

LETTERS

Preferential Solvation of Na^+ in *N,N*-Dimethylformamide–Water Binary Mixture

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Preferential solvation of Na^+ by *N,N*-dimethylformamide (DMF) in a DMF–water binary mixture is observed at the cluster level through mass spectrometry. Since DMF is highly electron donating, the Na^+ –DMF interaction is more favorable than the DMF– H_2O interaction. The observed clusters in a DMF–water mixture with and without NaCl, show that once a DMF molecule interacts with Na^+ , the DMF molecule hardly forms a hydrogen bond with a water molecule or cluster.

In water–organic solvent binary mixtures, molecular clusters are easily formed as a result of the balance of intermolecular interactions. Recently we have reported cluster structures in the binary mixtures between water and acetonitrile, dimethyl sulfoxide, methanol, ethanol, or propanol, depending on the mixing ratio between water and the organic solvent.^{1–7} We have suggested that the molecular clustering structures in these binary mixtures directly influence the solvation of a hydrophobic solute. For example, when phenol was added into these binary mixtures as a hydrophobic solute, it was preferentially solvated by the organic solvent molecules even at higher water contents.^{1,3,6,7} Water and an organic solvent cannot be mixed homogeneously at the molecular level; therefore, it is reasonably understood that the hydrophobic solutes form aggregates with the organic solvent molecules.

Preferential solvation is also expected for inorganic ions in water–organic solvent mixtures. Especially, since there are many organic solvents with electron donating ability higher than water, positive ions are likely to be solvated by the organic solvents. The study of the preferential solvation of ions will also provide new insight into the role of ions in biological molecular self-assembling processes, salting out behavior, etc. The salt effect on the phase separation of water–organic solvent mixtures has been studied in detail through neutron scattering experiments.^{8,9}

The preferential solvation of hydrophobic solutes in a water–organic solvent mixture is attributed to the weaker interaction between water and the hydrophobic molecule; that is, the exclusive interaction. On the contrary, the preferential solvation of the inorganic cation will be controlled by the attractive electrostatic interaction between the cation and the electron donating organic solvent molecule. To see the difference between these two types of preferential solvation at the cluster level, here we report the preferential solvation for Na^+ in *N,N*-dimethylformamide (DMF)–water mixture observed through mass spectrometry for clusters generated from fragmentation of liquid droplets. The observed clusters clearly demonstrate that the electrostatic interaction of DMF with Na^+ efficiently decreases the DMF– H_2O interaction.

The microscopic structures of solutions were analyzed through mass spectrometry of clusters generated from the solutions. Mass spectra of clusters in the DMF–water and in the DMF–water–NaCl solutions were measured by using specially designed mass spectrometers equipped with a thermospray-type and an electrospray-type nozzle, respectively. The principle of this method has been reported previously.^{10–16} For the measurement of the DMF–water solution (without NaCl), the liquid droplets, generated by the continuous flow of the sample solution into the vacuum chamber through the thermospray-type nozzle, are fragmented into (neutral) clusters via adiabatic expansion.^{10–12}

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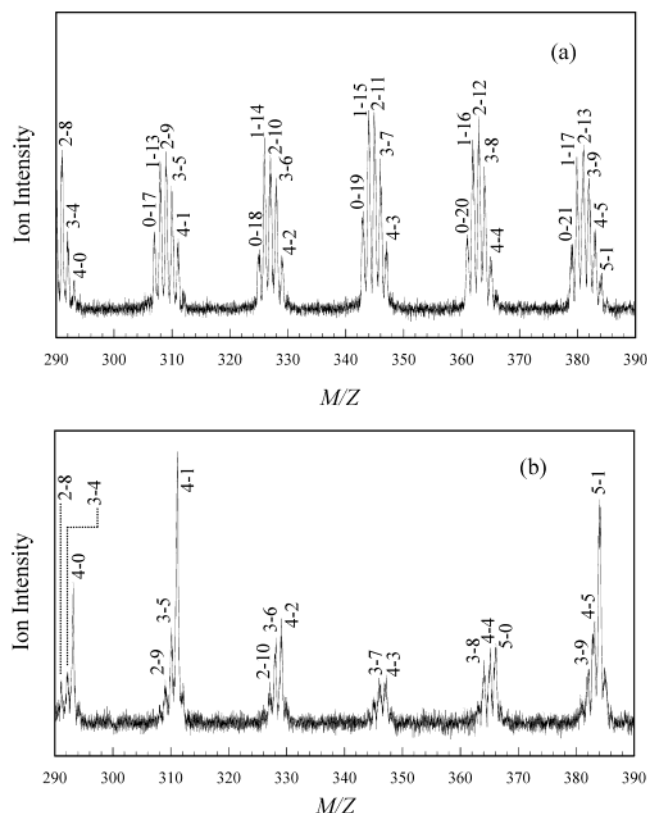


Figure 1. Mass spectra of clusters generated from aqueous (a) 5 wt% and (b) 20-wt% DMF solution. The paired numbers represent $m-n$ of $\text{H}^+(\text{DMF})_m(\text{H}_2\text{O})_n$; $m = 0$ represents water clusters, $\text{H}^+(\text{H}_2\text{O})_n$.

On the other hand, for the measurement of the DMF–water–NaCl solution, the electrospray-type mass spectrometer was used.^{13–16} The multicharged liquid droplets including excess Na^+ ions are generated by the electrospray principle in a high electric field. The multicharged liquid droplets are also fragmented to singly charged clusters via adiabatic expansion and electrostatic repulsion in the vacuum chamber. The resulting neutral and charged clusters were measured by a quadrupole mass spectrometer (Extrel, C-50) with and without electron impact ionization (30 eV), respectively.

