species $C_4H_{11}^+$(a) has the lower heat of formation but is not a "real" species while $C_4H_{11}^+$(b) of structure B is more stable toward dissociation. The barrier toward CH_4 + *sec*-$C_3H_7^+$ is 3.4 kcal/mol while the barrier toward *t*-$C_4H_9^+$ + H_2 should be somewhat higher.

The proton affinities for propane and isobutane calculated from the enthalpies of formation of the respective protonated a and b species are shown in Table I. Evidently protonation would lead mostly to protolysis into an alkyl ion and CH_4 or H_2. However, at low temperatures the species b should be observable provided that the protonating agent has a proton affinity which is higher than the proton affinity relating to the b species but not by more than 1-2 kcal/mol.

Ausloos,[27] Aquilanti,[28] and Harrison[29] have studied the protolysis of labeled propane and isobutane. This work has shown that the proton transferred by the acid (H_3^+ and CH_5^+) after protolysis appears in the neutral product. For example, in the protonation of propane the proton appears in the hydrogen when the products are $C_3H_7^+ + H_2$ and in the methane when the products are $C_2H_5^+ + CH_4$. It should be noted that this result is consistent with the assumption that protolysis proceeds via the three-center bonded structures A and B, since $C_3H_9^+$ A is essentially *sec*-$C_3H_7^+ \cdot H_2$ and $C_3H_9^+$ B is close to $C_2H_5^+ \cdot CH_4$. Both structures dissociate very easily after protonation of the C-H or the C-C bond so that little time is left for proton scrambling.

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Ionic Solvation by Aprotic Solvents. Gas Phase Solvation of the Alkali Ions by Acetonitrile

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Abstract: The ion equilibria in the gas phase ($M^+(CH_3CNz_{n-1} + CH_3CN = M^+(CH_3CN)_n$) were measured for Na^+, K^+, Rb^+, and Cs^+ for n = 1 to 5. The measured temperature dependence of the equilibrium constants $K_{n-1,n}$ led to the evaluation of $\Delta H°_{n-1,n}$, $\Delta G°_{n-1,n}$, and $\Delta S°_{n-1,n}$ for the above systems. Comparison with similar data for the halide negative ions and acetonitrile shows that the initial interactions (low n) are very much larger for positive ions than for negative ions. Electrostatic calculations for the complexes M^+CH_3CN, X^-CH_3CN, and M^+H_2O in which the charge distribution in the acetonitrile (and water) molecule is explicitly taken into account reproduce well the experimental $\Delta H_{0,1}$. These calculations show that the weak interaction of acetonitrile with negative ions is due to the diffuse distribution of the positive pole of the dipole over the C and H atoms of the molecule. On the other hand the concentrated negative charge on the accessible N atom leads to strong interactions with positive ions. The difference between positive and negative ion interactions with acetonitrile decreases as n is increased. At $n = 5$ the interactions with negative ions become slightly more favorable. Comparing the results for $M^+(CH_3CN)_n$ with those for $M^+(H_2O)_n$ one finds that for low n acetonitrile gives stronger binding. This is due to its higher dipole. However, as n increases the interactions with water become more favorable. The results can be used for an approximate prediction of the single ion free energies of solvation of the alkali and halide ions in acetonitrile. The present results agree best with the single ion energies of Case and Parsons. The measurements were performed with high pressure mass spectrometric apparatus.

Significant differences between the solvent effects of protic solvents (HOH, CH_3OH, etc.) and dipolar aprotic solvents like dimethylformamide, dimethyl sulfoxide, acetonitrile, and others have been observed in heterolic organic reactions.[1,2] These differences have been explained by the assumption that the solvation of negative ions by aprotic solvents is much weaker than that of positive ions of similar size and shape. Studies of the enthalpies of transfer[3] and activity coefficients[4] of alkali and halide ions in aprotic solvents have confirmed the weak solvation of negative ions. However, these investigations[3,4] were dependent on extra thermodynamic assumptions common to approaches in which properties of electrolytic so-

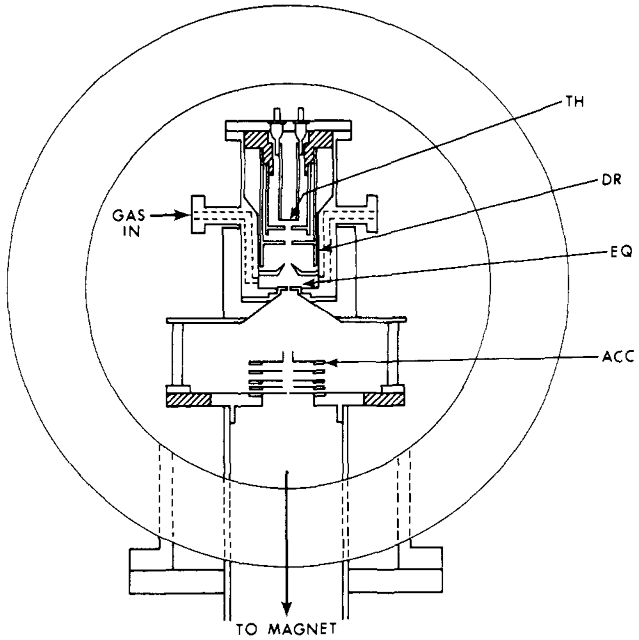

Figure 1. Ion apparatus. Ion source with TH = thermionic emission filament for production of alkali ions; DR = drift volume in which ions drift, through clustering gas, toward equilibration chamber; EQ = equilibration chamber which is free of electrical fields. Gas and ions escape through the ion exit slit at the botton into evacuated space. ACC ion acceleration plates by which ions are accelerated prior to mass separation in the magnet.

lutions containing positive and negative ions must be divided into those of separate positive and negative ions.

Since ion-molecule equilibria involving only positive or negative ions can be measured in the gas phase,[5-7] an investigation of the gas phase equilibria ($n-1, n$) involving the halide ions X^- and acetonitrile was made some time ago in the present laboratory.[8]

$$X^-(CH_3CN)_{n-1} + CH_3CN = X^-(CH_3CN)_n \quad (n-1, n)$$

van't Hoff plots of the equilibrium constants $K_{n-1,n}$ lead to $\Delta H°_{n-1,n}$ and $\Delta S°_{n-1,n}$ for the stepwise addition of solvent molecules to the ion. The present work reports measurements for acetonitrile and the alkali ions and compares the data for the positive alkali ions and the negative halide ions.

The equilibria ($n-1, n$) involving the alkali ions M^+ were measured in a specially designed alkali ion source capable of operating at acetonitrile gas pressures in the Torr range.

$$M^+(CH_3CN)_{n-1} + CH_3CN = M^+(CH_3CN)_n \quad (n-1, n)$$

The residence times of the ions in the ion source were sufficiently long for the ($n-1, n$) equilibrium to be achieved. The individual equilibria for different n were observed at different temperatures, the (0, 1) equilibrium occurring at the highest temperature. The equilibrium ion concentrations were detected by bleeding some of the gas and ions into an evacuated mass analysis system, i.e., mass spectrometer.

Experimental Section

The measurements were done in an alkali ion source capable of operating at neutral gas pressures of up to 4 Torr. The ion source shown in Figures 1 and 2 is somewhat similar to that used earlier for the alkali ion–water clustering experiments.[6,8] Changes of design were made so as to increase the leak tightness of the source, to improve the temperature homogeneity of the gas in the equilibration chamber, and to increase the intensity of the ion signal. The new ion source (Figure 1) consists of a heavy walled stainless steel cylinder. A lid which holds the filament and two electrodes is bolted to the top, and another small plate holding the ion exit slit is bolted to the bottom. Two channels, one for the gas supply and the other for connection to the capacitance manometer, are bored into the cylinder walls.

