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Hydration of Alkylammonium Ions in the Gas Phase

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Electrospray ionization−high-pressure mass spectrometry was used to determine the enthalpy, entropy, and Gibbs free energy for the equilibrium gas-phase ion−molecule association reactions of $C_mH_{2m+1}NH_3^+$ (m = 1−8), $(CH_3)_2NH_2^+$, and $(CH_3)_3NH^+$ with one to three water ligands. A subset of these ions has been studied previously, and the thermochemical properties determined in this investigation compare favorably with the previously published results, providing validation of our experimental technique and method. In addition, the present measurements show that the addition of a water ligand to the monohydrated alkylammonium ion results in an increased stabilization in its structure and binding.

Introduction

Biochemical reactions depend on their fundamental interactions with water. Knowledge of the energetics of such solute−water interactions, although extensive, is limited at the basic levels of understanding, such as the interactions involving small numbers of water molecules.[1,2] Studies of sequential equilibrium gas-phase ion−molecule reactions using water as a neutral ligand (see eq 1) span a period of 30 years,[3−8] and it is generally accepted that the sum of the free energies of adding the first few water molecules to an ion is sufficient to characterize the relative differences in bulk hydration energies between similar ions.[4,9]

$$\begin{aligned} M^+ + H_2O &\rightleftharpoons M^+H_2O \\ M^+H_2O + H_2O &\rightleftharpoons M^+(H_2O)_2 \\ M^+(H_2O)_2 + H_2O &\rightleftharpoons M^+(H_2O)_3 \\ M^+(H_2O)_{n-1} + H_2O &\rightleftharpoons M^+(H_2O)_n \qquad (1) \end{aligned}$$

Recently, the use of electrospray ionization has allowed for the extension of such thermodynamic studies to a wider variety of organic and inorganic ions that had not previously been accessible.[10−14] Measurement of equilibrium constants at a range of temperatures for reactions described by eq 1 leads to a determination of the standard free energies, $G^\circ_{n-1,n}$; enthalpies, $H^\circ_{n-1,n}$; and entropies, $S^\circ_{n-1,n}$, of hydration of an ion in each sequential reaction.

In this study, we have determined the hydration energetics of a series of *n*-alkylammonium ions, $C_mH_{2m+1}NH_3^+$ (m = 1−8), as well as the companion di- and trimethylammonium ions, under conditions resulting in the addition of one to three waters of hydration. Initially, the alkylammonium ions were chosen for study to compare our results with previously published work. As this model system was explored in some detail, we found a number of interesting aspects of the energetics that extend the understanding of the structure of water in gas-phase ionic systems.

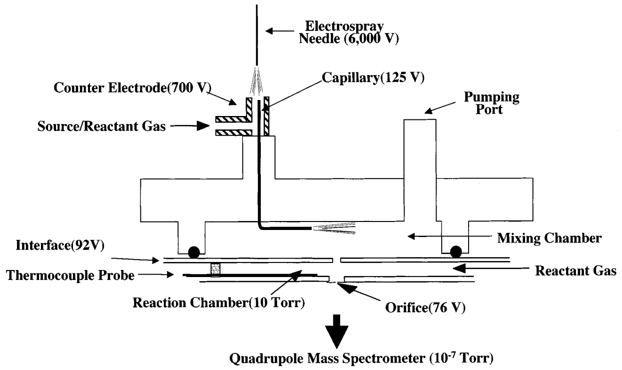

Figure 1. High-pressure electrospray ion source.

Experimental Section

Apparatus. The experimental apparatus is a modification of the standard PE-Sciex API-1 single-quadrupole mass spectrometer having a factory-built source housing heater(Thornhill, Ontario, Canada) and using an electrospray ionization (ESI) source. Modifications of the ion source were reproduced from designs used successfully by Kebarle and co-workers,[14] and the resulting source configuration is shown in Figure 1. Briefly, the standard electrospray needle was centered about 1 cm from the inlet of the sampling capillary, CAP. Cations were formed by pumping 0.1% alkylamine solutions prepared in doubly distilled deionized water through the electrospray needle at 5 μL/min using a Harvard Apparatus (Cambridge, MA) syringe pump, with the electrospray needle operated at +6000 V.

