a transparent difference spectrum in the 600–900-nm region, where the ground state usually does not absorb. We have found this to be the case in the Ni(II) porphyrins. One can generally make a similar argument concerning transient states in which an axial ligand is either bound or released in the excited state.

Thus, although the absorption changes in the red are of smaller amplitude than those in the blue, we suggest that this longer wavelength region is far more informative for the identification of metalloporphyrin transient states than is the Soret region.

## Summary

In this article we have examined the optical features that characterize the $^1(\pi,\pi^*)$, $^3(\pi,\pi^*)$, $^3(d,\pi^*)$, and (d,d) excited states of a variety of metalloporphyrins. All of the excited-state spectra exhibit strong absorption between 420 and 490 nm. This observation is not surprising in view of the likely common origin of the absorption in this region—transitions to excited states derived mainly from doubly excited configurations involving the $a_{1u}(\pi)$, $a_{2u}(\pi)$, and $e_g(\pi^*)$ orbitals. One conclusion to be drawn from our work is that the observation of strong absorption between the Soret- and Q-band bleachings must be used very cautiously as being indicative of a particular transient state.

Both the $^1(\pi,\pi^*)$ and the $^3(\pi,\pi^*)$ states feature a broad absorption that spans the visible and tails toward zero in the near infrared. In addition, the spectrum of the $^3(\pi,\pi^*)$ state almost always contains an absorption peak between 700 and 850 nm that rides atop this background. A similar long-wavelength absorption band is observed in the spectrum of the $^3(d,\pi^*)$ state, which allows some insight into the electronic origins of these bands. A second, weaker near-infrared transient absorption peak in the $^3(\pi,\pi^*)$ and $^3(d,\pi^*)$ spectra normally appears about 1400–1500 cm$^{-1}$ to shorter wavelengths, and we tentatively attribute it to a vibrational overtone of the long-wavelength transition. The spectrum of the $^3(d,\pi^*)$ state contains, in addition, a prominant band between 650 and 700 nm. The $^3(d,\pi^*)$ spectra are similar to spectra of metalloporphyrin $\pi$-anions. The observed (d,d) state spectra show a null spectrum to the red of the Q-band bleachings, as expected on the basis of straightforward electronic considerations. The $^1(\pi,\pi^*)$ excited-state spectra contain stimulated emission features that unambiguously identify this state. The Q(0,1) stimulated emission band, which appears as a negative feature that interrupts the broad transient absorption, lies ~1500 cm$^{-1}$ to the red of the Q(0,0) absorption band. On the basis of these observations, we suggest that the 600–900-nm region is better suited than the Soret region for helping to distinguish metalloporphyrin transient states. The analysis of fundamental optical properties of metalloporphyrin excited states that we have presented provides a very useful framework that will facilitate in vivo and in vitro transient absorption studies of these complexes.

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# Thermochemical Properties of Ion Complexes $Na^+(M)_n$ in the Gas Phase

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**Abstract:** Enthalpy, entropy, and Gibbs free energy changes for the ion–neutral association reactions $Na^+(M)_{n-1} + M \rightleftarrows Na^+(M)_n$, where M is acetone with $n = 1$–4, methanol with $n = 1$–4, and diethyl ether with $n = 1$–3, were measured using high-pressure mass spectrometry. From these data and earlier values, the order of the bonding energies of $Na^+M$ is found: $(MeOCH_2)_2 >$ acetone $> CH_3NH_2 > Et_2O > NH_3 > CH_3OH > H_2O > SO_2 > CO_2 > CO > HCl > N_2 > CH_4$. From our ab initio calculations and those of others, the interaction of $Na^+$ with M is found to be due mainly to electrostatic interactions. The enthalpy changes with the number of ligands, $n$, shows that the stability of $Na^+(M)_n$ decreases with $n$, and the larger the molecular size of the ligands, the more rapidly the stability decreases. The results indicate that the rapid decrease of the stability of cluster ions formed by sodium ion with larger size ligands is attributable to strong crowding in the cluster ions.

