ing. Optical excitation of RI^+ to RI^{*+} (11.22 ev for CH_3I^+, for example) permits charge transfer to and migration through 3MP (ionization potential $\sim$10.1 ev) followed by trapping on $(RI)_2$ to form $(RI)_2^+$. Such complexes have been observed for several alkyl iodides and bromides in the mass spectrometer.[20,21] For $(C_2H_5I)_2^+$ the ionization efficiency curve can be normalized to that for $C_2H_5I^+$ throughout, except for a small but well-defined maximum at 1.5 ev above onset and a second poorly defined maximum at 2.6 ev.[22] For $(c\text{-}C_5H_9I)_2^+$ a maximum occurs at 0.9 ev, and for $(n\text{-}C_5H_{11}I)_2^+$ maxima were found at 1.0 and 1.8 ev. The average values, since none is precise, are 1.1 ev for the first and 2.2 ev for the second. These maxima correspond to vertical transitions and should be compared with $(RI)_2^+$ optical band maxima which are 1.6 and 2.3 ev.

Evidence for $RI \cdot I$ complexes, observed under various other experimental conditions, have been reported. Ebert, et al.,[23] observed bands at 390 and 465 mμ following pulse radiolysis of cyclohexyl iodide. The first band is attributed to $C_6H_{11}I \cdot I$, the second to I_2^-. Timm[24] observed bands at 394 and 471 mμ following photolysis of C_2H_5I in isopentane–3-methylpentane

at $-196°$ and attributed the first to HI I and the second to $C_2H_5I \cdot I$. Thomas[25] observed an unresolved band with maxima at 312 and 352 mμ following pulse radiolysis of aqueous CH_3I and postulated $CH_3I \cdot I$.

The mechanisms by which energy is transferred from the major component to a minor component of a radiolytic system have been considered frequently. The alkyl iodide–alkane system serves as a model for illustrating the chemistry to be expected from one type of system as regards ionic processes. It is of interest that radical positive ions of relatively unstable alkyl iodides can survive charge recombination with I^-. It can be inferred, then, that alkane and alkene radical ions can also survive recombination with X^- when the electron affinity is $\sim$3 ev, or possibly less. Earlier indirect evidence had supported this interpretation,[26] based on dissipation of potential energy of the ion to its environment through electron affinity, polarization, and Coulombic energy.

The identification of charge-transfer complexes as products of ion recombination provides a useful new tool for radiation chemistry. To the best of our knowledge, the only identified products of charge recombination in radiation chemistry are those reported here and the excited species identified through recombination luminescence.[27]

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Competitive Solvation of the Hydrogen Ion by Water and Methanol Molecules Studied in the Gas Phase

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Abstract: Studies of the ions in irradiated water–methanol vapor mixtures show that the principal species are clusters, $(CH_3OH)_m(H_2O)_wH^+$. Methanol is taken up preferentially in clusters of small size. The preference for methanol decreases with size of the cluster. Water and methanol are taken up with equal preference for clusters with $m + w = 9$. Water is taken up preferentially in larger clusters. The results predict preferential solvation of the proton by water in macroclusters, *i.e.*, liquid water–methanol solutions. The preference for methanol does not show a distinct inner–outer shell behavior for clusters with $m + w \leq 6$. The data indicate that in a small cluster ($m + w = 3, 4$, or 5) the methanol molecules are equivalent among themselves, as are the water molecules. Thus the notation, $(CH_3OH)_{m-1}(H_2O)_w CH_3OH_2^+$ or $(CH_3OH)_m(H_2O)_{w-1}H_3O^+$, which indicates that the proton is more strongly bound to one particular molecule, would seem to be incorrect. Extrapolation of the data to clusters containing only the proton and one solvent molecule predict 11 kcal/mole for the difference between the proton affinity of methanol and water. This is close to estimates obtained by other means.

