



Chapter 2

Theory

2.1 The precipitation process(20,29)

Precipitation will not occur until a solution reaches and surpasses saturation. The first step of precipitation is nucleus formation or cluster formation, also called nucleation. The interaction between ions and between molecules which leads to cluster formation and eventually to the evolution of crystals has been linked to a chemical reaction. In the chemical reaction the activation energy is a barrier which must be overcome before products can be formed. Similarly, the energy barrier to nucleation must be overcome before crystallization can occur. One result of this energy barrier is the necessary creation of some degree of supersaturation before spontaneous crystallization will occur.

In solutions at normal temperature, the molecules or ions of solute are in constant motion and consequently are often within the sphere of influence of another molecule or ion. Hence, groups of molecules or ions are always present. There is, though, at the outset, a distinct difference between the clustering of ions and the

clustering of molecules. Because of their ionic charge, ions tend to associate with neutral or oppositely charged groups, whereas uncharged molecules do not suffer from this restriction.

Prior to nucleation there is continuous formation and dissolution of ionic or molecular clusters in equilibrium with all other clusters. If the concentration of solute ions or molecules is high enough, the clusters become sufficiently large to become consolidated into colloidal particles, where upon the supposedly irreversible crystal growth starts. Crystal growth can occur in two way. Firstly, if the solution is not supersated, the colloidal particles will be stable in the solution and may form aggregates. Alternatively, when the solution is supersaturated the colloidal particles themselves will grow to become fine crystals. In the same way, fine crystalline aggregates or single coarse crystals may be formed. Figure 2.1 shows type of precipitates as it depends on the degree of supersaturation and the nature of precipitate. The precipitates that have fast nucleation will make the solution drop below supersaturation when the colloidal particles occur. So the precipitates become colloidal aggregates.

