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Competitive Gas-Phase Solvation of Alkali Metal Ions by Water and Methanol

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On the basis of mass spectrometric measurements, the Gibbs energies $\Delta G_{x,y;x-1,y+1}$ for successive ligand exchange equilibria $MW_xA_y^+ + A \rightleftarrows MW_{x-1}A_{y+1}^+ + W$ ($W = H_2O$, $A = CH_3OH$) were determined for M = Li ($n = x + y = 2, 3, 4$), Na ($n = 2, 3, 4$), K ($n = 1, 2, 3$), Rb ($n = 1, 2$), and Cs ($n = 1, 2$). The exchange equilibria were established in a "high"-pressure ion source at 10 Torr of bath gas (N_2) containing water and methanol in the millitorr range and using MA_n^+ ions produced by electrospray. The corresponding entropies, $\Delta S_{x,y;x-1,y+1}$, were obtained from estimates based on theoretical calculations, and these values together with $\Delta G_{x,y;x-1,y+1}$ led to the enthalpies, $\Delta H_{x,y;x-1,y+1}$. Ab initio computations of $\Delta H_{x,y;x-1,y+1}$ for Li^+ and Na^+ systems were found to be in excellent agreement with the experimental values. Replacement of a water molecule with methanol is exothermic for small ion−solvent clusters, but the preferential takeup decreases with the total number of ligands and from Li^+ to Cs^+. This is ascribed to the increase in distance between the metal ion and the ligands, which increases the importance of the larger permanent dipole moment of water, relative to the larger polarizability of methanol.

1. Introduction

Solvation of metal ions is a fundamental field in chemistry, and it has as such drawn much attention. Indeed, the nature and the strength of the interactions of ions with solvent molecules have been studied extensively.[1] Such studies are of profound importance in biochemistry, because metal ions are known to be involved in several biochemical processes,[2] such as the polarization mechanisms of cells, and they may be crucial for the understanding of how proteins discriminate between metal ions even though it is still a puzzle how the Na^+−K^+ pump distinguishes between such closely related cations as Na^+ and K^+.[3]

A considerable amount of studies based on mass spectrometry techniques have been devoted to solvation phenomena of alkali metal ions in the gas phase to obtain the most direct information regarding the ion−solvent interactions.[4,5] Also it should be noticed that comparisons between gas-phase results and the behavior in solution may contribute significantly to the understanding of solvent effects, and that gas-phase studies can be useful to understand the ion behavior inside proteins where the environment may be closer to that observed in the gas phase.

Even though several papers dealing with solvation in organic and mixed solutions have appeared in the literature, little is actually known about the competitive solvation of small cations by water and alcohols.[1a,6] Investigations in the condensed phase of alkali[6a−c] (Li^+ to Rb^+) and magnesium[6d−f] metal ions in a mixture of water and methanol by various techniques seem to indicate a slight tendency for preferential solvation by water of these cations, but it should be emphasized that methanol is not completely excluded from the first solvent sphere.[6d−f] In contrast, gas-phase experiments regarding the competitive solvations of Li^+ and K^+ by water and methanol have shown a preferential solvation by methanol.[7,8] However, to our knowledge, no work has been devoted to study such competitive solvation in the case of the other alkali cations.

The concern of this paper is the competitive gas-phase solvation by water and methanol (which can be considered as a prototypical form of alcohols) of alkali metal cations from Li^+ to Cs^+. We have performed measurements of ion−molecule equilibria with a high-pressure mass spectrometer. Singly charged alkali metal ion complexes were produced from electrospraying alkali chloride or iodide solutions in methanol, and they were then converted to other ligand complexes by ion−molecule reactions in a gas-phase reaction chamber which contained water and methanol vapor in addition to bath gas nitrogen. The applications of electrospray ionization (ESI) to inorganic and organometallic chemistry have expanded rapidly, and now ESI has become a routine technique to generate singly as well as multiply charged metal ion complexes in the gas phase.[9] Ab initio computations have also been performed for the two smallest cations (Li^+ and Na^+) in $MW_xA_y^+$ aggregates (M = metal, W = water, and A = methanol) up to $n = x +$

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$y = 4$ at both the Hartree−Fock and the MP2 levels, using various basis sets.

2. Experimental and Computational Section

a. Apparatus. Measurements were done on a SCIEX triple quadrupole instrument. MA_n^+ were produced by electrospray from 10^{-4} M solutions of MCl or MI in methanol. Typical electrospray conditions: flow rate 2 μL/min; high voltage 4 kV. A detailed description of the ion source and the high-pressure reaction chamber has been given previously.[10] The pressure of nitrogen in the chamber was 10 Torr. A solution containing the weighed ratio of water and methanol was injected with a motor-driven microsyringe into the heated nitrogen gas flow. The partial pressure ratio is obtained from the weighed ratio of water and methanol. The uncertainty of the total pressure, calculated from the sample and nitrogen flow rates, is not of importance as it is not used in evaluation of the thermodynamical data.

It has earlier been shown that when there are trace amounts of water in the nitrogen (2 ppm corresponding to a pressure of ∼1.4 mTorr), hydration equilibria, $MW_{n-1}^+ + W \rightleftarrows MW_n^+$ are established.[4c,d] However, to check that the ligand exchange equilibria were truly achieved, experiments with different constant $P(W)/P(A)$ ratios were performed with a ligand pressure extending in some cases up to 120 mTorr. At high pressures the reaction coefficient should become invariant with pressure and thus equal to the equilibrium constant.

