Bonding Stability and Dehydration Constants for Hydrated Metal Ions[†]

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The bonding of water molecules with univalent metal ions (M^+) has been studied by electrospray ionization mass spectrometry (ESI-MS). Increasing the voltage between the skimmer cones (referred to as the cone voltage) induced the abstraction of water molecules from $M^+(H_2O)_n$ ions, for n equal to 1 or 2. The ions studied belonged to the alkali metals (M = H, Li, Na, K, Rb, and Cs) and to the copper family (M = Cu and Ag). The energies of water binding with the cations studied change in a different manner for alkali metal cations than for the Ag^+, Cu^+, and H^+ ions. A new method has been presented to determine the bonding stability and the dehydration constants for $M^+(H_2O)_n$ clusters.

Introduction

Water in biological systems contains numerous dissolved ions of both negative and positive charge, and gradients in the concentration of these ions play an important role in the passive transport of matter across semipermeable membranes in and out of living cells.[1] So, the study of ion hydration requires special attention.

The interaction of individual ions with individual solvent molecules is fundamental for understanding the solvation of ions. Determination of the detailed structure of bulk hydrogen-bonded systems is quite difficult. In liquid systems, in particular, the molecules and ions are in perpetual motion, because of both thermal excitations and quantum mechanical tunnelling. Most of these effects are substantially reduced in small clusters, which however still provide valuable insights into the structure and properties of the bulk.[1] Gas-phase solvated ions are cluster ions in which the core ion interacts with (is solvated by) one or more neutral molecules and may be of either polarity. Such ion−molecule complexes are governed by many of the same interactions that are at work in ion solvation in solution, and as such, their study offers a unique opportunity to gain insight into ion solvation at the microscopic level. By a judicious comparison of the derived thermochemical values for gas-phase clustering onto a selected ion, it will be possible to gain direct information on solvation energies in the bulk liquid state of the solvent whose clustering was under study.[2] So, studies of ion−solvent interactions in the gas phase constitute a bridge between gas phase and solution. Detailed information on ionic water clusters in the gas phase can be found in the recent review articles by Castleman and Bowen,[2] Niedner-Schatteburg and Bondybey,[1] and Beyer.[3]

The general method used for singly charged ion clusters such as $M^+(H_2O)_n$ is to generate M^+ in the gas phase in which the ligand molecule vapor is present.[4] The formation of $M^+(H_2O)_n$ then proceeds spontaneously by the third-body-dependent ion−solvent molecule association reactions. For the study of such ion clusters, mass spectrometry is an indispensable tool. Many experimental studies of $M^+(H_2O)_n$ clusters using mass spectrometers have been reported in the scientific literature. Here, only examples of such studies are mentioned. Džidić and Kebarle[5] and independently Keesee and Castleman[6] determined the enthalpies and entropies of the alkali-metal ion hydration in the gas phase using a mass spectrometer incorporating a high-pressure ion source. El-Shall et al.[7] used the laser vaporization/ionization high-pressure ion source mass spectrometer to study the hydration of Cu^+. Dalleska et al.[8] obtained the bond dissociation energies of water molecules to the first-row transition metal positive ions (from Ti^+ to Cu^+) by measurements of collision-induced dissociation in a guided ion beam mass spectrometer. Leize et al.[9] measured the relative intensities of the peaks corresponding to different alkali metal ions in the electrospray mass spectrum of aqueous solutions of alkali metal chlorides. They found a linear correlation between the peak intensities and the solvation energies for the alkali metal ions. Berg et al.[10] studied the stability and reactivity of hydrated magnesium, $Mg^+(H_2O)_n$, and hydrated aluminum, $Al^+(H_2O)_n$, cations using a Fourier transform-ion cyclotron resonance mass spectrometer. Recently, Iino et al.[11] reported solvation structures and coordination numbers of the hydrated Cu^+ and Ag^+ ions in the gas phase determined by infrared photodissociation spectroscopy.