A portion of the ion plume was drawn into the pressure-reducing capillary, CAP, and transmitted into the mixing chamber, MC. The MC was formed by mounting the stainless steel plate onto the standard interface plate, IN, but it was kept

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electrically insulated. The CAP was electrically connected to the MC plate, and the CAP exit aperture was parallel to the MC plate surface at a distance of approximately 4.5 mm. The CAP consisted of a 10-cm length of 0.02-in-i.d. × $^1/_{16}$-in-o.d. stainless steel capillary having a 90° bend approximately 14 mm from the exit aperture. The capillary was fixed into the MC plate using two arms of a SwageLok tee fitting with low-vapor-pressure epoxy. An electrically isolated $^1/_4$-in. stainless steel tube mounted coaxially to the CAP on the atmospheric-pressure side served as a counter electrode (CE) for the ESI and directed the countercurrent flow of source gas (SG), vide infra. The CAP terminates approximately 7.5 mm from the edge of the IN's 3-mm-diameter aperture. The reaction chamber, RC, was formed by the space between IN and the orifice plate, OR. The OR is electrically isolated from IN, as in the standard analytical configuration of the API source. The detection orifice connecting RC with the high-vacuum side of the instrument was a 100-μm-diameter aperture centered in a 50-μm-thick Ni foil. The distance between the MC and IN plates was 0.88 cm, and that between the IN and OR plates was 0.58 cm.

Ions enter the MC principally due to the reduced pressure from atmospheric pressure to the MC−RC regions. A pressure of 10 Torr was established in the MC−RC region by pumping on the approximately 1-cm-i.d. foreline connected to the back of the MC plate. A convectron-type thermocouple gauge was used to measure the pressure downstream from the pumping port; the pressure was assumed to be constant throughout the MC−RC region. Independent measurement of gas flow through CAP under typical operating conditions, 10 Torr in MC−RC and $\sim 6 \times 10^{-7}$ Torr in the quadrupole mass filter region, showed a flow rate of 760 L·Torr/min, a value comparable to the 518 L·Torr/min used by Klassen et al.[14] The flow rate through the mass spectrometer sampling orifice (OR) was approximately equal to 1.1 L·Torr/min using the Poiseuille equation to estimate the flow rate through the detection orifice.

Whereas the ideal equilibrium source would have no electric fields within the reaction regions, the fields within the reaction and detection regions of our apparatus were set to maximize ion intensities while minimizing the possibility of perturbing thermalized water cluster ion distributions. The electric field strengths used in this work were 3.9 V/cm·Torr in the MC and 2.7 V/cm·Torr in the RC. The possibility of mass discrimination in ion cluster ratios might still exist. Such discrimination errors would be most likely in this study for the ratio of the lowest-molecular-weight ionic species [$CH_3NH_3^+$] and its first hydration. Hovey and Likholyot[15] showed that the actual ion intensities need to be weighted by the square root of ion clusters' mass. This correction applied to this ratio would amount to a $\Delta G^\circ_{298\,K}$ of 0.2 kcal/mol, well within our experimental uncertainty.

Doubly distilled deionized water was delivered at flow rates of 0−15 μL/min from a second syringe pump (Harvard Apparatus model 22) to one arm of a heated Swagelok tee fitting upstream of the standard API-1 curtain gas flow meter. High-purity nitrogen gas was supplied to another arm of this fitting from a Whatman nitrogen generator (model 75-72). It was assumed that complete vaporization of the water within the tee occurred with no subsequent condensation in the lines leading to the source; condensation was not visually detected in the PFE tubing. Water concentrations were monitored continuously using a calibrated relative humidity probe (model RH 30-2, Omega Engineering) just upstream from the flow meter used to set the flow rate of the SG.

