			
5	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$			
6	$-A$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$				
7	$-A$	$-A$	$-H_2O$	$-H_2O$	$-H_2O$				
8	$-A$	$-A$	$-A$	$-A^b$	$-H_2O^b$	$-H_2O$	$-H_2O$		
9				$-A$	$-A$	$-A^b$	$-A^b$	$-A^b$	

[a] $-A$ denotes loss of amine and $-H_2O$ loss of water. [b] Not possible to confirm that the alternative decomposition route is absent.

Table VI. Unimolecular Decomposition Routes of Mixed Amine–Water Ion Clusters, $\{(A)_n \cdot (H_2O)_m\}H^+$, As Determined from the Presence of Metastable Peaks for Pyridine (C_5H_5N)[a]

	m							
n	1	2	3	4	5	6	7	8
1	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	
2	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	
3	$-H_2O$	$-H_2O$	$-H_2O^b$	$-H_2O^b$				
4	$-A$	$-H_2O$	$-H_2O^b$	$-H_2O$	$-H_2O$			
5		$-A$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$	$-H_2O$
6			$-A^b$	$-H_2O$				

[a] $-A$ denotes loss of amines and $-H_2O$ loss of water. [b] Not possible to confirm that the alternative decomposition route is absent.

solvation shell, with some hydrogen-bonding sites appearing to prefer water molecules and others methylamine molecules. The persistent loss of CH_3NH_2 from ion clusters with $n > 6$ and $m > 4$ would suggest that water alone is the preferred solvent in the tertiary solvation shell and beyond.

Table IIIb gives the results for the observed decomposition processes in water–dimethylamine ion clusters. From a consideration of the fragmentation pattern for clusters of the type $\{((CH_3)_2NH)_n \cdot H_2O\}H^+$ it can be seen that there is a transition in the decomposition route at $n = 4$. This gives the proton solvation unit as $((CH_3)_2NH)_4H^+$ or $(CH_3)_2NH_2^+((CH_3)_2NH)_3$. Although this unit contains the same number of amine molecules as found previously for methylamine, the result is unexpected because there has been a reduction in the number of available hydrogen-bonding sites through the addition of a second alkyl group. However, like the alcohols,[40,41] it is quite possible that the dimethylamine molecules extend out from the proton in a chain. As before, the reaction path transition point is offset by one through the addition of a second water molecule to the cluster $\{((CH_3)_2NH)_5 \cdot H_2O\}H^+$. Unlike methylamine, however, this behavior does not extend to $m = 3$. Again the fragmentation pattern can be used to produce a picture of the immediate environment of the solvated proton, and for this example it is possible to show that the pattern in Table IIIb is consistent with the formation of a chain of five amine molecules containing the proton and terminated at either end with water molecules. Figure 3 shows a schematic diagram of such a structure. The persistent loss of amine molecules from the larger ion clusters indicates that in the outer solvation shells water is the preferred solvent.

The observed fragmentation pattern for the water–ethylamine ion clusters presented in Table IVa is identical with that found for the water–methylamine system. This is despite an obvious increase in the size of the alkyl group and a small increase in molecular polarizability. The fragmentation pattern for the water–diethylamine ion clusters presented in Table IVb is quite different from the examples discussed previously. The proton solvation unit appears to be smaller, and the addition of single water molecules offsets the transition in decomposition route by a factor of 1 at least up to $n = 9$, and it is not absolutely certain that the process stops there. The proton solvation unit, as determined from the fragmentation pattern for $\{((CH_3CH_2)_2NH)_n \cdot H_2O\}H^+$ clusters, is $((CH_3CH_2)_2NH)_3H^+$ or $(CH_3CH_2)_2NH_2^+((CH_3CH_2)_2NH)_2$. This follows the pattern observed for NH_3, CH_3NH_2, and $CH_3CH_2NH_2$ in that each positively charged hydrogen atom on the protonated species has an amine molecule bound to it. Beyond this structure it is difficult to rationalize the decomposition pattern in terms of a developing secondary solvation shell. The argument used previously relied on the observed offset terminating after the addition of only two or three water molecules. One possible explanation is that the continued addition of water molecules serves to spread the cluster in two dimensions. This would have the effect of reducing any steric interactions which might exist between neighboring alkyl groups on different amine molecules. We shall return to the discussion of this particular example later in the paper.