Measurements were performed at different temperatures for some of the equilibria. The upper temperature limit of the reaction chamber was 480 K since higher temperatures interfered with the cryopumping used. This temperature is not sufficiently high for the generation of monoligated complexes of Li^+ and Na^+, since the bond energies for the diligated complexes are high and require higher temperatures for dissociation.[4]

The ion intensity ratios were detected with the last quadrupole Q_3, and the other quadrupoles were used as ion guides (RF only).

b. Determination of Thermochemical Data from Equilibrium Measurements. The reaction coefficient $Q_{x,y;x-1,y+1}$ (eq 2) for the water methanol exchange reaction (eq 1, short-cut notation (M:x,y;$x-1$,$y+1$)) is obtained from the measured ion intensities and the partial pressure ratio, $P(W)/P(A)$. The partial pressure ratio is calculated from the weighed ratio of water and methanol by use of the ideal gas law. If equilibrium is established, the reaction coefficient Q becomes independent of the reactant partial pressures and becomes equal to the equilibrium constant $K_{x,y;x-1,y+1}$. The change in Gibbs energy, $\Delta G_{x,y;x-1,y+1}$, can then be calculated from eq 3.

$$MW_xA_y^+(g) + A(g) \rightleftarrows MW_{x-1}A_{y+1}^+(g) + W(g) \qquad (1)$$

$$Q_{x,y;x-1,y+1} = \frac{I(MW_{x-1}A_{y+1}^+)\ P(W)}{I(MW_xA_y^+)\ P(A)} \qquad (2)$$

$$\Delta G_{x,y;x-1,y+1} = -RT \ln(K_{x,y;x-1,y+1}) \qquad (3)$$

The temperature range of the chamber is not large enough to allow determination of entropies and enthalpies from van't Hoff plots. However, the entropy change, $\Delta S_{x,y;x-1,y+1}$, for an exchange reaction involving similar ligands can be estimated. It consists of several terms. The intermediate complex $MW_xA_y^+\cdot A$ can lose either water or methanol; there are x ways to get $MW_{x-1}A_y^+ + W$ and $y + 1$ ways to get $MW_xA_y^+ + A$. When x is different from $y + 1$, the number of different pathways results in a nonzero entropy change for the exchange reaction as given by eq 4. We denote this entropy contribution as the

$$\Delta S_{x,y;x-1,y+1\cdot\mathrm{asym}} = R \ln\left(\frac{x}{y+1}\right) \qquad (4)$$

asymmetry term: it is positive for $x > y + 1$, zero for $x = y + 1$, and negative for $x < y + 1$. Translational, vibrational, and rotational entropy changes have also to be included to obtain the total entropy change (eq 5). The translational entropy change

$$\Delta S_{x,y;x-1,y+1} = \Delta S_{x,y;x-1,y+1.\mathrm{asym}} + \Delta S_{x,y;x-1,y+1\cdot\mathrm{trans}} + \Delta S_{x,y;x-1,y+1.\mathrm{rot}} + \Delta S_{x,y;x-1,y+1.\mathrm{vib}} \qquad (5)$$

is readily evaluated by means of the Sackur Tetrode equation (eq 6). m is the molecular weight. The rotational $\Delta S_{x,y;x-1,y+1\cdot\mathrm{rot}}$

$$\Delta S_{x,y;x-1,y+1.\mathrm{trans}} = \frac{3}{2} R \ln\left(\frac{m(MW_{x-1}A_{y+1})\ m(W)}{m(MW_xA_y)\ m(A)}\right) \qquad (6)$$

and vibrational $\Delta S_{x,y;x-1,y+1\cdot\mathrm{vib}}$ entropy changes are estimated on the basis of ab initio calculations of the rotational constants and vibrational frequencies for the Li^+ and Na^+ systems. In the Results and Discussion, it is shown that the rotational and vibrational entropy changes are almost of the same magnitude but opposite in sign so that they cancel each other. Hence, the total entropy change can be calculated to a good approximation just by considering the $\Delta S_{x,y;x-1,y+1\cdot\mathrm{asym}}$ and $\Delta S_{x,y;x-1,y+1.\mathrm{trans}}$ contributions.

The Gibbs energy change combined with the entropy change leads to the enthalpy change, $\Delta H_{x,y;x-1,y+1}$, using the classical thermodynamic relation.

c. Theoretical Details. Ab initio computations were carried out using the GAUSSIAN-94 system of programs.[11] For LiW_x^+ and NaW_x^+ ($n = 2, 3, 4$), the starting structures correspond to the most stable ones reported by Glendening and Feller[19b] for M = Li and Hashimoto and Morokuma[12] for M = Na. For $n = 4$ and M = Na, the study of Glendenning and Feller[19b] suggests that two structures are almost isoenergetic: the socalled "4 + 0" structure (which corresponds to a tetrahedral arrangement of four water molecules around the cationic center, a structure which was also considered in the study of Hashimoto and Morokuma), and the "3 + 1" one (where three molecules are directly bonded to the cationic center and the fourth one is hydrogen bonded to two of those molecules). However, when considering the binding enthalpies obtained by the latter authors, the "4 + 0" structure is predicted to be of lower energy by 0.5−2.4 kcal mol^{-1}, depending on the level of theory. Hence, only the "4 + 0" structure for NaW_4^+ was considered.

$MW_xA_y^+$ initial structures were obtained by substituting a water hydrogen by a methyl group on the MW_{x+1}^+ structures. All possible substitutions were investigated at the HF/6-31+G(d) level for $MW_xA_y^+$ structures for both M = Li and M = Na, and the harmonic vibrational frequencies of the most stable structures were obtained at this level of theory (up to $x + y = 3$ for Li and $x + y = 2$ for Na).

The geometries of the most stable structures so-obtained were then reoptimized at the HF/6-31+G(d,p) level, and their binding energies (BEs) refined at the MP2/6-31+G(2d,2p) level (up to $x + y = 4$ and $x < 3$ for Li^+ complexes and $x < 2$ for Na^+ complexes). To estimate the uncertainty due to the levels of theory chosen, computations were also performed on small $MW_xA_y^+$ structures (up to $x + y = 2$) at both the MP2/6-311+G(3df,2p) and MP4(sdtq)/6-31+G(2d,2p) levels (the results obtained at the latter levels of theory will however not be presented in detail in the present paper).