Measured concentrations of water vapor in nitrogen gas were introduced into the source through the same system normally used for curtain gas introduction in the API-1 instrument. The reagent gas, RG, was delivered at a total flow rate of 2.3 L·atm/min as follows. Reagent gas flow was split to purge the ESI plume (SG) at the entrance of the CAP at 2 L·atm/min, using the counter electrode assembly in which the CAP is mounted. Thus, the curtain gas was delivered at 0.3 L·atm/min to the reaction and mixing chambers. Water partial pressures of the RG were in the range of 0−100 mTorr at 10 Torr operating pressure in the mixing and reaction regions. The possibility of a gradient in water concentration between the RC, where the RG is admitted, and the MC, where ions are admitted and bulk pumping occurs, must be considered. Flow-dependent gradients are likely to be small in a system such as this source for two reasons. First, the connection between the RC and the MC is a relatively short tube of large cross section, and second, the gas flowing into the MC from the CAP has a composition very similar to the RG because of the use of the countercurrent flow (SG) at the entrance of the CAP. Kebarle and co-workers addressed the issue of neutral fractionation and found no effect on the observed ion ratios.[14]

Reaction temperatures were monitored directly with a thermocouple placed on the OR. Temperatures above ambient were attained using the built-in API-1 external source heater, a solid wire resistive heating element clamped to the exterior of the source housing. Subambient temperatures were realized by cooling the source housing with a liquid-nitrogen-cooled stream of "zero-grade" air gas flowing through the coils of $^1/_8$-in.-o.d. copper tubing wrapped around the source housing in a blanket of glass wool.

Materials. Gases, both nitrogen and zero-grade air, for these experiments were obtained from in-line purification systems. A Whatman (Haverhill, MA) model 76-803 zero-grade air generator was used to remove hydrocarbons and water vapor from laboratory high-pressure air lines. A Whatman (Haverhill, MA) model 75-72 nitrogen generator was used to produce 0.995 fractional purity nitrogen, free of hydrocarbons, oxygen, and water, using the same high-pressure laboratory air lines. Doubly distilled deionized water was obtained using a laboratory-scale water purifier manufactured by HydroServices (Research Triangle Park, NC) from house-distilled water. Reagent-grade alkylamine compounds were obtained from Sigma-Aldrich (St. Louis, MO).

Results and Discussion

Equilibrium Source Characteristics. A plot of the ion ratio of di- and monohydrated n-$CH_3CH_2NH_3^+$ over a range of electric fields in the RC is shown in Figure 2. The electric fields chosen for this work represent a compromise to obtain reliable levels of ion intensity for equilibrium studies. Constant ion ratios as a function of electric field strength seen in Figure 2 demonstrate the validity of the assumption that no perturbations in the ion ratios by electric fields occur within the reaction region. Increasing the electric field strength in the mixing chamber was found to have a negligible effect (data not shown). The values of electric field strength used in the present studies are comparable to and somewhat lower than values that have been used previously by Klassen et al.,[14] who operated under conditions of $E/p \approx 6.2$ V/cm·Torr in the MC and 2 V/cm·Torr in the RC region. Castleman and co-workers[16] operated their reaction cell of the equilibrium source with $E/p < 15$ V/cm·Torr and obtained good agreement with previous measurements made using the flowing afterglow technique. In another high-

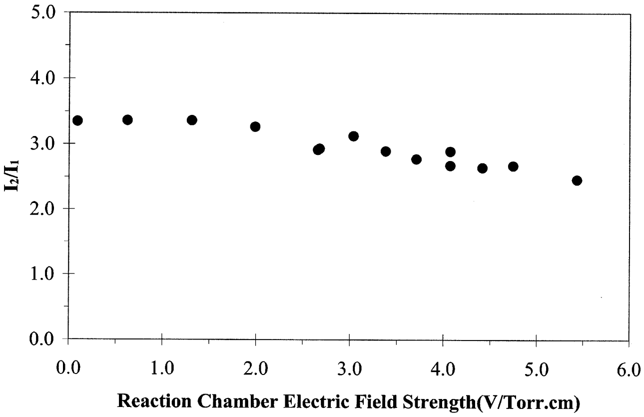

Figure 2. Variation of the ion intensity ratio n-$C_2H_5NH_3^+(H_2O)_2$ (I_2)/ n-$C_2H_5NH_3^+(H_2O)_1$ (I_1) with reaction electric field strength expressed in units of V/Torr·cm at $T = 291$ K and $P = 10$ Torr.