Concurrently, theoretical calculations were carried out for ion−water clusters to predict geometrical structures, binding energies, and heats of formation.[12−17]

Herein, $M^+(H_2O)_n$ clusters were investigated for the alkali metals (M = H, Li, Na, K, Rb, and Cs) and metals belonging to the copper family (M = Cu and Ag) by electrospray ionization mass spectrometry (ESI-MS). Since its introduction by Yamashita and Fenn in 1984,[18,19] the ESI-MS method has been widely used in biological research for fast and simultaneous detection of positive and negative ions.

ESI is a soft ionization technique, which means that the fragmentation of the target species is minimal and that the molecular weight of the parent ion(s) may be easily obtained. Fragmentation may be induced in ESI sources by increasing the cone voltage. The cone voltage setting determines the energy with which the ions are accelerated into the analyzer, which increases the energy of ion-neutral species collisions (the neutral species being the bath gas, typically nitrogen). This leads to collision-induced decomposition (CID).[20] In this study, increasing the cone voltage induced the abstraction of water molecules from the $M^+(H_2O)_n$ ions. We present a new method to determine

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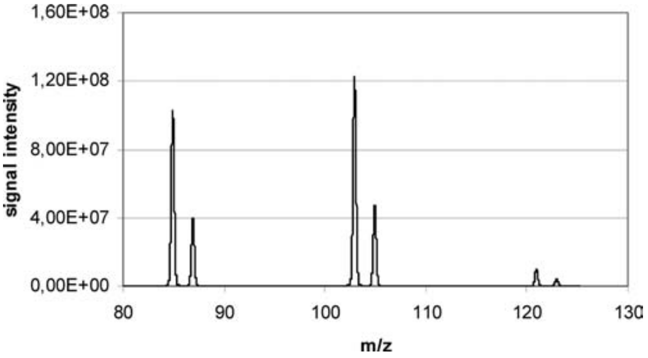

Figure 1. Positive ion mass spectrum of $RbClO_4$ at $V_C = 1$ V. The double peaks assigned to the Rb^+ ($m/z = 85$ and 87), $Rb^+(H_2O)$ ($m/z = 103$ and 105), and $Rb^+(H_2O)_2$ ($m/z = 121$ and 123) ions are due to the Rb isotopes (i.e., ^{85}Rb and ^{87}Rb).

the dehydration constants and the bonding stability of water molecules with M^+ ions. Our results can be useful in the examination of the ion hydration process.

Experimental Section

Materials. The salts used, HCOOH, CuCl, $LiClO_4$, $NaClO_4$, $KClO_4$, $RbClO_4$, $CsClO_4$, and $AgClO_4$ (PPH Polish Chemical Reagents "POCH" Gliwice or Merck, all salts: p.a.), were recrystallized twice or thrice, depending on the purity of the salt from doubly deionized water.

All solutions were prepared with doubly deionized water, whose conductivity was 0.05 $\mu S \cdot cm^{-1}$. The salt concentrations used were $2 \cdot 10^{-3}$ M. The CuCl concentration in the solution was about $6 \cdot 10^{-4}$ M because of the poor solubility of this salt.

Method. Electrospray mass spectra were recorded on a ZQ mass spectrometer (Waters & Micromass, Manchester, UK) equipped with an electrospray interface and probe. The solution studied was infused continuously at a flow rate of 40 $\mu L \cdot min^{-1}$. Nitrogen was used as both the nebulizing (80 $L \cdot min^{-1}$) and the desolvation gas (300 $L \cdot h^{-1}$). The source temperature was 120 °C. The electrospray capillary voltage was set to 3000 V, and the extractor was set to 4 V. The cone voltage (V_C) was varied from (1 to 44) V by increments of 1 V after every scan. Mass spectra were collected from m/z 2 to 180 (m and z are the mass and charge of the ion, respectively), in the positive ion mode, and the data were acquired in the multichannel analysis mode. Ions were scanned over the whole range in 0.5 s. The 10 scans were summed to obtain representative spectra. Mass analysis and isotope modeling were performed with the software provided by Micromass, Inc. The spectrometer was calibrated with a standard mixture of NaI and CsI. Any errors in the calibration were immediately visible by the difference between the theoretical and the measured m/z value. The ESI mass spectra were reproducible with a fluctuation of the peak intensities of ± 5 %. Further analysis was performed on the averaged mass spectra obtained from three consecutive experiments.