The interaction of ions with solvent molecules has been studied for many years in liquid solutions. More recently considerable advances in this field were made by applying the powerful techniques of nmr and esr. Starting a few years ago we have published work[1-4]

in which a new approach is used, namely, the study of ion–solvent interactions in the gas phase. This approach has the very special advantage of studying ion–solvent molecule complexes (ions surrounded by a cluster of solvent molecules) without the interference of the bulk of the solvent. The method is thus specially

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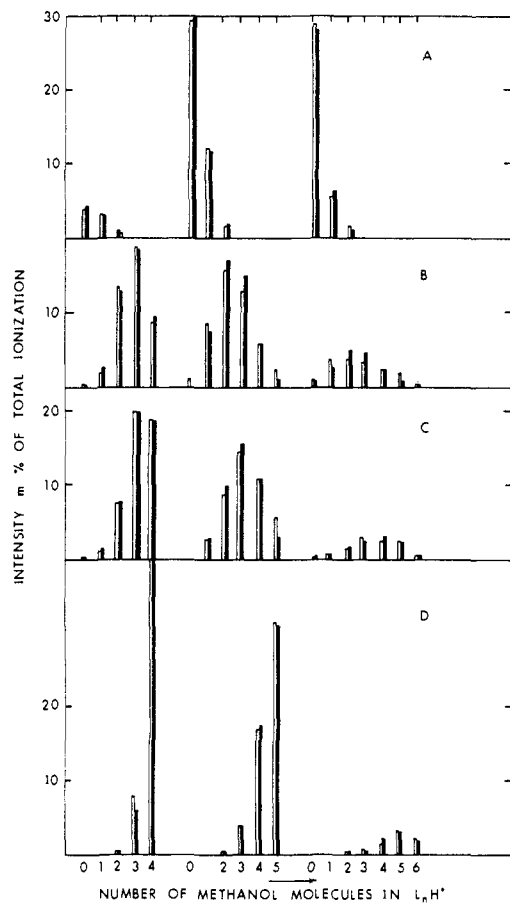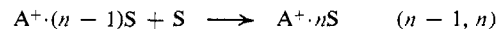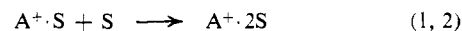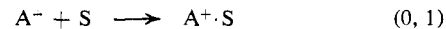
Figure 1. Ion intensities of clusters observed in water–methanol vapor mixtures at 5 torr total pressure and 50°. L in L_nH^+ stands for either a water or methanol molecule: (A) traces of methanol, (B) 2.3, (C) 5, and (D) 20 mole % methanol in vapor; □ observed values, ■ calculated values. The calculated values were obtained by fitting probability distributions to the experimental data (see text). Data show that methanol is taken up preferentially in clusters. Preferential take-up decreases with cluster size. Take-up of methanol shifts intensity distributions to lower ligand number n.

suited to provide information on the intimate interactions between the central ion and the solvent molecules in the incomplete or complete first and second solvation shells.

The gas-phase studies are based on mass spectrometric measurement of the relative concentrations of ionic species A^+S_n or B^-S_n, where A^+ and B^- are any positive and negative ion and S are solvent molecules. The measurement of the relative concentrations is obtained by bleeding a probe of the gas into an ion mass analysis system, i.e., a vacuum chamber attached to a mass spectrometer. In the vacuum chamber the gas is pumped out while the ions are captured by electric fields, accelerated and focused, and then mass analyzed by some conventional means (magnetic separation quadrupole filter, etc.). After mass analysis, the ion beam intensities are detected as electrical currents.

Several types of solvation studies can be undertaken if the relative concentrations of the ionic species are known. For example, enthalpies and entropies of individual solvent molecule addition steps can be obtained. The ion A^+ is produced in the gas phase by some form of ionizing radiation or thermal means. If the atmosphere surrounding the ion contains the vapor of a polar

molecule (solvent S), a number of clustering reactions will occur.

$$A^- + S \longrightarrow A^+ \cdot S \qquad (0, 1)$$

$$A^+ \cdot S + S \longrightarrow A^+ \cdot 2S \qquad (1, 2)$$

$$A^+ \cdot (n - 1)S + S \longrightarrow A^+ \cdot nS \qquad (n - 1, n)$$

At equilibrium the following relations will hold

$$\Delta F_{0,n} = \Delta F°_{0,1} + \Delta F°_{1,2} + \ldots + \Delta F°_{n-1,n} \qquad (I)$$

$$\Delta F°_{n-1,n} = -RT \ln \frac{P_{A^+ \cdot nS}}{P_{A^+ \cdot (n-1)S}P_S} = -RT \ln K_{n-1,n} \qquad (II)$$

where P_X is the partial pressure of X.

