Nucleation and supersaturation in porous media (revisited)

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ABSTRACT

Supersaturation-Nucleation-Time (S-N-T) diagrams are shown to be a useful tool to predict nucleation during reactive-transport processes in porous media. Such diagrams can be determined experimentally or estimated from theoretical calculations based on classical nucleation theory. With this aim, a ‘pragmatic’ understanding of the nucleation rate equation is adopted here and the meaning and magnitude of the interfacial tension and induction time discussed. Theoretical diagrams and experimental data are shown to match fairly well as long as there is an appropriate choice of the ‘relevant’ volume for induction-time calculations.

KEYWORDS: nucleation, supersaturation, porous media.

Introduction

NUCLEATION is in the scientific spotlight, as shown by the number of reviews published on the subject in the last few years, particularly in relation to crystal nucleation in solution (Benning and Waychunas, 2008; Vekilov, 2010; Yi and Rutledge, 2012; Gebauer et al., 2014). These additions to the literature are no doubt related to the detection of stable solute species, referred to as pre-nucleation clusters (PNCs), which are supposed to mediate the development of the crystal phase from the aqueous solution (Gebauer et al., 2008; Gebauer and Cölfen, 2011). That breakthrough challenges our idea of the mechanisms involved in the nucleation process as defined in classical nucleation theory (CNT). The use of state-of-the-art techniques (Pouget et al., 2009) and molecular simulation methods (Demichelis et al., 2011) reveals the nature of PNCs and making the statement “now you see them” (Meldrum and Sear, 2008) convincing, at least in the case of calcium carbonate. Other inorganic systems such as certain iron oxy-hydroxides (e.g. Yuwono et al., 2010), calcium phosphates (e.g. Wang et al., 2012), and silica could be reasonably accommodated in the new nucleation paradigm, although the recognition as PNCs of certain oligomers, amorphous nano-clusters, and other “primary” particles is a source of controversy (Gebauer et al., 2014). Moreover, the stability of many of these species and their effect on nucleation barriers remains a point for discussion (De Yoreo, 2013). Finally, even if ‘primary’ particles exist in a given aqueous system, the formation of precursor phases by aggregation may not occur (Baumgartner et al., 2013), and the process can still be described within the CNT framework.

Much work needs to be done to extend the aggregation-based mechanism to inorganic systems other than CaCO3, and therefore nucleation will continue to be a leading topic in the years to come. In the meantime, kinetic modelling of nucleation is typically performed using the classical nucleation rate equation, with some exceptions in systems that are known to involve amorphous precursor phases (e.g. Rodriguez-Blanco et al., 2011). CNT is used not only in

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industrial crystallization protocols (Sangwal, 2007) but also in geochemical modelling (Fritz and Noguera, 2009) and in fundamental studies of precipitation and co-precipitation on mineral surfaces (Fernández-Martínez et al., 2013; Shtukenberg et al., 2005).

In CNT, the nucleation rate (the number of nuclei, \( N \), formed per unit volume and time: \( J = N/Vt \)) depends exponentially on the free energy change (\( \Delta G_c \)) involved in the formation of a nucleus of critical size, i.e.

\[
J = \Gamma \exp \left( -\frac{\Delta G_c}{kT} \right)
\]

(1)

where \( k \) is the Boltzmann constant, \( T \) the absolute temperature, and \( \Gamma \) a pre-exponential factor. In turn, \( \Delta G_c \) depends significantly on the supersaturation (\( S \)), according to

\[
\Delta G_c = \frac{\beta \omega^2 \sigma^3}{(kT \ln S)^2}
\]

