On heterogeneous nucleation during the precipitation of barium sulfate

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ARTICLE INFO

ABSTRACT

Mechanisms of primary nucleation of crystals are commonly differentiated into homogeneous nucleation due to molecular collisions, and heterogeneous nucleation originating from the surface of existing heterogeneous seed particles. In theory, all heterogeneous seeds should be activated and the kinetics of homogeneous nucleation should become dominant at high supersaturation. Hence, we suppose that heterogeneous nucleation becomes negligible at very high supersaturation, e.g., at technical precipitation of barium sulfate. Nevertheless, it is often assumed in literature that heterogeneous nucleation dominates the nucleation rate even at very high supersaturation. We assume that the particle size of precipitated barium sulfate is not influenced by the presence of foreign particles above a certain high supersaturation. To prove this assumption, precipitation experiments were carried out at very high nominal activity-based supersaturation in the presence of varying amounts of barium sulfate seeds and reaction-inert silica seeds. The influence of this seed material on the particle size obtained and on the depletion of supersaturation is investigated. Our experiments prove that the heterogeneous seeds used have no influence on the particle size or the depletion of supersaturation, and that heterogeneous nucleation is to be neglected in the case of barium sulfate precipitation at very high supersaturation.

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1. Introduction

Two kinds of primary nucleation mechanisms are distinguished in literature: homogeneous and heterogeneous nucleation (Söhnel and Garside, 1992; Mullin, 1993; Kashchiev, 2000; Mersmann, 2001; Myerson, 2002; Sangwal, 2007). It is a common view that the nucleation rate for both mechanisms shows a nonlinear dependence on the prevailing, activity-based supersaturation

$$S_{a,0} \equiv \frac{a_{i,0}}{a_i^*} \tag{1}$$

(see Fig. 1). We use the term nominal, activity-based, supersaturation (Symbol $S_{a,0}$) in the following to refer to the fact that, as a rule, the actual supersaturation in such experiments may be lower than the nominal supersaturation calculated from the feed compositions, either because of the impossibility to mix the feed streams instantaneously or because of an instantaneously commencing depletion of supersaturation during this mixing process.

Homogeneous nucleation is described by the classical nucleation theory (Volmer and Weber, 1926) and occurs from a clear solution. It is not active at low supersaturation, because activation energy for nucleation has to be superseded. At higher supersaturation, it attains increasingly high rates. The maximum rate would be the rate of molecular collision. By contrast, the formation of nuclei in heterogeneous nucleation is assumed to be catalyzed by the surface of existing particles or by the wall of the process equipment. Because these surfaces reduce, but do not neutralize the said work of nucleation, this mechanism is also inactive at low supersaturation. However, it is expected that a lower supersaturation than for homogeneous nucleation is required for heterogeneous nucleation to become active. Nevertheless, the availability of a heterogeneous surface which can be activated is limited. Therefore, the heterogeneous nucleation rate will attain a maximum value. Hence, homogeneous nucleation will be the determining nucleation mechanism at supersaturations which we name "very high." The physicochemical characteristics of the heterogeneous surface will determine whether it acts catalytically or not.

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http://dx.doi.org/10.1016/j.cherd.2016.07.024

Nomenclature

Symbols

A_{BET}	BET surface (m^2/g)
A_V	Specific volume-based surface (m^2/m^3)
a	Activity (mol/m^3)
$\tilde{c}$	Molar concentration (mol/m^3)
c	Mass concentration (kg/m^3)
f	Frequency distribution function ($1/m$)
G	Growth rate (m/s)
J	Nucleation rate ($1/m^3 s$)
n	Number of particles per volume and size class ($1/m^4$)
K_{SP}	Solubility product (mol^2/l^2) or (mol^4/l^4)
k_B	Boltzmann constant
q_3	Volume-based particle size frequency distribution ($1/m$)
R	Free lattice ion ratio
RI	Refractive index
S_a	Activity-based degree of supersaturation
Sh	Sherwood number
T	Temperature (K)
t	Time (s)
t_R	Residence time in reaction tube (s)
V_m	Molar volume of barium sulfate (m^3/mol)
$\bar{x}$	Mean size of logarithmic distribution function (m)
x	Particle size (m)
γ_{cl}	Interfacial energy between crystal and liquid (J/m^2)
κ	Conductivity (S/m)
ν	Stoichiometric coefficient
σ	Deviation of logarithmic distribution function