Thus knowledge of the equilibrium concentrations of the clustered species $A^+ \cdot nS$ obtained from experiments at different pressures of S will allow the determination of $K_{n-1,n}$ and $\Delta F_{n-1,n}$. Such measurements done at different temperatures will lead to the evaluation of $\Delta H_{n-1,n}$ and $\Delta S_{n-1,n}$. Studies of the systems $NH_4^+(NH_3)_n$[3] and $H^+(H_2O)_n$[1,5] based on the above outline have been published.

The present work is related to the above work but deals with the competitive solvation of one given ion, in this case the hydrogen ion, by two different solvents: methanol and water. The study is done at a single temperature. The partial pressures of methanol and water are varied and the resulting clusters $(CH_3OH)_m$-$(H_2O)_w H^+$ observed. The water–methanol system is a classical example of a mixed solvent and has received considerable attention in liquid solutions. Considering that the proton affinity of methanol is some 10–20 kcal higher than that of water[6] but that, on the other hand, the dielectric constant of water is considerably higher than that of methanol, one can ask the following questions. Is the proton preferentially solvated by methanol in a small cluster where $w + m$ is not larger than 10? Is the proton preferentially solvated by water in a macrocluster, i.e., liquid solution? If the surroundings of the proton in liquid solution are enriched in water, is then the proton nevertheless attached to one methanol molecule forming $CH_3OH_2^+$? We believe that the experiments described below provide some interesting information on these questions.

Experimental Section

Most of the results were obtained with the α-particle high-pressure mass spectrometer which has been described in previous publications.[2,7] Water and methanol vapor were mixed by admitting known pressures of the vapors separately into two interconnecting 2-l. glass bulbs. Opening the stopcock between the bulbs permitted mixing. The bulbs were connected by means of a short 15-mm glass tube to the ion source. All parts of the system were thermostated at 50°. This elevated temperature allowed fairly reliable dosing of the compounds in the mixture. Two series of runs at 2.5 and 5 torr total pressure were made. Mixtures of less than a few per cent of methanol (or water) could not be prepared reliably due to surface adsorption of the vapors.

A separate series of experiments was performed on a mass spectrometer utilizing a proton beam as ionizing medium.[5,8,9] The ion source of this instrument had the conventional Nier-type rectangular shape, a repeller, and an ion exit slit. The collimated 100-kev proton beam entered and exited the ion source through two 5×10^{-6} in. nickel foils. The distance between beam and ion

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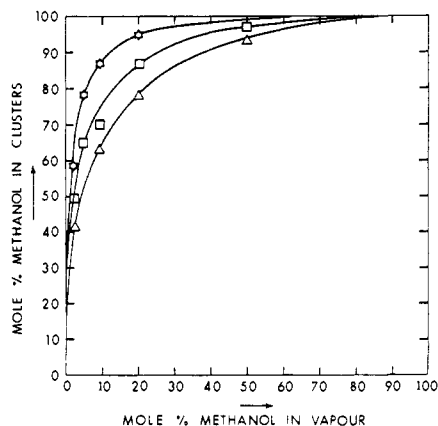(9) J. G. Collins, Ph.D. Thesis, University of Alberta, Edmonton.

Figure 2. Methanol content of clusters L_nH^+: ☆, L_4H^+; ◻, L_5H^+; △, L_6H^+.

Figure 3. Plot of preference factor γ for methanol $vs.$ mole % methanol in vapor: ◻, 2.5 torr; ◯, 5 torr total pressure.

Figure 4. Change of relative intensities of cluster groups L_nH^+ with methanol content. Take-up of methanol reduces n.

exit slit was 4 mm. The repeller field strength was 10 v/cm. The water–methanol mixtures were prepared by bleeding these gases through two separate inlet systems with separate leaks to the ion source. The ion source temperature was 30°. The partial pressure of the gases was established by direct measurement of the pressure in the ion source with a McLeod gauge. A total pressure of 0.36 torr was used.

Results and Discussion

The water–methanol experiments on the α-particle mass spectrometer consisted of two series of runs taken at a constant ion source temperature of 50° and two constant total pressures, 2.3 and 5 torr. Mass spectra were obtained of mixtures in which the mole fraction of methanol was increased stepwise, starting with pure water.