(2)

where \( \omega \) is the molecular volume in the solid phase, \( \beta \) is a factor that depends on the shape of the nucleus, and \( \sigma \) is the interfacial tension. Most readers are likely to be aware of the weak points implicit in CNT, such as the idea of applying macroscopic concepts (surface and volume) to molecular-scale objects or the assumption that the interfacial tension does not depend on the size of the nuclei. While there is a general agreement on these weak points, the method by which the controlling parameters in equations 1 and 2 are estimated is widely disregarded. For example, the interfacial tension is recognized to represent all the excess energy accumulated in the vicinity of the solution–cluster interface, but in practice, \( \sigma \) is an ‘artificial’ parameter that cannot be determined by direct and unambiguous experiments (Söhnel, 1982). In fact, the opposite approach must be adopted: the only interfacial tension values that are relevant in modelling nucleation kinetics are those obtained in nucleation experiments, i.e. from nucleation-rate or induction-time measurements. Although the term ‘interfacial tension’ is used interchangeably in the literature, the nucleation-derived \( \sigma \) has a different meaning and value from the “surface energies” obtained by contact-angle measurements (Wu and Nancollas, 1999) or water-adsorption calorimetry (Forbes et al., 2011). Moreover, the CNT-derived \( \sigma \) values depend on the aqueous speciation model, the expression chosen for the supersaturation, and the shape factor chosen for the nuclei (Prieto et al., 2012). This fact was well known by the pioneers in this field (Söhnel, 1982) but is frequently disregarded in the literature. Therefore, to model the nucleation kinetics in a given system, all the input data must be consistent with the value of \( \sigma \) chosen for the calculation. Thus, the CNT expression in equation 1 can be imagined as a species of fitting function in which the main fitting parameter is \( \sigma \). The nucleation barrier depends heavily (\( \Delta G_c \propto \sigma^3 \)) on this empirical magnitude, whereas other less influential parameters (particularly those included in the pre-exponential factor) can be tuned to optimize the results. From that point of view, \( \Delta G_c \) plays a similar role to the energy barriers to form activated complexes, which are typical in chemical kinetics. Moreover, phenomena such as the singular nucleation behaviour of sparingly soluble compounds in ionic solutions (Kowacz et al., 2010) could be modelled by CNT, provided that ad hoc nucleation-derived \( \sigma \) data were available.

According to this pragmatic understanding of CNT, the present study models the nucleation behaviour observed in previous experiments (Putnis et al., 1995), taking baryte as an example system. Such experiments were conducted in U-shaped tubes in which the reacting ions counter-diffuse through a column of porous silica hydrogel. Because the gel properties inhibit advection and convection, the crystallization medium is purely diffusive. Crystals tend to nucleate approximately midway through the diffusion column, which is the zone where the supersaturation builds up most rapidly because the counter-diffusing ions ‘meet’ there. Hydrogel media have been used widely to simulate precipitation and reactive transport in natural environments (Fernández-Díaz et al., 1996; Prieto et al., 2002) and are currently used in bio-mineralization studies (Sancho-Tomás et al., 2013; Nindiyasari et al., 2014). In nature, precipitation frequently occurs in pores of rocks, soils and sediments. Moreover, crystallization of salts in porous building materials (masonry, cement, mortar) has been recognized as crucial for their weathering and decay (Rodríguez-Navarro et al., 2002). Developing predictive models for the nucleation behaviour in these types of systems is worthwhile, therefore. With this aim, we use a type of supersaturation-nucleation-time diagram (S-N-T) that allows the interpretation of nucleation pathways in solution systems. S-N-T diagrams are reminiscent of the
temperature-transformation-time (T-T-T)
diagrams used to interpret sub-solidus transforma-
tions in mineralogy and metallurgy (Putnis, 1992)
and can be used similarly. The choice of baryte as
an example system is not arbitrary. Baryte-scale
formation is a problem in many industrial
processes where knowledge of the nucleation
kinetics is essential for developing anti-scale
strategies. However, while most precipitation
studies have been performed using vigorously
stirred solutions, in many scenarios the nucleation
of baryte occurs in pores or small cavities where
the confined solution can become more highly
supersaturated than an analogous free solution
(Putnis and Mauhe, 2001; Rodríguez-Ruiz et al.,
2014). The present study confirms that hydrogels
are excellent media to emulate nucleation of
minerals in such conditions of confinement.