In recent years, considerable attention has been directed to studies of the nature of clusters formed by the attachment of molecules to ions in the gas phase.[1] This has been motivated in part due to realization that studies of clusters in the gas phase provide requisite data for elucidating the nature and extent of ion–solvent interactions, which are important in solution chemistry. The results give detailed information on forces operating in individual complexes, but without interference arising from the presence of the bulk solvent. Furthermore, it is evident that research in this area is also particularly valuable in the field of interphase physics,[2] which is concerned with understanding the details of the collective effects responsible for phase transitions (nucleation phenomena), the development of surfaces, and ultimately solvation phenomenon and formation of the condensed state.

Among the various methods available to study ion clusters, high-pressure mass spectrometry (HPMS) is one of the most useful to measure their thermodynamic properties.[3-5] During past years, a number of bonding energies of metal ions with various ligands have been determined by HPMS in our laboratory.[2,5] Although the bonding energies of $Na^+$ with $H_2O$, $NH_3$, and other molecules have been available,[6-9] little work has been done on the interaction between $Na^+$ and organic molecules, especially those comprising important solvents. Systems of some interest include protic solvents

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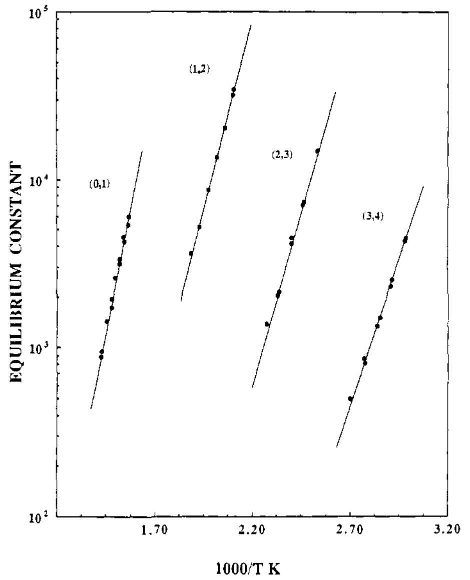

**Figure 1.** van't Hoff plots for the association reactions of $Na^+(CH_3OH)_{n-1,n} + CH_3OH \rightleftarrows Na^+(CH_3OH)_n$.

(such as $CH_3OH$) and dipolar aprotic ones (such as acetone and $Et_2O$).

The purpose of the present study is to provide data on reactions of $Na^+$ with typical organic solvents. The standard free energy, enthalpy, and entropy changes for the following association reactions are reported herein.

$$Na^+(M)_{n-1} + M \rightleftarrows Na^+(M)_n \qquad (1)$$

where M is acetone, methanol, and diethyl ether.

## Experimental Section

The apparatus used to conduct the present experiments has been described previously.[7] Briefly, sodium ion is produced thermionically by resistively heating a coated platinum filament. The coating consists of one part $Al_2O_3$, two parts $SiO_2$, and one part $NaNO_3$. After production from filament, the $Na^+$ ion undergoes numerous collisions with a carrier gas containing the ligand at a preestablished concentration. The collisions effect both thermalization and clustering. The sodium ion and resulting cluster ions are directed by means of a repeller assembly and further controlled by two electrodes, the gating grid, and top gate, which drift ions into the reaction cell region. The top gate has a wire mesh to reduce field penetration into reaction cell region, where sodium ion and clustering ions undergo further clustering and achieve both a thermal and chemical equilibrium condition. The reaction cell is controlled to maintain a stable, desired temperature and pressure. In the present experiment, the pressure of the reaction cell is kept at a selected value between 3 and 10 Torr of a comprised mixture of ligands and argon carrier gas. The present experiments were made in the temperature range 320–750 K. Cluster ions that effuse through the 75- or 100-$\mu$m-diameter orifice separating the reaction cell and vacuum chamber are focused into a quadrupole filter by an ion lens. In order to prevent possible breakup of cluster ions during sampling, the potential on the first plate of the ion lens is restricted to as low a value as possible (below 5 V). After passing through the quadrupole mass filter, the cluster ions are detected by channeltron electron multiplier (CEM) in a pulse-counting mode. The signal from CEM is amplified and collected by a multichannel analyzer.