In pure water, at 5 torr, the abundant ionic species are $H^+(H_2O)_n$, the intense peaks occurring for $n = 3$ to 7 with a maximum at $n = 5$. The addition of less than 0.1% methanol[10] causes some of the clusters to accept one or even two methanol molecules (Figure 1) Further increase of the mole fraction of methanol brings about a continued rapid increase of the methanol content in the clusters as shown by the ion intensity distributions obtained with 2.3, 5, and 20% methanol in the vapor (Figure 1). (To simplify the notation we shall use W for a water molecule, M for methanol, and L for either water of methanol.) The average molecular methanol content of the different ions as a function of the mole per cent methanol in the vapor is shown in Figure 2. It is evident from Figures 1 and 2 that methanol is taken up preferentially in the ions. For example, from Figure 2 we see that for a vapor composition containing only 5 mole % methanol, the cluster groups L_4H^+, L_5H^+, and L_6H^+ contain an average of 80, 65, and 55% of methanol molecules. In order to express the preference for methanol more quantitatively we can define a preference factor γ_n which equals the ratio of methanol to water molecules in the cluster group L_nH^+ over the ratio of methanol to water molecules in the gas phase. Calling the fraction of methanol to total molecules (in L_nH^+) equal to μ_n and that of water ω_n, we can express γ_n by eq III, where P_W and P_M stand for the partial pressures

$$\gamma_n = \frac{\mu_n P_W}{\omega_n P_M} \quad (III)$$

(10) Accurate concentration of methanol could not be established due to adsorption phenomena; see Experimental Section.
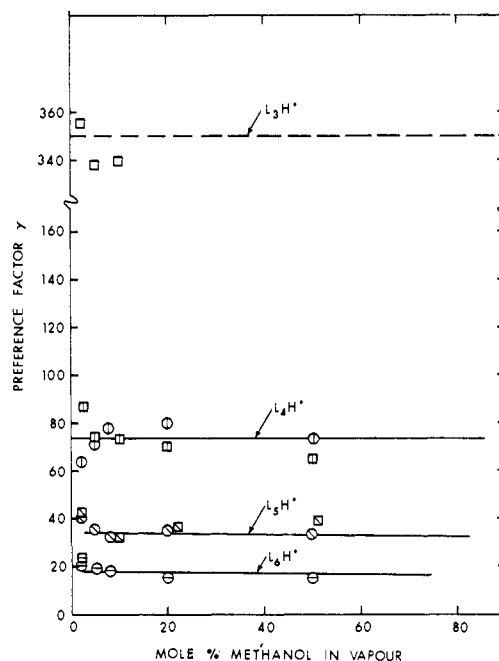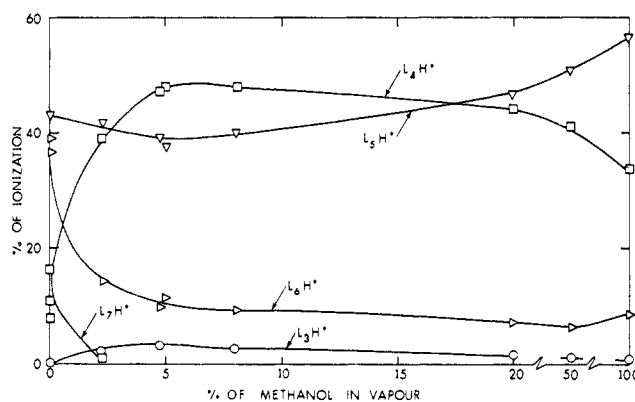
of water and methanol vapors. As an illustration we will apply (III) to the 5% methanol data quoted above, obtaining $\gamma_4 = 76$, $\gamma_5 = 35$, and $\gamma_6 = 23$. Figure 3 shows such calculated γ's for different methanol vapor concentrations. It can be seen that they are essentially constant, some change being indicated only at low methanol vapor concentrations. Figure 4 shows the relative intensities of the cluster groups L_nH^+ as a function of the methanol content of the vapor. We see that the preferential take-up of methanol in the clusters is accompanied by a reduction of the cluster size. Thus it is observed that the L_7H^+ cluster, which is 10% of the total cluster population in pure water, decreases to an insignificant percentage after the addition of 5% methanol in the vapor. In the same concentration range L_6H^+ is found to decrease from 39 to 10%. On the other hand, the smaller clusters L_4H^+ and L_3H^+ show corresponding increases. Considering the average uptake of methanol molecules in this range, one can conclude that when two or three molecules of methanol are taken up, three or four (respectively) molecules
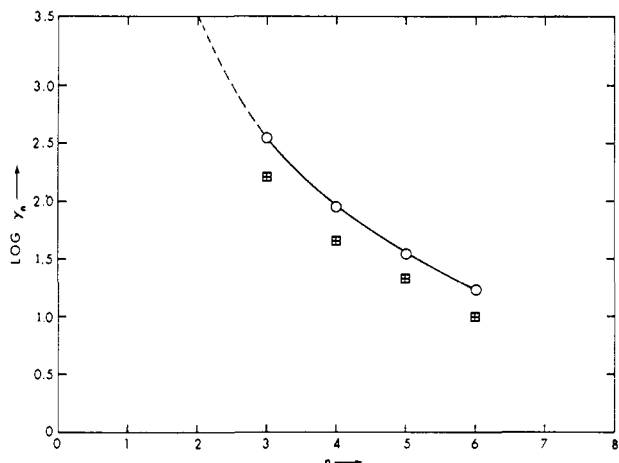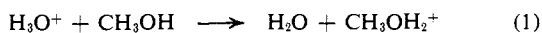
Figure 5. Plot of factor $\bar{\gamma}_n$ (which expresses preference for methanol in cluster group L_nH^+) vs. n. $\bar{\gamma}_n$ is average of γ_n given in Figure 3: ⊙, 5 and 2.5 torr total pressure results obtained on the α mass spectrometer; ⊞, data from proton beam mass spectrometer obtained at 0.23 torr total pressure. Extrapolation of data leads to preference for water above $n = 9$.