Sub- and superscripts

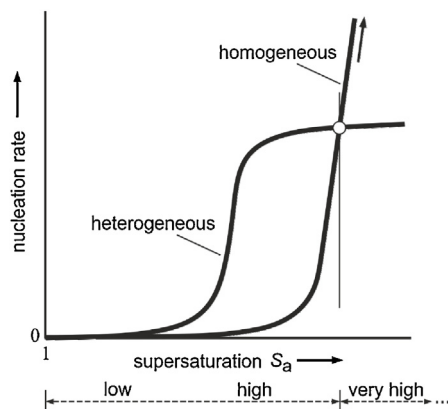|	
0	Initial, at $t = 0$
50, 3	Mean volume-based
*	Solid–liquid equilibrium
crit	Critical
free	Free ion
het	Heterogeneous
hom	Homogeneous
i	Component
max	Maximum
min	Minimum
n	Nucleation mechanism
poi	Point of inflection

Fig. 1 – Principal dependency of homogeneous and heterogeneous nucleation rates on supersaturation.

ing) (Mealor and Townshend, 1966; Nielsen, 1969; Packter et al., 1981; Mohanty et al., 1988; Angerhöfer, 1994; He et al., 1995; Schubert and Mersmann, 1996; Kashchiev and Van Rosmalen, 2003; Kucher et al., 2006, 2008). Other sources describe that barium sulfate grows by aggregation in this range of supersaturation (Melikhov and Vukovic, 1975; Judat and Kind, 2004; Roelands et al., 2006; Kügler et al., 2015; Ruiz-Agudo et al., 2015).

Which kind of seed particles should have acted as heterogeneous nuclei is not revealed in the literature cited above. Only general remarks about "rust," "dust," "foreign substrate" and "other submicroscopic impurities" are given (Mealor and Townshend, 1966; Nielsen, 1969; Packter et al., 1981; Roelands et al., 2006; Walton, 1963). Schubert and Mersmann (1996) carried out barium sulfate precipitation experiments with specific types of seed particles (silica (SiO_2), alumina (Al_2O_3) and titania (TiO_2)). They found that the rate of nucleation depends on both the area of seed surface and, according to classical nucleation theory, the physicochemistry of the surface, which is responsible for the reduction of free enthalpy of nucleating a critical cluster. However, it was not possible for them to characterize the nanoparticles obtained physicochemically due to limited analytical methods (Schubert, 1998). They precipitated barium sulfate in a T-mixer and then let the particles precipitated increase their size up to micrometers to be able to measure their particle size distribution by static light scattering. For this growth process, both necessary reagent solutions (barium hydroxide, sulfuric acid) were added carefully to the suspension of nanoparticles obtained. All precipitation experiments were carried out at stoichiometric conditions ($R \equiv \tilde{c}_{Ba}^{free}/\tilde{c}_{SO_4}^{free} = 1$). The current knowledge is that stoichiometric precipitation of barium sulfate leads to agglomeration of the primary particles (Kucher et al., 2006; Kügler et al., 2015; Schubert and Mersmann, 2000; Schwarzer and Peukert, 2002). Despite this effect, they found that particle numbers increased significantly upon adding seed particles and, therefore, they concluded that the mechanism of heterogeneous nucleation was dominant.

Following the above definition of supersaturation S_a, low solubility substances are prone to considerable supersaturation values, particularly during technical precipitation processes with high reagent concentration $\tilde{c}_i$ (Mersmann, 2001; Kind, 2002). A comparison between four arbitrary, but differently soluble inorganic salts proves that the degree of supersaturation S_a attains considerable numbers even at low reagent concentration $\tilde{c}_i$ (see Table 1).

It can be seen from Table 1 that barium sulfate particularly leads to considerable supersaturation. The question arises whether, in this case, homogeneous nucleation dominates and whether the supersaturation has to be considered as being high or very high (see Fig. 1). Regarding this question, many authors have observed a wide range of nucleation rates for barium sulfate and concluded from their experimental findings that heterogeneous nucleation is active up to supersaturations of $S_{a,0} \leq 500$ (equal to $\tilde{c}_{BaSO_4} = 0.02$ mol/l after mix-

Table 1 – Activity-based supersaturation S_a of some metal salts ranked by their solubility. The mean activity coefficients are calculated with the semiempirical model of Bromley (1973); solubility products, ion association constants and carbonate equilibrium are considered (Monnin, 1999; Parkhurst and Appelo, 2013).

i	$-\log(K_{SP,i})$	$\tilde{c}_i$ in mol/l		
		0.001	0.01	0.1
$BaSO_4$	9.82	$S_a = 67$	343	1233
$BaCO_3$	8.56	13	76	270
$SrSO_4$	6.62	1.4	7.7	29
$CaSO_4 \cdot 2H_2O$	4.58	0.14[a]	0.78[a]	2.6

[a] $S_a < 1$: undersaturated.