Methods

Precipitation experiments

The experiments addressed here were described
broadly in the original papers by Putnis et al.
(1995) and Prieto et al. (1990). The U-tube
arrangement in which two solution reservoirs are
separated by a diffusion column of silica hydrogel
is shown in Fig. 1. The gel contains ~95.6 vol.%
solution within interconnecting pores of diameters
0.1–0.5 μm. However, the pore size is not uniform
(Henisch, 1988) and secondary pores with
diameters >10 μm are common. The initial gel
pH is 5.5, and the working temperature is 25ºC. In
such a device, the experimental inputs are the U-
tube dimensions and the initial concentration of
the reactants, while the primary outputs are the
location of the crystallization zone (cz) and the
time (tw) at which the first crystallites are observed
by optical microscopy at ×500 magnification.
These data, as provided by Putnis et al. (1995) and
related papers, are shown in Table 1. The
secondary parameters have been recalculated
here to make them consistent with the overall
calculation procedure. Solution speciation, mass-
transfer, and supersaturation have been computed
using the geochemical code PHREEQC (Parkhurst
and Appelo, 2013) and its default database.
PHREEQC allows modelling of one-dimensional

![Fig. 1. Typical U-tube arrangement. The horizontal branch (28 cm) connects two vertical branches (10 cm) which
contain the parent solutions. The SEM image shows a typical baryte crystal grown by this technique.]

| Code | Parent solutions (M) | t_w (h ± 6) | cz (cm ± 1) | Ω^th × 10^3 | R_O (h⁻¹) | t_R (h) |
|------|----------------------|-------------|-------------|-------------|-----------|---------|
| BRT-1 | 0.5 0.5              | 380*        | 14          | 11.9 ± 1.2  | 190       | 62.6    |
| BRT-2 | 0.5 0.3              | 432         | 16          | 10.7 ± 0.9  | 144       | 74.1    |
| BRT-3 | 0.3 0.5              | 458         | 14          | 11.5 ± 0.9  | 136       | 84.3    |
| BRT-4 | 0.5 0.1              | 476         | 18          | 7.30 ± 0.6  | 90        | 81.1    |
| BRT-5 | 0.3 0.3              | 480         | 15          | 8.18 ± 1.5  | 94        | 87.1    |
| BRT-6 | 0.1 0.5              | 504         | 13          | 8.11 ± 0.5  | 80        | 101.4   |
| BRT-7 | 0.1 0.1              | 572         | 15          | 4.06 ± 0.3  | 35        | 116.1   |

* Note that in Prieto et al. (1990) and Putnis et al. (1995) this value was mistakenly compiled as 360 h.
diffusion with the same algorithm that was used by Henisch and García-Ruiz (1986) to model the diffusion and precipitation patterns in gel columns. The newly obtained parameters ($\Omega^h$ and $R_\Omega$) differ from the original ones but correlate similarly with each other.

For sparingly soluble minerals, the thermodynamic supersaturation is given by the quotient between the ionic activity product in the current solution and the thermodynamic solubility product. In the case of baryte:

$$\Omega = \{\text{Ba}^{2+}\} \cdot \{\text{SO}_4^{2-}\}/\Omega_{\text{Hrt}}$$

In Table 1, $\Omega^h$ represents the value of $\Omega$ at $t_w$, and column $R_\Omega$ lists the supersaturation rate ($d\Omega/dt$) at $t_w$. The waiting time $t_w$ can be considered as representative of nucleation: once a crystal nucleates, the growth to reach a visible size ($\times 500$) is very fast due to the high supersaturation level in the nucleation area (Table 1). Even so, the imprecision in determining the nucleation event can be expected to depend on the observer’s care and thoroughness. Here, we have chosen deliberately an overestimated value of $\pm 6$ h, considering a 3 h monitoring interval. This imprecision is not very significant ($<2\%$) when compared with the $t_w$ values but needs to be incorporated in the calculations. The last column in Table 1 ($t_R$) represents the time elapsed to reach $\Omega^h$ at a constant rate equal to $R_\Omega$.