## Results

Equilibrium constants were measured as a function of temperature for the gas-phase association reactions given by eq 1 with M being methanol, $n$ = 1–4, acetone, $n$ = 1–4, and diethyl ether, $n$ = 1–3.

Experimental results are displayed in the form of van't Hoff plots in Figures 1–3. The results are based on 1 atm as the standard state. During the course of the measurements, experiments were performed to ensure that the measured equilibrium constant was not affected by experimental conditions. One of the factors that might influence the attainment of equilibrium is the top gate voltage. As mentioned in the Experimental Section, one uses the top gate to reduce the field penetration into reaction cell and to effect the efficient drifting of ions to the sampling orifice. Hence, the residence time of reactant ions in the reaction cell is controlled by the top gate voltage; the higher the top gate voltage, the shorter the residence time. If the voltage is set too high, the residence time might become too short for the reactions to achieve equilibrium. Thus, the top gate voltage should be kept as low as possible so that the equilibrium is not altered by residence time or possibly by energy above thermal imparted to the ions by the field. The effect of the top gate voltage on the equilibrium was studied before undertaking measurement of the equilibrium constants. Figure 4 shows the top gate voltage check plots for the three (0,1) clustering reactions. Unlike some earlier results,[10,11] in which the top gate voltage (above 20 V) influenced strongly the first clustering reactions of metal ions with small ligands such as $H_2O$ and $NH_3$, the deduced equilibrium constants of the present reactions did not change with top gate voltage in the region 10–70 V. One possible reason is that the ligands employed in the present study have a large number of degrees of freedom. Hence, the formed metastable complex $(Na^+M)^*$ will have a longer lifetime

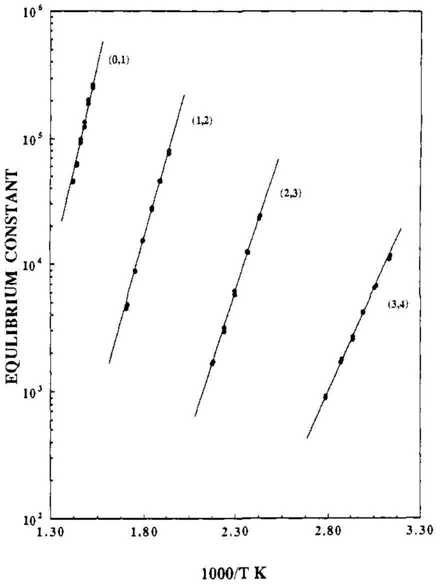

**Figure 2.** van't Hoff plots for the association reactions of $Na^+(acetone)_{n-1,n}$ + acetone $\rightleftarrows$ $Na^+(acetone)_n$.

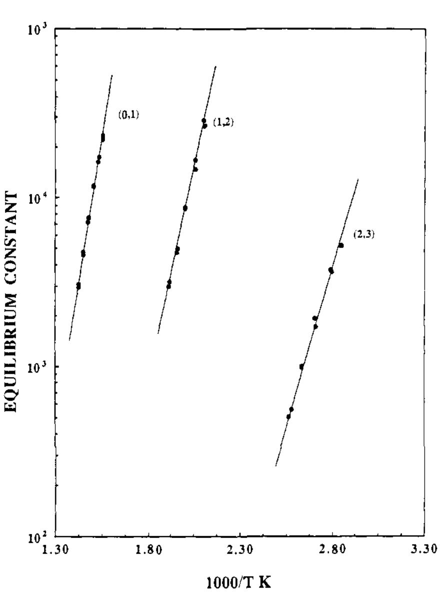

**Figure 3.** van't Hoff plots for the association reactions of $Na^+(Et_2O)_{n-1,n} + Et_2O \rightleftarrows Na^+(Et_2O)_n$.

