No. 2108

Elucidation of the Mechanism to Include b Bromine Ions into Sodium Chloride Crystals

Yoshiyuki SHIRAKAWA, Yuhei TSUGAWA

Department of Chemical Engineering & Materials Science, Doshisha University

Summary

NaCl crystals produced by the Japanese salt-making process contain a relatively large amount of impurity ions from seawater. In general, most of the impurities contained in crystalline products are derived from the mother liquor, which remains a problem in the production of high-purity and high-quality salts. The concentration of K and Br ions by the uptake phenomenon reaches several hundreds to 1,000 ppm in the product, and it cannot be completely removed by washing the products and the uptake mechanism is poor understood. If we can understand this mechanism and suppress the uptake, it is expected that the manufacturing cost of high-purity NaCl will be reduced. On the other hand, overseas, iodine and fluorine, which are essential trace elements, are added to the salt. However, since these are sprayed as an aqueous solution, they have a problem that they volatilize with time and their contents decrease. Since F and I ions are halogens like Cl and Br ions, if the mechanism of Cl and Br ion uptake can be understood, it can be applied to the uptake of F and I ions and may be immobilized in the crystal.

In this study, we analyzed the solution structure near the interface between NaCl crystal and NaCl-NaBr or NaCl-NaI aqueous solution in the early stage of crystal growth by molecular dynamics (MD) simulation and investigated the ionic behavior in the presence of impurities. As a result, it was found that the impurity ion (Br^-, I^-) concentration near the crystal-solution interface was higher than the saturated concentration, which was significantly different from the composition of the bulk. This result suggests that even if the impurity ion concentration is unsaturated, it may crystallize due to local supersaturation near the interface. In addition, Br^- and I^- showed different impurity effects on the crystal growth rate. In the presence of Br^-, NaCl tends to form a solid solution with NaBr, and since the dehydration energy of Br^- is smaller than that of Cl^-, Br^- tends to dehydrate. However, since the growth rate of Br^- is slower than that of Cl^-, the rate-determining of Br^- reduces the overall crystal growth rate. On the other hand, in the presence of I^-, NaCl is difficult to form a solid solution with NaI, and the dehydration energy of I^- is higher than that of Cl^-, so that I^- is difficult to dehydrate. Therefore, it was found that I^- was hardly incorporated into the crystal surface and was present at a high concentration near the interface and slowed down the crystal growth rate.