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Microscopic environment of metal ion controlled by the balance between preferential solvation and coordination

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The preferential solvation and the coordination characterizing metal ions (Mg^{2+} and Zn^{2+}) in solution, which control the microscopic environments around the metal ions, were directly observed through the mass spectrometric analysis of clusters isolated from liquid droplets.

The interaction of metal ions and organic compounds in water are vital for living activities.[1–5] For example, Mg^{2+} is essential for stabilization and replication of DNA, whereas Zn^{2+} causes a destabilization. Although Mg^{2+} and Zn^{2+} have similar ionic radius and charge,[6–8] the effect on the biological process is in contrast. To know the role of metal ions, the information on the microscopic environment of ion will become indispensable. Here we report on an experimental approach to study the microscopic environments around metal ions (Mg^{2+}, Zn^{2+}) in aqueous solutions containing an organic compound. Electrospray mass spectrometry permits the isolation of metal–solvent, metal–ligand and metal–ligand–solvent clusters from the solution into the gas phase.

The clusters in electrolyte solutions were measured by the specially designed mass spectrometer equipped with an electrospray interface as described previously.[9–12] The mass spectrometer is composed of a homemade electrospray interface, a quadrupole mass filter (Extrel, C50), and a five-stage differentially pumped vacuum system. Based on the electrospray principle, positively or negatively multi-charged liquid droplets including excess cations or anions are generated, according to the polarity of the electric field between the electrospray nozzle and the mass filter. The multi-charged liquid droplets are then fragmented into clusters *via* adiabatic expansion and electrostatic repulsion in the vacuum chamber. The charged clusters including cations or anions are analyzed without further external ionization.

In this mass spectrometer, a nozzle, three skimmers and a quadrupole mass filter are aligned coaxially to reduce collisioned interactions.[9] The electric voltages supplied to the nozzle and the three skimmers (E_1, E_2, E_3, E_4) are (4100, 300, 290, 200) and (−4600, −320, −310, −240) for the positive and negative ion measurement, respectively. It has already been reported that the initial distribution of ionic clusters without having collisioned influence was observed at the small $E_2 - E_3$ difference (around 10 V), and that the collisioned influence leading to the desolvation was promoted at the large $E_2 - E_3$ difference (around 90 V).[9,13] The used electric voltages and the nozzle–skimmer–mass filter coaxial alignment keep the collisioned influence small.

Fig. 1(a) and (b) shows the mass spectra of positively and negatively charged clusters generated from a solution of $MgCl_2$ (1.0×10^{-3} mol dm^{-3}) in a 1-BuOH–H_2O (molar ratio = 1 : 100) mixture. For positive ion measurement [Fig. 1(a)], $Mg^{2+}(1\text{-BuOH})_a$, where a = 3–10, clusters are observed dominantly. $Mg^{2+}(H_2O)_x$, where x = 5–12 and $Mg^{2+}Cl^-(1\text{-BuOH})_b$, where b = 2–6, are also observed but with relatively weak intensities. In comparing the mass distribution of $Mg^{2+}(1\text{-BuOH})_a$, $Mg^{2+}Cl^-(1\text{-BuOH})_b$, and $Mg^{2+}(H_2O)_x$, it is clear that Mg^{2+} is preferentially solvated by 1-BuOH in the 1-BuOH–H_2O mixed solvent. The interactions of Mg^{2+} with the counterion Cl^- and H_2O are obviously restrained by this preferential solvation. On the other hand, as for the negative ion clusters shown in Fig. 1(b), $Cl^-(H_2O)_m$, where m = 0, 1, 2, 3, and $Cl^-(1\text{-BuOH})(H_2O)_n$, where n = 0, 1, 2, are observed. Both H_2O and 1-BuOH molecules exist around Cl^-. The strong preferential solvation by 1-BuOH as observed for Mg^{2+} cannot be recognized for Cl^-. The formation of non-solvated Cl^- suggests that the solvation for Cl^- is weaker than that for Mg^{2+}, which correlates with ΔH of hydration: $\Delta H_{\text{hyd}}(Mg^{2+}) = -1908$ kJ mol^{-1}, $\Delta H_{\text{hyd}}(Cl^-) = -362.8$ kJ mol^{-1}. Even though the hydration of Mg^{2+} is energetically more favourable than that of Cl^-, the intensity ratio $Mg^{2+}(H_2O)_x/Mg^{2+}(1\text{-BuOH})_a$ is much smaller than $Cl^-(H_2O)_m/Cl^-(1\text{-BuOH})$. This also indicates the difference in the ion–solvent (H_2O and 1-BuOH) interactions between $Mg^{2+}$and Cl^-.