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**Table I.** Thermochemical Properties of the Association Reactions of $Na^+(M)_{n-1,n} + M \rightleftarrows Na^+(M)_n$

| | $-\Delta H°_{n-1,n}$, kcal/mol | | | | $-\Delta S°_{n-1,n}$, cal/mol·K | | | | $-\Delta G°_{n-1,n}$, kcal/mol | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(n-1),n$ | acetone | $CH_3OH$ | $Et_2O$ | $H_2O$[a] | acetone | $CH_3OH$ | $Et_2O$ | $H_2O$[a] | acetone | $CH_3OH$ | $Et_2O$ | $H_2O$[a] |
| 0,1 | 33.4 ± 0.2 | 26.6 ± 0.2 | 31.0 ± 0.3 | 24.0 | 26.1 ± 0.2 | 24.3 ± 0.3 | 28.2 ± 0.5 | 21.5 | 25.6 | 23.1 | 22.5 | 17.6 |
| 1,2 | 25.2 ± 0.1 | 20.2 ± 0.2 | 22.9 ± 0.3 | 19.8 | 24.6 ± 0.3 | 21.7 ± 0.4 | 28.0 ± 0.7 | 22.2 | 17.8 | 13.7 | 14.5 | 13.2 |
| 2,3 | 20.7 ± 0.2 | 17.4 ± 0.4 | 16.4 ± 0.3 | 15.8 | 30.0 ± 0.4 | 25.1 ± 0.8 | 29.5 ± 0.7 | 21.9 | 11.6 | 9.9 | 7.6 | 9.3 |
| 3,4 | 14.7 ± 0.2 | 15.7 ± 0.2 | | 13.8 | 27.3 ± 0.6 | 30.0 ± 0.5 | | 25.0 | 6.5 | 6.7 | | 6.3 |

[a] Reference 6.

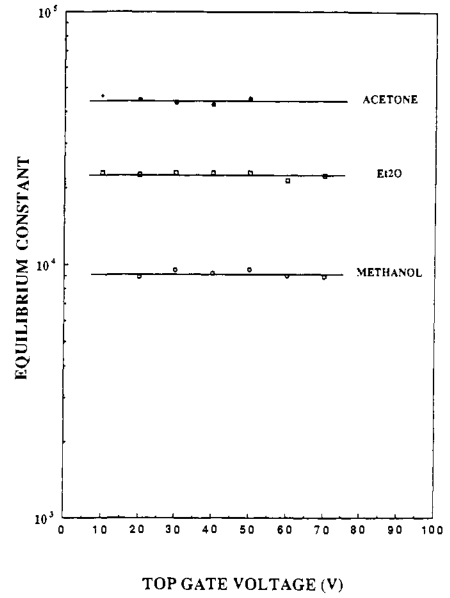

**Figure 4.** Typical plots to check the possible influence of the top gate voltage on acquiring equilibration for the three first clustering reactions of sodium ion with methanol ($P$ = 4.8 Torr, 10% methanol in Ar), acetone ($P$ = 4.5 Torr, 2.5% acetone in Ar), and diethyl ether ($P$ = 3.5 Torr, 2.75% diethyl ether in Ar).

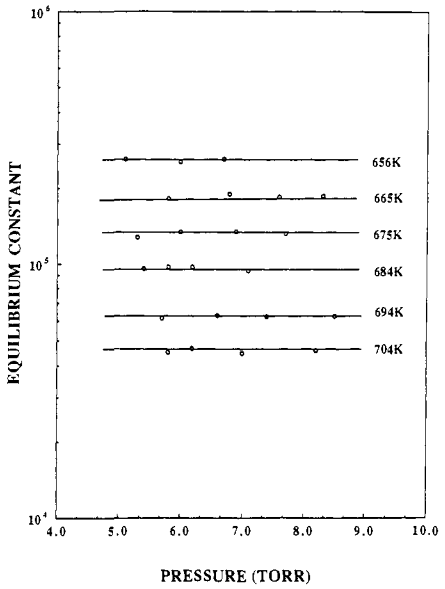

**Figure 5.** Typical pressure plots to check for any influence on acquiring equilibration for the association reaction $Na^+ + \text{acetone} \rightleftarrows Na^+(\text{acetone})$ at six temperatures.