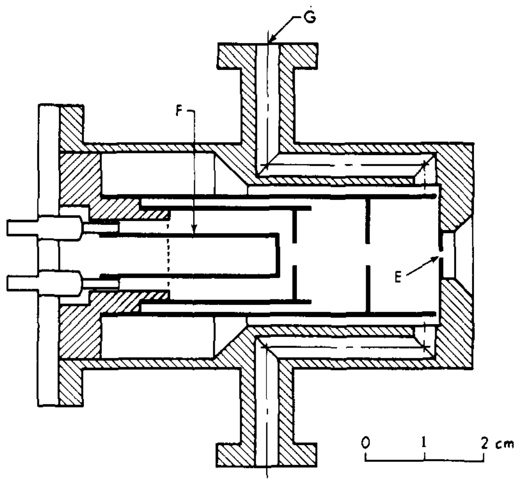

Figure 2. Cross-sectional view of the ion source, drift tube: F, filament; E, exit slit; G, gas in.

The positive alkali ions were produced by thermionic emission from the heated filament. The filament was a 7 mm by 2 mm strip of platinum gauze coated with an alkali-alumosilicate melt.[10] The ions emitted from the filament (~1 μA) drifted toward the equilibration chamber under the influence of an electrical field produced by the voltages (relative to ground): filament + 2000 V, first electrode 2180 V, second electrode 2090 V, equilibration chamber 2000 V. The principal function of the two drift electrodes was to act as thermal radiation shields and heat transfer barriers between the hot filament and the equilibration chamber. The 9 mm deep equilibration chamber was field free. The top of the chamber was formed by a thick walled lid with a small central hole. The lid fitted tightly into the inside of the ion source. At the botton of the equilibration chamber a small slit (0.01 × 1 mm) allowed gas and ions to escape into the evacuated space housing the ion acceleration, magnetic separation, and ion detection system.

The number of ions starting from the filament and passing through the various stages of the ion source was measured by means of suitably placed (temporary) electrodes. In the presence of gas by far the largest ion loss (a factor of $\sim 10^6$ at 1 Torr) occurred in the equilibration chamber. This could have been expected since in this chamber the ions become quickly thermalized and then diffuse in all directions. The ratio of chamber wall to ion exit slit area is $\sim 5 \times 10^5$.

The temperature of the equilibrium chamber was measured by two thermocouples embedded in the wall. The ion source could be heated by a metal heater jacket containing heater elements. It could be also cooled by a metal cooling jacket containing channels through which various thermostated cooling fluids wer circulated.

The ion source could be easily converted into a drift tube as shown in Figure 2. In this case a uniform drift field could be applied right over the whole space down to the ion exit slit.

In some experiments with the equilibration chamber the ions were pulsed by suitable gating voltage between the filament and the first electrode. Two ions like K^+ and $K^+ \cdot CH_3CN$ which are in equilibrium have identical mobilities. Therefore their intensity–time distributions should have the same shapes. The intensity–time distribution after pulsing the positive ions production was observed by means of multiscaler detection, collecting ions with a given mass. This test allowed one to eliminate conditions under which equilibrium was not achieved. A number of other tests dealing with the equilibrium and thermal nature of the ions in the equilibration chamber were also performed. Details for these tests and more information on thepparatus can be found in the dissertation of Davidson.[11]

It was found that the drift source gave equilibrium constants in agreement with the equilibration chamber results when the E/P value was less than 2 Volt/(cm Torr). This source could be operated either in the pulsed or continuous mode. However, all measurements reported in the next section were obtained with the field free equilibration chamber, since the drift source was not found to offer any specific advantages for the equilibrium measurements, and since it was thought that the equilibrium chamber arrangement offered superior temperature homogeneity, particularly at low temperatures.

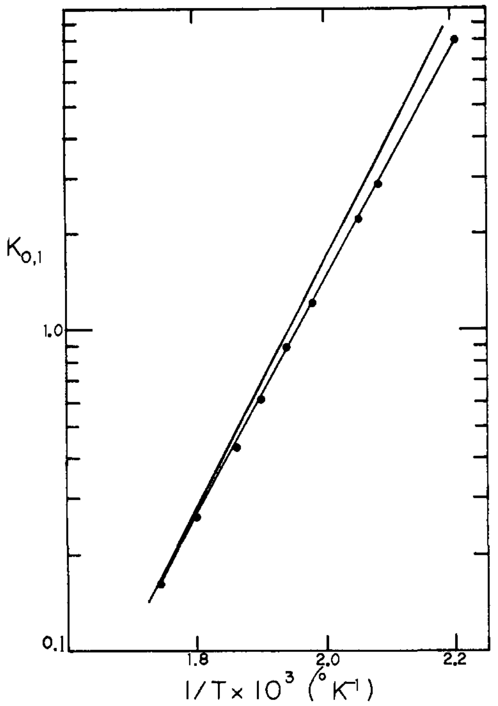

Figure 3. A comparison of $K_{0,1}$ obtained in this study (●) with that of Searles[9] (—) for the reaction $K^+ + H_2O = K^+(H_2O)$.

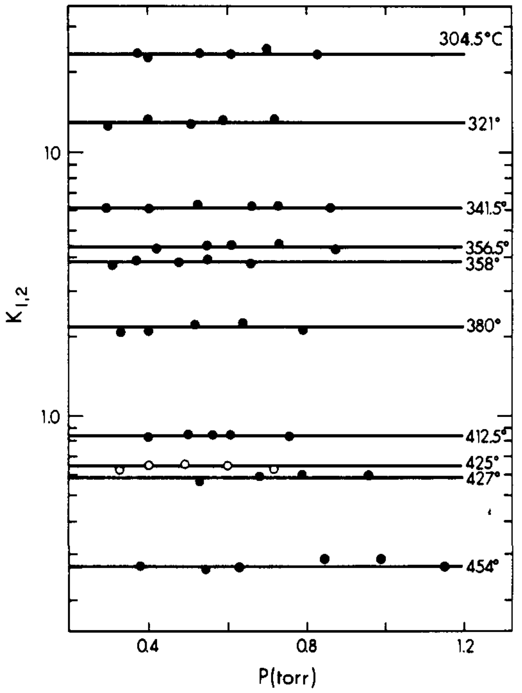

Figure 4. Equilibrium constants $K_{1,2}$ (Torr^{-1}) vs. acetonitrile pressure for reaction $Na^+(CH_3CN) + CH_3CN = Na^+(CH_3CN)_2$.

Results and Discussion

(a) **Results. General.** Some earlier equilibria measurements were repeated with the present new source in order to examine the degree of agreement. These tests involved the clustering of water to the potassium ion. Good agreement with previous results[9] was obtained for the $K_{3,4}$ equilibrium which is measured near room temperature. The results for the $K_{0,1}$ equilibrium were not in complete agreement. The two van't Hoff plots are shown in Figure 3. The new slope is somewhat lower. The new data lead to $\Delta H°_{0,1} = -16.9$ kcal/mol, $\Delta G°_{0,1} = -11.0$ kcal/mol (at 298 K), and $\Delta S°_{0,1} = -19.9$ eu. These can be compared with the corresponding previous results:[9] -17.9, -11.4, and -21.6. We do not known which determination is more accurate nor do we know the exact reason causing the different results. The data illustrate the error that can be expected from two different experimental arrangements. It is interesting to note that the new $\Delta H_{0,1}$ is closer to a recent theoretical result of 15.7 kcal/mol obtained by Kistenmacher, Popkie, and Clementi.[12]

The equilibrium constants $K_{n,n-1}$ for the reactions n, $n - 1$ were determined at a given temperature using several different acetonitrile pressures.

$$M^+(CH_3CN)_n = M^+(CH_3CN)_{n-1} + CH_3CN \quad (n, n-1)$$

Shown in Figure 4 are the $K_{1,2}$ observed with $M^+ = Na^+$. The constants are found to change little in the experimentally used pressure range. Similar data were obtained for the other $K_{n,n-1}$ involving Na^+ and the other alkali ions. The resulting van't Hoff plots are shown in Figures 4-8. The $K_{0,1}$ to $K_{4,5}$ for K^+, Rb^+, and Cs^+ could be determined. For Na^+ only $K_{1,2}$ to $K_{4,5}$ were determined. The determination of $K_{0,1}(Na^+)$ required temperatures higher than 700 K. Various difficulties were experienced at such high temperatures so that the determination of $K_{0,1}$ was abandoned. For similar reasons, the equilibria involving Li^+ were not studied.

