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Establishment of Controlling Various Crystallization Behaviors by Conductivity - Mechanism of Nucleation, Growth and Impurity Effect from NaCl Solution -

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Summary

Introduction　Various kinds of crystallization behavior such as nucleation, growth, impurity effect and impurity distribution etc. in manufacturing process of pharmaceutical and food are unstable and causes the difficulty of controlling and predicting crystal quality. In our laboratory, models of secondary nucleation and distribution of impurity have been designed and have played an important role to clarify their behaviors. In this study, the aim is to understand behaviors in crystallizer with the electrolyte solution of NaCl and $NH_4H_2PO_4$ by means of electrical conductivity and self-produced turbidity meter.

Experimental　Prove of electrical conductivity is introduced in crystallizer of double jacket type to measure the conductivity of the solution. Also, brightness of the solution is calculated from motion picture by microscope of pen type.

(Exp. 1)　It is difficult to catch the change of ion concentration from the conductivity because temperature dependency of solubility of NaCl is lower. Accordingly, inside of crystallizer is observed by the change of brightness obtained from microscope in anti-solvent crystallization process. Alcohol (ethanol and 1-propanol) as an anti-solvent is dropped into crystallizer pooled with NaCl solution (volume; 300 ml, rotation speed; 300 rpm, saturation temperature; 15^{o}C) and small crystal is precipitated. Dropping amount is 50 ml and the speed is changed as an operating condition. After dropping, size distribution of filtrated and dried crystal is measured by laser diffraction method.

(Exp. 2)　Change of ion concentration in precipitation process is measured by electrical conductivity because temperature dependency of solubility of $NH_4H_2PO_4$ (MAP: Mono-Ammonium Phosphate) is higher. Accordingly, information of nucleation and crystal growth could be obtained. First, saturated solution at 15^{o}C is prepared in 300 ml vessel and the temperature is cooled down to 10^{o}C. Secondly, seed crystal (size; 275 µm, weight; 2 g) is inserted into the supersaturated solution and the conductivity is measured at every one second. Finally, crystal size distribution and aspect ratio of average size are measured after crystallization. In this experiment, concentrations of metal ion (Al^{3+}) and/or chelate agent (EDTA; Ethylen diamine tetra acetic acid) are changed as an operating condition to investigate nucleation, growth and impurity effect.

Results and discussion

(Exp. 1)　Brightness increases quickly in the case of higher dropping speed because more NaCl crystal is precipitated. On the other hand, crystal size is smaller when the speed is faster. Smaller crystal is obtained by fast dropping because anti-solvent is diffused soon.

(Exp. 2)　Higher Al^{3+} concentration in MAP crystallization process causes lower crystal growth rate. Same amount of chelate agent for Al^{3+} concentration shows recovery effect of growth rate. On the other hand, needle crystal is obtained if solution includes metal ion or metal chelate complex. This is reason why impurity with positive charge is adsorbed on (100) face only. Also, crystallization process of smaller aspect ratio causes more secondary nucleation.