The enthalpy changes corresponding to the substitution reactions of a water molecule by a methanol one were computed

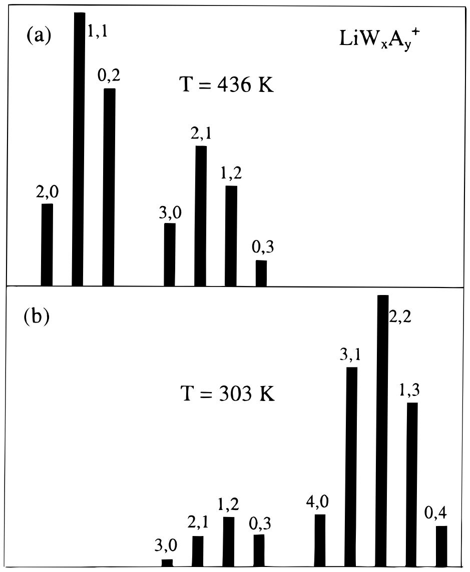

Figure 1. $Li(H_2O)_x(CH_3OH)_y^+$ intensity distributions obtained when methanol complexes of Li^+ are supplied to the reaction chamber which contains H_2O and MeOH at a constant partial pressure ratio (5.6). x,y: $Li(H_2O)_x(CH_3OH)_y^+$. Temperature of the reaction chamber: 436 K (a) and 303 K (b).

from the $\Delta E_{x,y;x-1,y+1}$ values (corresponding to the difference in the BEs of the $MW_{x-1}A_{y+1}^+$ and $MW_xA_y^+$ clusters) and by accounting for the thermal corrections (at 298 K and 1 atm), estimated using the harmonic approximation with Hartree–Fock frequencies. Those were scaled by the empirical factor 0.90 as recently proposed by Scott and Radom,[13] to account for their overestimation at this level of theory.[14] From our computations, it appears that theoretical $\Delta H_{x,y;x-1,y+1}$ values are very close to the $\Delta E_{x,y;x-1,y+1}$ ones (within less than 0.05 kcal mol^{-1} up to $x + y = 3$ for M = Li and $x + y = 2$ for M = Na). Hence, for the greater clusters, the theoretical $\Delta E_{x,y;x-1,y+1}$ values were assimilated with the $\Delta H_{x,y;x-1,y+1}$ ones. Last, to estimate the uncertainty of our computations, the basis set superposition errors (BSSEs) were estimated up to $x + y = 3$ at the MP2/6-311+G(2d,2p) level using the full counterpoise method (CP).[15]

3. Results and Discussion

a. Experimental Results: Gibbs Energies. The ion intensity distributions for complexes of Li^+ observed at two different temperatures (436 and 303 K) and a water-to-methanol ratio of 5.6 are shown in Figure 1. On the basis of these intensities, the reaction coefficients were calculated. In Figure 2 are shown the four reaction coefficients for the four successive ligand exchange reactions, (Li:4,0;3,1), (Li:3,1;2,2), (Li:2,2;1,3), and (Li:1,3;0,4), at different pressures (P(W) + P(A)) and at different water-to-methanol ratios (5.6 and 13.1). At higher pressures than about 10 mTorr the reaction coefficients become invariant with pressure and the water-to-methanol ratio, and therefore the reactions can be considered at equilibrium. The initial ions entering the reaction chamber are MA_n^+, resulting in higher values of Q at low pressures. However, lower values of Q than the equilibrium constant K have also been observed. Hence, reliable values can only be extracted at higher pressures than 10 mTorr. For both exchanges K is larger than unity, leading to negative $\Delta G_{x,y;x-1,y+1}$ values. Similar results were obtained for exchange in $LiW_xA_y^+$, $n = x + y = 2, 3$. Also for complexes of Na^+, K^+, and Cs^+ equilibrium was reached at high pressures. However, the intensity distribution of Rb^+ complexes was highly dependent on the water-to-methanol ratio and the total ligand pressure at room temperature, indicating that the exchange reactions are too slow for equilibrium to be established within the residence time in the reaction chamber (approximately 100 μs).[10] At higher temperatures equilibrium was more closely approached. We do not understand the reason for the different behavior of the Rb^+ complexes.

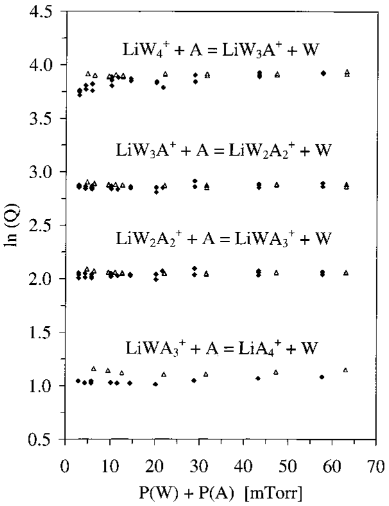

Figure 2. Achievement of the equilibrium plot for $Li(H_2O)_x(CH_3OH)_y^+ + CH_3OH \rightleftarrows Li(H_2O)_{x-1}(CH_3OH)_{y+1}$, $n = x + y = 4$. Temperature of the reaction chamber: 303 K. $P(H_2O)/P(CH_3OH) = 5.6$ (◆), $P(H_2O)/P(CH_3OH) = 13.1$ (△).

From the equilibrium constants the Gibbs energy changes, $\Delta G_{x,y;x-1,y+1}$, were calculated and are summarized in Table 1. The uncertainty is estimated to 0.1 kcal mol^{-1}. Included in the table is the value for the reaction (Li:1,0;0,1) determined by Taft et al. using ion cyclotron resonance mass spectrometry.[16]

b. Entropy Results. As mentioned above, our experimental apparatus does not allow us to evaluate accurate van't Hoff plots, and therefore to derive the entropy changes of the substitution reactions. However, for the equilibria that could be observed over a large temperature interval, only very small changes in the $\Delta G_{x,y;x-1,y+1}$ values with temperature were determined (cf. Table 1). From this observation, the magnitude of the entropy changes for the substitution reaction is therefore estimated to be included within 0–4 cal mol^{-1} K^{-1}.

The different contributions (i.e., translational, rotational, and vibrational) to the exchange reaction entropy changes obtained from computations at the HF/6-31+G(d) level for LiW_xA_y systems (up to $x + y = 3$) are shown in Table 2. In contrast to Woodin and Beauchamp,[17] who concluded that rotational entropy effects have to be considered for this reaction but assumed the vibrational entropy change to be negligible, the results summarized in Table 2 clearly indicate that both these contributions are significant for all of the exchange reactions (Li:x,y;$x-1$,$y+1$). However, as seen from the table, the vibrational entropy change is numerically very close to the rotational one, but opposite in sign so that these two terms cancel each other. A similar result was also found for Na^+ systems. This implies that entropy changes for the substitution reactions are expected to be quantitatively well estimated by considering only the asymmetry and translational terms.