The $\Delta G°$, $\Delta H°$, and $\Delta S°$ values obtained from the van't Hoff plots are summarized in Table I. These data will be discussed after some useful results from electrostatic calculations have been introduced.

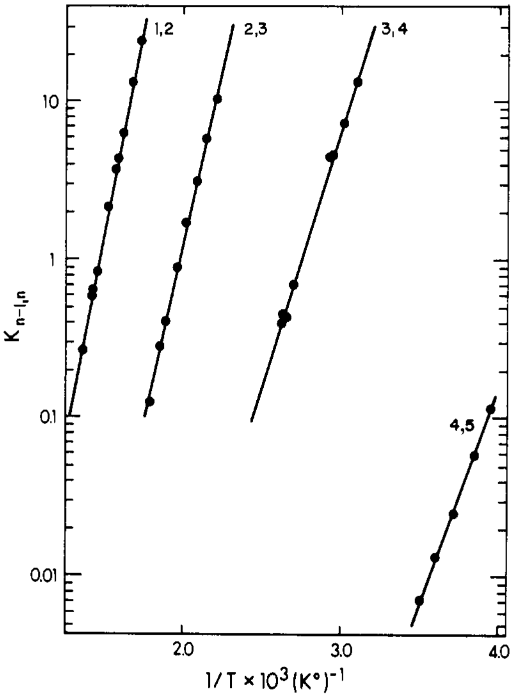

Figure 5. van't Hoff plots of equilibrium constants $K_{n-1,n}$ for the reactions of Na^+ with acetonitrile molecules.

(b) Electrostatic Calculations of the Binding Energies for $M^+(H_2O)$, $M^+(CH_3CN)$, and $X^-(CH_3CN)$. Comparison with Experimental Results. A simple electrostatic calculation involving point dipoles and point polarizabilities would predict identical binding energies to a positive and negative ion of the same radius. Since the central characteristic of aprotic solvents is their unequal solvation of positive and negative ions, it is obvious that more refined calculations, taking into account the charge distribution in the solvent molecule, must be made.As pointed out earlier[8] aprotic solvents are characterized by permanent dipoles in which the positive charge is diffusely

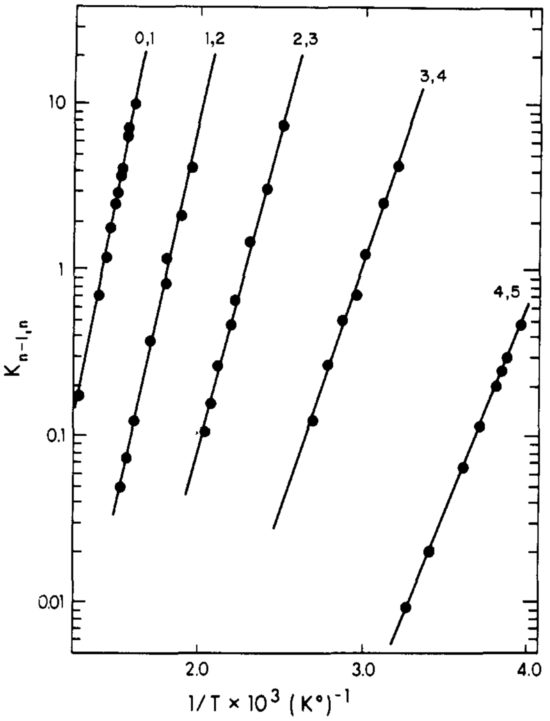

Figure 6. van't Hoff plots of the equilibrium constants for the gas phase solvation of the potassium ion by acetonitrile: (■) points from the potassium-sodium source.

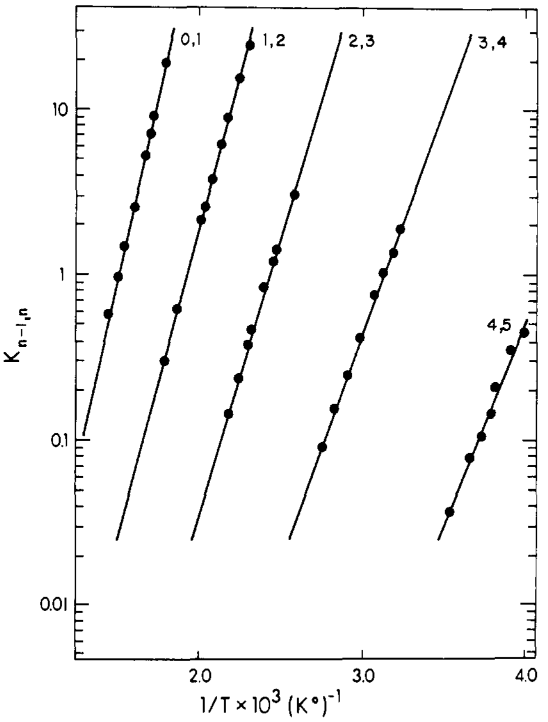

Figure 7. van't Hoff plots of the equilibrium constants for the gas phase solvation of the rubidium ion by acetonitrile.

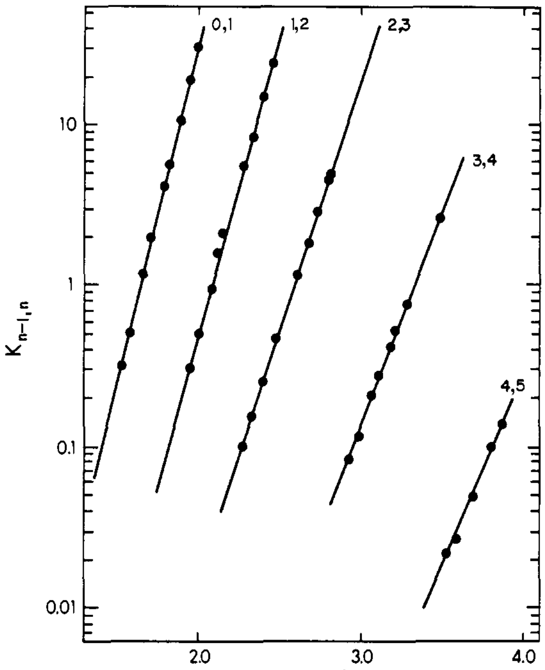

Figure 8. van't Hoff plots of the equilibrium constants for the gas phase solvation of the cesium ion by acetonitrile.