**CNT calculations**

There are numerous compilations of CNT-derived $\sigma$ values in the literature, but most of them come from the same original papers by Nielsen (1967), Garten and Head (1973) and a small number of others. These original data were determined using concentrations instead of activities to express the supersaturation or simply introducing correction terms that represent the rate of attachment of monomers (growth units or molecules) to the critical nuclei. Different approximations to derive this factor can be seen in the literature (Walton, 1969; Lasaga, 1998; Kashchiev, 2000; Sangwal, 2007). When the attachment is controlled by the diffusion of growth units from the solution bulk to the nucleus surface, a comprehensive formulation (Kashchiev, 2000) results in:

$$\Gamma = Z \frac{DN_1}{r_c} A_c N_0$$

where $N_0$ and $N_1$ are concentrations that represent the number of nucleation sites and the number of monomers per unit volume of fluid, respectively. $D$ is the diffusion coefficient of the monomers in the fluid phase, and $A_c$ is the surface area of the critical nucleus, assumed to be a sphere of radius $r_c$ (with $r_c = 2\sigma\delta/kT \ln\Omega$). The term $DN_1/r_c$ stands for the incoming diffusion flux of monomers to the nucleus surface. Finally, the Zeldovich factor ($Z$) arises from the steady-state treatment of the problem:

$$Z = \left( \frac{\Delta G_c}{3\pi kT n_c^2} \right)^{1/3}$$

where $n_c$ is the number of monomers in the critical nucleus. For homogeneous (HON) nucleation, every molecular position can be considered a potential nucleation site (Kashchiev and Rosmalen, 2003). Therefore, $N_0$ can be equated to $1/v_w$, where $v_w$ is the volume of a water molecule in the solution. The calculations were implemented in Mathcad (MathSoft Inc.) using the parameters compiled in Table 2. The concentration of monomers ($N_1$) depends on the super-
saturation and was calculated in each case using PHREEQC. Simulations of 3D-heterogeneous nucleation (HEN) on foreign micro-particles have been performed using a unified operational formula in which HON is treated as a limiting case of HEN with $\sigma$ replaced by an effective interfacial tension defined as:

$$\sigma_{\text{eff}} = \Phi \sigma$$ (7)

where the coefficient $\Phi$ is a number between 0 and 1 (Sangwal, 2007; Liu, 1999) that depends on both the substrate–nucleus interaction and the geometry of the assemblage.

**Calculation results and discussion**

**Critical supersaturation and threshold supersaturation**

The classical nucleation rate equation is based on the assumption that supersaturation is reached instantaneously. For a given supersaturation, the nucleation rate adopts a specific value, and we can represent a function that relates the two parameters. Figure 2 represents such a function for baryte. As shown, the nucleation rate increases so dramatically with supersaturation that the occurrence of a critical value is usually admitted. Above this value, the nucleation becomes catastrophic ($J \rightarrow \infty$), and below this value, nucleation decreases quickly to zero. The critical supersaturation is considered to be representative of the metastability limit, which marks the width of the so-called metastable zone. However, the critical supersaturation needs to be defined by choosing an arbitrary value of $J$ (typically $1 \text{s}^{-1} \text{cm}^{-3}$), and therefore, the metastability limit is ambiguous. Moreover, in most scenarios, supersaturation is not reached instantaneously but increases continuously until nucleation (whether HEN or HON) occurs. That phenomenon also occurs in counter-diffusion experiments, for which the concept of threshold supersaturation was first defined (Putnis et al., 1995; Prieto et al., 1990). The threshold supersaturation, $\Omega^\text{th}$, is the effective supersaturation at which nucleation occurs and has been shown to depend on the reaction path followed by the system.