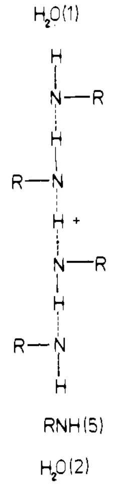

Figure 3. As for Figure 2, but for dimethylamine with R ≡ $(CH_3)_2$.

From the water–propylamine results shown in Table V it can be seen that the proton solvation unit is $(CH_3CH_2CH_2NH_2)_5H^+$ or $CH_3CH_2CH_2NH_3^+(CH_3CH_2CH_2NH_2)_4$. This is larger than those found for the other primary amines, and the increased size has the effect of making an extra hydrogen-bonding site available to the secondary solvation shell. By adopting the procedure used to explain the water–methylamine results it is possible to show that the pattern in Table V is consistent with the formation of a mixed secondary solvation shell composed of four water molecules and three propylamine molecules. This results in the structure $\{(CH_3CH_2CH_2NH_2)_8 \cdot (H_2O)_4\}H^+$ where all the available hydrogen-bonding sites on the proton solvation unit are occupied. Such a structure is shown schematically in Figure 4. Although a symmetric configuration has again been drawn, it must be appreciated that there is a large number of possible molecular permutations. From these results it would appear that the extra hydrogen-bonding site is occupied by an amine molecule and that it is located in a different type of site from those we have assumed are occupied by the other two amine molecules in the secondary solvation shell. The cluster $\{(CH_3CH_2CH_2NH_2)_8 \cdot (H_2O)_4\}H^+$ loses an amine molecule whereas the complete secondary solvation shells for the other primary amines both lose water molecules. However,

Table VII. Solvent Preference of the Hydrogen Ion in Water–Amine Systems

amine	proton solvation unit	secondary solvation shell	tertiary shell and beyond
NH_3	$NH_4^+(NH_3)_4$	H_2O	H_2O^b
CH_3NH_2	$CH_3NH_3^+(CH_3NH_2)_3$	mixed CH_3NH_2/H_2O	H_2O
$CH_3CH_2NH_2$	$CH_3CH_2NH_3^+(CH_3CH_2NH_2)_3$	mixed $CH_3CH_2NH_2/H_2O$	H_2O
$CH_3CH_2CH_2NH_2$	$CH_3CH_2CH_2NH_3^+(CH_3CH_2CH_2NH_2)_4$	mixed $CH_3CH_2CH_2NH_2/H_2O$	H_2O
$(CH_3)_2NH$	$(CH_3)_2NH_2^+(CH_3)_2NH)_3$	H_2O	H_2O
$(CH_3CH_2)_2NH$	$(CH_3CH_2)_2NH_2^+((CH_3CH_2)_2NH)_2$	cannot be resolved	H_2O^b
$(CH_3)_3N$	$(CH_3)_3NH^+((CH_3)_3N)_2{}^a$	not appropriate, see text	
$(CH_3CH_2)_3N$	$(CH_3CH_2)_3NH^+N(CH_2CH_3)_3$		
C_5H_5N	$C_5H_5NH^+(C_5H_5N)_2$		

[a] Possibly. [b] Most probably.

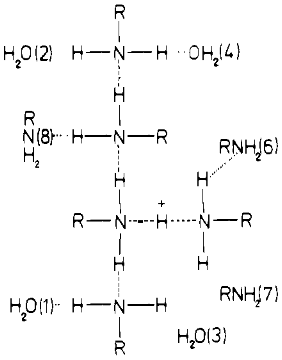

Figure 4. As for Figure 2, but for propylamine with R ≡ $CH_3CH_2CH_2$.

in view of the qualitative nature of these results and the possibility of some uncertainty in the assignment of metastable peaks from the decomposition of high-mass clusters, it would not be prudent to develop this line of reasoning too far.