The cluster analysis and principal component analysis were performed using the Statistica program.

Results and Discussion

Aqueous solutions of salt of alkali metals, copper, and silver were studied, and their positive ion mass spectra were recorded. An example mass spectrum is shown in Figure 1.

Peak intensities (I) depend on the cone voltage (V_C) in the mass spectrometer. So, the ESI mass spectra of the salts studied were recorded at different values of the cone voltage. In these spectra the mass signals assigned to the M^+ and $M^+(H_2O)_n$ ions, where n is 1 or 2, were considered. Signals for $n = 3$ were observed only for M = H and Ag. Example changes in the peak intensity measured as a function of the cone voltage are presented in Figure 2. The curves are bell-like shaped for the $M^+(H_2O)$ and $M^+(H_2O)_2$ ions.

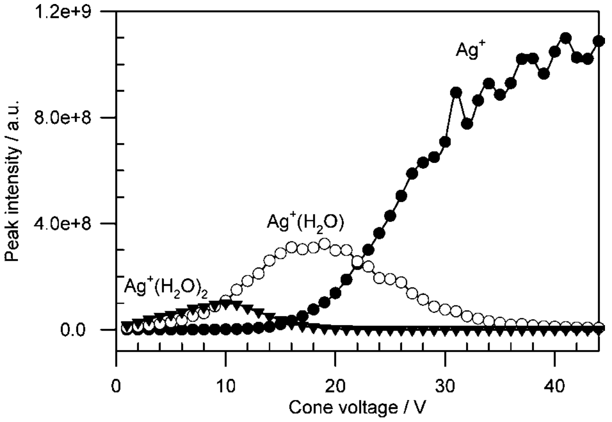

Figure 2. Intensities, I, of the mass peaks assigned to the Ag^+, $Ag^+(H_2O)$, and $Ag^+(H_2O)_2$ ions as a function of the cone voltage, V_C.

The decrease in the peak intensity recorded on the right side of the maximum of I with increasing cone voltage is caused by the disappearance of the complex ion studied, due to the dehydration process:

$$M^+(H_2O)_2 \rightarrow M^+(H_2O) + H_2O \qquad (1)$$

$$M^+(H_2O) \rightarrow M^+ + H_2O \qquad (2)$$

The experimental curves of $I = f(V_C)$ obtained for the salt studied are shown in Figure 3.

The curve shapes and the maximum position in the plots of I versus V_C reflect the physicochemical properties, like the mass, mobility, momentum, and the stability of the ions studied.

Binding Stability of Water Molecules with the M^+ Ions. The ion fragmentation is a chemical reaction reflecting the ion stability. Changes in the intensity of the peak appearing on the right side of the maximum of I with increasing cone voltage (see Figures 3b,c) depend on the stability of the $M^+(H_2O)_n$ ion. The greater the peak intensity decrease, the less stable the complex ion and the easier its fragmentation. The slope (dI/dV_C) of the linear section of this intensity decrease versus increasing cone voltage can be a measure of the $M^+(H_2O)_n$ ion stability. The greater the negative dI/dV_C value, the less stable is the binding of a water molecule with the M^+ ion. To the dI/dV_C values independent of concentration of the complex ions in the gas phase, the graphs of I versus V_C were normalized to the maximum intensity assumed to be 1. The $d(I/I_{max})/dV_C$ values, determined for the $M^+(H_2O)_n$ ions (to the accuracy of ± 0.01), are collected in Table 1.

The binding energy of a water molecule with ion A^+ is higher than that with ion B^+ (where A^+ and B^+ are any metal ions), if the $A^+(H_2O)_n$ ion is more stable than the $B^+(H_2O)_n$ ion. So, as follows from Table 1, the binding stability, that is, the binding energies of water molecules with the alkali metal cations studied, increases in the order $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+ < H^+$. On the other hand, one can see that the metal cations belonging to the copper family are ordered according to increasing binding energies with water molecules as follows: $Ag^+ < Cu^+$. Moreover, for all metal cations studied the $M^+(H_2O)$ ion is more stable