**Table II.** Thermochemical Quantities for $Na^+$–M

| M | $D_0(Na^+{-}M)$, kcal mol | $-\Delta G°_{0,1}$, kcal/mol | $-\Delta S°_{0,1}$, cal/mol·K | ref |
|---|---|---|---|---|
| DME[a] | 47.2 | 36.9 | 34.6 | 9 |
| acetone | 33.4 | 25.6 | 26.1 | this work |
| $CH_3NH_2$ | 32.1 | 23.1 | 30.3 | 13 |
| $Et_2O$ | 31.0 | 22.5 | 28.2 | this work |
| $NH_3$ | 29.1 | 21.4 | 25.7 | 7 |
| $CH_3OH$ | 26.6 | 19.3 | 24.3 | this work |
| $H_2O$ | 24.0 | 17.6 | 21.5 | 6 |
| $SO_2$ | 18.9 | 14.9 | 20.2 | 9 |
| $CO_2$ | 15.9 | 9.9 | 20.1 | 9 |
| CO | 12.5 | 6.5 | 20.4 | 9 |
| HCl | 12.2 | 6.1 | 20.4 | 9 |
| $N_2$ | 8.0 | 2.5 | 18.6 | 9 |
| $CH_4$ | 7.2 | 3.0 | 14.1 | 9 |

[a] DME = $(MeOCH_2)_2$.

against unimolecular decomposition and can be more readily thermalized,[12] whereby the clustering reactions achieve equilibrium more rapidly.

Another possible factor is the carrier gas pressure, which might produce effects on (i) the thermalization of ions, (ii) the extent of sufficient collisions for the attainment of equilibrium, and (iii) problems with ion sampling. Therefore, a study is also made to find the region in which the equilibrium constants do not change with pressure. A typical pressure check for the first clustering reaction of $Na^+$ with acetone is displayed in Figure 5. In the pressure region from 4 to 9 Torr, the equilibrium constant is seen to be independent of pressure, and the pressure check further establishes that an equilibrium condition is attained. Furthermore, the plots indicate that there is no sampling problem due to the expansion of gas from the reaction cell into the detection chamber. All data in Figures 1–3, used to deduce the requisite thermochemical values, were measured under the experimental conditions determined by the top gate voltage and pressure studies described in the foregoing.

A least-squares fit of the data points displayed in Figures 1–3 for each reaction was used to determine both the slopes and intercepts of the lines shown in the van't Hoff plots. Thereby, the enthalpy and entropy changes of the reactions were determined, respectively. These values and those from ref 6 for water are listed in Table I, together with the Gibbs free energy changes at 298 K for each reaction. The error limits for the enthalpy and entropy changes correspond to one standard deviation based on the least-squares fit.

## Discussion

**(1) Bonding Energies $D_0(Na^+{-}M)$.** Except for a small energy correction, which is usually on the order of $^1/_2$ kcal/mol, the value of $-\Delta H°_{0,1}$ is equivalent to the bond dissociation energy $D_0(Na^+{-}M)$.[5] An interesting comparison is that of the relative bond dissociation energies, $D_0(Na^+{-}M)$, for sodium ion with different ligands. From the results of this work and others,[5,13] a list of $D_0(Na^+{-}M)$ is compiled in Table II with entropy and Gibbs free energy changes. The results indicate that the order of the strength of the bonding of the sodium ion with 13 different ligands is consistent with the inequality:

$$\text{DME} > \text{acetone} > CH_3NH_2 > Et_2O > NH_3 > CH_3OH > H_2O > SO_2 > CO_2 > CO > HCl > N_2 > CH_4$$

Clementi et al.[14] have made ab initio calculations for bonding of the $Na^+{-}H_2O$ cluster. The bonding energy that they calculated is in excellent agreement with experimental data.[6] The Mulliken population analysis showed a charge transfer of only 0.013e from

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[12] Passarella, R.; Castleman. A. W., Jr. submitted for publication in *J. Phys. Chem.*

[13] Guo, B. C.; Castleman, A. W., Jr., unpublished results.