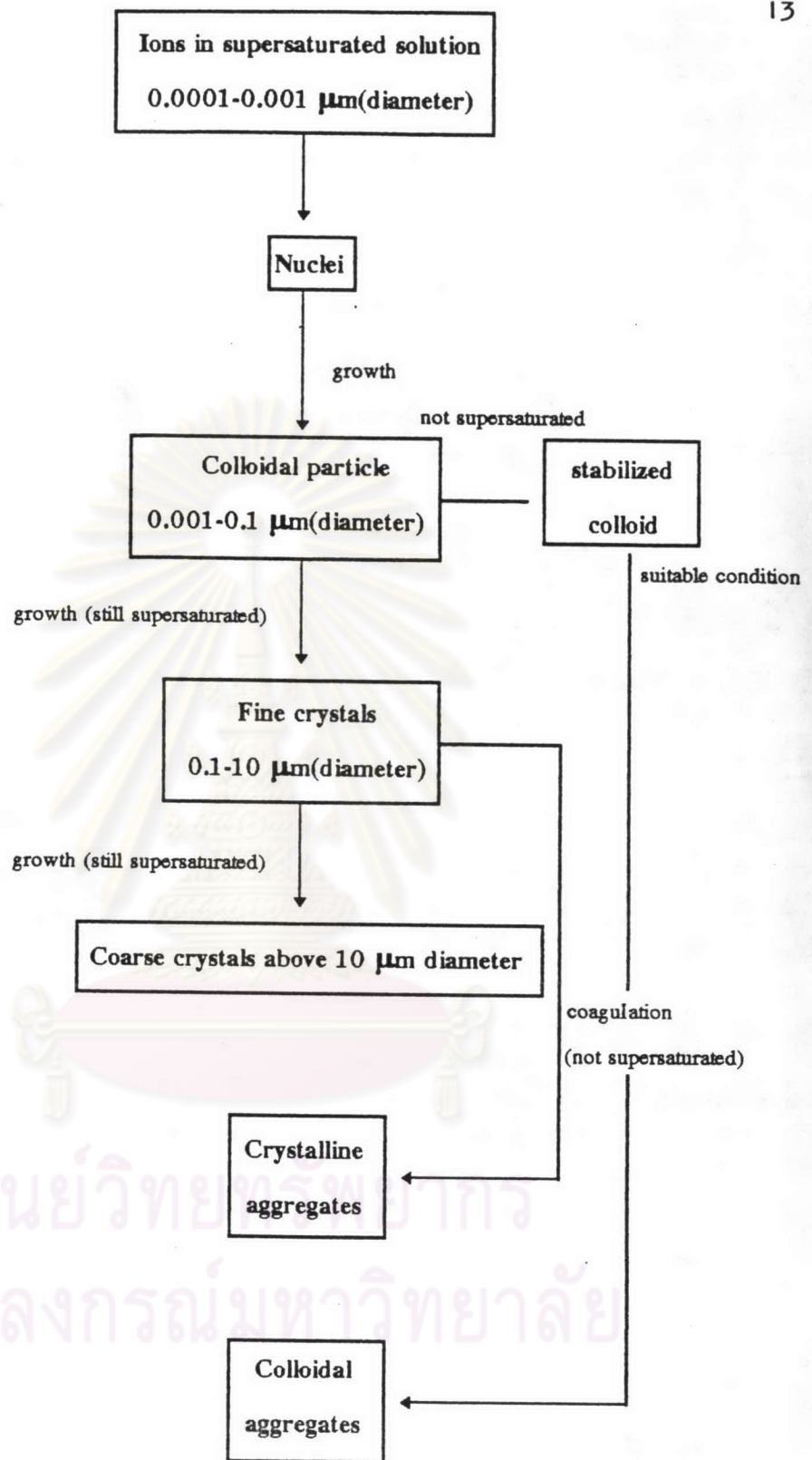


Fig.2.1 Flow chart of precipitation process

From above, there are two hypothesis to explain precipitation, coagulation hypothesis(22) and super-saturation hypothesis(14), and generally postulating that the nucleation of particles is discontinuous. Recent theories postulate that colloid formation and crystal growth of the reacting system when coupled with diffusion leads to periodic precipitation. The former hypothesis mainly suffered from an inadequate treatment of nucleation and crystal growth. These shortcomings do no longer exist. Therefore, this thesis tends to give preference to the super-saturation hypothesis. It will be shown that the main implications of the coagulation hypothesis are no longer neglected. The super-saturation approach is a comprehensive theory based on mathematical analytic solutions of Fick's law. Its strength is easy and quantitative relation to experimental parameters; its shortcoming is restriction to infinite and semi-infinite systems, which significantly differs from realistic experimental set-ups. When considering the very different shapes of concentration profiles for diffusion in finite and infinite systems, then such analytic approach is suited to explain the mechanisms involved, but not to model the actual reaction progress over extended periods of time.

In the following sections, an outline of the different aspects is given which work together to bring about



the phenomenon of periodic precipitation.

Thermodynamic aspects (28)

2.1-a Stability limits

Thermodynamic equilibrium determines the stability ranges of coexisting phases. It thus puts forward a necessary condition for the formation of a new phase. The occurrence of a solid precipitate from an aqueous solution requires that the solid is stable, i.e., that its solubility limit is exceeded. This can be accomplished in different ways, for example by temperature changes. The temperature is driven beyond the limit of stable solubility. This is usually a lower temperature threshold, and less commonly an upper one ("retrograde solubility").

by evaporation. The concentrations of dissolved components are driven beyond their limits of stable solubility by partial extraction of the solvent from the solution.

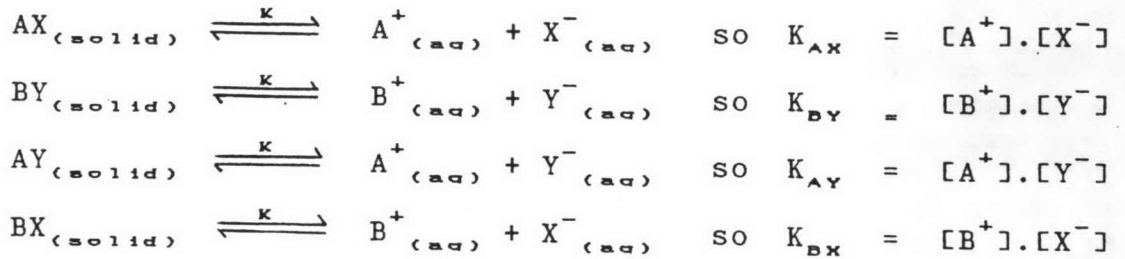
by diffusion.