Table I. Experimental Thermodynamic Values for the Gas Phase Reactions $M^+(CH_3CN)_{n-1} + CH_3CN \rightleftarrows M^+(CH_3CN)_n$ $(n-1, n)$

Reaction $(n-1, n)$	$-\Delta H_{n-1,n}$, kcal/mol	$-\Delta G_{n-1,n}$,[a] kcal/mol	$-\Delta S_{n-1,n}$,[a] eu
	Na^+		
1, 2	24.4 ± 0.3	17.6 ± 0.4	22.7 ± 0.5
2, 3	20.6 ± 0.5	12.3 ± 0.5	27.5 ± 0.9
3, 4	14.9 ± 0.2	6.61 ± 0.3	27.9 ± 0.6
4, 5	12.7 ± 0.2	0.39 ± 0.3	41.2 ± 0.7
	K^+		
0, 1	24.4 ± 0.4	18.0 ± 0.5	21.5 ± 0.7
1, 2	20.6 ± 0.5	13.4 ± 0.5	24.2 ± 0.5
2, 3	18.2 ± 0.3	9.8 ± 0.3	28.3 ± 0.6
3, 4	13.6 ± 0.4	5.44 ± 0.4	27.5 ± 1.2
4, 5	11.5 ± 0.1	1.43 ± 0.1	33.7 ± 0.3
	Rb^+		
0, 1	20.7 ± 0.3	15.3 ± 0.3	18.1 ± 0.5
1, 2	17.7 ± 0.2	11.4 ± 0.3	20.9 ± 0.5
2, 3	15.7 ± 0.2	8.30 ± 0.3	24.8 ± 0.5
3, 4	12.5 ± 0.2	4.80 ± 0.3	25.7 ± 0.5
4, 5	11.1 ± 0.6	1.42 ± 0.8	32.5 ± 2.1
	Cs^+		
0, 1	19.2 ± 0.1	13.7 ± 0.1	18.6 ± 0.2
1, 2	16.7 ± 0.3	10.2 ± 0.3	21.6 ± 0.6
2, 3	14.3 ± 0.1	7.2 ± 0.2	24.0 ± 0.4
3, 4	12.1 ± 0.1	4.01 ± 0.2	27.0 ± 0.4
4, 5	10.9 ± 0.3	1.06 ± 0.5	32.9 ± 1.2

[a] Standard state 1 atm and 298 K. The error limits given correspond to standard deviation from least-squares plots. The absolute error is probably considerably larger. It is estimated to be ~1 kcal/mol for the enthalpy and free energy and ~4 eu for the entropy changes.

distributed over a large part of the molecule while the negative charge is concentrated in a small, accessible end of the molecule. This typical aprotic distribution is shown in Figure 9 for acetonitrile. Considering such a distribution, qualitatively, it becomes immediately clear that the binding energies to negative ions should be weaker than those to positive ions. The calculations described below give a quantitative confirmation of this notion.

The total stabilization energy E_t between a single solvent molecule and an ion was calculated[11] in the usual manner as a sum of the four terms shown in eq 1.

$$E_t = E_{dip} + E_{ind} + E_{dis} + E_{rep} \qquad (1)$$

The ion-permanent dipole energy was obtained from eq 2,

$$E_{\mathrm{dip}} = 334 \sum_i Q_i/R_i \qquad (2)$$

where Q_i is the point charge on the ith atom of the solvent molecule, R_i is the distance between the center of the ion and the ith atom, and 334 is a numerical factor giving E_{dip} in kilocalories per mole for R in ångströms and Q in atomic units. The point charges Q used for water and acetonitrile are shown in Figure 9. These values were obtained on the basis of the net Mulliken electron populations calculated by Pople.[13] However, these electron populations did not predict the correct dipole moments. Therefore they were multiplied by an adjustment factor (.63 for water and 1.91 for acetonitrile)[27] whose value was selected to give point charges which lead to the correct dipole moments, 1.81 D for water and 3.97 D for acetonitrile.

The induced dipole interaction was calculated from eq 3

$$E_{\mathrm{ind}} = -167 \sum (\alpha_l \cos^2\theta + \alpha_t \sin^2\theta)(R_{ij})^{-4} \qquad (3)$$

where ij represents the bond between atoms i and j of the ligand, θ is the angle of this bond with respect to the ion, R_{ij} is the distance between the ion and the polarizability centroid of the bond, and α_l and α_t are the lateral and transverse bond polarizabilities. Details on the choice of bond polarizabilities α_l and α_t a the location of the polarizability centroids are given elsewhere.[11]

The dispersion energy was evaluated by the modified[14] London equation

$$E_{\mathrm{dis}} = -\tfrac{3}{2}\frac{\alpha_l\alpha_S}{R_{lS}{}^6}\frac{I_lI_S}{I_l + I_S} \qquad (4)$$

α_l and α_S are the polarizabilities of the ion and the solvent molecule, I's are the corresponding ionization potentials. Following the suggestion by Pitzer[15] the ionization potentials were multiplied by a correction factor. The correction term J = 2.5 previously used by Eliezer and Krindel[16] for calculations involving alkali ions and water was used also in the present work for water and acetonitrile. Since the London equation is anisotropic a correction was made[11] to take into account the directional distribution of the electron charge density in acetonitrile and water.

The repulsion energy was evaluated by assuming an exponential dependence on distance (see eq 5) since this form, rather than the Lennard-Jones R^{-12} potential, was found more reliable for the ion–neutral distances involved in the ion–solvent molecule complexes. The exponential form was used recently with good success in two similar calculations.[16,18] The constants C_{1j} and a_{1j} in eq 5 are characteristic of the ion and the atoms j of the solvent molecule.

$$E_{\mathrm{rep}} = \sum_j C_{1j}e^{-a_{1j}r_{1j}} \qquad (5)$$

For positive ions interacting with water or acetonitrile only the ion–oxygen atom repulsion was taken into account. For the negative ion–acetonitrile calculations, the bond axis of the acetonitrile molecule was assumed to be passing through the center of the negative ion such that the ion made symmetric contact with the three hydrogens. Since that orientation also brings the methyl carbon atom close to the negative ion the repulsions of the three hydrogens and the carbon atom were taken into account. The constants C_{1j} and a_{1j} were determined from data of Amdur,[17] following the procedure of Eliezer and Krindel.[16] The actual values used and details of the procedure used are given in Davidson's thesis.[11]

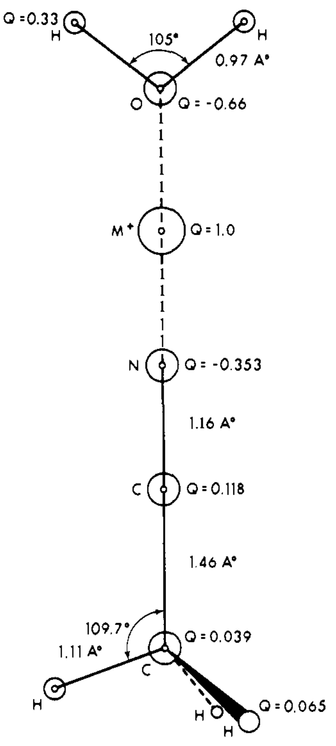

Figure 9. Bond distances, angles, and point charge distribution for water and acetonitrile. Q in units of electron charge.[27]

Table II. Calculated Electrostatic Potential Energies[a] for the Reactions $M^+ + H_2O = M^+(H_2O)$, $M^+ + CH_3CN = M^+(CH_3CN)$, and $X^- + CH_3CN = X^-(CH_3CN)$[17]