So far only the results for the primary and secondary amines have been discussed. In terms of clustering, the distinction between these and the tertiary amines involves more than just a difference in the number of alkyl groups. Both the primary and secondary amines can contribute hydrogen-bonding sites to the ion cluster, and these serve to extend the network or chain. In contrast, when a pyridine or tertiary amine molecule forms a hydrogen bond it terminates the chain or network to which it is attached. From Tables IIIc, IVc, and VI it can be seen that the proton solvation units as determined from the fragmentation patterns are $((CH_3)_3N)_3H^+$, $((CH_3CH_2)_3N)_2H^+$, and $(C_5H_5N)_3H^+$, respectively. The stable pyridine ion cluster is smaller than that suggested by Holland and Castleman;[44] their results indicate that $(C_5H_5N)_4H^+$ is the stable unit. However, it will be shown below that the behavior of these ion clusters with respect to fragmentation is quite different from the other amines discussed previously and that metastable peak intensities may not be the most useful guide for determining the size of the proton solvation unit. With the formation of solvation units of the type suggested above, the resultant ion cluster offers no further sites for hydrogen bond formation. In particular, there are no sites available for the attachment of water molecules. However, the results in Tables IIIc, IVc, and VI show that the presence of one or more water molecules does influence the decomposition pattern of these ion clusters in a manner similar to that observed for the other amines. In a recent study of mixed ion clusters of water with ethers and ketones,[69] it was observed that the combination $X_{m+2}(H_2O)_mH^+$ (the notation is different from that used in ref 69) resulted in the formation of very stable ion clusters with quite characteristic fragmentation properties. Exactly the same behavior is observed in the case of the trialkylamines; ions with the combination $\{(A)_{n=m+2}\cdot(H_2O)_m\}H^+$ are the most intense in each of the respective mass spectra, and ions for which $n > m + 2$ are either not detected or have very low intensities. Also apart from the trimethylamine result at $n = 3$ and $m = 1$, ion clusters with the combination $n = m + 2$ decompose in a different manner to other configurations.

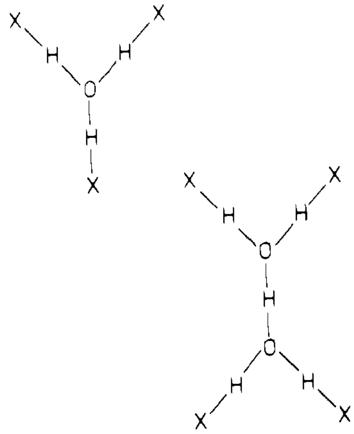

Figure 5. Proposed hydrogen-bonded structures for the $X_{m+2}(H_2O)_mH^+$ clusters; X = trimethylamine, triethylamine, or pyridine. Further examples can be found in ref 69.

Both the above observations are consistent with the water–ether results in particular.[69] The previous study also suggested that this pattern of behavior begins to break down when $n > 6$, and that is supported by the present results. At first sight this would not appear to account for the water–pyridine results because clusters with the combination $n = m+2$ fragment in exactly the same manner as those for which $n < m + 2$. Only the clusters with $n > m + 2$ behave differently. However, the ether/ketone results[69] revealed a correlation between fragmentation behavior and the dipole moment of X. It was observed that if the dipole moment of X was greater than that of water, then a metastable peak was observed for the loss of H_2O from the stable ion cluster structure $X_{m+2}(H_2O)_mH^+$. A metastable peak for loss of X was present if its dipole moment was less than that of water. From the dipole moment values given in Table I it can be seen that both the water–trialkylamine and water–pyridine fragmentation patterns correspond almost exactly to the type of behavior expected from stable cluster structures of the form $X_{m+2}(H_2O)_mH^+$. There is no evidence of a similar correlation with molecular polarizability. Some of the structures used to account for the ether/ketone results are given in Figure 5,[69] and it can be seen that for each of these configurations all the available hydrogen-bonding sites are occupied. The marked similarity between the present results and those reported for the water–ether and water–ketone systems[69] leads us to believe that the $\{(A)_{n=m+2}\cdot(H_2O)_m\}H^+$ clusters for pyridine and the trialkylamines have structures identical with those given in Figure 5.