Solubility limits are lowered locally by a solvent/solvent interdiffusion process (e.g. water vs. ethanol). Alternatively, a local solubility product of a specific compound is increased locally as a result of solute/solute interdiffusion. Either way, the system is eventually driven beyond a stability limit.

In the present study, only the latter case, and more specific the solute/solute interdiffusion process is of interest.

2.1-b Solubilities of aqueous electrolytes

The theory is outlined for the example of a reciprocal univalent aqueous electrolyte system with compounds AX, BY. The reciprocal compounds are AY and BX. Let the dissolved compounds be completely dissociated, i.e., as $A^+_{(aq.)}$, $X^-_{(aq.)}$, $B^+_{(aq.)}$ and $Y^-_{(aq.)}$. Then, let K_{AX} , K_{BY} , K_{AY} , K_{BX} be the local solubility products of compounds AX, BY, AY and BX;



A stable solution is established when all K are smaller than the respective solubility limits $K_j(s)$, $j = AX, BY, AY, BX$. For $K > K_j(s)$, the system is supersaturated. Thus the parameter $K/K_j(s)$ describes the position of the system with respect to thermodynamic equilibrium.

The experimental set-up considered shall be a gel column of glass powder and agar gel open to either one or both ends to reservoirs filled with dissolved AX or BY solution, respectively. The gel may contain AX or BY . This is the most general case. Examples of the specific boundary conditions are given in Fig.2.2.

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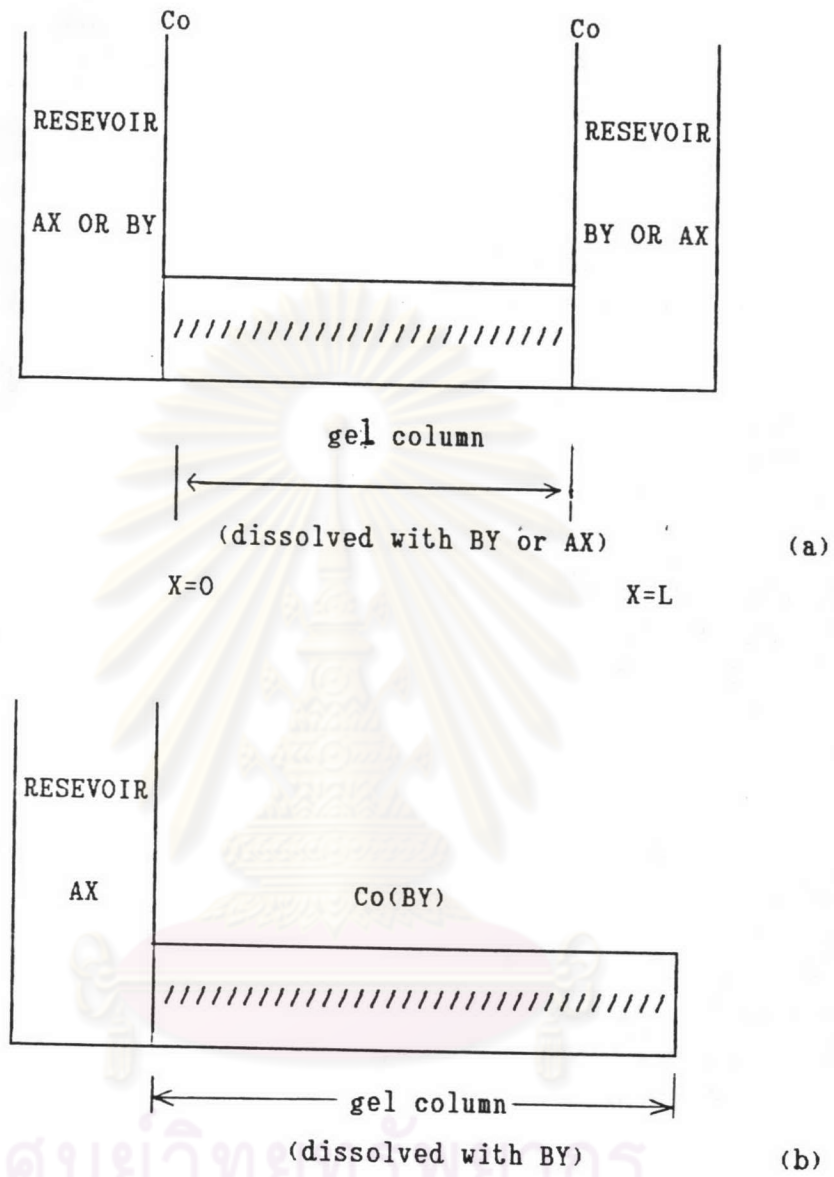


Fig.2.2 Sketch of the experimental set-up for diffusion and precipitation experiments.