[14] Kistenmacher, H.; Popkie, H.; Clementi, E. *J. Chem. Phys.* **1973**, *58*, 1689. Clementi, E.; Popkie, H. *J. Chem. Phys.* **1972**, *57*, 1850.

water to the sodium ion, which indicates that bonding between sodium ion and water is almost purely electrostatic.

As part of the present study, we performed ab initio geometry optimization calculations on the $Na^+$–$CH_3OH$ cluster using the HONDO/6 program with the 3G basis set. Our results show that negligible electron transfer occurs from methanol to the sodium ion, which also suggests that electrostatic bonding dominates in the case of the $Na^+$–$CH_3OH$ cluster. Moreover, the good agreement of experimental bonding energies and those calculated from electrostatic considerations[15–18] also suggests that bonding of sodium ion with other ligands is mainly electrostatic interaction. Thus it is quite safe to assume that the bonding between sodium ion and all of the other ligands listed in Table II is also predominantly electrostatic in origin.

There are four main contributions to the electrostatic interactions.[15] These are (i) ion–dipole moment interaction determined by the dipole moment of ligand, (ii) ion-induced dipole moment, (iii) dispersion interactions determined by the polarizability of ligand, and (iv) the repulsive interaction between ion and ligand, which produces a negative contribution to the total electrostatic force. Among them, the ion–dipole moment interaction is the one of dominant magnitude.

The bonding energy of $Na^+$–DME [DME = $(MeOCH_2)_2$] complex is extremely high. The strong bonding is created by the structure of DME. Unlike other ligands listed in Table II, DME has two functional sites for attachment of a sodium ion; that is, bonding of sodium ion with DME occurs by interaction with two sites. The bonding is similar to that of a sodium ion with two ligands that have one functional site, from which it follows that the bonding energy should be almost equal to that of a sodium ion with two one-functional site ligands. By way of comparison, Kebarle and co-workers[19] have studied the reactions of potassium ion with organic compounds, which have two bonding sites for metal ions. They also found that the bonding of potassium ion with these molecules was very strong.

Ab initio study of the complex $Na^+$–*N,N*-methylethylacetamide has shown that, in the most stable structure, the sodium ion is along the line of the C=O bond axis.[20] The same alignment is expected to occur in the $Na^+$–acetone complex. The main interaction occurs with the carbonyl oxygen and the carbonyl bond dipole. Since acetone has a large dipole moment (2.88 D)[22] and the carbonyl oxygen is more negative, it is expected that the bonding between the sodium ion and acetone should be the strongest one among the one-functional site ligands listed in Table II.

From Table II, one of the interesting features of the data is seen by comparing the relative bonding of $H_2O$ and $NH_3$ with their alkyl-substituting molecules. The bonding energies of the $Na^+$–M complex increase with an increase of the alkyl size and number, even though the dipole moments of methyl-substituting molecules do not change and may even decrease with the substitution of H by the alkyl group.[22] When one methyl group substitutes one hydrogen in water or ammonia, the bonding increases almost 3 kcal/mol. Two ethyl groups substitute two hydrogens in water, and the bonding increases almost 7 kcal/mol. The same phenomenon has been observed by Kebarle and his co-workers[21] in the $K^+$–M case.

Though ion–dipole interactions normally play a main role in the electrostatic interactions, sometimes strong ion-induced dipole and dispersion interactions contribute substantially to the bonding of ions and molecules. Therefore, cluster ions can display stronger bonding with ligands which have smaller dipole moments if there are compensating larger polarizabilities. The effect of improvement of bonding energy by ion-induced dipole moment interactions and dispersion interactions has been observed from experiment.[7] For example, $NH_3$ has a smaller dipole moment (1.47 D) than $H_2O$ (1.87 D), while the polarizability of $NH_3$ (2.26) is larger than that of $H_2O$ (1.45).[22] The bonding energy of the $Na^+$–$NH_3$ cluster determined from experiment[7] is almost 5.1 kcal/mol larger than that of $Na^+$–$H_2O$ cluster.[6] Electrostatic calculations performed by Kebarle et al.[21] also indicated that, in the $K^+$–M case, dipole moments either did not change or even decreased with the substitution of H by alkyl group, whereupon the bonding becomes less favorable. But, polarization and quadrupole moments of the substituted molecules increase so greatly that the change in induced dipole and dispersion interactions more than compensates, whereby enhanced bonding is obtained. In the present case, we believe that the same arguments apply concerning the effect of polarizability on improving the bonding energy of cluster ions with alkyl-substituting molecules because the bonding of $Na^+$–M is mainly electrostatic and the bonding features of $Na^+$–M are about the same as those of $K^+$–M.