Entropy changes based on these two terms are shown in Table 3 for all of the studied exchange reactions. The order of magnitude is 1–4 cal mol^{-1} K^{-1} in accordance with the crude estimate based on the temperature variation experiments described above. The entropy change is positive for the reactions (Li:3,0;2,1) and (Na:3,0;2,1) and negative for the reactions (Li:1,2;0,3) and (Na:1,1;0,2) as the exoergicity, respectively,

TABLE 1: Experimental $\Delta G_{x,y;x-1,y+1}$ Values (kcal mol^{-1}) for $MW_xA_y^+ + A \rightleftarrows MW_{x-1}A_{y+1}^+ + W$[a]

			Li				Na			K		Rb			Cs	
n	*x*,*y*	*x*−1,*y*+1	302	436	470	373[b]	303[c]	372	432	302	443	337	376	402[d]	304	315
1	1,0	0,1				−3.9					−1.6	−1.2	−1.4	−1.4	−1.2	−1.3
2	2,0	1,1		−3.3	−3.3		−2.1	−2.2	−2.2	−1.6		−1.5			−1.4	
	1,1	0,2		−1.9	−1.9		−1.5	−1.1	−1.0	−0.8		−0.9			−0.7	
3	3,0	2,1	−2.7	−2.9	−3.0		−1.9	−2.1	−2.3	−1.6						
	2,1	1,2	−1.9	−1.9	−1.9		−1.3	−1.3		−1.0						
	1,2	0,3	−1.2	−0.9	−0.9		−0.6	−0.6		−0.3						
4	4,0	3,1	−2.3				−1.8									
	3,1	2,2	−1.7				−1.2									
	2,2	1,3	−1.2				−0.7									
	1,3	0,4	−0.7				−0.3									

[a] Estimated uncertainty 0.1 kcal mol^{-1}. For each metal ion, the chamber temperature is given in Kelvin. [b] From ref 16. [c] Low intensity of $NaW_xA_y^+$, $n = x + y = 2$. [d] Value obtained from measurements of the individual desolvation reactions: $RbW^+ \rightleftarrows Rb^+ + W$ ($\Delta H_{1,0;0,0} = 15.9$ kcal mol^{-1}, $\Delta S_{1,0;0,0} = 21.6$ cal mol^{-1} K^{-1}, 298 K, cf. ref. 4a) and $RbA^+ \rightleftarrows Rb^+ + A$ ($\Delta G_{0,1;0,0} = 8.8$ kcal mol^{-1}, temperature 402 K, present work).

TABLE 2: Translational ($\Delta S_{\mathrm{trans}}$), Asymmetric ($\Delta S_{\mathrm{asym}}$), Rotational ($\Delta S_{\mathrm{rot}}$), and Vibrational ($\Delta S_{\mathrm{vib}}$) Contributions (cal mol^{-1} K^{-1}) to the $\Delta S_{x,y;x-1,y+1}$ Entropy Changes of the Exchange Reactions (Li:x,y;$x-1$,$y+1$) up to $x + y = 3$, Obtained from ab Initio Computations at the HF/6-31+G(d) Level[a]

n	*x*,*y*	*x*−1,*y*+1	$\Delta S_{\mathrm{trans}}$	ΔS_{asym}	ΔS_{rot}	ΔS_{vib}	ΔS
1	1,0	0,1	−0.35	0	−3.28	3.33	−0.28
2	2,0	1,1	−0.87	1.39	−4.38	4.84	0.98
	1,1	0,2	−1.06	−1.39	−5.52	5.65	−2.32
3	3,0	2,1	−1.10	2.20	−5.97	5.95	1.08
	2,1	1,2	−1.20	0	−6.18	6.14	−1.24
	1,2	0,3	−1.27	−2.20	−6.22	6.21	−3.48

[a] The vibrational contributions, ΔS_{vib} values, correspond to unscaled harmonic frequencies (the difference in the ΔS_{vib} is at most 0.2 cal mol^{-1} K^{-1} when considering frequencies scaled by the empirical factor 0.90).

TABLE 3: Computed $\Delta S_{x,y;x-1,y+1}$ Values (cal mol^{-1} K^{-1}) for $MW_xA_y^+ + A \rightleftarrows MW_{x-1}A_{y+1}^+ + W$, as Obtained from Eqs 4 (ΔS_{asym}) and 6 ($\Delta S_{\mathrm{trans}}$)

n	*x*,*y*	*x*−1,*y*+1	Li	Na	K	Rb	Cs
1	1,0	0,1	−0.4	−0.8	−1.1	−1.3	−1.5
2	2,0	1,1	0.5	0.3	0.2	0.0	−0.1
	1,1	0,2	−2.4	−2.6	−2.7	−2.8	−2.9
3	3,0	2,1	1.1	1.0	0.9		
	2,1	1,2	−1.2	−1.3	−1.4		
	1,2	0,3	−3.5	−3.5	−3.6		
4	4,0	3,1	1.5	1.5			
	3,1	2,2	−0.5	−0.6			
	2,2	1,3	−2.2	−2.2			
	1,3	0,4	−4.2	−4.2			

increases and decreases with temperature. Furthermore, for a certain number of ligands *n*, the exoergicity for successive exchanges decreases, which is ascribed to the asymmetry term of the entropy change.

From our ab initio computations, the theoretical $\Delta H_{x,y;x-1,y+1}$ values are predicted to be the same, for $x + y$ constant (cf. sections c and d).[18] This allows us to test the reliability of our calculated $\Delta S_{x,y;x-1,y+1}$ values by comparing the two members of eq 7, where the $\Delta G_{x,y;x-1,y+1}$ and *T* values are taken from

$$\Delta S_{x-1,y+1;x-2,y+2} - \Delta S_{x,y;x-1,y+1} = -(\Delta G_{x-1,y+1;x-2,y+2} - \Delta G_{x,y;x-1,y+1})/T \quad (7)$$