To minimize desolvation from clusters, the pressure gradient from the nozzle to the quadrupole mass filter is held as small as possible, by use of four-stage and five-stage differential pumping system for the thermospray-type and the electrospray-type measurement, respectively. To reduce collisional interactions, the nozzle is situated coaxially to the skimmers and the quadrupole mass filter.

Mass spectra of clusters isolated from aqueous 5 wt % DMF solution are shown in Figure 1a. Water clusters, $\text{H}^+(\text{H}_2\text{O})_n$, and hydrated DMF clusters, $\text{H}^+(\text{DMF})_m(\text{H}_2\text{O})_n$, are observed as a series of clusters with varying m and n . In the series of $\text{H}^+(\text{DMF})_m(\text{H}_2\text{O})_n$ clusters of $m = 1, 2, 3$, and 4, the main structures are composed of water molecules, that is, $\text{H}^+(\text{DMF})_m(\text{H}_2\text{O})_n$ with $m < n$ are observed dominantly. The H_2O – H_2O hydrogen bonding interaction forms main structures in the solution, and DMF molecules are dispersed among the hydrogen bonded water clusters. Such a cluster structure, which is mainly composed of hydrogen bonding water, was observed at DMF concentrations lower than 10 wt%. This indicates that DMF molecules have a strong affinity to the hydrogen-bonding network of water in the region of less than 10 wt%.

When a concentration of DMF is increased to 20 wt%, the cluster structure is obviously reorganized. In the region of m/z

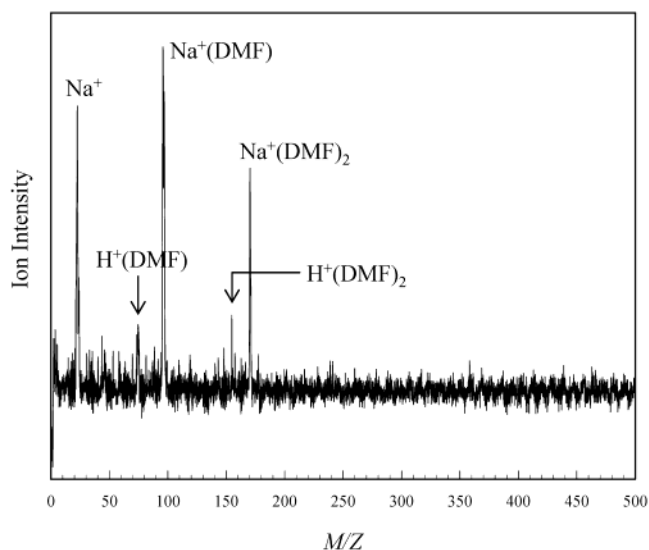


Figure 2. Mass spectrum of clusters generated from aqueous 5 wt% DMF solution including NaCl (1×10^{-3} mol/L).

= 290–390 in Figure 1b, the series of $\text{H}^+(\text{DMF})_m(\text{H}_2\text{O})_n$ clusters of $m = 0$ and 1 are hardly observed, and the clusters of $m = 2$ are observable but with weak intensities. In the series of the clusters of $m = 4$, the nonhydrated and monohydrated clusters, the peak $m-n$: 4–0 and 4–1, are observed more dominantly than the highly hydrated clusters. The same property can be confirmed for the series of $m = 5$. Instead of the water clusters and the DMF hydrate clusters as observed in Figure 1a, the DMF self-aggregation is remarkably promoted.

When NaCl is added into the DMF–water mixture, Na^+ is expected to be preferentially solvated by the DMF molecule, because DMF is a more donating solvent than water (donor number: 26.6 (DMF), 18.0 (water)).¹⁷ The main interest is how the cluster in the DMF–water mixture is related to the preferential solvation for Na^+ . Figure 2 shows the mass spectra of clusters generated from aqueous 5 wt% DMF solution including NaCl (1×10^{-3} mol/L), through the electrospray method. Na^+ and its interaction with DMF, $\text{Na}^+(\text{DMF})_{1,2}$, are observed as prominent species. This clearly indicates that Na^+ is preferentially solvated by DMF molecules in aqueous 5 wt% DMF solution, rather than by water. It should be noted that the neutral clusters such as hydrated DMF are not observed here, because only the clusters including a cation are observed in this electrospray mass spectrometry.

Comparing the cluster structure of aqueous 5 wt% DMF solutions with and without NaCl (Figure 1a and Figure 2), it is found that the clustering of DMF is drastically changed by the interaction with Na^+ . In the absence of NaCl, DMF molecules exhibit hydrogen-bonding interaction with coexistent $\text{H}^+(\text{H}_2\text{O})_n$ clusters. On the other hand, by the addition of NaCl into this aqueous 5 wt% DMF solution, a portion of the DMF molecules interact with Na^+ preferentially rather than with water clusters. This demonstrates that once a DMF molecule interacts with Na^+ , that DMF molecule does not form a hydrogen bond with the coexisting water molecules and clusters. The DMF– Na^+ electrostatic interaction is more favorable than the DMF–water hydrogen-bonding interaction. Na^+ gathers DMF selectively, irrespective of the DMF–water cluster structure. This is in strong contrast with the preferential solvation of the hydrophobic solutes reported previously, where the preferential solvation is strongly controlled by the cluster structures depending on the water concentration.^{1,3,6,7}

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