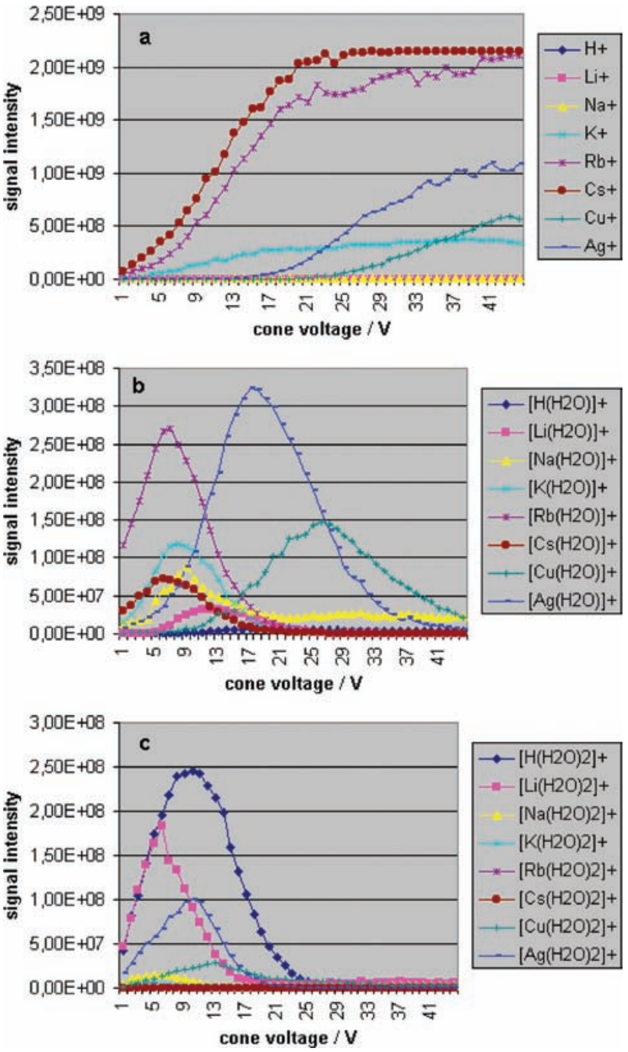

Figure 3. $I = f(V_C)$ curves obtained for (a) M^+, (b) $M^+(H_2O)$, and (c) $M^+(H_2O)_2$ ions. The curve for the H^+ ion has not been obtained because of a too low *m*/*z* value of this ion. From among the multiple signals (assigned to a given ion in the ESI mass spectrum) arising due to the element isotopes, the highest peak (for which the noise contribution is the least) was considered.

Table 1. Values of $d(I/I_{max})/dV_C$ Obtained for the $M^+(H_2O)_n$ Ions and the Dehydration Constants, K_1 and K_2, Determined According to Equations 5 and 6, Respectively

	$d(I/I_{max})/dV_C/V^{-1}$		K_1/a_{H_2O}	K_2/a_{H_2O}
M^+	$M^+(H_2O)_2$	$M^+(H_2O)$	*n*: 2 → 1	*n*: 1 → 0
H	−0.0889	−0.0377	0.0059	
Li	−0.1067	−0.052	0.0346	0.0006
Na	−0.1379	−0.0753	3.859	0.04
K	−0.1601	−0.0902	18.24	0.629
Rb	−0.2049	−0.0983	62.5	1.993
Cs	−0.2133	−0.1072	122.3	5.779
Cu	−0.120	−0.0585	0.751	0.533
Ag	−0.1405	−0.0732	1.081	0.319

than $M^+(H_2O)_2$, which means that the binding energy of the M^+ ion with a single water molecule is higher than one with two water molecules. In conclusion, the binding energies decrease with the increasing ionic radius of the metal and the number of ligands. These trends are consistent with an electrostatic bonding mechanism. Ligands are less strongly bound to larger ions because the ligands cannot approach them too closely. On the other hand, increasing the ligand number reduces the bond energy due to increasing the ligand−ligand repulsion and the delocalization of the central ion charge.