Fig. 2 shows the mass spectra of positive and negative ion clusters generated from a solution of $ZnCl_2$ (1.0×10^{-3} mol dm^{-3}) in a 1-BuOH–H_2O (molar ratio = 1 : 100) mixture. For positive ion clusters (Fig. 2(a)), $Zn^{2+}(1\text{-BuOH})_c$, where c = 3–9, and $ZnCl^+(1\text{-BuOH})_d$, where d = 1–4, are observed, which is similar to the preferential solvation for Mg^{2+} by 1-BuOH as shown in Fig. 1(a). However, the microscopic environment of Zn^{2+} was not as simple as surrounded by only 1-BuOH. The $[Zn_3Cl_4]^{2+}(1\text{-BuOH})_e$, where e = 0–7, clusters are also observed as outstanding peaks in Fig. 2(a), which indicates relatively strong interaction of Zn^{2+} with Cl^- comparable to the

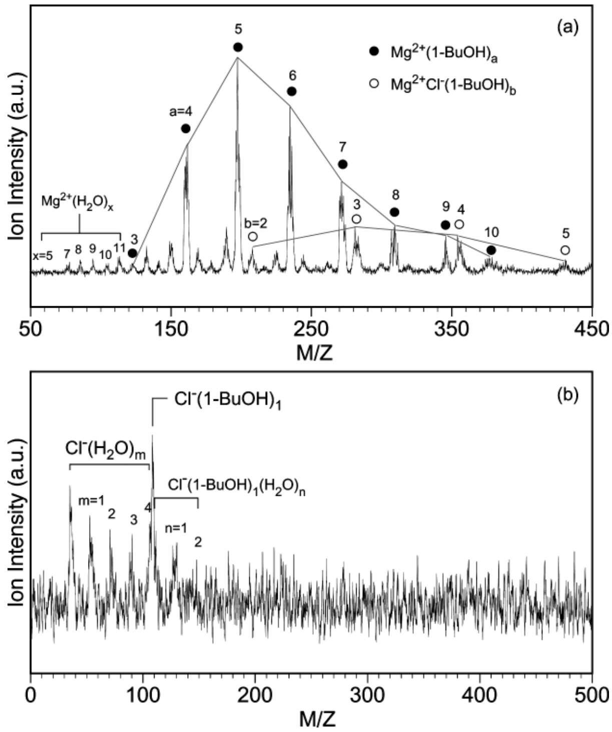

Fig. 1 Mass spectra of clusters generated from 1-BuOH–H_2O solutions (molar ratio = 1 : 100) including $MgCl_2$ (1×10^{-3} mol dm^{-3}). (a) positive ion (b) negative ion. The numeral on each peak corresponds to the number of solvent molecule in the clusters.