(a) two source reservoirs,

(b) one source reservoir.

Let us now restrict the following initial system configuration like this : The gel column is open at one end only and contains dissolved BY at an initial concentration $C_{o(BY)}$, connected to a reservoir containing dissolved AX at an initial concentration $C_{o(AX)}$. It is obvious that the local solubility products $K_{AX} = [A^+].[X^-]$ and $K_{BY} = [B^+].[Y^-]$ cannot be increased beyond their respective initial reservoir values $K_{AX(o)}$ and $K_{BY(o)}$, by interdiffusion. By contrast, $K_{AY} = [A^+].[Y^-]$ and $K_{BX} = [B^+].[X^-]$ might reach their solubility limits. Let us now select a combination of A, B, X and Y in such a way that the solubility limit ; $K_{BX(s)} > K_{AX(s)} \approx K_{BY(s)} \gg K_{AY(s)}$. Then only AY can form a stable solid phase. The molar Gibbs free energy of dissolution of AY is given by

$$G_{diss} = RT \ln \frac{K_{AY}}{K_{AY(s)}}$$

We have to distinguish among the following local conditions :

$$K_{AY} < K_{AY(s)} : G_{diss} < 0 ; \text{solid AY is in equilibrium with the solution ;}$$

$K_{AY} = K_{AY(s)}$: $G_{diss} = 0$; solid AY is in equilibrium with the solution ;

$K_{AY} > K_{AY(s)}$: $G_{diss} > 0$; local super-saturation with respect to AY ; solid AY already present grows ; prerequisite for the formation of previously nonexistent solid AY : If $K_{AY} > K_{AY(s)}$ is not established, then solid AY will not form.

2.1-c Ostwald's concept of supersaturation

From the experiments of Ostwald, the relation between solubility limits and precipitation as shown in figure 2.3 is derived. It comprises the effects of both concentration and temperature. The saturation limit is AA', The solution in the area between AA' and LL' is called metastable supersaturated solution. The solution in this area is not in equilibrium, it will be precipitate only when heterogeneous nucleation (seeding) occurs. In this case, it will be precipitate until the concentration of the solution decrease to the saturation limit (AA'). If the solution reaches beyond the critical supersaturation, Then spontaneous precipitation will occur. (Via homogeneous nucleation)