The qualitative conclusions derived from the above results are summarized in Table VII. We shall now proceed to discuss some of the overall features of these and to comment on the implications they may have with regard to hydrogen ion solvation in binary liquid mixtures. The development of a relationship between fragmentation pattern and ion cluster structure relies on one quite major assumption. The possibility that a number of alternative configurations could exist for a given n and m combination has already been considered several times in this discussion. Our analysis of the experimental data requires that metastable peak

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(69) Stace, A. J.; Moore, C. *J. Phys. Chem.* **1982**, *86*, 3681.

formation results from the unimolecular decomposition of a single n and m configuration; only then is it possible to relate structure and fragmentation pattern. Thus, during their residence time in the ion source ($\simeq 10^{-6}$ s), it will be necessary for the ion clusters to rearrange and shed molecules in order to adopt the most stable structure appropriate for a given set of n and m values. Internal energy will for the most part dictate both the effectiveness of the rearrangement process and the ultimate size of an ion cluster when it is finally extracted from the source. Three observations lead us to believe that the assumption of a single ion cluster configuration is reasonable: (1) If the competitive shift criterion used to predict relative metastable peak intensities is applied to ions in the source, then a natural ordering within clusters will arise because they will use their internal energy to discard the most weakly bound molecules first. (2) Most ion clusters appear to give only one metastable peak. If there were several versions of a particular cluster, then more metastable peaks for loss of both H_2O and A from the same n and m values might be observed. (3) Where independent verification is possible the fragmentation pattern and subsequent interpretation does conform to what would be predicted for a single structure cluster.[64,65] What remains uncertain is the nature of that structure.

The structures presented in Figures 2–5 and Table VII represent those configurations where the molecules are bound to the proton by hydrogen bonds. However, the rather open nature of some of these structures means that small molecules, such as H_2O and CH_3NH_2, could quite easily occupy non-hydrogen-bonding interstitial sites close to the proton.[41] Because the occupants of such sites are going to be far more susceptible to displacement through thermal motion, it is perhaps more realistic to consider proton solvation as consisting of a "transient" and a "persistent" shell structure. The difference between the two being defined not only in terms of relative lifetimes but also in terms of the types of interactions responsible for their presence. The "transient" solvent structure will arise from a combination of thermal motion and potential interactions of the type c and d discussed above, while hydrogen bonding will be primarily responsible for the "persistent" structure. Obviously, the present experiment will only allow us to probe the latter.

From Table VIII it can be seen that the general features of the solvent structure in the primary and secondary amines are approximately the same. In small clusters the hydrogen ion is preferentially solvated by amine molecules; but as the solvent structure develops into the secondary and tertiary shells so the preference gradually changes in favor of water, The constitution of the shells is consistent with the view that initial preference of the proton for amine molecules arises from the formation of charge-enhanced hydrogen bonds between the cationic hydrogen atoms on the protonated amine and the other members of the proton solvation unit.[70] The polarizability of the alkyl group of the amine will make an important contribution to this type of bonding.[15] With the formation of the secondary solvation shells it becomes evident that the influence of the positive charge is starting to decline. Under these circumstances water molecules, which are capable of forming stronger hydrogen bonds in the absence of a positive charge, begin to preferentially occupy the vacant hydrogen-bonding sites. The formation of the tertiary solvation shell completes the replacement of amine by water as the preferred solvent. When features of the primary and secondary amine results are compared with those of the tertiary amines and pyridine, one major difference is very obvious. Whereas the solvation shells of the former all present what is essentially a hydrophilic exterior to the bulk solvent in the form of vacant hydrogen-bonding sites, the exteriors of the latter, as can be seen from Figure 5, consist of hydrocarbon groups which will display hydrophobic properties. In terms of ion solvation in two-component mixtures such behavior on the part of the tertiary amines could have important consequences. Selective ion sequestering as a mechanism for transporting water-soluble ions through a membrane requires preferential solvation of the ion within a shell of hydrocarbon-soluble molecules.[29] Any one of the structures proposed in Figure 5 for the tertiary amines or pyridine would satisfy that requirement. Also there are no obvious reasons why other simple ions, such as Na^+ or K^+, should not behave in exactly the same manner as H^+. Certainly in the case of H_2O and NH_3 these metal ions display a solvent preference.[43,44,67,68] In a binary solution, reactions driven by free energy differences could lead to the preferential solvation of an ion by the sequestering agent.[29]

