6.4 Fundamentals

6.4.1 Solubility, Supersaturation and Particle Size

The leading property of bulk crystalline material is its particle size (distribution). Obviously, a high nucleation rate will lead to fine material and *vice versa* a low nucleation rate is required for coarse product. Experience teaches that sparingly soluble substances lead to fine material and only rather well soluble substances can be crystallized to coarse bulk material. The reason behind this observation lies in the definition of supersaturation: The driving force for nucleation is the difference in chemical potential between the material in the dissolved state and the crystalline state. By some rearrangement and simplification this difference may be expressed as supersaturation ratio S_A of the crystallizing substance A

$$S_A = \frac{x_A}{x_A^*}, \tag{6.1}$$

with x_A being the mass fraction of A in the solution and x_A^* being the mass fraction of A in equilibrium with its crystalline phase, *i.e.* the solubility of A. From eqn (6.1) it is obvious that rather high supersaturation is obtained at low solubility and low supersaturation is obtained at high solubility. Hence, well soluble substances are crystallized at low nucleation rates compared to sparingly soluble substances and thus become coarse.[38] This is the explanation for the observation that crystallization of well soluble substances leads to product in the size range above 10 μm while precipitation of sparingly soluble substances leads to fine material even in the nano-range.[14]

6.4.2 Growth Rate, Particle Size, Residence Time and Crystallizer Volume

Furthermore, it is observed that continuous crystallization of well soluble substances often leads to linear growth rates G in the order of $5–10 \times 10^{-8}$ m s^{-1}, see ref. 38. This observation allows for a crude first estimation of the required mean residence time (also called: draw-down time) for crystals of a targeted mean size $L_{4,3}$

$$\tau \equiv \frac{M_{\mathrm{A,cryst\ in\ crystallizer}}}{\dot{M}_{\mathrm{A}}} \approx \frac{L_{4,3}}{G}. \tag{6.2}$$

The mean residence time, τ, of the crystals in the crystallizer is the mean time which is available for growth of the crystals. It is defined by the mass of crystalline substance A suspended in the crystallizer, $M_{\mathrm{A,cryst\ in\ crystallizer}}$, divided by the mass flow of A produced by the crystallizer, $\dot{M}_{\mathrm{A}}$. In reality each crystal has its own residence time and, hence, there is a residence time distribution. Typical technical values for the mean residence time for a 100–500 μm sized product is in the order of 1–5 h. More exact figures have to be obtained from adequate laboratory experiments.