

## Direct Observation of the $\text{Li}^+$ -18-Crown-6 Complex Working as $\text{H}_2\text{O}$ Capture in Acetone–Water Mixture

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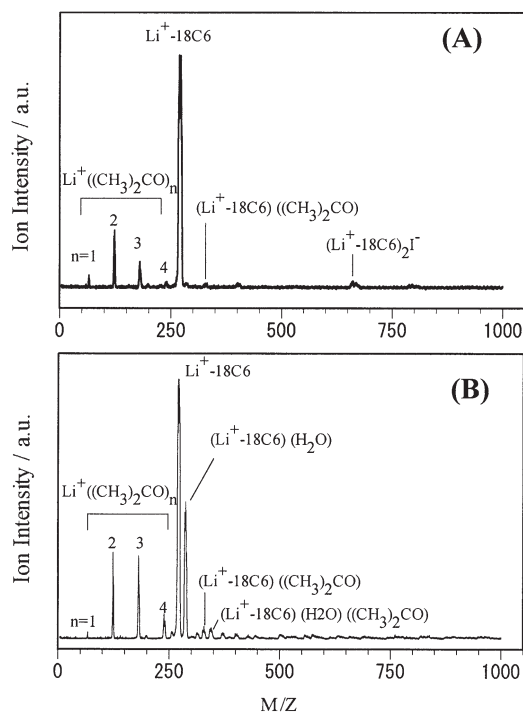
The complex formation of alkali metal ion ( $\text{Li}^+$  or  $\text{Na}^+$ ) with 18-crown-6 in an acetone–water mixed solvent was studied by means of the specially designed mass spectrometer. The  $\text{Li}^+$ -18-crown-6 complex can hold one  $\text{H}_2\text{O}$  in its cavity in the mixed solvent, whereas the  $\text{Na}^+$ -18-crown-6 complex hardly holds an  $\text{H}_2\text{O}$ .

It is well known that crown ethers form complex with alkali metal ions as depending on the cavity size and the ionic radius. As for the complex formation constant of 18-crown-6 (18C6) with a series of alkali metal ions, they are in the order of  $\text{K}^+ > \text{Rb}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+$  in polar solvents.<sup>1–3</sup> On the other hand, ab initio theoretical studies suggested that binding enthalpy is in the order of  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  in the gas phase, but this sequence changes with the hydration to the free metal ion and its complex.<sup>4</sup> The solvation on solutes plays an important role on the property and structure of the crown ether complex in solution. The theoretical studies<sup>4</sup> also suggested that 18C6 is partially wrapped around the  $\text{Li}^+$  in an optimized structure of the  $\text{Li}^+$ -18C6 complex, because an ionic radius of the  $\text{Li}^+$  is too small to fill the cavity of 18C6. When the  $\text{Li}^+$ -18C6 complex interacts with water (the hydration number = 1, 2, or 4), the wrapped structure should be changed into the nearly planar structure (the  $D_{3d}$  conformation) and one or two water molecules can exist in the cavity of the complex. In the crystalline state, the dihydrated  $\text{Li}^+$ -18C6 complex was reported.<sup>5</sup> Here we focus on this  $\text{Li}^+$ -18C6–water interaction in acetone by means of the specially designed mass spectrometer. To see the effect of the free space in the 18C6 cavity, the  $\text{Li}^+$ -18C6–water interaction will be compared with the  $\text{Na}^+$ -18C6–water interaction. In this study, we have found out experimentally that  $\text{Li}^+$ -18C6 complex in a solution has a distinguished property to capture selectively one  $\text{H}_2\text{O}$  in its cavity.

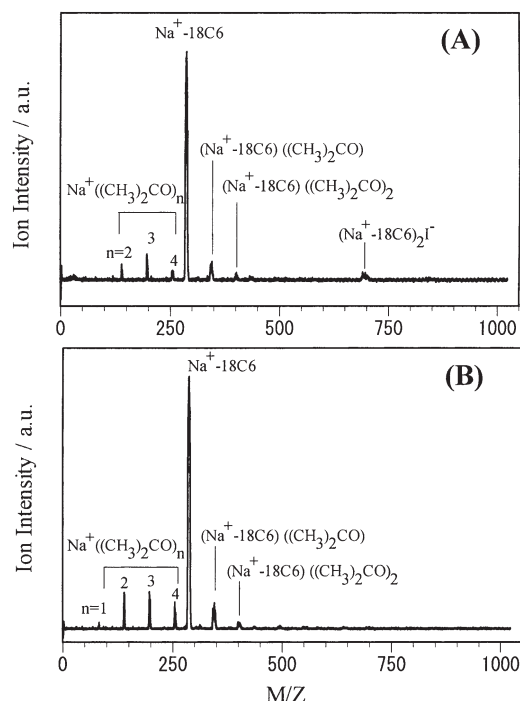
In order to measure the mass spectra, we used a mass spectrometer specially designed for the measurement of clusters in an electrolyte solution. We have already reported the experimental details and the correlation between the observed cluster structures and intermolecular interactions in the solutions.<sup>6</sup> The instrument is composed of a five-stage differentially pumped vacuum system, a homemade electrospray interface and a quadrupole mass spectrometer. The sample solution was injected into the five-stage differentially pumped vacuum system by an HPLC pump with a flow rate of  $0.01 \text{ mL min}^{-1}$  through a fused silica capillary tube (i.d. 0.1 mm). The multicharged liquid droplets including excess cations were generated through the homemade electrospray interface. The resulting multicharged liquid droplets were led from the first chamber (650 Torr) to the fifth chamber ( $1 \times 10^{-6}$  Torr) through the pressure difference and a

gradient of the electric field. During the flight of the liquid droplets, they are fragmented into clusters, molecules or ions via adiabatic expansion and electrostatic repulsion. The resulting positively charged clusters including ions were analyzed in the fifth chamber by a quadrupole mass spectrometer (Extrel C50) without any external ionization. Through this mass spectrometry, measurable molecules are only those that interact relatively strongly with positive ions. The relatively weakly interacting molecules with the ions are vaporized via fragmentation. Moreover, the electrically neutral clusters are not observed without external ionization. Therefore, the mass distribution observed here reflects the relatively strong interaction between the positive ions and coexisting molecules in the solution.