	R	$-E_{\mathrm{dip}}$	$-E_{\mathrm{ind}}$	$-E_{\mathrm{dis}}$	E_{rep}	$-E_t$	$-\Delta H_{\mathrm{exptl}}$
				$M^+(H_2O)$			
Na^+	2.17[d]	24.73	6.39	1.40	8.51	24.00	24.0[b]
K^+	2.59[d]	17.79	3.36	1.72	5.95	16.92	17.9[b] (16.9)[c]
Rb^+	2.75[d]	15.89	2.70	2.39	5.90	15.08	15.9[b]
Cs^+	2.84[d]	14.95	2.40	2.96	5.98	14.46	13.7[b]
				$M^+(CH_3CN)$			
							$-\Delta H$
Na^+	2.12[f]	28.39	11.92	1.84	10.82	31.33	(31)[e]
K^+	2.57[f]	21.31	6.56	2.46	7.90	22.43	24.4[e]
Rb^+	2.74[f]	19.33	5.35	3.50	8.07	20.11	20.7[e]
Cs^+	2.84[f]	18.30	4.77	4.28	7.98	19.38	19.2[e]
				$X^-(CH_3CN)$			
F^-	2.55[g]	19.06	6.17	0.88	5.52	20.59	16.0[h]
Cl^-	3.10[g]	14.51	3.21	1.06	3.86	14.93	13.4[h]
Br^-	3.37[g]	12.84	2.43	0.93	3.36	12.84	12.9[h]
I^-	3.49[g]	12.24	2.18	1.05	3.29	12.18	11.9[h]

[a] In kcal/mol. [b] From ref 6. [c] From ref 9. [d] Distance from M^+ to oxygen atom in Å. [e] Present work. [f] Distance from M^+ to N atom in Å. [g] Distance from X^- to methyl carbon. [h] From ref 8.

The total energy E_t at the equilibrium distance was obtained by minimization of the energy. These E_t and the corresponding distances are shown in Table II. The experimentally measured $\Delta H_{0,1}$ values from Table I are also included for comparison. The E_t are not directly comparable with $\Delta H_{0,1}$. The major differences are the zero point energies for three new vibrations in the ion–molecule complex. These amount to about 2 kcal/mol[12] such that $E_t + 2 \approx \Delta H_{0,1}$ (kcal/mol). Since the purpose of the present calculation is to obtain qualitative insights this small theoretically expected difference between E_t and $\Delta H_{0,1}$ will not be considered further.

Good agreement between E_t and $\Delta H_{0,1}$ is found for all the cases considered, i.e., $M^+(H_2O)$, $M^+(CH_3CN)$, and $X^-(CH_3CN)$. It is interesting to note that $E_{\mathrm{ind}} + E_{\mathrm{dis}}$ nearly cancel E_{rep} such that $E_t \approx E_{\mathrm{dip}}$. This very useful qualitative

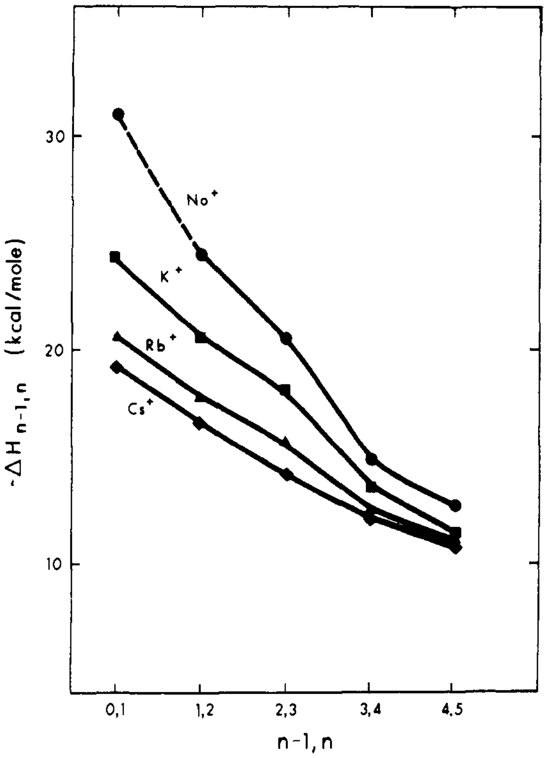

Figure 10. Enthalpies for the clustering reactions $M^+(CH_3CN)_{n-1} + CH_3CN = M^+(CH_3CN)_n$; M = Na, K, Rb, Cs. The dashed line indicates an extrapolated value.

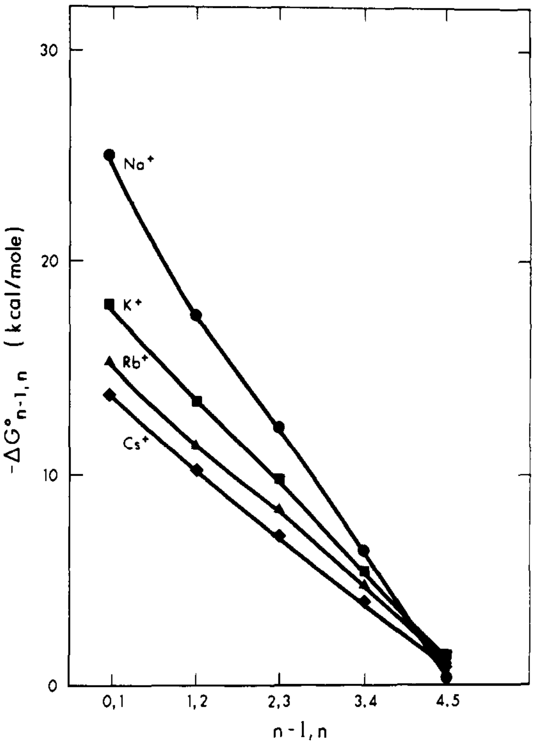

Figure 11. Standard free energies at 298 K for the clustering reactions $M^+(CH_3CN)_{n-1} + CH_3CN = M^+(CH_3CN)$. $\Delta G^\circ_{0,1}$ for Na^+ obtained by extrapolation.

simplification shows that the ion–permanent dipole interactions alone are sufficient for characterization of the binding energies. Thus the present calculations confirm the assumption that the weak bonding of acetonitrile to negative ions is a consequence of the diffuse charge distribution of the permanent dipole in this aprotic solvent. It is important to realize that very much the same effect should operate in DMSO where the positive charge is spread over the methyl groups and the sulfur atom, while the negative charge is concentrated on the accessible (to the ion) oxygen atom. Thus the unequal solvation of positive and negative ions by "aprotic" solvents is only indirectly due to their aprotic character, directly decisive is the nature of the charge distribution constituting the dipole.

The binding energy of acetonitrile to the alkali ions is seen to be considerably stronger than that of water. This undoubtedly reflects the much higher dipole moment of acetonitrile. Toward positive ions this high dipole moment can be fully effective since the negative pole is on the relatively small and accessible nitrogen atom. Other electrostatic calculations[16,18] and some SCF–LCAO–MO ab initio calculations[12,19] have been done for the alkali hydrates. These literature values are all close to the experimental results and thus also to the present electrostatic calculations. They have not been included in Table **II**, since the present work deals primarily with acetonitrile. The ab initio calculations have shown that there is practically no electron transfer from the molecules to the ion, i.e., that the bonding is almost exclusively "electrostatic". Other interesting insights can also be found in these treatments.[20,21]