Table 1. From our calculations, a good agreement is obtained for Li$^+$, Na$^+$, and K$^+$ at all temperatures: the difference between calculation and experiment is at most 0.3 cal mol^{-1} K^{-1}. For Rb$^+$, the deviation is high (1 cal mol^{-1} K^{-1}), which is ascribed to the difficulty of obtaining Gibbs energies for exchange reactions of this ion. For Cs$^+$ the calculated entropy difference is overestimated by 0.5 cal mol^{-1} K^{-1}, indicating that the rotational and vibrational terms do not completely cancel each other for heavy metal ions where the center of mass is very close to the metal center. From the above, we estimate the error in the calculated entropy changes to be ±0.5 cal mol^{-1} K^{-1}.

c. Enthalpy Results. The calculated entropy changes and the Gibbs energy changes lead to the enthalpy changes (Table 4). From the uncertainty in the entropy calculation, the uncertainty in the enthalpy changes is estimated to be ±0.2 kcal mol^{-1}. For all equilibria, the exchange of water for methanol is an exothermic reaction, and $\Delta H_{x,y;x-1,y+1}$ is independent of *x* and *y* for $n = x + y$ constant; there is a small difference between $\Delta H_{2,0;1,1}$ and $\Delta H_{1,1;0,2}$ for M = Rb (cf. the above section). Overall, the exothermicity decreases with *n*, from M = Li to Cs.

d. Comparison of Experimental and Theoretical Results for Li$^+$ and Na$^+$ Systems. The calculated binding energies (BEs) corresponding to $MW_xA_y^+$ ($x + y = 1-4$) systems for M = Li and M = Na are summarized in Tables 5 and 6 at the HF/6-31+G(d,p) and MP2/6-31+G(2d,2p) levels of theory. The BSSE estimates at the MP2/6-31+G(2d,2p) level are also shown in those tables. For MW_x^+ systems ($x = 1-4$), all of our results are in good agreement with those previously published by Feller et al.[19] for Li$^+$ systems and Hashimoto and Morokuma[12] for Na$^+$ systems. In particular, for the latter systems, Hashimoto and Morokuma reported the following BEs at the MP2/6-31+G(d)//HF/6-31+G(d) level for $x = 1-4$: 26.2, 49.9, 69.8, and 85.9 kcal mol^{-1}, which are greater than our BEs at the MP2/6-31+G(2d,2p)//HF/6-31+G(d,p) level by about 10% (cf. Table 5). However, it has to be noticed that the BEs of MW_x^+ systems are very sensitive to the basis set extension and that, usually, a more extended basis set results in smaller BEs.[20] From our computations, it also appears that the HF/6-31+G(d,p) level overestimates the BEs for both $LiW_xA_y^+$ and $NaW_xA_y^+$ systems as compared to those obtained at the MP2/6-31+G(2d,2p) level by about 10%, up to $x + y = 4$. However, for $\Delta E_{x,y;x-1,y+1}$ those estimated at the HF/6-31+G(d,p) level are numerically underestimated as compared to MP2/6-31+G(2d,2p) computations for both Li$^+$ and Na$^+$ systems, by about 0.5 kcal mol^{-1}, whatever the aggregate size. Regarding the BSSE values, it appears that even if they represent from 3% to 5% of the aggregate BEs, they are almost constant for $x + y$ constant (cf. Tables 5 and 6), suggesting that they have almost no influence on the estimates of $\Delta E_{x,y;x-1,y+1}$ values. As there is still some controversy about whether the counterpoise method is appropriate for a correct estimate of the BSSE,[21] all theoretical energetic values mentioned in this paper do not include the BSSE correction. It is worth noting that, considering the BSSE values

TABLE 4: Experimental and Theoretical Values of $\Delta H_{x,y;x-1,y+1}$ (kcal mol^{-1}) for $MW_xA_y^+ + A \rightleftarrows MW_{x-1}A_{y+1}^+ + W$[a]

n	x,y	x−1,y+1	Li			Na			K	Rb	Cs
1	1,0	0,1	−4.0[b]	*−3.1*	*−3.4*	−2.6[c]	*−1.5*	*−1.9*	−2.1	−1.8	−1.7
2	2,0	1,1	−3.1	*−2.4*	*−3.0*	−2.1	*−1.2*	*−1.7*	−1.5	−1.5	−1.4
	1,1	0,2	−3.0	*−2.3*	*−2.9*	−2.2	*−1.2*	*−1.7*	−1.6	−1.8	−1.6
3	3,0	2,1	−2.4	*−1.7*	*−2.4*	−1.7	*−0.9*	*−1.4*	−1.3		
	2,1	1,2	−2.4	*−1.6*	*−2.4*	−1.7	*−0.8*	*−1.4*	−1.4		
	1,2	0,3	−2.4	*−1.6*	*−2.5*	−1.8	*−0.8*	*−1.4*	−1.4		
4	4,0	3,1	−1.8	*−1.1*	*−1.9*	−1.4	*−0.6*	*−1.2*			
	3,1	2,2	−1.8	*−1.1*	*−2.0*	−1.4	*−0.6*				
	2,2	1,3	−1.9	*−0.9*		−1.4	*−0.6*				
	1,3	0,4	−2.0	*−1.0*		−1.6	*−0.6*				

[a] The experimental uncertainty is estimated at 0.2 kcal mol^{-1}. For Li and Na, theoretical results at the HF/6-31+G(d,p) and MP2/6-31+G(2d,2p) levels, respectively, are italicized. [b] Enthalpy change calculated from the Gibbs energy change reported in ref 16 and the entropy change from Table 3. [c] Value obtained from measurements of the individual desolvation reactions: $NaW^+ \rightleftarrows Na^+ + W$ ($\Delta H_{1,0;0,0} = 24.0$ kcal mol^{-1}, taken from ref 4a) and $NaA^+ \rightleftarrows Na^+ + A$ ($\Delta H_{0,1;0,0}$ - 26.6 kcal mol^{-1}, taken from ref 24).