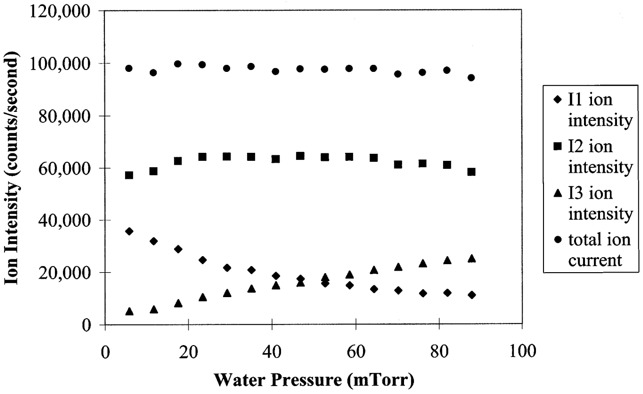

Figure 3. Ion intensity of n-$C_2H_5NH_3^+(H_2O)_{1,2,3}$ versus water pressure (mTorr) at 291 K and 10 Torr. [$I_1 = n$-$C_2H_5NH_3^+(H_2O)_1$, $I_2 = n$-$C_2H_5NH_3^+(H_2O)_2$, $I_3 = n$-$C_2H_5NH_3^+(H_2O)_3$].

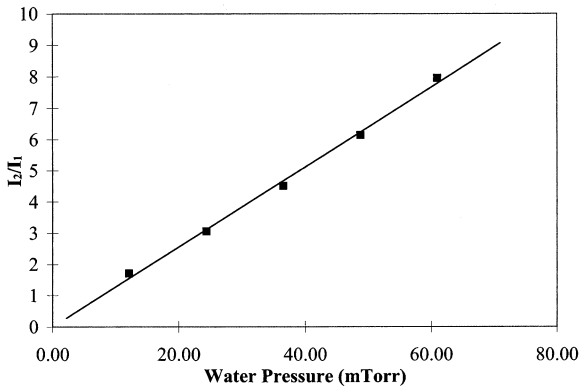

Figure 4. Ion intensity ratio n-$C_2H_5NH_3^+(H_2O)_2$ (I_2)/ n-$C_2H_5NH_3^+(H_2O)_1$ (I_1) as a function of water pressure (mTorr) and at 287 K. The slope of the straight line correspond to the equilibrium constant $K_{1,2}$. A trace amount of water vapor is present in the reaction chamber when no water vapor is added to the reagent gas because the alkylamines were prepared in water and the electrospray ionization process was done at atmospheric pressure.

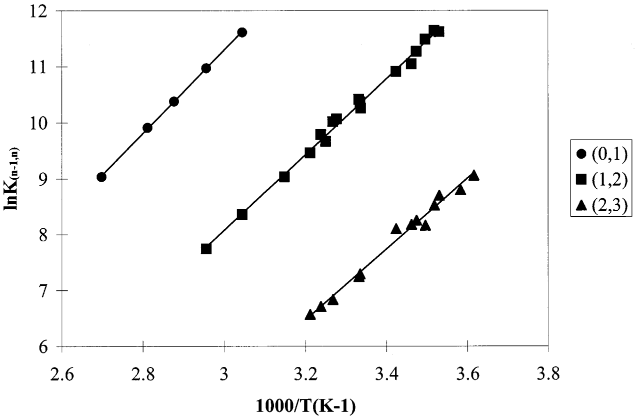

Figure 5. van't Hoff plots (natural logarithm of the equilibrium constant versus the reciprocal absolute temperature) of the (0, 1) ●, (1, 2) ■, and (2, 3) ▲ hydrations of n-$C_2H_5NH_3^+$.

pressure mass spectrometry study by Castleman and co-workers, measured equilibrium constants were found to remain unperturbed for values of $E/p < 9$ V/cm·Torr.[17] Ion intensities for n-$C_2H_5NH_3^+(H_2O)_n$ versus H_2O pressure are shown in Figure 3. The total ion intensity remains constant, demonstrating that no significant ion mass discrimination is occurring in the sampling process.