of water are displaced. Obviously, methanol, in small clusters, interacts more strongly with the proton but its larger molecular volume is not conducive to growth of the cluster.

The preferential take-up of methanol in clusters of small size is not surprising. It has been established by mass spectrometric measurements at low pressures[6] that reaction 1 proceeding in the gas phase is exothermic by some 10–20 kcal. The exothermicity of the reaction, which represents the difference between the proton affinities of methanol and water, is due to the positive inductive effect of the methyl group which stabilizes the $CH_3OH_2^+$ ion. The attachment of a second molecule of methanol to the $CH_3OH_2^+$ should again be favored over water since the electron-releasing property of the methyl group in the second methanol molecule will have a stabilizing effect in any reasonable structure of the M_2H^+ ion. One may expect that with further growth of the clusters the selective take-up of methanol will continue but generally with a diminishing preference. The decrease of preference should be due to the larger volume of the methanol molecule and the diminishing importance of the electron-releasing ability of the methyl group for methanol molecules located at increasing distances from the ionic charge. The electronic effect of the methyl group at larger distances can be assumed to affect the solvation interactions by increasing the polarizability of methanol (relative to water). The dipole moments of water and methanol are 1.85 and 1.69 D., while the polarizabilities are 1.48 and 3.23 A.[3] The potential energy of the ion–dipole interaction decreases with the square of the distance while that of the polarizability decreases with the fourth power. The considerably higher polarizability of methanol which contributes to its preferential take-up at close range is thus of little help at larger distances.

The expected decrease of preference for methanol with increasing cluster size is confirmed by the experimental results. The effect is shown particularly clearly in Figure 5 where log $\bar{\gamma}_n$ has been plotted vs. n. We see

$$H_3O^+ + CH_3OH \longrightarrow H_2O + CH_3OH_2^+ \qquad (1)$$

that $\bar{\gamma}_n$ becomes approximately equal to unity for $n = 9$. Thus water is taken up preferentially in clusters with n larger than 9. Also shown in Figure 5 are $\bar{\gamma}_n$ obtained with the proton beam mass spectrometer at 0.36 torr total pressure and 30° (see Experimental Section). The values for $\bar{\gamma}_n$ are somewhat lower but are generally similar and show the same trend as the 5-torr data of the α-particle spectrometer. We have done a more detailed comparison of the condition in the two instruments using pure water. The experiments[5,9] show that clustering equilibrium conditions are approached in the proton beam instrument only above 0.3-torr ion source pressure. Thus the differences between the data in Figure 5 must be due largely to less complete equilibrium in the proton instrument. All methanol–water data obtained on the proton instrument were, in general, similar to those obtained with the α-particle spectrometer and will therefore not be further discussed.