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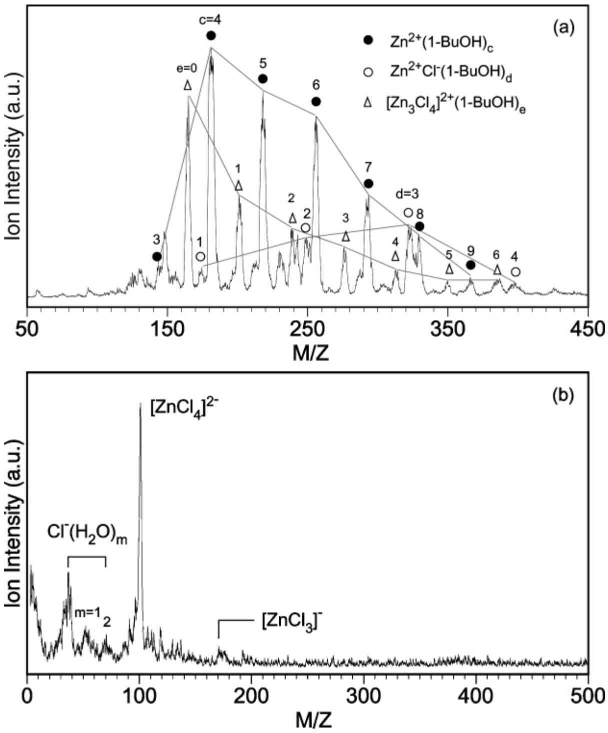
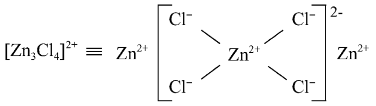


Fig. 2 Mass spectra of clusters generated from 1-BuOH–H_2O solutions (molar ratio = 1 : 100) including $ZnCl_2$ (1×10^{-3} mol dm^{-3}). (a) positive ion (b) negative ion. The numeral on each peak corresponds to the number of solvent molecule in the clusters.

solvation by 1-BuOH. This suggests that Cl^- behaves as a ligand to form $[ZnCl_4]^{2-}$. The $[Zn_3Cl_4]^{2+}$ is thought to correspond to the following clusters including the complex ion $[ZnCl_4]^{2-}$, which is a counter anion to Zn^{2+}.



To confirm the existence of $[ZnCl_4]^{2-}$, the measurement of the negative ion clusters for the same solution was carried out. In Fig. 2(b), $[ZnCl_4]^{2-}$ is observed dominantly, and solvated Cl^- clusters with water ($Cl^-(H_2O)_m$) are also observed. The observation of $[ZnCl_4]^{2-}$ clearly indicates that the interaction between Zn^{2+} and Cl^- is strong in solution. The preferential solvation with 1-BuOH and the complexation with Cl^-, that is, coordination, were found to determine the microscopic environment of Zn^{2+}in solution.

The microscopic environment around Mg^{2+} and Zn^{2+} in the solution is found to be controlled by the balance between the preferential solvation and the coordination as shown in Fig. 1 and 2. The microscopic environment around Mg^{2+} is mainly controlled by the preferential solvation by 1-BuOH, while that for Zn^{2+} is controlled not only by the preferential solvation but also by the coordination. The difference in physicochemical properties between Mg^{2+} and Zn^{2+} in solution is clearly demonstrated here, which is correlated with the reported values of the stability constant of complexes.[14] The mass distributions of $Mg^{2+}(1\text{-BuOH})_a$ and $Zn^{2+}(1\text{-BuOH})_c$ look alike, and those of $Mg^{2+}Cl^-(1\text{-BuOH})_b$ and $Zn^{2+}Cl^-(1\text{-BuOH})_d$ also look alike. This indicates that the preferential solvation by 1-BuOH is controlled by the charge density of the metal ions. Moreover, we have observed that in a 1-BuOH–H_2O (1 : 100) mixture without including ions, the 1-BuOH forms self-association clusters through hydrogen bonding and hydrophobic interactions, and the hydrogen bonding network of H_2O is disintegrated. Such a cluster structure in the 1-BuOH–H_2O mixture should be related to the preferential solvation.[15,16]

It should be noted that the balance between the preferential solvation and the coordination was easily influenced by the coexisting ligand. When acetylacetone (Hacac), whose dissociated enol anion (acetylacetonate (acac)) having coordination ability much higher than Cl^-, was added instead of 1-BuOH, almost Zn^{2+} formed complex with acac; on the other hand, 36% of Mg^{2+} formed complex with acac and 64% of Mg^{2+} was preferentially solvated by Hacac. The microscopic environments around metal ions are determined by the varying balance between the formation of coordinated complex and the preferential solvation. The mass spectrometric analysis of clusters presented here would be the only experimental method to measure this balance directly.

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