Figure 3 shows the increase in supersaturation in $cz$ as a function of time in the case of experiment BRT-1 (see Table 1 also). The highest value is $\Omega^\text{th}$. The supersaturation increases to reach an almost constant value of $R_\omega$. The inset shows at a larger scale that there is a linear trend for long diffusion times. The supersaturation rate, $R_\omega$, is given by the slope of this line. Figure 3 also shows $t_{\text{th}}$, i.e. the waiting time when supersaturation increases from zero to $\Omega^\text{th}$ at a constant rate equal to $R_\omega$. According to the experiments of Putnis et al. (1995), inspection of Table 1 shows

| Mechanism | $\sigma_{\text{eff}}$ (J cm$^{-2}$) | $\Phi$ | $D$ (cm$^2$ s$^{-1}$) | $\omega$ (cm$^3$) | $N_0$ (cm$^{-3}$) | $\beta$ | $V$ (cm$^3$) |
|-----------|----------------|------|----------------|-------------|-------------|------|-------------|
| HON       | $1.34 \times 10^{-5}$ | 1    | $9.37 \times 10^{-6}$ | $8.6 \times 10^{-23}$ | $3.33 \times 10^{22}$ | 16$\pi$/3 | 1.91       |
| HEN       | $1.06 \times 10^{-5}$ | 0.79 | $9.37 \times 10^{-6}$ | $8.6 \times 10^{-23}$ | $2.50 \times 10^7$  | 16$\pi$/3 | 1.91       |
| HON-0.1 μm | $1.34 \times 10^{-5}$ | 1    | $9.3 \times 10^{-6}$  | $8.65 \times 10^{-23}$ | $3.33 \times 10^{22}$ | 16$\pi$/3 | $5. \times 10^{-16}$ |
| HON-1 μm  | $1.34 \times 10^{-5}$ | 1    | $9.3 \times 10^{-6}$  | $8.65 \times 10^{-23}$ | $3.33 \times 10^{22}$ | 16$\pi$/3 | $5. \times 10^{-13}$ |
| HON-100 μm | $1.34 \times 10^{-5}$ | 1    | $9.3 \times 10^{-6}$  | $8.65 \times 10^{-23}$ | $3.33 \times 10^{22}$ | 16$\pi$/3 | $5. \times 10^{-7}$ |
| HEN-1 μm  | $9.38 \times 10^{-6}$ | 0.7  | $9.3 \times 10^{-6}$  | $8.65 \times 10^{-23}$ | $2.5 \times 10^7$  | 16$\pi$/3 | $5. \times 10^{-7}$ |
| HEN-1 μm  | $1.01 \times 10^{-5}$ | 0.75 | $9.3 \times 10^{-6}$  | $8.65 \times 10^{-23}$ | $2.5 \times 10^7$  | 16$\pi$/3 | $5. \times 10^{-7}$ |
| HEN-1 μm  | $1.07 \times 10^{-5}$ | 0.8  | $9.3 \times 10^{-6}$  | $8.65 \times 10^{-23}$ | $3.33 \times 10^{22}$ | 16$\pi$/3 | $5. \times 10^{-7}$ |
that the greater the supersaturation rate, the
greater the threshold supersaturation. The varia-
tion of $\Omega^\text{th}$ with $R_O$ fits an empirical relationship
that used to be familiar in the industrial crystal-
lization literature (Putnis et al., 1995). The
theoretical understanding of that correlation still
requires deeper insight, however.

**Induction time and waiting time**

The induction time, i.e. the time ($t_i$) that elapses
between the ‘instantaneous’ creation of super-
saturation and the detection of nucleation, is
another important concept in CNT. This time is
related to the ability of the solution to remain
supersaturated and, with some misgivings, can be
considered an “experimental observable”
(Kashchiev and van Rosmalen, 2003). In contrast,
the waiting time ($t_w$) represents the total time
involved in the transport–reaction process, from
the beginning of the experiment to the moment at
which $\Omega^\text{th}$ is reached and nucleation occurs.