A plot of ion ratio vs water concentration for a pair of ion species present in the n-$C_2H_5NH_3^+$ system is shown in Figure 4 with a line fitted by a linear regression. The slope of the regression lines is the equilibrium constant of the reaction and the experimentally determined intercepts was found to be 0 within acceptable limits. Using equilibrium constants determined at several different temperatures over the range of 0−120 °C, van't Hoff plots were constructed for each alkylammonium ion−water system. An example of a typical van't Hoff plot is shown in Figure 5 for the n-$C_2H_5NH_3^+$ system. After fitting linear regressions to the data, values of the slope and intercept of these plots were used to calculate, respectively, the enthalpy and entropy changes for the reactions, along with 95% confidence for these parameters. The values of enthalpy and entropy determined from this treatment are summarized in Table 1 for the standard state of 1 atm. Values in Table 1 were used to calculate $\Delta G^\circ_{298\,\mathrm{K}}$ for each water−ammonium ion system assuming a temperature invariance in enthapy.[18]

The values given in Table 1 cover additions of from one to three waters for all of the n-alkylammonium ions between C_1 and C_8 as well as two additional methylammonium ions, $(CH_3)_2NH_2^+$ and $(CH_3)_3NH^+$. Approximately half of these 30 ammonium ion−water cluster combinations have been determined previously. With the exception of the first uptake of water to the hexylammonium ion and the second and third uptakes of water to the octylammonium ion, the first to the third uptakes of water were fully studied for the methyl-, dimethyl-, trimethyl-, ethyl-, and propylammonium systems. In general, there is quite reasonable agreement between the values determined in this work and those determined previously.[6,7,12−14,19−21]

As seen in Table 1, entropy changes are fairly constant over all alkylammonium ions for each water addition. This is reasonable because the entropy change for water addition is dominated by the loss of three translational degrees of freedom as can be demonstrated from fundamental considerations of statistical thermodynamics.[22] However, we observe that the average differences between the entropy changes for (0,1) to (1,2) (−26.0 ± 1.2 and −27.8 ± 1.4 cal/K·mol, $p = 0.004$) are statistically different. That is, there is a significant decrease in the average entropy change for the addition of the second water to the cluster. Kebarle and co-workers suggested that $\Delta\Delta S^\circ$ values can be evaluated on the basis of symmetry number changes of an equilibrium reactions.[12] On the other hand, this small but significant decrease in $\Delta\Delta S^\circ$ might arise from entropy changes in internal modes of the cluster ion. We speculate that this change is associated with the losses of vibrational degrees of freedom arising from the formation of an internal hydrogen bond. In a previous study, Meotner and Deakyne observed a

TABLE 1: Hydration Energies of Alkylammonium Ion Reactions of $M^+(H_2O)_{n-1} \rightarrow M^+(H_2O)_n$