(c) **Interactions with More than One Solvent Molecule.** The change of $\Delta H^\circ_{n-1,n}$ and $\Delta G^\circ_{n-1,n}$ with n is shown in Figures 10 and 11. These figures are based on the experimental results from Table I. Both ΔH and ΔG are seen to decrease rapidly with n. The decrease observed with the smaller ions is faster than that for the larger ones. For sodium the decrease is so fast that a crossover occurs for $n = 5$; i.e., the $-\Delta G^\circ_{4,5}(Na^+)$ is lower than $-\Delta G^\circ_{4,5}$ for the other ions. The large decrease of stability for the addition of the fifth molecule can be very directly observed in the Na^+–acetonitrile van't Hoff plots (Figure 5), where the very big gap between the 3,4 and 4,5 lines is very noticeable. Similar but smaller gaps occur also in the van't Hoff plots of the other alkali ions (Figures 6–8). The smallest gap is found for the largest ion Cs^+. This suggests that the relatively large weakening of interaction with the fifth molecule is due to crowding of the molecules in the first "shell". The fifth molecule going into the first "shell" imposes constraints on the freedom of all molecules. This is reflected in the particularly unfavorable entropy change. For example, for sodium $\Delta S^\circ_{4,5}(Na^+) = -41.2$ eu is much larger than $\Delta S^\circ_{3,4}(Na^+) = -27.9$ eu. The five molecules in the first "shell" need not be imagined to all have exactly equal distance to the ion. Differencein ion–molecule distances were predicted in the recent calculations of alkali ion–water clusters of Kistenmacher et al.[20] We expect acetonitrile molecules to have a particularly strong tendency to crowd near the ion, i.e., in the first "shell", since removal of an acetonitrile molecule to the second "shell" should be particularly unfavorable compared with water. The increase of the ion–molecule distance in the second shell is larger since acetonitrile is a long molecule. Furthermore, because of the aprotic nature of acetonitrile, bonding of the outer shell molecule to the inner shell molecules is also weak. It is interesting in this connection to compare the experimental results for the acetonitrile (A) interactions with those for water (W) molecules. A useful and very direct comparison can be obtained by an examination of the superimposed van't Hoff plots for Na^+ shown in Figure 12. Looking at Figure 12 one notices first the already discussed stronger interactions with acetonitrile on the addition of the first molecule. This effect carries over to subsequent additions of solvent molecules at low n. However, the decrease of $K_{n-1,n}$ with n is much more rapid with acetonitrile than water. This leads to $K_{3,4}(A)$ and $K_{3,4}(W)$ becoming nearly equal. Past $K_{3,4}$ the water interactions become stronger, i.e., $K_{n-1,n}(W)$ becomes bigger than $K_{n-1,n}(A)$. The gap between $K_{3,4}(A)$ and $K_{4,5}(A)$ is so large that both $K_{4,5}(W)$ and $K_{5,6}(W)$ are much higher than $K_{4,5}(A)$.

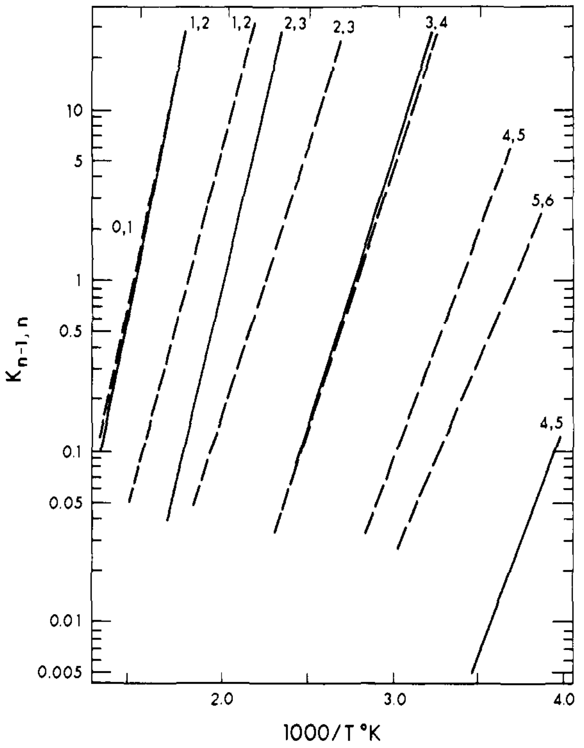

Figure 12. van t Hoff plots for the gas phase solvation of the sodium ion by acetonitrile (solid lines) and water[6] (dashed lines).

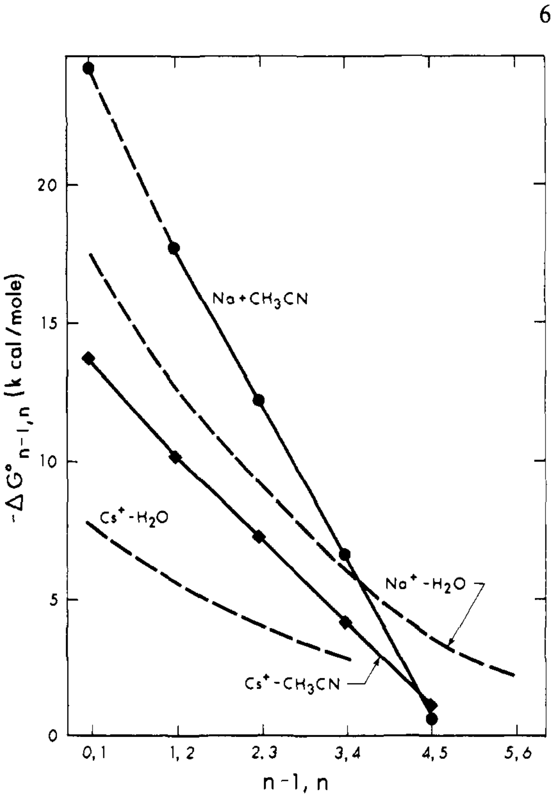

Figure 13. A comparison of the free energy changes $\Delta G°_{n-1,n}$ for gas phase solvation of the small Na^+ and the large Cs^+ by water and acetonitrile. Standard state 1 atm, 298 K.

A comparison of the free energy changes $\Delta G°_{n-1,n}$ (at room temperature) for water and acetonitrile reacting with the small Na^+ and the large Cs^+ is shown in Figure 13. This figure also shows very clearly the much faster decrease of the acetonitrile interactions with increasing n. For Na^+ the water interactions become more favorable at (3, 4) while for Cs^+ the crossover occurs at somewhat higher n. It is most likely that the water interactions remain more favorable for all higher n. It is not 'possible on the basis of the present limited data (Figure 13) to predict whether total single ion free energies of solvation for the alkali ions will be higher in water or in acetonitrile. However, as will be shown in the next section a comparison between available $(n - 1, n)$ data for the alkali and halide ions in acetonitrile may be used to predict plausible single ion free energies of solvation in acetonitrile.

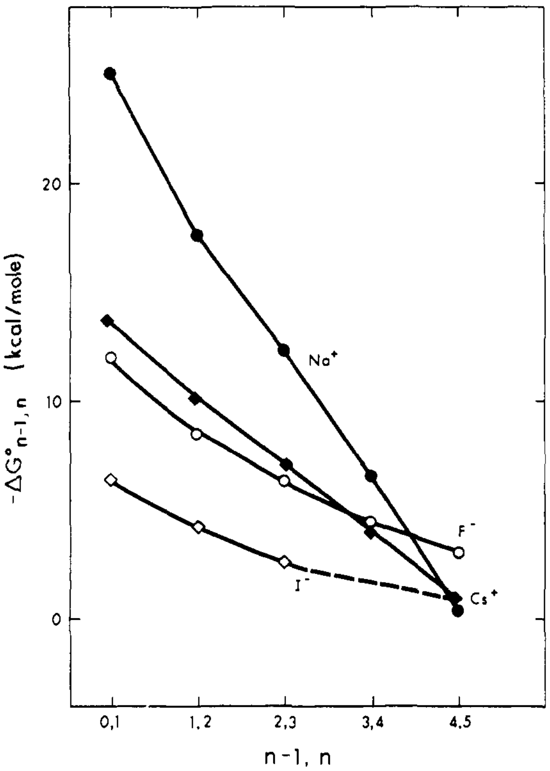

Figure 14. A comparison of the free energy changes $\Delta G°_{n-1,n}$ for positive and negative ions and acetonitrile. Standard state 1 atm, 298 K.