There are a number of differences between the amines both in terms of the size and in terms of constitution of the various solvation shells. Whether or not any of these are responsible for differences in basicity remains to be seen. From our analysis of the data in Tables II, IIIa, and IVa it would appear that the presence of a proton in a mixed water–ammonia or water–primary amine solution could create short-range three-dimensional order within the liquid. With pyridine and the tertiary amines the ordering would be essentially two dimensional, and such structures, particularly those containing pyridine, will be susceptible to the formation of an extensive "transient" solvation shell. Of the secondary amines, dimethylamine behaves in a manner similar to that expected of the water–alcohol ion clusters. Both types of molecule provide just a single hydrogen-bonding site with the result that the "persistent" solvation unit adopts a chainlike structure. This is equivalent to short-range order in only one dimension. The earlier analysis of the water–diethylamine ion cluster fragmentation pattern led us to conclude that the observed behavior could not be attributed to structures associated with the development of regular solvation shells, cf. the water–dimethylamine system. In fact the pattern in Table IVb is not too dissimilar from that observed for the water–trialkylamine systems. One reason for this may be that steric interference prevents the ion clusters from adopting optimum structures similar to those suggested for dimethylamine, i.e., Figure 3. By choosing structures of the type suggested for the trialkylamines this interference may be reduced. Steric interference may also be one of the reasons why the proton solvation unit for diethylamine is smaller than that for dimethylamine. It is interesting to note that the proton solvation unit suggested for the alcohols was also of the form $(ROH)_3H^+$.[41,70,71] In general the solvation units proposed for ethylamine series conform to what would be expected from a progressive reduction in the number of available hydrogen-bonding sites in going from NH_4^+ to $(CH_3CH_2)_3NH^+$. Given the discussion above we would suggest that such behavior arises from a combination of both electronic and steric factors.

A qualitative correlation can be drawn between the basicity of an individual amine and the behavior exhibited in Table VII. Consider first the distinction between a weak and a strong base which has been deduced from other gas-phase studies.[24,25,38] In general, a strong base will be effective in delocalizing the charge of the proton internally. This will have the effect of reducing the ability of the protonated amine to form a network of charge-enhanced hydrogen bonds. In contrast, a weak base will retain most of the positive charge at the site of protonation. This assists the amine to form strong hydrogen bonds, which then become instrumental in delocalizing the positive charge through the solvent. This distinction also has some significance in the application of eq 1–3, particularly in the determination of r_i.[24,32] Thus, in terms of the present experiment it might be expected that the stronger bases will form smaller proton solvation units and that solvent preference will more rapidly change in favor of water, i.e., after the addition of only a few amine molecules. With regard to the proton solvation units, this conclusion is borne out by a comparison of dimethylamine with diethylamine and trimethylamine with triethylamine. Within each pair the latter mentioned amine is the stronger base. Similarly, propylamine is a slightly weaker base than either methylamine or ethylamine. If the water–alcohol cluster results are aso taken into consideration, then our experiments show that these very weak bases can have solvation units as large as $n = 13$.[40,41] The development of a similar correlation through an alkylamine series is confused by changes in the number

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(70) Hirao, K.; Sano, M.; Yamabe, S. *Chem. Phys. Lett.* **1982**, *87*, 181.