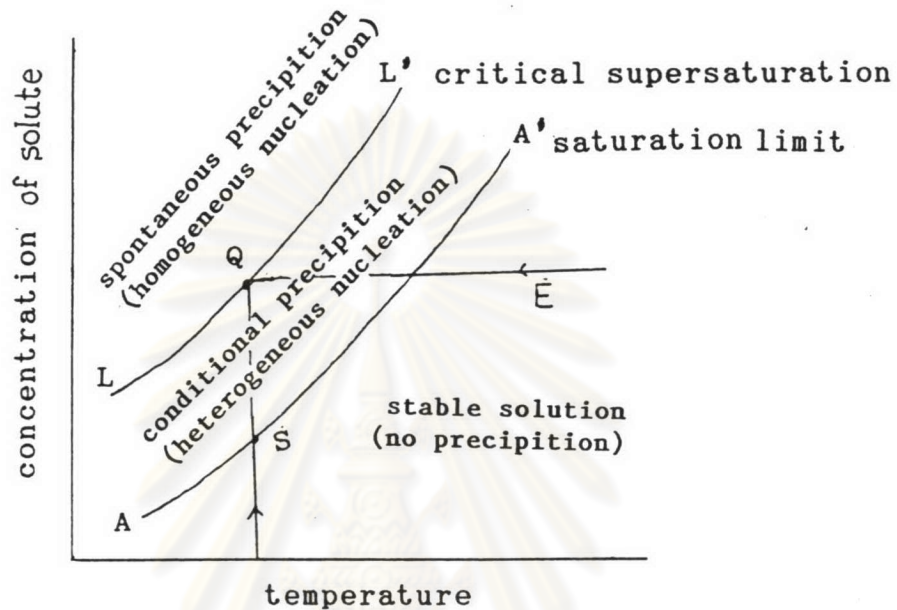


Fig. 2.3 solubility curve

So, when we mix a solution of compounds AX and BY, precipitation will not occur if the system stays below point S of the AA' curve. Precipitate will not occur. If the concentration is increased until point Q, the solution starts to give spontaneous nucleation without need the help of seeding and precipitation will occur. Likewise, when the temperature is decreased to point Q at curve LL', then spontaneous precipitation will occur. The ratios of the concentration of solutes at points Q and S in the

saturation limit curves is called degree of supersaturation. This is in agreement with the concepts of thermodynamic stability in section 2.1 and phase formation in the section 2.3

Diffusion

2.2-a Electrolyte interdiffusion

Diffusion is the very important factor for periodic precipitation. It makes the ions of the electrolyte in reservoir meet the ions in the gel and to build up local supersaturation. So the periodic precipitation process is largely dominated by diffusion. Theoretical treatment has been based on application of Fick's diffusion law ;

$$\frac{\partial C_{AX}}{\partial t} = D \frac{\partial^2 C_{AX}}{\partial x^2}$$

$$\frac{\partial C_{BY}}{\partial t} = D \frac{\partial^2 C_{BY}}{\partial x^2}$$



where C = concentraion,

x = the distance from the gel-solution interface with the positive direction in the direction of the diffusion,

D = diffusion coefficient,

t = time of diffusion.

Venzl(30) studied a post nucleation theory based on diffusion, dissolution, nucleation and supersaturation by using mathematical analysis to determine the location of the next band.

The experimental set-up considered in this thesis work is recalled (see Fig.2.2). This is a finite gel column, open at either one or two ends to reservoirs filled with dissolved AX or BY. The gel column may contain dissolved AX or BY, too. If $K < K_{(e)}$, then nothing else but counter-diffusion occurs, which is govoned by the chemical diffusion coefficients of A^+ , X^- , B^+ , Y^- and H_2O . Taking into account the restrictions due to

- the electroneutrality condition,

- the zero effective current condition,

then three independent diffusion coefficients are operative, e.q., $D(H_2O)$, $D(A^+)$, $D(B^+)$. When the reservoirs are infinitely large and well stirred, then we have the case

of "diffusion into or out of a slab", which is a standard problem of diffusion mathematics. Respective solutions are given in classic monographs like(31-32). The solution for the case of infinitely large reservoirs with complete absence of convection is known. It is a simple superimposition of two error functions.

In the present study, the case of close-to-infinitely large reservoirs was not realized by the experimental set-up. Beside other difficulties, it would have lead to an unduly high consumption of chemicals. On the other hand, finite reservoirs undergo depletion during interdiffusion. This inflicts tremendous difficulties on the theoretical treatment. From this point of view, a numeric approach(1) is the most suitable way to check for the effect of certain boundary conditions on the temporal development of concentration profiles.

2.2-b Influence of an inert gel

The effect of the gel on interdiffusion is often described as not influencing the process except for suppressing convection. If this is true, then the effective diffusion coefficient $D(\text{eff})$ in such an inert porous system is given by the product

$$D(\text{eff}) \approx D.P$$

with D = diffusion coefficient in the aqueous solution, P = gel porosity equivalent to the water content of the gel. In carbohydrate gels with $P \geq 0.99$, the gel has indeed no such geometric influence on the diffusion process. Even in silica gels with P typically ranging from 0.5 to 0.9, this influence remains minor. It is, however, pronounced in dense gels(22) bringing about a retardation of the diffusion process and, in turn, significantly smaller spacing of periodic precipitates. To conclude, for the systems investigated in the present study, the above influence can be neglected.

