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Effects of Impurity Atomic Ions on Salt Nanocrystal Structures

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Summary

Incorporation of impurity ions such as bromide ions into sodium chloride crystals has been one of the problems in the production of highly pure salt from seawater. Several studies were reported concerning to the effects of impurity ions in the salt crystal growth. However, there was no report of molecular-level study on salt nanocrystals so far. In the present study, we have examined how the nanocrystal structures are changed by incorporation, by using ion mobility mass spectrometry combined with theoretical calculation.

In the experiment, we have examined intensity distributions and collision cross sections of Br^--incorporated salt nanocrystal positive and negative ions, $Na_nCl_{n-2}Br^+$ and $Na_{n-1}Cl_{n-1}Br^-$ by a home-made experimental apparatus of ion mobility-mass spectrometry, which were developed in the former research project. The equilibrium structures of these cluster ions were also determined by quantum chemical calculations based on density functional theory, and the collision cross sections of the structures were obtained theoretically. Then the observed ion structures were finally assigned by comparing the experimental cross sections with theoretical ones.

As a result of the positive ion experiment, $Na_nCl_{n-2}Br^+$ showed a size dependence of the cross sections which is similar to that of $Na_nCl_{n-1}^+$, and they had cross sections with about 1-2 $Å^2$ larger than $Na_nCl_{n-1}^+$. On the other hand, equilibrium structures of $Na_nCl_{n-2}Br^+$ were almost the same with those of $Na_nCl_{n-1}^+$, including the order of the stability. In conclusion, the structures of $Na_nCl_{n-2}Br^+$ were assigned to the most stable ones from the comparison between the experimental and theoretical cross sections. We obtained the qualitatively similar results also for the negative ions.

We are now planning measurements for the cluster ions with wider sizes and different charge states, using a new apparatus with electrospray ion source.