ammonium ion	$(n - 1, n)$	$-\Delta H°$ (kcal/mol)	$-\Delta S°$ (cal/K·mol)	$-\Delta G°_{298\,K}$ (kcal/mol)	ref
$CH_3NH_3^+$	(0, 1)	14.9 ± 1.1	19.9 ± 3.1	9.0 ± 2.0	
		16.8 ± 0.5	21.8 ± 1.0	10.3 ± 0.7	7
		18.8 ± 0.3	26.3 ± 0.7	11.0 ± 0.4	6
				10.7	19
	(1, 2)	13.1 ± 0.6	21.5 ± 1.9	6.7 ± 1.2	
		14.6 ± 0.5	24.2 ± 1.0	7.4 ± 0.7	7
		14.6 ± 0.3	26.7 ± 0.7	6.7 ± 0.3	6
				7.5	19
	(2, 3)	12.2 ± 0.6	24.5 ± 1.9	4.9 ± 1.2	
		12.3 ± 0.5	24.1 ± 1.0	5.1 ± 0.7	7
		12.4 ± 0.8	26.4 ± 2.3	4.5 ± 1.0	6
				5.2	19
$(CH_3)_2NH_2^+$	(0, 1)	14.4 ± 0.4	22.1 ± 1.3	7.8 ± 0.8	
		15.0 ± 0.5	22.9 ± 1.0	8.2 ± 0.7	7
				9.1	19
	(1, 2)	13.8 ± 0.7	26.8 ± 2.3	5.8 ± 1.4	
		13.5 ± 0.5	24.7 ± 1.0	6.1 ± 0.7	7
				6.2	19
	(2, 3)	11.6 ± 0.8	26.2 ± 2.9	3.8 ± 1.8	
		11.3 ± 0.5	24.4 ± 1.0	4.0 ± 0.7	7
				4.2	19
$(CH_3)_3NH^+$	(0, 1)	14.9 ± 1.0	26.8 ± 3.2	6.9 ± 2.0	
		14.5 ± 0.5	24.1 ± 1.0	7.3 ± 0.7	7
		14.5	24.1	7.3	20
		14.5	24.4	7.2	21
				7.6	19
	(1, 2)	12.9 ± 0.9	29.7 ± 2.9	4.0 ± 1.8	
		11.4 ± 0.5	24.8 ± 1.0	4.0 ± 0.7	7
				4.3	19
	(2, 3)	10.0 ± 0.5	24.9 ± 1.0	2.6 ± 0.7	7
				3.4	19
n-$C_2H_5NH_3^+$	(0, 1)	14.2 ± 0.2	19.5 ± 0.4	8.3 ± 0.3	
		17.5 ± 0.5	25.9 ± 1.0	9.8 ± 0.7	7
		17.5 ± 0.4	25.9 ± 0.9	9.8 ± 0.5	6
	(1, 2)	12.7 ± 0.2	21.6 ± 0.8	6.3 ± 0.5	
		14.7 ± 0.5	29.7 ± 1.0	5.8 ± 0.7	7
		14.7 ± 0.2	29.7 ± 0.7	5.8 ± 0.3	6
	(2, 3)	11.8 ± 0.4	24.7 ± 1.5	4.5 ± 0.9	
		13.2 ± 0.5	30.8 ± 1.0	4.0 ± 0.7	7
		13.2 ± 1.2	30.8 ± 3.6	4.0 ± 1.6	6
n-$C_3H_7NH_3^+$	(0, 1)	15.3 ± 0.3	24.0 ± 1.0	8.2 ± 0.7	
		15.1 ± 0.5	21.5 ± 1.0	8.7 ± 0.7	7
		15.6	22.8	8.8	12
	(1, 2)	13.8 ± 0.5	26.2 ± 1.8	6.0 ± 1.1	
		11.6 ± 0.5	21.3 ± 1.0	5.3 ± 0.7	7
				6.7 (290 K)	13
				6.4 (293 K)	14
	(2, 3)	10.7 ± 0.6	21.2 ± 2.0	4.3 ± 1.2	
		10.3 ± 0.5	23.1 ± 1.0	3.4 ± 0.7	7
				4.8 (290 K)	13
				4.6 (293 K)	14
n-$C_4H_9NH_3^+$	(0, 1)	16.0 ± 0.5	26.4 ± 1.5	8.1 ± 0.9	
	(1, 2)	13.6 ± 0.3	26.0 ± 1.1	5.8 ± 0.7	
	(2, 3)	11.7 ± 0.4	24.9 ± 1.5	4.2 ± 0.9	
n-$C_5H_{11}NH_3^+$	(0, 1)	14.8 ± 0.2	23.2 ± 0.7	7.9 ± 0.4	
	(1, 2)	13.6 ± 0.4	26.0 ± 1.4	5.8 ± 0.9	
	(2, 3)	10.8 ± 1.0	22.3 ± 3.6	4.2 ± 2.2	
n-$C_6H_{13}NH_3^+$	(0, 1)	15.1 ± 0.4	24.2 ± 1.0	7.9 ± 0.7	
		15.2	22.8	8.4	12
	(1, 2)	13.5 ± 0.5	25.8 ± 1.5	5.8 ± 0.9	
	(2, 3)	10.4 ± 0.7	20.9 ± 2.5	4.2 ± 1.6	
n-$C_7H_{15}NH_3^+$	(0, 1)	15.2 ± 0.3	24.7 ± 0.9	7.9 ± 0.5	
	(1, 2)	13.1 ± 0.2	24.7 ± 0.7	5.7 ± 0.4	
	(2, 3)	11.6 ± 0.6	25.2 ± 2.2	4.1 ± 1.4	
n-$C_8H_{17}NH_3^+$	(0, 1)	15.7 ± 0.4	26.0 ± 1.0	7.9 ± 0.7	
				8.5 (293 K)	14
	(1, 2)	13.9 ± 0.3	27.3 ± 1.0	5.8 ± 0.6	
				6.1 (293 K)	13
	(2, 3)	11.7 ± 0.6	25.4 ± 2.2	4.1 ± 1.3	
				5.0 (293 K)	13