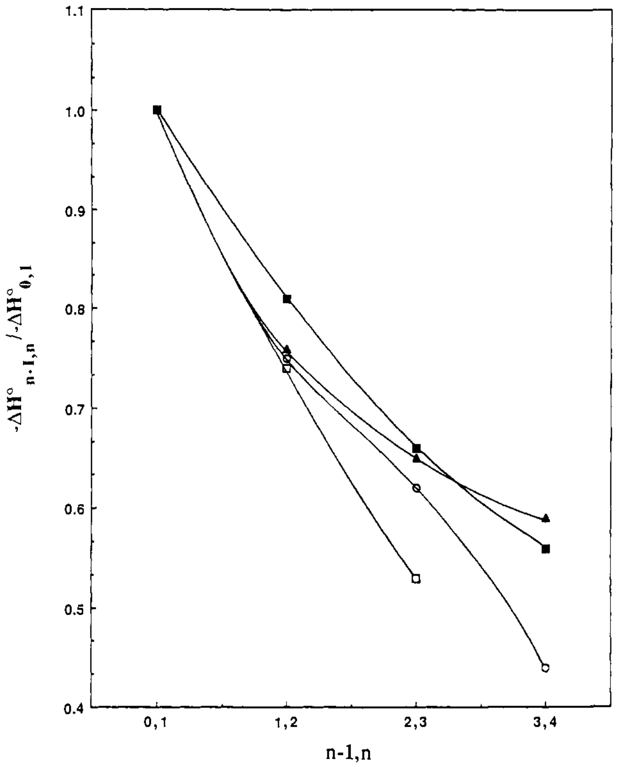

Figure 6. Relative stepwise enthalpy changes to $-\Delta H^\circ_{0,1}$ for the addition of $Et_2O$ (□), $H_2O$ (■), acetone (○), and methanol (▲) onto sodium ion as a function of the clustering step.

**(2) Stability of $Na^+(M)_n$.** Another interesting comparison is that of the trends in the stability of $Na^+(M)_n$, related to the $-\Delta H^\circ_{n-1,n}$. Table I lists the stepwise enthalpy changes for the addition of acetone, diethyl ether, methanol, and water as a function of the clustering step. Figure 6 displays the stepwise enthalpy changes relative to $-\Delta H^\circ_{0,1}$. The data are based on experimental results of the present study and earlier ones.[6] The magnitude of the enthalpy change, $-\Delta H^\circ_{n-1,n}$, is seen to decrease with *n*. The enthalpy changes for the addition of $Et_2O$ to sodium ion are seen to decrease the most rapidly and to decrease more rapidly for acetone than for methanol.

It is not surprising that successive enthalpy changes decrease with ligand number *n* because the bonding is mostly electrostatic, and the total ligand–ligand interaction in the smaller ion clusters is repulsive due largely to the dipole moment of the attached ligands.[16] The more ligands in the cluster ions, the stronger the repulsion and the less stable the cluster ions. Similarly, the larger the ligand, the greater the crowding in the cluster ions and hence the less stable the cluster ions. If the interaction of the system is purely electrostatic, it is generally expected that the minimum

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(15) Spears, K. G. *J. Chem. Phys.* **1972**, *57*, 1850.
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(21) Davidson, W. R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6133.
(22) *Handbook of Chemistry and Physics*, 66th ed.; Chemical Rubber Co.: Cleveland, OH, 1986.

energy configuration consists of an ion in the center of opposing ligands, and the most stable structure of $Na^+(M)_n$ should have the highest symmetry where all ligands go into the first shell. In fact, some ab initio and other calculations about the hydration of alkali ions[16,23-25] support the above argument. Therefore, it is expected that for the organic ligands under consideration here, if all go into the first shell, $Na^+(M)_2$ is linear, $Na^+(M)_3$ will have a trigonal structure, and $Na^+(M)_4$ will be tetrahedral.