The observation that γ_n remains approximately constant with methanol content of the cluster group L_nH^+ (see Figure 3) is surprising. One would have expected the preference for methanol in a given L_nH^+ to be governed by the number of methanol molecules already present in L_nH^+. As mentioned before, the curves for L_4H^+, L_5H^+, and L_6H^+ (Figure 3) show some changes in the range 2.5–8% methanol in the vapor. The data indicate an increase of γ with decreasing methanol content of the cluster. Unfortunately, the experimental scatter in this range is so large that the trend is obscured. We conclude that a variation of γ_n with methanol content of the cluster L_nH^+ probably occurs but that this variation is considerably smaller than the change of $\bar{\gamma}_n$ with n which is displayed in Figure 5.

The approximate constancy of γ_n with methanol content of the cluster suggests that the relative concentration of the component ions $M_nM_{n-m}H^+$ of the cluster group L_nH^+ could be fitted by a probability distribution. For example, for the cluster L_3H^+, the relative intensities of $W_3H^+:W_2MH^+:WM_2H^+:M_3H^+$ predicted by probability are given by the terms of the binomial expression $(\omega + \mu)^3 = \omega^3 + 3\omega^2\mu + 3\omega\mu^2 + \mu^3 = 1$. The ion intensities indicated as "calculated" in Figure 2 were obtained by such a procedure. The ω and μ used were the average proportion of water and methanol molecules in the given cluster group L_nH^+ obtained from the experimental data. To facilitate comparison we then multiplied the individual terms of the binomial expansion by the total intensity of the given cluster group L_nH^+. As seen in Figure 1 the probability distributions give a relatively good fit.

The possibility of fitting approximate probability distributions to the experimental data allows conclusions to be made on two interesting questions. The first question is whether an inner and outer shell are formed with distinct selectivity for water and methanol. The second question concerns the nature of the central ion; i.e., are we to consider the central ion as H^+, $CH_3OH_2^+$, or H_3O^+? With regard to the first question, it is instructive to compare the present data with earlier results on the competitive solvation of NH_4^+ by NH_3 and H_2O molecules.[2] In that work cluster distributions of $L_nNH_4^+$ were observed (L now stands for water or ammonia molecules) which could be fitted by probability distributions treating all ligands as equivalent

only as long as n was equal to or less than 4. The γ_n obtained for $n \leq 4$ did not change much and showed a near 20-fold preference for ammonia. The ion intensities for clusters with $n > 4$ could not be fitted by treating all ligand molecules as equivalent. A good fit with probability distributions could be obtained only by dividing the ligands into two groups: one containing four molecules and the other $n - 4$. This treatment led to two γ's: one for the four molecules which were assigned to an inner shell in which the 20-fold preference for the NH_3 existed, and one for the remaining molecules which were assigned to an outer shell. The γ_n (outer shell) showed a 30- to 40-fold preference for water. The possibility, in the present work, of fitting the L_nH^+ with a single probability distribution up to $n = 6$ means that no inner and outer shell with distinct preference for methanol or water can be assigned to this system. Some understanding of the reasons for the differences between the two systems can be obtained by a consideration of the structures involved. The cluster $(NH_3)_4NH_4^+$ probably contains NH_4^+ as a central ion surrounded tetrahedrally by the four ammonia ligands, whose nitrogen atoms point toward the central charge. A model shows that this arrangement produces a compact structure. The preservation of a distinct inner ammonia shell on the addition of several additional molecules is thus not surprising. The protonated water–methanol system is considerably more complex. No compact structure of three, four, or five molecules can be conceived. This structural difference is probably responsible for the lack of a distinct inner–outer shell behavior of the preference for methanol. Our data extend only up to $n = 6$ and thus do not allow us to say whether beyond $n = 6$ an outer shell develops with a discontinuous jump in the decrease of the preference for methanol. In any case, extrapolation of our data to higher n predicts that in macroclusters or liquid solutions the ion will be preferentially solvated by water. This result is in agreement with predictions of the Debye[11] equation (based on a structureless liquid model) which for water–methanol mixtures predicts that the vicnity of small cations will be enriched in water. Experimental determinations of the selective solvation of the Cr^{3+} ion in water–methanol solutions by King[12] and co-workers show that this ion is selectively solvated by water.