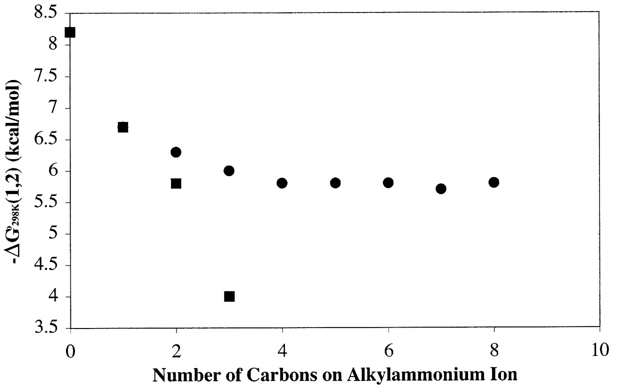

Figure 6. $\Delta G°_{298\,K}(1,2)$ vs carbon length of n-alkylammonium ions (●) and number of methyl groups attached to the ammonium ion (■). $\Delta G°_{298\,K}(1,2)$ for the ammonium ion is taken from ref 5.

similar trend, where the second water in a dihydrate of $(CH_3)_4N^+$ was proposed to bind to the first water molecule by forming a strong hydrogen bond instead of binding to the ion.[23]

The contribution arising from the increasing alkyl chain length is shown in Figure 6 for the case of the addition of the second water to each of the monohydrated alkylammonium ions. A similar trend in $\Delta G°_{298\,K}$ for the (0,1) and (2,3) hydration studies is observed; see column five of Table 1. Figure 6 illustrates the initial rapid decrease in $\Delta G°_{298\,K}$ for short chain lengths of n-alkylammonium ions and a constant free energy change for chain lengths greater than four or five methylene groups. This is entirely consistent with our earlier observation with magic-number cationic water clusters.[24] That is, the water molecules preferentially cluster about the quaternary nitrogen, the charged site, and the alkyl chains lie away from the ion. This concept is confirmed by the behavior of the di- and trimethylammonium ions shown in Figure 6. For the same number of carbons in an ion cluster, the shielding effects of the methyl groups bound directly to the nitrogen dramatically decreases the hydration free energy change relative to that of the analogous n-alkyl chain. This nonlinear trend in free energy within increasing chain length might be an example of the "straight-chain anomaly" that has been observed.[25,26] Such an irregularity is observed when the critical length of the alkyl chain is attained, resulting in weak interactions between the ionic site and the more distant alkyl groups.

Conclusions

An exhaustive study of the equilibrium clustering of one to three waters with alkylammonium ions shows a pattern of behavior consistent with water clusters forming around the charged portion of the ion and being influenced by the nature of the attached hydrophobic groups. Detailed analysis of the entropy values derived from these measurements suggests the possibility of detecting the entropy change associated with the formation of an internal hydrogen bond. These results attempt to build the foundation necessary for the determination of the hydration energies of basic amino acids (histidine, lysine, and arginine) and to gain a greater understanding of the nature and reactivity of biologically relevant ions in the gas phase.

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