TABLE 5: Ab Initio Results at the HF/6-31+G(d,p) and MP2/6-31+G(2d,2p) Levels for Li^+ Systems (hartrees)[a]

	HF/ 6-31+G(d,p)	MP2/ 6-31+G(2d,2p)	BE_{HF}	BE_{MP2}	BSSE
Li^+	−7.235 54	−7.235 52			
W	−76.031 23	−76.262 99			
A	−115.052 40	−115.431 17			
LiW^+	−83.324 55	−83.551 65	36.26	33.35	1.07
LiA^+	−122.350 58	−122.725 29	39.31	36.77	1.05
LiW_2^+	−159.406 65	−159.862 35	68.18	63.28	2.78
$LiWA^+$	−198.431 66	−199.035 24	70.59	66.24	2.74
LiA_2^+	−237.456 54	−238.208 04	72.92	69.14	2.71
LiW_3^+	−235.476 39	−236.162 17	92.34	86.40	4.03
LiW_2A^+	−274.500 25	−275.334 16	94.03	88.79	4.28
$LiWA_2^+$	−313.523 97	−314.506 12	95.63	91.16	3.82
LiA_3^+	−352.547 60	−353.678 25	97.18	93.64	3.81
LiW_4^+	−311.535 069	−312.453 35	109.57	104.08	
LiW_3A^+	−350.557 96	−351.624 62	110.65	106.02	
$LiW_2A_2^+$	−389.580 80	−390.795 93	111.70	107.99	
$LiWA_3^+$	−428.603 38		112.58		
LiA_4^+	−467.626 12		113.57		

[a] BE: complex binding energy (kcal mol^{-1}). BSSE: basis set superposition error estimate at the MP2/6-31+G(2d,2p) level (kcal mol^{-1}).

TABLE 6: Ab Initio Results at the HF/6-31+G(d,p) and MP2/6-31+G(2d,2p) Levels for Na^+ Systems (hartrees)[a]

	HF/ 6-31+G(d,p)	MP2/ 6-31+G(2d,2p)	BE_{HF}	BE_{MP2}	BSSE
Na^+	−161.659 29	−161.658 73			
NaW^+	−237.731 47	−237.959 42	25.70	23.66	0.67
NaA^+	−276.755 04	−277.130 69	27.20	25.60	0.64
NaW_2^+	−313.799 78	−314.255 61	48.96	44.49	1.94
$NaWA^+$	−352.822 87	−353.426 46	50.17	46.17	1.91
NaA_2^+	−391.845 89	−392.597 26	51.33	47.81	1.88
NaW_3^+	−389.861 94	−390.546 21	68.37	61.82	2.47
NaW_2A^+	−428.884 48	−429.716 67	69.23	63.21	2.56
$NaWA_2^+$	−467.906 98	−468.887 02	70.07	64.61	2.43
NaA_3^+	−506.929 44	−508.057 49	70.88	66.05	2.49
NaW_4^+	−465.918 23	−466.832 09	84.10	76.18	
NaW_3A^+	−504.940 28	−506.002 15	84.65	77.36	
$NaW_2A_2^+$	−543.962 33		85.20		
$NaWA_3^+$	−582.984 32		85.72		
NaA_4^+	−622.006 32		86.24		

[a] BE: complex binding energy (kcal mol^{-1}). BSSE: basis set superposition error estimate at the MP2/6-31+G(2d,2p) level (kcal mol^{-1}).

given in Tables 5 and 6, the uncertainty regarding the theoretical $\Delta E_{x,y;x-1,y+1}$ value appears to be 0.2 kcal mol^{-1}, which corresponds to the experimental uncertainty.

Table 4 contains the experimental enthalpy changes together with results of ab initio computations for Li^+ and Na^+ systems. The experimental $\Delta H_{x,y;x-1,y+1}$ values for successive water methanol exchange reactions are equal, which is verified by the theoretical data for both Li^+ and Na^+, regardless of the level of theory. Theoretically, this result is also confirmed at higher levels of theory: our computations at both the MP2/6-311+G-(3df,2p) and MP4(stdq)/6-31+G(2d,2p) levels also show that the enthalpy changes are equal for Li and Na systems, with values included in the range of those obtained at the HF/6-31+G(d,p) and MP2/6-31+G(2d,2p) levels.[22] Furthermore, both experimental and theoretical $\Delta H_{x,y;x-1,y+1}$ values numerically decrease with n.

The change in enthalpy for (Li:1,0;0,1), which is based on the Gibbs energy from Taft et al.,[16] is lower than our values for (Li:2,0;1,1) and (K:1,0;0,1) as expected, but it deviates by 0.6 kcal mol^{-1} from the MP2/6-31+G(2d,2p) value. Threshold collision-induced dissociation experiments of $MW_xA_y^+$ provide another way of determining the bond enthalpy difference between water and methanol. Experimentally, Rodgers and Armentrout have recently reported a difference of 5.5 kcal mol^{-1} at 0 K between bond dissociation enthalpies $D(WLi^+{-}A)$ and $D(ALi^+{-}W)$ in agreement with the difference between the individual enthalpies: $D(Li^+{-}A) - D(Li^+{-}W) = 5.2$ kcal mol^{-1}.[4e,23] This value is considerably higher than the value of Taft et al.[16] and our theoretical values. Unfortunately, no threshold data exist for complexes of Li^+ with more than two ligands, so a direct comparison with equilibrium results is not possible.

Guo et al.[24] have determined the change in enthalpy for successive addition of methanol to NaA_y^+ ($y = 0, 1, 2, 3$). For $y = 0$ (Na:0,0;0,1), a value of −26.6 kcal mol^{-1} was obtained. Combined with the value for (Na:0,0;1,0), −24.0 kcal mol^{-1},[4b] the enthalpy change for the exchange reaction (Na:1,0;0,1) is −2.6 kcal mol^{-1} (included in Table 4). This value fits very well with our data: it is higher than that for (Li:1,0;0,1) but lower than those for (K:1,0;0,1) (−2.1 kcal mol^{-1}) and (Na:2,0;1,1) (−2.1 kcal mol^{-1}) as expected. In addition, the absolute value is reasonable: the experimental increase in the enthalpy change from $n = 2$ to $n = 3$ is 0.4 kcal mol^{-1}, which is the same from $n = 1$ to $n = 2$.

e. K^+ Systems. Exchange of water for methanol in complexes of potassium has previously been investigated by Evans et al. by indirect measurements.[8] They report an enthalpy change of −21.9 kcal mol^{-1} for (K:0,0;0,1), and thus this reaction is 4.0 kcal mol^{-1} more exothermic than the corresponding reaction with water (K:0,0;1,0) (−17.9 kcal mol^{-1}), i.e., (K:1,0;0,1), −4.0 kcal mol^{-1}. Compared with −2.6 kcal mol^{-1} for the reaction (Na:1,0;0,1), −4.0 kcal mol^{-1} seems far too low. The value we obtain for (K:1,0;0,1) is −2.1 kcal mol^{-1} (Table 4), which is higher than that for (Na:1,0;0,1). Furthermore, in contrast to our work, the enthalpy changes for successive exchange

