

## 1. Introduction

Crystallization is a separation and purification process used in the production of a wide range of materials from bulk commodity chemicals to speciality chemicals and pharmaceuticals in terms of purity and crystal size distribution (CSD).

In order to design a crystallization process it needs kinetic data especially those of crystal growth. The techniques used to measure crystal growth rates can be divided into two main groups. The first group is comprised of methods that rely on the growth of a single crystals to obtain the needed data. The second set of methods involves the growth of a suspension of crystals in solution. The aim is to allow the crystals to grow at a known growth rate without any nucleation occurring. This implies, therefore, that the supersaturations used in these experiments must be controlled.

It has been known, that the shape and purity of the crystals are influenced by impurities, which alter the kinetic parameters as the rates of nucleation, growth and dissolution and even the shape of the crystals. The effect of impurities on the crystallization kinetics, most probably, is due to the impurity adsorption on the crystal surface. *Therefore, an understanding of impurity effects is a great interest.*

The present investigations are concentrated to discuss all issues concerning the influence of impurities on the crystal growth processes only for inorganic salts in aqueous solutions. To show that the impurity's action can be changed by process conditions like supersaturation and temperature level. Therefore, this thesis should be an attempted to discuss the thermodynamic and kinetic effects, caused by the impurity's effect, on the crystal growth processes. Furthermore, new explanations for the effect of impurities by measuring crystal surface potential should be introduced.

The growth of crystals in a supersaturation solution is a very complex process that has not been completely understood up to now. The main reason of this complexity is the number of mass transfer steps and the heat transfer involved in the process [1-3]. In a supersaturated solution, the first step is a new surface by nucleation then a diffusion of solute to the surface, following the adsorption of solute on the surface and integration of solute into the crystal lattice. The further steps, which were almost always ignored, are heat related effects from the liberation of the crystallization heat when the crystal grow, and from the heat transfer connected with the mass transfer from and to the phase boundary (liquid/solid). Different physical laws govern all these steps and the present state of science is not able to explain all the phenomena in crystallization.

Growth rate dispersion (GRD) is one of those phenomena which are difficult to explain. Crystallization is a surface phenomenon, but in fact, surface properties were often omitted. Especially, in dissolution no other step than diffusion was considered. As it is already shown by Fabain [4] and Fabain and Ulrich [5] that the dissolution rate of  $K_2SO_4$  shows a dissolution rate dispersion (DRD), which is not possible to explain by the present knowledge that accepts only dissolution as a diffusion-controlled phenomenon. Therefore, other surface phenomena should be taken into account to overcome these explanation difficulties.

Consequently, the presence of small amounts of transition metal ions in aqueous solutions (as impurities) may effect whole crystallization process. The structure of the solution is only effected by the presence of hydronium ions in the solution. The interaction between the present species and the solvent depends on the structure properties in the solution due to the present ions. The smaller the ion is the stronger is the interaction (higher hydration energy) between the ion and water molecules in the coordination sphere. Up to todate, most studies do not consider a hydration of univalent, divalent and trivalent positive ions (cations) in aqueous solution to generate hydronium ions and may be changed the pH value of the solution and hence the potential and the charge of the diffusion layer will be effected.

It has been shown a long time ago that most particles in aqueous solutions are charged for various reasons, such as ionization of surface groups, specific adsorption or desorption of ions. This causes to the formation of the electrical double layer. Any ion, which will be incorporated into the crystal lattice, should pass this electrical double layer which gives extra resistance to the crystal growth. If the formation of the electrical double layer is accepted, external effects on this layer and on the crystallization kinetics can be explained more easily. Unfortunately, there is no detailed experimental research on the surface charge (potential) determination of highly soluble salts in the literature. This can be made e.g. by zeta Potential determination, but the high conductivity of saturated solutions causes some measurement problems. Therefore, the importance of surface potential in the crystal growth kinetics should be investigated by measuring  $\zeta$ -potential in order to emphasize that the hydration of lattice ions does have a significant influence on the surface charge. I.e. the external effects on the electrical double layer and hence on the crystallization kinetics can be explained more easily by measuring of  $\zeta$ -potential.