Figures 1A and 1B show the mass spectra of clusters isolated from solutions of 18C6 ( $0.001 \text{ mol dm}^{-3}$ ) in the presence of  $\text{LiI}$  ( $0.001 \text{ mol dm}^{-3}$ ) in pure acetone and in an acetone–water mixture (molar ratio 65:35), respectively. For the pure acetone solution (Figure 1A), the  $\text{Li}^+$ -18C6 complex is formed predominantly, and the  $\text{Li}^+$  free from the 18C6 is observed as solvated ions such as  $\text{Li}^+(\text{CH}_3)_2\text{CO}_n$ ;  $n = 1-4$ . As minor species,  $(\text{Li}^+-18\text{C6})((\text{CH}_3)_2\text{CO})$  and  $(\text{Li}^+-18\text{C6})_2\text{I}^-$  are also recognized. On



**Figure 1.** Mass spectra of ion clusters isolated from solutions containing  $\text{LiI}$  ( $0.001 \text{ mol dm}^{-3}$ ), 18C6 ( $0.001 \text{ mol dm}^{-3}$ ), and solvent: (A) acetone, (B) acetone–water (molar ratio 65:35).



**Figure 2.** Mass spectra of ion clusters isolated from solutions containing NaI ( $0.001 \text{ mol dm}^{-3}$ ), 18C6 ( $0.001 \text{ mol dm}^{-3}$ ), and solvent: (A) acetone, (B) acetone–water (molar ratio 65:35).

the other hand, for the acetone–water solution (Figure 1B), the  $\text{Li}^+$ –18C6 complex and the  $\text{Li}^+$ –18C6– $\text{H}_2\text{O}$  complex are obviously formed. The  $\text{Li}^+$  free from the 18C6 is preferentially solvated by acetone, which is the same as in pure acetone. The interaction of  $\text{Li}^+$  with water is found to be limited only in the 18C6 cavity. In other words, the  $\text{Li}^+$ –18C6 complex captures one  $\text{H}_2\text{O}$  molecule from the acetone–water mixture. If the  $\text{H}_2\text{O}$  in the  $\text{Li}^+$ –18C6– $\text{H}_2\text{O}$  complex is located in the cavity, the formation of the same kind of complex will be decreased by replacing  $\text{Li}^+$  by  $\text{Na}^+$ .

Figures 2A and 2B show the mass spectra observed for NaI–18C6 system ( $c_{18\text{C}6} = 0.001 \text{ mol dm}^{-3}$ ,  $c_{\text{NaI}} = 0.001 \text{ mol dm}^{-3}$ ) in pure acetone and in the acetone–water mixture (molar ratio 65:35), respectively. In both solvents, the  $\text{Na}^+$ –18C6 complex is formed predominantly, and the  $\text{Na}^+$  free from 18C6 is solvated by the acetone. As we expected, the interaction of the  $\text{Na}^+$ –18C6 complex with an  $\text{H}_2\text{O}$  hardly takes place.

Gutmann donor number ( $DN$ ) is widely used as a parameter representing the strength of the solvation to a metal ion, and the values of  $DN$  for acetone (17) and water (18) are almost the same. Hence, the stable state of the monohydrated species of the  $\text{Li}^+$ –18C6 complex cannot be fully explained by the solva-

tion ability of  $\text{H}_2\text{O}$  to the  $\text{Li}^+$ . In fact, the  $\text{Li}^+$ ,  $\text{Na}^+$ , and the  $\text{Na}^+$ –18C6 complex are preferentially solvated by the acetone in the acetone–water mixed solvent.

Ab initio theoretical studies suggested a nearly planar structure (the  $D_{3d}$  conformation) for the  $\text{Li}^+$ –18C6 complex when the complex interacts with water (the hydration number = 1, 2, or 4).<sup>4</sup> While the dihydrated  $\text{Li}^+$ –18C6 complex was reported in the crystalline state,<sup>5</sup> we revealed in this study that the first hydration to the  $\text{Li}^+$ –18C6 complex was strong, and the second and more hydration were relatively weak in the solution. We checked on the nearly planar structure of the  $\text{Li}^+$ –18C6 complex including one  $\text{H}_2\text{O}$  molecule by using the CPK model. In this model, the  $\text{Li}^+$  binds three oxygen atoms of 18C6 in its cavity. The  $\text{H}_2\text{O}$  molecule is able to bind both one of ether oxygen atoms by hydrogen bonding and the  $\text{Li}^+$  concurrently. We can interpret the stable state of the monohydrated species of the  $\text{Li}^+$ –18C6 complex by the strong bridged bonding of the  $\text{H}_2\text{O}$  molecule.

Although  $\text{Li}^+$  is preferentially solvated by the acetone in the acetone–water mixed solvent, the  $\text{Li}^+$ –18C6 complex can selectively capture one  $\text{H}_2\text{O}$  in its cavity. This indicates that the  $\text{Li}^+$ –18C6 complex has strong affinity to an  $\text{H}_2\text{O}$ . It should be also noted that the  $\text{H}_2\text{O}$  in the acetone–water mixture would contribute to solvate  $\text{I}^-$ . In Figures 1B and 2B, the hydration of  $\text{I}^-$  decreases the ion–counterion interaction.

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