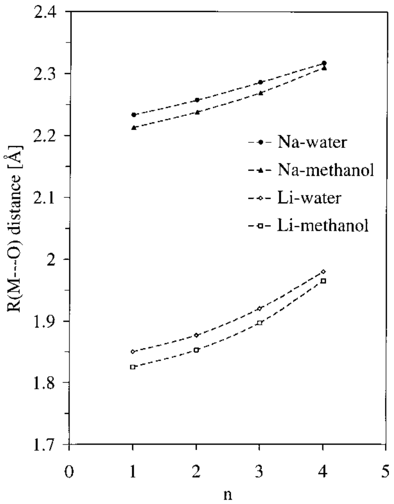

Figure 3. R(M$\cdots$O) distances (Å) for Li^+ and Na^+ systems from ab initio computations at the HF/6-31+G(d,p) level.

reactions vary considerably; the following values are reported:[8] (K:2,0;1,1), −3.5; (K:1,1;0,2), −2.4; (K:3,0;2,1), −3.4; (K:2,1;1,2), −0.5; (K:1,2;0,3), −3.3 kcal mol^{-1}. There seems to be no chemical reason for such a large variation, and it is apparently due to experimental uncertainty. They report entropy changes associated with the exchange reactions in the range between 6.3 and 15.0 cal mol^{-1} K^{-1}. These seem to be unreasonably high; cf. the entropy of an association reaction of approximately 23 cal mol^{-1} K^{-1}.[4c] We therefore believe that our values are an improvement on the already existing thermodynamic data on K^+ systems.

f. Preferential Gas-Phase Solvation. The exchange of water for methanol in the investigated complexes is an exothermic reaction. A preference of methanol over water in complexes of Li^+ and K^+ was also observed by Yamashita and Fenn[7] and Evans et al.[8] Kebarle et al.[25] have found that methanol is taken up preferentially in proton clusters of small size but that water is taken up preferentially in larger clusters ($n > 9$). This was explained by the higher polarizability α of methanol relative to water (1.45 (H_2O) and 3.3 (CH_3OH) $Å^3$)[26] and the higher dipole moment μ_D of water relative to methanol (1.85 (H_2O) and 1.70 (CH_3OH) D).[26] The potential energy of the ion−induced dipole interaction decreases with the fourth power of the distance r, whereas the potential energy of the ion−dipole interaction decreases with the square of r (eq 8).[27] q is the charge on the

$$V(r) = -\frac{\alpha q^2}{2r^4} - \frac{q\mu_D}{r^2}\cos(\theta) \qquad (8)$$

ion and θ the angle the dipole makes with the line of centers. Hence, the dipole moment is of importance when the solvent molecule is far away from the ion, while the polarizability is the determining factor at close approach. The distance to the ligands increases from Li^+ to Cs^+ due to the increasing metal ion radius, explaining why the preference for methanol decreases. Similarly, the ligand repulsion increases with the number of ligands, resulting in increased distances between the metal ion and the ligands and hence a decrease in the preference for methanol as observed. This is verified by the ab initio calculations: the R(M$\cdots$O) distances (corresponding to water and methanol oxygen) obtained from our computations at the HF/6-31+G(d,p) level are plotted versus $n = x + y$ in Figure 3. It is seen that R(M$\cdots$O) distances increase from about 1.83 ($n = 1$) to 1.98 ($n = 4$) Å in the case of M = Li and from 2.22 ($n = 1$) to 2.31 ($n = 4$) Å for M = Na. However, water R(M$\cdots$O) distances are greater than methanol ones, by about 0.02 Å, regardless of the value of n and the nature of M (cf. Figure 3).

TABLE 7: Values of $\Delta H_{n,0;0,n}$ (kcal mol^{-1}) for $MW_n^+ + nA \rightleftarrows MA_n^+ + nW$[a]

n	Li	Na	K	Rb	Cs
1	−3.4[b]	−2.6[c]	−2.1	−1.8	−1.7
2	−6.1	−4.3	−3.1	−3.3	−3.0
3	−7.2	−5.2	−4.1		
4	−7.5	−5.8			

[a] Estimated uncertainty 0.2 kcal mol^{-1}. [b] From ab initio computations at the MP2/6-31+G(2d,2p)//HF/6-31+G(d,p) level. [c] Value obtained from measurements of the individual desolvation reactions: $NaW^+ \rightleftarrows Na^+ + W$ ($\Delta H_{1,0;0,0}$ = 24.0 kcal mol^{-1}, taken from ref 4a) and $NaA^+ \rightleftarrows Na^+ + A$ ($\Delta H_{0,1;0,0}$ = 26.6 kcal mol^{-1}, taken from ref 24).

g. Structure of the Solvent Shell. Ab initio calculations performed by Feller et al.[19] have shown that the lowest energy conformation of LiW_4^+ corresponds to a structure in which every water molecule is directly bonded to Li^+ ("4 + 0" structure). For LiW_5^+ a "4 + 1" structure in which four water molecules are coordinated to Li^+ and the remaining water is in the second shell hydrogen bonded to two of the waters in the first shell was found to be more favorable than the "5 + 0" structure in which all five water molecules are directly coordinated to Li^+. Collision-induced dissociation measurements on LiW_x^+, x = 1, 2, ..., 6, by Rodgers and Armentrout, also indicated that the first solvent shell contains a maximum of four water ligands.[4e] In addition, a hydration number of 4 for Li^+ has been determined by X-ray diffraction experiments in aqueous solution.[28]

The enthalpy changes, $\Delta H_{x,y;x-1,y+1}$, for successive water methanol exchange in four-coordinate Li^+ complexes are equal, about −1.9 ± 0.2 kcal mol^{-1} (Table 4), indicating that also in mixed water−methanol complexes, $LiW_xA_y^+$ ($x + y = 4$), and in the methanol complex, LiA_4^+, the first solvent shell contains four molecules (which was the hypothesis used for our theoretical computations), and isomeric structures where a ligand is situated in the second shell are of minor importance.