(71) Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 7939.

of available hydrogen-bonding sites. However, alkyl substitution, and in particular the step from NH_3 to primary amine, does appear to influence the constitution of the secondary solvation shell (see Table VII). The variation in the number of available hydrogen-bonding sites also appears to suppress any correlation which may exist between molecular polarizability and solvation unit size.[41] In the alcohols the number of sites always remains constant, which means that allowing for steric factors the structures of the solvation units are probably all quite similar. As a result the size of a unit could easily be sensitive to a variation in the contribution of the ion–induced dipole to the overall strength of each charge-enhanced hydrogen bond. Only for the primary amines is it evident that the molecule with the highest polarizability has the largest proton solvation unit. In the secondary and tertiary amines it may be more important to take into consideration the polarizabilities of individual alkyl groups.

Within the range of amines studied in this paper the largest difference in basicity occurs between the alkylamines and pyridine. The gas-phase basicity of the latter is approximately the same as that of propylamine, but the pK_a values differ by over 5 orders of magnitude.[24] Pyridine and its substituted forms have been the subject of numerous gas- and liquid-phase thermodynamic studies.[39,72–77] For the most part, however, these have concentrated on substituent effects and used the unsubstituted pyridine as a reference point. Our results show that pyridine certainly behaves differently from the trialkylamines, and the estimated size of the proton solvation unit ($(C_5H_5N)_3H^+$ in Table VII and $(C_5H_5N)_4H^+$ by Holland and Castleman[44]) would suggest that the positive charge is not delocalized within the ring system to any great extent. A clue to pyridine's weak basicity may come from a study of ion clusters of the type $C_5H_5NH^+(H_2O)_m$. Preliminary results[59] suggest that when m is large (>10) these clusters begin to lose pyridine. This would confirm the suggestion that the basicity of water clusters increases as a function of size[39] and that once large enough they may actually "deprotonate" the pyridinium ion.[76] Kebarle[34] has suggested that $CH_3CH_2OH_2^+(H_2O)_m$ clusters may behave in a similar fashion; but we have found no evidence in our experiments to support this view.[40]

Conclusion

In the present paper we have extended our study of hydrogen ion solvation in mixed clusters to include water–amine systems. Similar to the water–alcohol results[40,41] it is observed that the solvent preference of hydrogen ions changes as a function of cluster size. In its immediate environment the proton prefers amine molecules, but as the size of the cluster increases it is found that the long-range interaction of the proton with water molecules becomes stronger than that with additional amine molecules. The analysis of the water–alcohol results included a detailed discussion of proton mobility.[40,41] It was suggested that on the time scale of the experiment the distribution of proton positions would appear highly averaged and maximized at a configuration of lowest potential energy. Although it could not be confirmed from the experimental data, $(ROH)_3H^+$ was offered as one such configuration. From the present experimental results we have been able to positively identify a series of these configurations for a number of different amines; these we have labeled proton solvation units. Additional information from the ion cluster fragmentation patterns has allowed us to establish the presence of discrete secondary solvation shells in ammonia and the primary and secondary amines. A number of factors appear to contribute to the size, shape, and constitution of the solvation shells. The prime contribution in most of the amines is the number of available hydrogen-bonding sites. The fact that charge-enhanced hydrogen bonding appears to be responsible for the stability of the proton solvation unit would suggest that electrostatic interactions are also important. The gradual transition from charge-enhanced to normal hydrogen bonding has been identified as being responsible for the change in solvent preference from amine to water molecules. The results also indicate that steric interference could also influence the solvation process. In addition to the presence of a "persistent" solvent structure arising from hydrogen bonding, we have also recognized that there could exist an extensive "transient" solvent structure due to small molecules occupying non-hydrogen-bonding sites close to the proton.

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Registry No. NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3N$, 75-50-3; $CH_3CH_2NH_2$, 75-04-7; $(CH_3CH_2)_2NH$, 109-89-7; $(CH_3CH_2)_3N$, 121-44-8; $CH_3CH_2CH_2NH_2$, 107-10-8; C_5H_5N, 110-86-1; hydrogen ion, 12408-02-5; water, 7732-18-5.

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