Following the comprehensive review by
Kashchiev and van Rosmalen (2003), “when the
appearance of the very first supernucleus in the
solution volume is the event that brings the
solution out of metastability”, the induction time
is given by:

$$t_i = 1/JV$$

where $V$ is the solution volume. As Kashchiev and
van Rosmalen (2003) noted, equation 8 implies
setting $N = 1$ at $t = t_i$ in the expression $J = N/Vt$.

As discussed below, porous media are highly
effective at suppressing nucleation. As a conse-
quence, crystallization occurs at high supersatura-
tion, and the nucleation density ($N/V$) is typically
very low. For this reason (and because of the
hydrogel transparency), the gel technique provides
certain research opportunities that nucleation in
free solutions cannot provide. The low nucleation
density allows us to detect and count the very first
crystallites in the crystallization zone. In fact,
certain typical papers on crystallization in gels
(Prieto et al., 1990) report not only $t_w$ and $cz$ but
also the number of crystallites observed. That
feature makes equation 8 suitable for exploring the
nucleation behaviour in this study.

Figure 4 shows an S-N-T diagram calculated for
HON (solid line) using the parameters in Table 2.
The calculation has been performed considering the whole volume of the crystallization zone \( V = \pi r^2 h = 1.91 \text{ cm}^3 \). The HEN diagram (dashed line) is somewhat speculative because parameters such as the concentration of active nucleation sites \( N_0 \) and \( \Phi \) are difficult to estimate. Here, we have chosen \( N_0 = 2.5 \times 10^7 \text{ cm}^{-3} \) from the data obtained by Garten and Head (1973) for baryte nucleation. Figure 5 shows the crystal counts obtained by these authors as a function of supersaturation. The strong increase above a certain supersaturation level is representative of HON, whereas at a lower supersaturation, the number of nuclei is virtually independent of supersaturation and can be considered representative of the concentration of active HEN sites.

The diagram in Fig. 4 can be used to assess whether nucleation will or will not occur in an evolutionary system and at what degree of supersaturation. However, the diagram does not seem to work with gel experiments. As shown in

Fig. 4. S-N-T diagrams calculated for HON and HEN of baryte using the parameters in Table 2. The HEN diagram has been calculated using the number of active sites from experimental data by Garten and Head (1973).

Fig. 5. Nucleation density of baryte in ‘free’ solutions as a function of supersaturation (recalculated from Garten and Head, 1973).

Fig. 6. Comparison of the experimental values of \( \Omega^\text{th} \) with the theoretical S-N-T curves. The open circles show the induction times to be expected at equivalent supersaturations in 1.91 cm\(^3\) of ‘free’ solution.
Fig. 6, the experimental $\Omega^\text{th}$ data points correspond to longer times in comparison with the theoretical nucleation curves. The experimental values of $\Omega^\text{th}$ have been plotted on the ordinate against $t_R$ on the abscissa, i.e. considering a stationary supersaturation rate. The open circles show the induction times to be expected at equivalent supersaturation in 1.91 cm$^3$ of ‘free’ solution. As observed, $t_i$ and $t_R$ differ by orders of magnitude.

**The pore size effect**

As seen in equation 8, the induction time depends on the solution volume that we consider: the larger $V$, the shorter $t_i$, in agreement with the probabilistic nature of nucleation. A problem arises because choosing the ‘relevant’ volume for nucleation-rate calculations is not always easy. The diagram in Fig. 4 was calculated by considering the whole volume of the crystallization zone, which does not seem to be the right choice. The fact that porous media are highly effective at suppressing nucleation lies at the core of this problem. During cluster formation, the solution vicinity becomes poor in solute, and the disappearance of a subcritical cluster is ensured if no exchange brings new growth units into its vicinity (Prieto et al., 2002). This effect is particularly important in fine porous media, where the solution is trapped in small pores connected by tortuous routes, and solute transport occurs by diffusion. Under these conditions, each single pore can be envisioned as a crystallization chamber, and we can use the pore size as the ‘relevant’ volume in equation 8.