Dehydration Constants. The thermodynamic dehydration constants, *K*, for the reactions described by eqs 1 and 2 are defined as:

$$K_1 = f_{M^+(H_2O)}[M^+(H_2O)]a_{H_2O}/f_{M^+(H_2O)_2}[M^+(H_2O)_2] \tag{3}$$

$$K_2 = f_{M^+}[M^+]a_{H_2O}/f_{M^+(H_2O)}[M^+(H_2O)] \tag{4}$$

where $[M^+(H_2O)]$, $[M^+(H_2O)_2]$, and $[M^+]$ are the molar concentrations of $M^+(H_2O)$, $M^+(H_2O)_2$, and M^+ ions, respectively, $f_{M^+(H_2O)}$, $f_{M^+(H_2O)_2}$, and f_{M^+} are their corresponding activity coefficients, and a_{H_2O} is the water activity. When the solution is very dilute, all of the activity coefficients are equal to unity. The relationship between the peak height, I_X, observed in the mass spectrum at the *m*/*z* value for ion X and the concentration of this ion in solution, [X], can be expressed as $[X] = t_X \cdot I_X$, where t_X is a proportionality constant. This constant is called a transfer coefficient, which depends on relative vaporization and ionization efficiencies of different molecular species.[21] The t_X coefficient is related to all instrumental and chemical effects that decrease or enhance the mass spectrometric signal for ion X. One can expect that the values of the transfer coefficients of M^+, $M^+(H_2O)$, and $M^+(H_2O)_2$ ions are nearly equal for a given metal cation. Under this assumption, eqs 3 and 4 reduce to the following:

$$K_1 = I_{M^+(H_2O)}a_{H_2O}/I_{M^+(H_2O)_2} \tag{5}$$

$$K_2 = I_{M^+}a_{H_2O}/I_{M^+(H_2O)} \tag{6}$$

The K_1 and K_2 values have been determined from the experimental curves of $I = f(V_C)$ shown in Figure 3 after prior smoothing of the curves. Maximum intensity is read off the curve for a given ion and is used as the denominator of constant *K*; V_C, at which this maximum intensity is observed, is noted as $V_{C,Imax}$. The intensity value obtained from the curve for a respective ion at V_C equal to $V_{C,Imax}$ mentioned above was used in the numerator of constant *K*. For example, for the dehydration process of hydrogen ions, the maximum intensity was read off the curve shown in Figure 3c for the $H^+(H_2O)_2$ ions (i.e., the intensity value at $V_{C,Imax} = 10$ V) and was assumed as the denominator of K_1. The intensity value read off the curve presented in Figure 3b for the $H^+(H_2O)$ ions at $V_C = 10$ V was used as the numerator of the K_1 constant. The determined K_1 and K_2 values are collected in Table 1.

As follows from the Table 1 data, the series of alkali metal cations ordered according to increasing K_1 and K_2 values is $H^+ < Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. The metal cations belonging to the copper family are arranged in a separate series. The series presented here of alkali metal cations is the reverse of the series of those cations ordered according to increasing binding stability, that is, the binding energies of water molecules with the cations (see previous section). The constants of K_2 and K_1 are related to the $M^+(H_2O)$ and $M^+(H_2O)_2$ ion stabilities, respectively, because the stabilities of those complex ions are connected with the run of the reactions described by eqs 2 and 1, respectively. For all metal cations studied, K_2 values are smaller than K_1 values, which supports the earlier conclusion that the $M^+(H_2O)$ ion is more stable than $M^+(H_2O)_2$.

Concluding, the higher the binding energy (i.e., the more stable the binding) of the M^+ ion with water molecules is, the worse the dehydration of this ion and, consequently, the smaller *K* values for this ion.