Figure 6 shows that the relative enthalpy change for the second addition of a ligand to the sodium ion is almost the same for all three organic molecules studied. But, beginning from the third step of addition, the relative enthalpy changes illustrate different trends for different ligands. The data in Table I show that $-\Delta H^\circ_{2,3}$ is 1 kcal/mol smaller for $Et_2O$ than for methanol, though $-\Delta H^\circ_{0,1}$ and $-\Delta H^\circ_{1,2}$ is much larger for $Et_2O$ than for methanol. In the same way, $-\Delta H^\circ_{n-1,n}$ for acetate becomes smaller than that for methanol at the fourth step addition. These results reflect the extent of the crowding in the cluster ions due to the addition of more ligands. In linear $Na^+(M)_2$, the two ligands lie on opposite sides of the sodium ion. Because of the large distance between ligands, the crowding does not cause a big difference in $Na^+(M)_2$ with different ligands.

Next, it is interesting to consider the fate of the third and fourth ligand. Theoretical calculations[16,23-25] have indicated that the third and fourth water go into the first shell to form trigonal $Na^+(H_2O)_3$ and tetrahedral $Na^+(H_2O)_4$, which is supported by the experimental fact that there is no abrupt change in the bond energy for the third and fourth addition of water. In the case of $Et_2O$, at the third addition step, molecular size begins to create a crowding effect on the cluster ion. Since $Et_2O$ has the largest molecular size among the ligands listed in Table I, the $Na^+(Et_2O)_3$ cluster becomes strongly crowded and mutual repulsion of $Et_2O$ may increase so that the stability of the cluster drops quickly. Alternatively, it is possible that the third $Et_2O$ goes into the second shell to avoid crowding. However, we expect that the ligand should go into first shell. $Et_2O$ is a large, as well as a long, molecule, and if it goes into second shell, the distance should be much longer between sodium ion and $Et_2O$ than between sodium and water in the second shell. Bonding of outer shell $Et_2O$ to inner shell $Et_2O$ is also weak due to its aprotic nature. Thereupon, the attraction would be greatly reduced, with a concomitant reduction in the stability of the cluster ion. Hence, in such a situation, the $-\Delta H^\circ_{2,3}$ should be much smaller than that obtained from experiment. In fact, the measured $-\Delta H^\circ_{2,3}$ is about 1 kcal/mol larger for $Et_2O$ than for water, which is thought to be in the first shell. Similarly, at the third addition step, the smaller difference in molecular size between acetone and methanol does not yet display a clearly different crowding effect in these cluster ions. But, the size effect on the stability of cluster ions becomes strong at the fourth addition step so that $-\Delta H^\circ_{3,4}$ for acetone drops rapidly and even becomes smaller than that for methanol.

An interesting result of this study is the similar trends in the enthalpy changes for both $Na^+(CH_3OH)_n$ and $Na^+(H_2O)_n$ systems with $n$ ranging from 1 to 4. The similarities are unexpected since the molecular size of methanol is much larger than water. Note that a similar result has been observed for $K^+(CH_3OH)_{1-4}$ and $K^+(H_2O)_{1-4}$ systems in our laboratory.[26] One possible explanation is that there may be a fortuitous balancing of the bonding effects due to the different molecular sizes of the two molecules and their relative properties. At different distances of interaction between the ions and ligands there may be compensating effects from the bonding contributions due to the different dipole moments and polarizabilities of the two molecules. The molecular size of methanol is larger than water, but at the fourth addition step, the crowding in $Na^+(CH_3OH)_4$ compared with that in $Na^+(H_2O)_4$ is not strong enough to reduce dramatically the stability of $Na^+(CH_3OH)_4$. Thus, no big drop of $-\Delta H^\circ_{3,4}$ was found for the methanol system.

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