(d) Comparison of the Results for the Alkali Ions and Halide Ions and Acetonitrile and Relationship with Total Single Ion Free Energies of Solvation. The free energy changes $\Delta G°_{n-1,n}$ for acetonitrile interacting with the small ions of similar size Na^+ and F^- and the large ions Cs^+ and I^- are shown in Figure 14. The initial much stronger interaction at low n with positive ions was discussed and explained in section (b). As n is increased the difference between the positive and negative ion decreases, a result that is expected. Surprisingly a crossover is indicated by the data both for the small and large ions. Thus the (4, 5) interaction is stronger for F^- than for Na^+ even though the isoelectronic F^- has the larger radius, since its nuclear charge is two units lower. Since acetonitrile presumably interacts via its three H atoms with the negative ion (see section (b)), crowding should occur sooner for the negative ions than positive ions. This means that the crossover cannot be explained on the basis of crowding of the first shell. Since with increase of n the average ion-molecule distance increases, a more rapid decrease of the ion-molecule polarizability interaction can be expected for positive ions since for these ions the high polarizability -C≡N end of the molecule is closest to the ion. However, while the decrease of this interaction will be more rapid for positive ions that effect need not lead to crossover. We conclude that the crossover, if real, is of a temporary nature, i.e., it involves some specific favorable structures at $n \approx 5$ or 6 which occur for negative ion. However, we believe that this reversal holds only for a narrow interval of n. For high n the interactions should become normal, i.e., identical for positive and negative ions of the same radius.

An attempt can be made to use the present experimental data for an estimate of the total free energies of solvation of

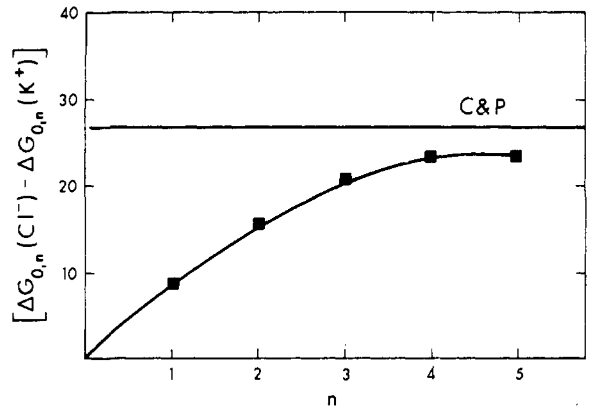

Figure 15. Plot of $D_n = \Delta G^\circ{}_{0,n}(\mathrm{Cl}^-) - \Delta G^\circ{}_{0,n}(\mathrm{K}^+)$ vs. n, the number of acetonitrile molecules on the ion. Horizontal straight line corresponds to $\Delta G^\circ{}_s(\mathrm{Cl}^-) - \Delta G^\circ{}_s(\mathrm{K}^+)$, the total single ion free energies of solvation in acetonitrile obtained by Case and Parsons.[21] Values in kcal/mol, 278 K.

single ions in acetonitrile. The total single ion free energies of solvation can be related to the gas phase results by eq 6 where $\Delta G^\circ{}_{0,n} = \Delta G_{0,1} + \Delta G_{1,2} + \ldots \Delta G_{n-1,n}$ and D_n is just an abbreviation for the difference.

$$\Delta G^\circ{}_{0,n}(\mathrm{X}^-) - \Delta G^\circ{}_{0,n}(\mathrm{M}^+) = D_n \qquad (6)$$

Obviously D_n for very large n should be equal to the difference of the total single ion free energies of solvation $\Delta G^\circ{}_s$, i.e., eq 7 should be valid for large n.

$$D_n = \Delta G^\circ{}_s(\mathrm{X}^-) - \Delta G^\circ{}_s(\mathrm{M}^+) \qquad (7)$$

Equation 7 can be combined with eq 8, which expresses the free energy of solvation of the ion pair $\mathrm{M^+X^-}$, to give eq 9.

$$\Delta G^\circ{}_s(\mathrm{M}^+,\mathrm{X}^-) = \Delta G^\circ{}_s(\mathrm{M}^+) + \Delta G^\circ{}_s(\mathrm{X}^-) \qquad (8)$$

$$2\Delta G^\circ{}_s(\mathrm{X}^-) = D_n + \Delta G^\circ{}_s(\mathrm{M^+X^-}) \qquad (9)$$

Thus, if experimental data for sufficiently high n were available, the single ion solvation energies could be determined from (9) since experimental $\Delta G^\circ{}_s(\mathrm{M}^+,\mathrm{X}^-)$ have been determined for the alkali halides in acetonitrile.

Shown in Figure 15 is the difference D_n for the isoelectronic pair Cl^-, K^+. Also shown is the difference of the total single ion free energies of solvation in acetonitrile obtained from the data of Case and Parsons.[21] These acetonitrile data[27] were obtained by voltapotential measurements like those of Randles[22] (for water) and are therefore probably the most reliable set. As evident from Figure 15, D_n gradually increases with n and at D_5 (the highest available D_n) comes fairly close to Parsons' result. If the assumption is made that eq 7 is valid for n as low as 5 one can obtain via eq 8 and 9 single ion solvation energies. $\Delta G^\circ{}_s(\mathrm{X}^-)$ and $\Delta G^\circ{}_s(\mathrm{M}^+)$ obtained in such a manner are shown in Table III. The ion pair data $\Delta G^\circ{}_s(\mathrm{M}^+,\mathrm{X}^-)$ required for eq 9 were taken from Padova.[23] The $\Delta G^\circ{}_s(\mathrm{M}^+)$ for a given positive ion can be obtained from $\Delta G^\circ{}_{0,5}(\mathrm{X}^-)$ involving different negative ions. As can be noted (see Table III) these multiple results are quite consistent. For example, the values for Na^+ are 95.2, 96.5, and 96.8 kcal/mol obtained from $\Delta G_{0,5}(\mathrm{X}^-)$ of Cl^-, Br^-, and I^-. A similar situation exists also for the negative ions. The averages of the results in Table III are compared in Table IV with the single ion free energies of solvation available in the literature. Table IV includes also a set of data which were obtained by a procedure which is somewhat different. In order to obtain single ion solvation energies it is necessary to separate $\Delta G^\circ{}_s(\mathrm{M}^+,\mathrm{X}^-)$ for only one ion pair. Then the other ions can be obtained from the remaining $\Delta G^\circ{}_s(\mathrm{M}^+,\mathrm{X}^-)$. The ions K^+ and Cl^- were selected as such a pair and the $\Delta G^\circ{}_{0,5}(\mathrm{K}^+)$ and $\Delta G^\circ{}_{0,5}(\mathrm{Cl}^-)$ were used in conjunction with the Padova[23] $\Delta G^\circ(\mathrm{M}^+,\mathrm{X}^-)$ to obtain the consistent set (footnote b) in Table IV. As can be seen the values from the averages (footnote a) and the consistent set (footnote b) are within 1 kcal/mol.