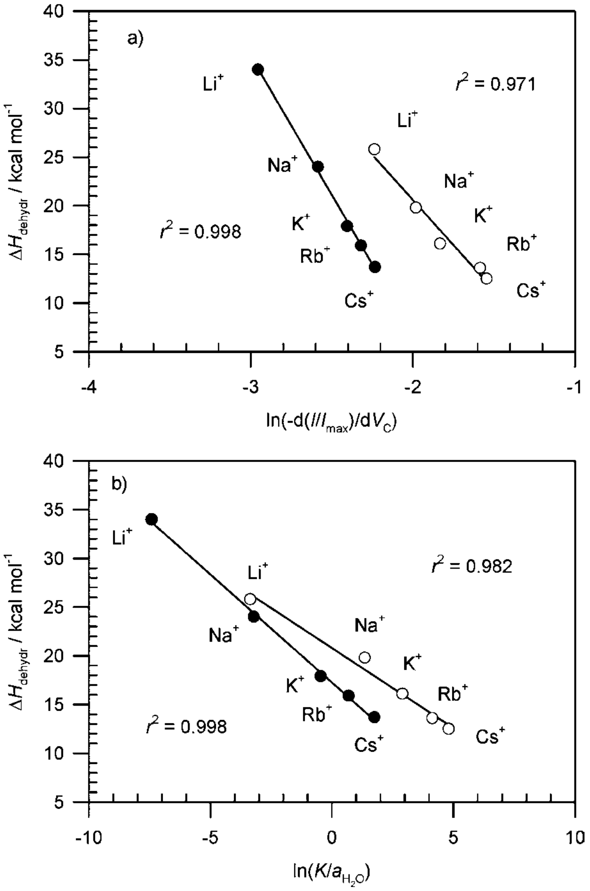

Figure 4. Plots of dehydration enthalpies, ΔH_{dehydr}, versus (a) $\ln(-d(I/I_{max})/dV_C)$ and (b) $\ln(K/a_{H_2O})$ for alkali metal cations. The ΔH_{dehydr} values were taken from ref 5. The ΔH_{dehydr} values have not been given for the H^+, Ag^+, and Cu^+ ions. Open circles correspond to the reaction described by eq 1, in which *n* changes from 2 to 1, while filled circles correspond to the reaction described by eq 2, in which *n* changes from 1 to 0. The values of the coefficients of determination, r^2, are given for the lines.

Correlation of Experimental Results with Literature Data. Linear correlations were found between the values of dehydration enthalpies, ΔH_{dehydr} (determined by Džidić and Kebarle[5]), and the $d(I/I_{max})/dV_C$ and K values (this work) for alkali metal cations (see Figure 4).

We have also correlated our $d(I/I_{max})/dV_C$ and K values with the Marcus values[22] of the standard Gibbs energy (ΔG_{dehydr}) and standard enthalpy (ΔH_{dehydr}) of ion dehydration. As shown in Figure 5, the obtained dependences are linear with the points assigned to Ag^+, Cu^+, and H^+ ions on a different line than the points assigned to the other cations. This means that Ag^+, Cu^+, and H^+ ions form a separate ion group and their properties differ from those of the other cations.

Moreover, a linear correlation has been found between the K values and the width of the first hydration shell, Δr (see Figure 6). The thicker hydration shell of the M^+ cation means the stronger hydration of this ion; consequently, the dehydration process of this ion is more difficult, so the lower K values (i.e., the more negative $\ln K$ values) are observed for this metal cation. As shown in Figure 6, the points assigned to Ag^+ and Cu^+ ions are not on the same line as those assigned to the alkali metal cations.

To verify the correctness of the suggestion that the two groups of the metal ions exist, the affinity of the M^+ ions to water molecules has been studied by cluster analysis (CA) and principal component analysis (PCA). The CA and PCA are the chemometric techniques that have been applied to the mathematical analysis of the intensity distribution and similarity of the $I = f(V_C)$ curves obtained for M^+ complexes with water molecules. Cluster analysis and principal component analysis of the bell-like shape curves are shown in Figure 7. In the CA the Euclidean distance, that is, the geometric distance between

