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# Study of Incorporation of Impurity Atomic Ions into Salt Nanocrystals

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Summary

Incorporation of impurity ions such as potassium, bromide, and iodide ions into sodium chloride crystals has been one of the problems in the production of highly pure salt from seawater. Several studies were already reported concerning to this problem. However, there have been no molecular-level studies about the incorporation phenomenon so far. In the present study, we have examined how efficiently the incorporation proceeds as a function of nanocrystal size and how the nanocrystal structures are changed by incorporation, by using ion mobility mass spectrometry combined with theoretical calculation.

In the experiment, we firstly examined intensities of $Br^-$-incorporated salt nanocrystal positive and negative ions, $Na_nCl_{n-2}Br^+$ and $Na_{n-1}Cl_{n-1}Br^-$ in the mass spectra. Then we compared the intensities with the expected intensities which were estimated from the relative concentrations of Br and Cl supplied in the sample. As a result, we found that the incorporation probabilities were lower than the expected value for all size ($n$) of positive ions. On the other hand, for the small size of negative ions, it was found that the probabilities were higher than expected, and that they decreased rapidly with $n$. These findings were explained by the energies for the substitution reaction of Cl with Br, and also by the averaged bond lengths in the nanocrystals.

The equilibrium structures of $Br^-$- or $I^-$-incorporated salt nanocrystal ions were also discussed from the comparison between collision cross sections determined by ion mobility measurement and those obtained by quantum chemical calculations. The ion structures were finally assigned to be the most stable structures, in which one of the $Cl^-$ in the salt nanocrystal was replaced with $Br^-$ or $I^-$.

We are now planning ion mobility measurements with higher resolution for the nanocrystal ions with wider sizes and different charge states, using a new apparatus with electrospray ionization source. Then we are further aiming at unveiling the bulk phenomena at the molecular level.