Table III. Total Alkali Halide Solvation Free Energies in Acetonitrile and Experimental Differences in Free Energies Determined in the Gas Phase

MX	$-\Delta G^\circ{}_s(\mathrm{M^+X^-})$[a]	D_5[b]	$-\Delta G^\circ{}_s(\mathrm{M}^+)$[c]	$-\Delta G^\circ{}_s(\mathrm{X}^-)$[c]
NaCl	154.5	35.8	95.2	59.4
NaBr	153.0	40.1	96.5	56.4
NaI	148.0	45.7	96.8	51.2
KCl	139.0	22.9	81.0	58.0
KBr	137.5	27.2	82.3	55.2
KI	132.5	32.8	82.6	49.9
RbCl	134.5	16.1	75.3	59.2
RbBr	133.0	20.4	76.7	56.3
RbI	128.0	26.0	77.0	51.0
CsCl	125.5	11.0	68.3	57.2
CsBr	124.0	15.3	69.6	54.4
CsI	119.0	20.9	69.9	49.1

[a] Free energy of solvation from gas phase to acetonitrile for M^+ and X^- in kcal/mol, see ref 23. [b] $\Delta G^\circ{}_{0,5}(\mathrm{X}^-) - \Delta G^\circ{}_{0,5}(\mathrm{M}^+)$ in kcal/mol, standard state 1 atm. Values for X^- from ref 8, values for M^+ from the present work. [c] Approximate single ion free energies of solvation from gas phase to acetonitrile in kcal/mol evaluated from eq 8 and 9.

Table IV. Comparison of the Approximate Single Ion Free Energies of Solvation in Acetonitrile Predicted from (8) and (9) with Literature Values

	$-\Delta G^\circ{}_s$, kcal/mol				
	Present work[a,b]		Parsons[c]	Parker[d]	Coetzee[e]
Na^+	96.2[a]	97[b]	98.8	94.9	91.7
K^+	82.0	81	83.0	78.7	76.1
Rb^+	76.3	76.5	78.2	73.9	71.7
Cs^+	69.3	67.5	70.3		64.2
Cl^-	58.5	58	55.7		63.2
Br^-	55.6	56.5	54.2	57.3	60.0
I^-	50.3	51.5	49.5	52.7	55.4

[a] Averages of values from Table III. [b] Values based on $-\Delta G^\circ{}_s(\mathrm{K}^+) = 81$ and $-\Delta G^\circ{}_s(\mathrm{Cl}^-) = 58$ kcal/mol; see Table III. [c] Case and Parsons,[21] voltapotential measurements of Ag^+ in acetonitrile. [d] Parker;[24] $\Delta G_{\mathrm{tr}}(\mathrm{Ph_4As^+}) = \Delta G_{\mathrm{tr}}(\mathrm{Ph_4B^-})$ assumption. Parker gives single ion free energies of transfer ΔG from water to acetonitrile. These were converted into $\Delta G^\circ{}_{\mathrm{solv}}$ acetonitrile by adding them to the single ion free energies of hydration of Randles.[22] [e] Coetzee;[26] polarography and modified Born equation.

The present results (Table IV) are closest to the values of Parsons[21] obtained by voltapotential measurements involving a gas interface. These results should be the most accurate since they do not involve an extra thermodynamic assumption. The data of Parker[24] which utilize the widely used (see also Kolthoff[25]) assumption $\Delta G_{\mathrm{tr}}(\mathrm{Ph_4As^+}) = \Delta G_{\mathrm{tr}}(\mathrm{Ph_4B^-})$ are also not very significantly different from the present results. Coetzee's[26] early results are the farthest off.

Approximate single ion enthalpies of solvation could have been obtained by eq 8 and 9 written for the corresponding ΔH changes. Since the uncertainties in the ΔH determinations are larger and the available $\Delta H_{n-1,n}$ range limited we did not think it worthwhile to evaluate the single ion enthalpies of solvation.

It is indeed surprising that $\Delta G^\circ{}_{0,n}(\mathrm{X}^-) - \Delta G^\circ{}_{0,n}(\mathrm{M}^+) = D_n$ should converge to the single ion solvation difference for values of n as low as $n = 5$. Of course one cannot be certain that this is not an accidental result. It is conceivable but somewhat unlikely that D_n will change, i.e., experience some oscillation at higher n. Unfortunately measurements of $\Delta G°_{n-1,n}$ for high n are difficult because condensation of the solvent vapor occurs at the walls of the reaction chamber. This happens at the point where the vapor pressure of the gas phase cluster $M^+(S)_n$ becomes larger than the vapor pressure of the solvent S (with a flat surface). A new experimental approach is being presently tried in our laboratory which promises to overcome the above difficulty. Controlled adiabatic expansion is used to cool the gas below its dew point, while the walls of the flow system are kept at temperatures above the dew point. If these measurements prove successful, they might provide information not only on the single ion solvation energies but also on the question of the accommodation of a cluster consisting of an ion and several solvent molecules S into a cavity of the (liquid) solvent. Evidently if eq 7 becomes valid already for relatively low n, solvation of the clusters $X^-(S)_n$ and $M^+(S)_n$ (with this n) into the liquid solvent S must release the same amount of energy. This would mean that the solvent structure at the interface of the cavity will be able to change equally well for the accommodation of the positive and negative cluster. If this can occur at low n it would mean that there is considerable structural flexibility in the clusters and the solvent.

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(27) NOTE ADDED IN PROOF. Because of an inadvertent mistake, the adjustment factor by which the net atomic charges of acetonitrile[13] must be multiplied is not 1.91 as given in the text but 1.68. The corrected changes for acetonitrile (see Figure 9) are N −0.311, C 0.035, C(methyl) 0.104 and H 0.057. A recalculation shows that the equilibrium distance between the positive ion and acetonitrile increases by ~0.01 Å and the negative ion and acetonitrile by ~0.02 Å (see Table II). The total binding energies decrease by less than 4%. Since these changes are very small, the conclusions given in the discussion remain unchanged.

Binding Energies and Stabilities of Potassium Ion Complexes from Studies of the Gas Phase Ion Equilibria[1] $K^+ + M = K^+M$

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Abstract: The ΔG, ΔH, and ΔS values for the gas phase reactions $K^+ + M = K^+M$ were determined from the temperature dependence of the corresponding equilibria observed with a mass spectrometer equipped with a special high pressure ion source and a potassium ion thermionic emitter. The compounds M were the nitrogen and oxygen bases: NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, n-propylamine, pyridine, aniline, H_2O, $(CH_3)_2O$, and $(C_2H_5)_2O$. Recent theoretical SCF-MO calculations of K^+OH_2 have shown that the bond is largely of electrostatic nature. Classical electrostatic calculations were performed in the present work for K^+M where $M = OH_2$, NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$. The results were found in good agreement with the experimental determinations. A comparison between the stability of the complexes K^+M and the Bronsted basicities (proton affinities of M) is made. The difference between the stabilities of the K^+ complexes with nitrogen and oxygen bases is very much smaller than the difference between the proton affinities. This is shown to be a consequence of the electrostatic character of the K^+M bonding. The increases of stability with methyl substitution in the ammonia methylamines series is very much smaller for K^+M complexes than for the corresponding H^+M. A brief comparison with the boron complexes $(CH_3)_3BM$, observed in the gas phase, is also made.

A program of studies based on ion-molecule equilibria in the gas phase was initiated in the present laboratory several years ago.[2,3] An important part of this research were studies of alkali ion-solvent molecule equilibria. Data for the alkali ions interacting with water molecules in the equilibria $(n-1, n)$ for $n = 1$ to $n = 6$ or 7 were published earlier.[4]

$$M^+(OH_2)_{n-1} + OH_2 = M^+(OH_2)_n \qquad (n-1, n)$$

Recently a similar study involving the aprotic solvent acetonitrile[5] was also completed. The $\Delta H°_{n-1,n}$ and $\Delta S°_{n-1,n}$ obtained from van't Hoff plots of the equilibrium constants $K_{n-1,n}$ have been of value in giving the strength of the interaction with the first molecule (vis $\Delta H°_{0,1}$ and $\Delta S°_{0,1}$) and the changes of these interactions on successive additions of further molecules. The determination of such successive ion equilibria is generally straightforward, but nevertheless time consuming.