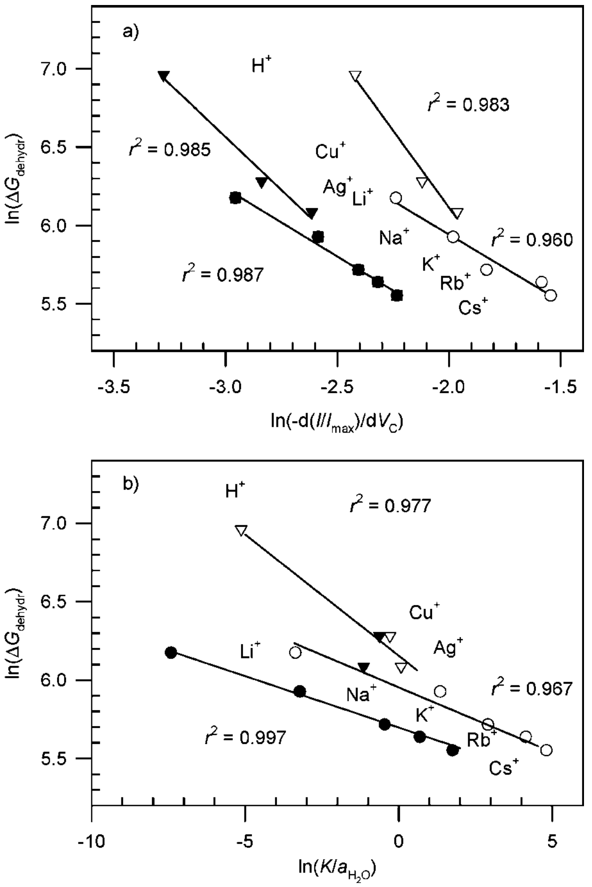

Figure 5. Plots of $\ln(\Delta G_{dehydr})$ versus (a) the $\ln(-d(I/I_{max})/dV_C)$ and (b) the $\ln(K/a_{H_2O})$ values determined for reaction 1 (open symbols) and for reaction 2 (filled symbols). The values of the coefficients of determination, r^2, are given for the lines. The ΔG_{dehydr} values were taken from ref 22. When the ΔH_{dehydr} values were taken from ref 22 instead of the ΔG_{dehydr} values, the obtained plots were very similar to those presented here.

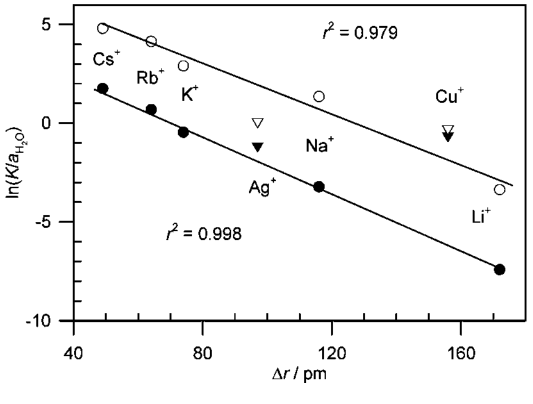

Figure 6. Correlation between the Δr values and the $\ln(K/a_{H_2O})$ values determined for reaction 1 (open symbols) and for reaction 2 (filled symbols). The values of the coefficients of determination, r^2, are given for the lines. The Δr values were taken from ref 23. The Δr value has not been given for the H^+ ion.

