

isotherms can be applied to express the equilibrium coverage of the surface. Assuming that the Langmuir isotherm applies, the equilibrium coverage is expressed as:

$$\theta_{\text{eq}} = \frac{Kc_i}{1 + Kc_i} \quad (2.9)$$

where  $K$  ( $\text{m}^3 \text{kg}^{-1}$ ) is the Langmuir constant and  $c_i$  ( $\text{kg m}^{-3}$ ) is the impurity concentration. Then, the growth rate inhibition, related to the growth rate in pure media, can be written as:

$$G_i = G(1 - \alpha\theta_{\text{eq}}) \quad (2.10)$$

where  $\alpha$  (–) accounts for the effectiveness of impurity on growth rate inhibition.<sup>11</sup> It is important to highlight that the growth rate inhibition is facet-specific, therefore growth rate inhibitors can be used to selectively block the growth rate of selected crystal facets, enabling efficient crystal shape control.<sup>12</sup>

### 2.2.4 Modeling Crystal Agglomeration

In certain crystallization systems the unification of crystals, including by flocculation, aggregation and agglomeration, occurs, which can influence the crystal size distribution (CSD), and so has to be taken into account in the model development. From a mechanistic perspective, it is important but difficult to distinguish among these mechanisms. Generally speaking, a flocculate is a group of particles that are connected by weak cohesive forces. Agglomeration is the unification of primary particles by cementation through a crystalline bridge. The formation of this bridge requires crystal growth, therefore, agglomeration occurs in supersaturated solutions and these groups are harder to destroy. The bonding forces in aggregates are stronger than in flocculates, but weaker than in agglomerates. Agglomeration is dominant under the approximately 10  $\mu\text{m}$  size range, including the submicron range, and it is generally negligible for crystals exceeding 50  $\mu\text{m}$ .<sup>13</sup> Therefore, agglomeration is naturally accompanied by high nucleation rates, typically those in reaction crystallization/precipitation.

For isotropic crystals the agglomeration does not conserve the shape, but it conserves the volume. It is a general agglomeration modeling assumption to consider the linear size of the agglomerate as the sphere-equivalent diameter. For the shape of binary agglomerates this might be a crude assumption, but for highly agglomerating systems spherical agglomerates are likely to be formed, as Figure 2.5 presents.

The rate of agglomeration between two crystals (with sizes  $L$  and  $\lambda$ ) is described by the agglomeration function ( $\beta$ ):

$$\beta(L, \lambda) = \alpha_0 \beta_0(L, \lambda) \quad (2.11)$$

where  $\alpha_0$  (–) is an agglomeration constant and  $\beta_0$  ( $\text{s}^{-1}$ ) is the agglomeration kernel.