In the case of NaW_4^+ the "3 + 1" and "4 + 0" structures are close in energy,[19b,c] but the "4 + 0" structure is enthalpically more stable than the "3 + 1" structure. Therefore, the discussion given above for Li^+ systems is transferable to Na^+ systems.

h. Desolvation from Cationized Water and Methanol Clusters and the Approach to the Bulk Limit. Since values of $\Delta H_{x,y;x-1,y+1}$ are known for $(x,y) = (n,0), (n-1,1), ..., (1,n-1)$, the enthalpy for the exchange of n water molecules with n methanol molecules (eq 9) can easily be obtained by summation (eq 10). Such values are shown in Table 7. The

$$MW_n^+(g) + nA(g) \rightleftarrows MA_n^+(g) + nW(g) \qquad (9)$$

$$\Delta H_{n,0;0,n} = \sum_{x,y=n,0}^{1,n-1} \Delta H_{x,y;x-1,y+1} \qquad (x = n - y) \quad (10)$$

exothermicity increases with n, but the increase becomes smaller and smaller; e.g., for M = Li, $\Delta H_{n-1,0;0,n-1} - \Delta H_{n,0;0,n}$ is 3.4 ($n = 1$, calculated), 2.7 ($n = 2$, based on calculation and experiment), 1.1 ($n = 3$), and 0.3 ($n = 4$) kcal mol^{-1}. The difference between $\Delta H_{n-1,0;0,n-1}$ and $\Delta H_{n,0;0,n}$ is equal to the difference in enthalpy between the desolvation reactions 11 and 12, $\Delta H_{n,n-1}(A) - \Delta H_{n,n-1}(W)$ (eq 13). In Figure 4, $\Delta H_{n,n-1}(A) - \Delta H_{n,n-1}(W)$ is plotted as a function of n for the

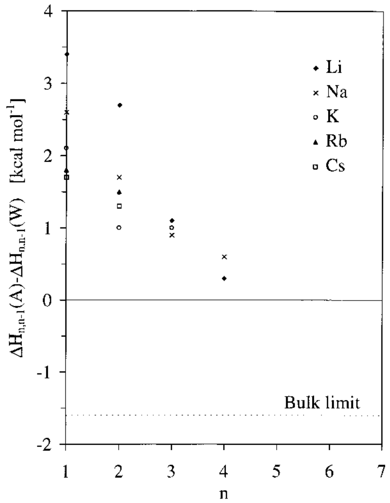

Figure 4. Difference in enthalpy between desolvation reactions of $M(H_2O)_n^+$ and $M(CH_3OH)_n^+$ (eqs 11 and 12) as a function of cluster size. The bulk limit corresponds to the difference in the vaporization enthalpies of water and of methanol.

$$MW_n^+ \rightleftarrows MW_{n-1}^+ + W \qquad \Delta H_{n,n-1}(W) \qquad (11)$$

$$MA_n^+ \rightleftarrows MA_{n-1}^+ + A \qquad \Delta H_{n,n-1}(A) \qquad (12)$$

$$\Delta H_{n,n-1}(A) - \Delta H_{n,n-1}(W) = \Delta H_{n-1,0;0,n-1} - \Delta H_{n,0;0,n} \quad (13)$$

different alkali metal ions. For $n = 1-4$, the difference is positive; thus, the desolvation enthalpy for a methanol cluster is higher than for a water cluster. It is seen from extrapolation that $\Delta H_{n,n-1}(A) - \Delta H_{n,n-1}(W)$ is approximately zero in the region 5−7, which means that in this cluster size region the desolvation enthalpy is almost the same for water and methanol. The dependence on the alkali metal ion diminishes with n as expected. For small clusters ($n = 1, 2$) the ion−solvent interactions are clearly very important. For n larger than approximately 7, $\Delta H_{n,n-1}(A) - \Delta H_{n,n-1}(W)$ is negative, and the desolvation enthalpy for a cationized water cluster is higher than for a cationized methanol cluster. In the limit of n infinity, i.e., an infinitely dilute solution, the metal ion has no influence on the thermodynamics of desolvation, and $\Delta H_{n,n-1}(A) - \Delta H_{n,n-1}(W)$ becomes equal to the difference in enthalpy of vaporization between methanol and water (-1.6 kcal mol^{-1}).[26] The bulk limit is represented by the broken line in the figure.

As mentioned in the Introduction, it seems that in a mixed water methanol solution the first solvation shell is primarily made of water molecules. This contrasts with the gas-phase solvation of bare alkali metal ions at low n, where methanol is preferred for direct coordination to the metal ion. However, in solution the structure of the second solvation shell is of importance. The first solvation shell of Li^+ contains four molecules, most probably in both water and methanol solution, but the number of possible hydrogen bonds to the next shell differs: e.g., $Li(H_2O)_4^+$ can hydrogen bond to eight molecules, whereas the number is only four for $Li(CH_3OH)_4^+$. Hence, water molecules in the first shell permit a more extensive hydrogen bond network between the first and second shells. This assumption is in line with MP2 ab initio computations on dimer molecules, which have shown that the interaction of a water molecule with the methyl group of methanol is about 6 times less strong than a typical hydrogen bond.[29] As the maximum number of water and methanol molecules is four in this work, our results describe the thermodynamics without the implications of a second shell.

4. Conclusion

Thermodynamic values for exchange of water for methanol in alkali metal complexes have been reported. Both experimental and theoretical techniques were needed to obtain reliable results. Changes in Gibbs energy were determined by high-pressure mass spectrometry, and on the basis of simple calculations of the entropy changes, the enthalpy changes were obtained. Ab initio computations on Li^+ and Na^+ systems support this strategy. Therefore, our data complement and, we believe, improve on the existing values determined by other workers.

In this study the complexes contain from one to four ligands, which means that the implications of a second shell do not have to be considered. Clearly, investigations on five-coordinate alkali metal ion complexes or doubly charged complexes which are formed with a higher number of ligands would be valuable to determine the role of a secondary solvation shell.

Additional Information. The *xyz* coordinates of the calculated structures are available on request (e-mail: michel.masella@cea.fr).

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