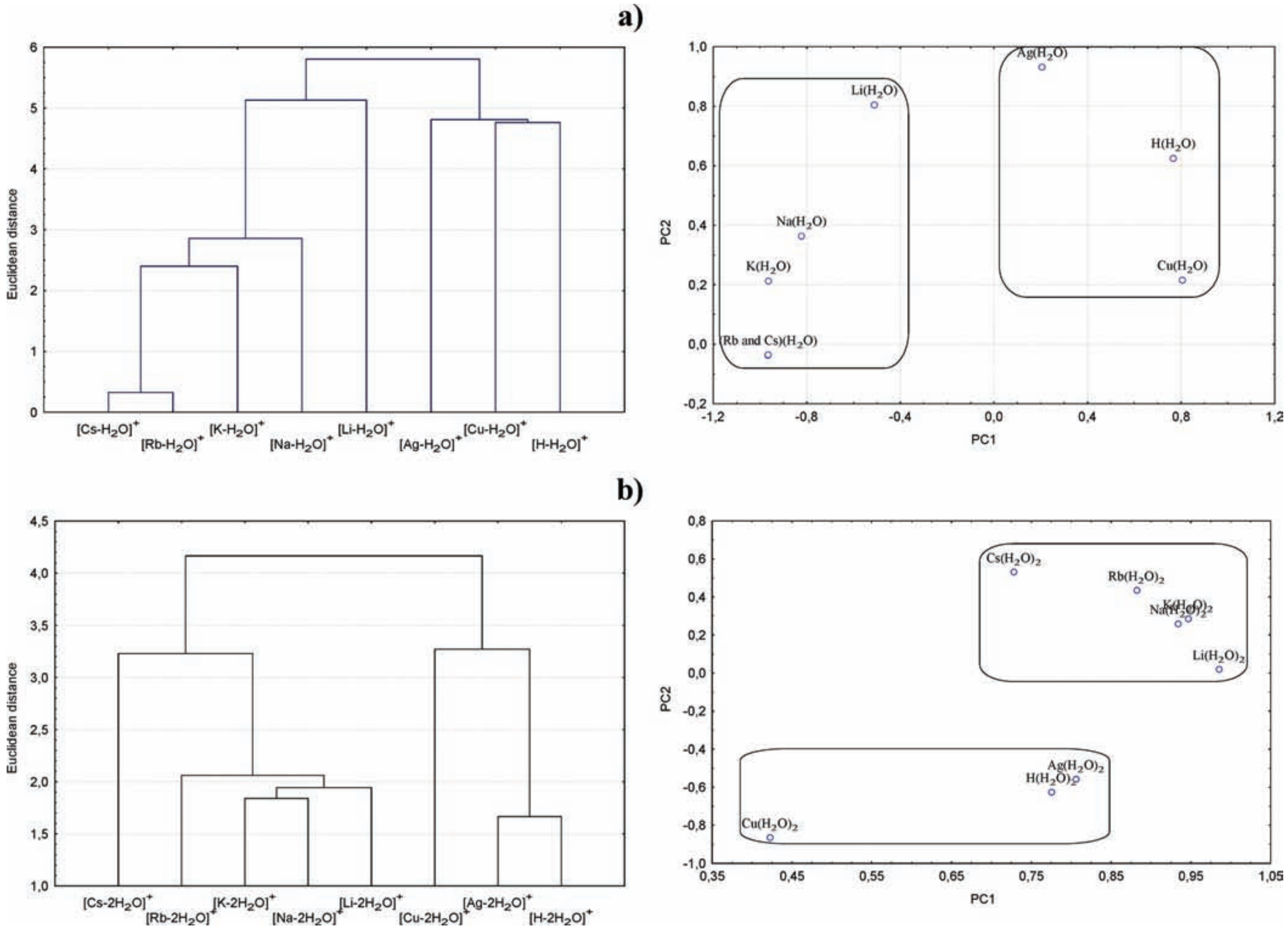

Figure 7. Cluster analysis (on the left side) and principal component analysis (on the right side) of the bell-like shape curves (as presented in Figure 3b,c) obtained for (a) $M^+(H_2O)$ and (b) $M^+(H_2O)_2$.

grouping objects (i.e., metal ions in our case) in the space, is the numerical measure of similarity. In the PCA the distance between the points assigned to the ions studied is a measure of similarity. As follows from Figures 7a,b, in both cases, that is, for complexes with one and two water molecules, respectively, two distinct groups of similarity between the M^+ ions studied are visible in both analyses. The cations of alkali metals, with the exception of the hydrogen cation, make one group, while the cations of hydrogen, copper, and silver make a separate cluster.

So, similar intercationic relations can be drawn from Figures 5 and 7. Generally, irrespective of the number of bound water molecules, the cations of alkali metals, with the exception of the hydrogen cation, make one group of similarity, while the cations of hydrogen, copper, and silver make the other group of similarity. It means that the physicochemical properties (like the mass, mobility, momentum, and the binding stability of water molecules) change in a different manner for alkali metal cations than for the Ag^+, Cu^+, and H^+ ions.

Conclusion

The binding of water molecules with the cations of alkali metals, copper, and silver has been investigated by ESI-MS. As demonstrated in this work, the binding energies of water molecules with the alkali metal cations studied increase in the order $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$. On the other hand, according to increasing binding energies with water molecules, hydrogen ions and the metal cations belonging to the copper family are arranged into a separate series of $Ag^+ < Cu^+ < H^+$.

An easy method has been proposed for the determination of the dehydration constants and the stability of the $M^+(H_2O)_n$ ions for n equal to 1 or 2. Linear correlations have been found between our experimental results and literature values of the dehydration energies.

The results presented in this work can be useful in the examination of the ion dehydration process.

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