Figure 7 shows two S-N-T diagrams calculated in this way for pore sizes of 1 μm and 0.1 μm (see Table 2). The experimental results plot between both curves, which demonstrate that the relevant volume in determining the nucleation behaviour is probably the pore volume and that the largest pores must be the preferential nucleation places. Although the HEN curve has not been represented, the high threshold supersaturation points towards an HON mechanism. The only exception occurs in experiment BRT-7. In this case, $\Omega^\text{th}$ and $R_\Omega$ are comparatively very small and a HEN mechanism could be expected. In counter-diffusion experiments the gel is said to be inert because it does not take part in the precipitation reaction. Nevertheless, in the same way as in free solutions, in real systems nucleation may occur on foreign nanoparticles or active centres present in either the polymeric framework or the interstitial solution. Anyway, Fig. 7 illustrates that S-N-T diagrams can be a suitable tool to assess HEN conditions in rocks, sediments, soils, etc., where the prediction of precipitation reactions is complicated not only by the porous nature of these media but also by their interaction with the precipitate (Stack et al., 2014).

Porous media are known to affect the transport of solutes through a diversity of mechanisms such as adsorption, absorption and precipitation.
However, the existence of a pore-size dependence of the metastability of supersaturated solutions is less known and not often considered in reactive-transport modeling. Such dependence usually results in inhibition of precipitation in nanopores and preference for the precipitation in macropores. Stack et al. (2014) studied the kinetics of precipitation of calcium carbonate in an amorphous-silica medium that contained two categories of pore sizes, macro pores ($\Omega > 30 \, \mu m$) and nanopores ($\Omega = 8-30 \, nm$). Those authors observed precipitation exclusively in the macropores and demonstrated how the interaction between substrate and precipitate is a controlling factor, with more “favorable” interactions allowing precipitation to occur in smaller pores. In fact, precipitation on nanopores can be enhanced using additives that increase the “favourability” of the substrate–precipitate interaction (Stack et al., 2014).

In the CNT framework, such ‘favourability’ can be expressed in terms of the HEN coefficient, $\Phi$. The smaller $\Phi$ is, the smaller the effective interfacial tension, $\sigma_{eff}$ (see equation 7) and the larger the HEN probability. The effect is shown in Figure 8a for the nucleation of baryte in 1 $\mu m$-sized pores. Figure 8b illustrates the influence of the pore size in the case of HON in a porous medium with two categories (100 $\mu m$ and 0.1 $\mu m$) of pores. As can be seen, for $\Omega = 6000$ the induction time differs by nine orders of magnitude! Obviously, nucleation would occur in the 100 $\mu m$ pores. Only in case that the supply of reactants continued and $\Omega$ increased or kept constant for a long time, precipitation could eventually occur in the nanopores. These two examples show separately the main factors involved in the precipitation behaviour in porous media. In practice, the scenario will be a complex combination of both examples in which the interplay of nucleation mechanisms, pore-size effects, and supersaturation evolution will determine the final outcome.

Conclusions

S-N-T diagrams are shown to be a useful tool for interpreting and predicting nucleation behaviour in porous media. Such diagrams can be determined experimentally or estimated from CNT-based calculations. With this aim, the present author has adopted a pragmatic understanding of CNT in which the nucleation rate expression is imagined as a species of fitting function with the interfacial tension being the main fitting parameter. The method can be extended to a diversity of scenarios. The correct choice of the relevant volume for the studied system becomes clearer when one considers that nucleation in porous rocks is favoured in fractures and open spaces, where a faster supply of growth units is ensured.

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