We can turn now to the question whether in a small cluster containing both water and methanol the proton interacts much more strongly with one molecule than with the others. Considering the higher proton affinity of methanol this one molecule should be methanol. With our data we can examine whether the intensity distribution of the members of a cluster L_nH^+ can be fitted by probability distributions, treating all methanol molecules as identical, or whether a better fit of the experimental data is obtained by assuming one methanol molecule to be tightly bound to the proton and thus part of the central ion, i.e., is the cluster $M_mW_{n-m}H^+$ more correctly described by the formula $M_{m-1}W_{n-m}$-

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(12) J. C. Jayne and E. L. King, J. Am. Chem. Soc., 86, 3989 (1964).

$CH_3OH_2^+$. The data obtained with 2.5% and higher methanol concentration in the vapor are not sensitive to the choice of the central ion since in these spectra the clusters contain only very small (i.e., possibly based on background peaks) intensities of pure water clusters. It can be shown that these spectra can be fitted almost equally well by distributions in which one assumes the ion to be $M_{m-1}W_{n-m}CH_3OH_2^+$. The distributions for this ion are obtained by the binomial expansion of $(\mu' + \omega')^{n-1}$, μ' and ω' being the fractions of methanol and water ligands (obtained from the experimental intensities) of the cluster group by omitting the proton carrying methanol molecule from the count. A good discrimination between the fits based on $CH_3OH_2^+$ or H^+ can be obtained only from experiments where the intensities of the pure water and methanol containing clusters are of comparable magnitude. This is the case for the data obtained with traces of methanol[13] (top spectrum, Figure 1). The calculated fit shown in this spectrum was obtained on the basis of treating all methanol molecules as equivalent among themselves and all water molecules as equivalent among themselves, i.e., formula $M_mW_{n-m}H^+$. No fit of the data can be obtained by treating one of the methanol molecules as part of a central ion $CH_3OH_2^+$. The result that the two molecules of methanol in a cluster like $M_2W_2H^+$ are equivalent and can be replaced with equal ease by water must mean that the two methanol molecules are equally strongly bonded to the cluster and thus probably equally strongly bonded to the proton.

Accepting the central assumption of this work, namely, that the relative ion intensities represent near equilibrium relative concentrations of the clusters in the ion source, one can obtain various thermodynamic data. Thus, considering any two ions one can obtain the difference between their energies of formation from their intensity ratio and the known pressures of water and methanol. A particularly simple and interesting case is represented by the exchange reaction 2. The

$$W_nH^+ + nM \longrightarrow M_nH^- + nW \tag{2}$$

free-energy change of this reaction is given by eq IV, where I_2 and I_1 stand for the ion intensities of M_nH^+

$$\Delta F_n^\circ = -RT \ln K_n = -RT \ln \frac{I_2P_W}{I_1P_M} \tag{IV}$$

and W_nH^+. Assuming that the probability distributions represent the data well, on substituting for I_2/I_1 one obtains

$$\Delta F_n^\circ = -RT \ln \gamma_n^n \tag{V}$$

For the clusters $n = 4$–7, substitution of the γ's from Figure 5 leads to the values $-\Delta F_4 = 12.9$, $-\Delta F_5 = 11.5$, $-\Delta F_4 = 11.6$, $-\Delta F_3 = 11.4$ kcal/mole. These changes of ΔF_n° should be close to the enthalpy changes ΔH_n° since only a small change of entropy is expected for reaction 2. Noticing that ΔF_n remains approximately constant, we can extrapolate $\Delta F_1^\circ \approx \Delta H_1 \approx -11$ kcal/mole. The enthalpy change ΔH_1° corresponds to the difference between the proton affinities of water and methanol. Ion–molecule reaction data obtained at low pressure predict a ΔH_1 of around -14 kcal.[6]