2.2-c Influence of a gel with ion exchange capacity

The situation changes completely when a gel exhibits some ion exchange capacity. This may be neglected for some carbohydrate gels, but is definitely not negligible in silica gels and in systems containing extended glass surfaces. The $\equiv\text{Si-OH}$ groups have a certain affinity towards cations, thus partially immobilizing them. For univalent cations, this reads



This may lead to the consequence that for low concentrations of R, anionic diffusion may become rate-controlling. Besides this, the pH value will certainly shift the above equilibrium and thus influence the course of diffusion. The maximum ion exchange capacity of a silica gel may be estimated as lined out below:

The O...O distance in the $[\text{SiO}_4]$ tetrahedron is $a_0 \approx 0.26 \text{ nm}$. Let us roughly adopt the presence of one hydroxyl site per surface area $a_0 a_0$. This corresponds to a surface concentration of

$$N_A = 1/a_0^2 \approx 1.5 \times 10^{19} \text{ m}^{-2} ,$$

or, expressed as molar quantity,

$$n_A \approx 2.5 \times 10^{-5} \text{ mol/m}^2 .$$

A material with a specific surface area B thus provides a mass-related concentration of surface hydroxyl groups of

$$n_M = n_A B , n_M \text{ in mol/g} .$$

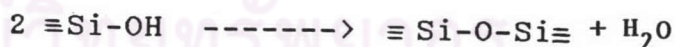
An agar gel with a silica wt. fraction y assumes an overall density

$$\rho = \frac{1}{y/\rho_1 + (1-y)/\rho_2}$$

with $\rho_1 = 2.2 \text{ g/cm}^3$, $\rho_2 = 1.0 \text{ g/cm}^3$. Thus, the volume concentration of surface hydroxyl groups is given by

$$n_v = n_A B \rho, \quad n_v \text{ in mol/cm}^3.$$

Anticipating the experimental conditions for silica gels (i.e., $y = 0.11$ to 0.4 ; $B = 50$ to $300 \text{ m}^2/\text{g}$), the value for n_v amounts to 0.002 to 0.008 mol/cm^3 . In fact, a major fraction of this high ion exchange capacity will not be available since it is involved in the gel formation process forming bridges among the colloidal particles like



and another major fraction may not be accessible by large cation for steric reasons. Yet, when allowing for the fact that 1 cm^3 of a gel filled with a 1 molar univalent electrolyte does not contain more than 0.001 mol of cations, then an influence of the silica gel on the diffusion process is certain. Unfortunately, none of the existing

theories or approaches make proper allowance for this effect.

Phase formation

2.3-a Nature of Nucleus(20)

Nucleation phenomena can be presented in two formulations, depending on the nature of nucleus. Either the initiating nucleus resembles a minute piece of bulk crystal and may be treated by the "embryo in cavity" model, or, at the other extreme, the nucleus is diffuse with the solvated ions being virtually unchanged from their individual state. These conditions correspond to tight binding for strong interaction or weak binding for strong solvation, and are depicted in Fig.2.4 and Fig.2.5. The mathematical analysis of nucleation in these two situations will be quite different. The first case may be represented in terms of a classical formulation resembling that proposed by Volmer and others(33);the second requires a nonclassical analysis which might be treated by kinetic or thermodynamic reasoning.

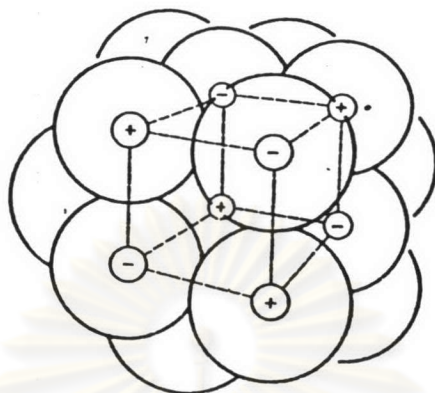


Fig. 2.4 Nature of nucleus , classic formulation

Fig.2.4 In this model the formation of an ionic embryo involves a strong interaction between ions so that the internal lattice solvation is overcome and the configuration becomes that of a small piece of crystal in a solvent cavity. The ions are in fact relaxed from their normal (bulk) lattice positions and, apart from the usual thermodynamic difficulties in dealing with small clusters, the ionic or molecular "volume" cannot strictly be identified with that of the bulk crystalline phase. Integration of all these details in a concise model is not possible. Instead, the classical theory of homogeneous nucleation will be presented in the following section.



Fig. 2.5 Nature of nucleus , nonclassical analysis

Fig.2.5 A cross-section diagram of a weakly interacting diffuse ionic cluster. Ionic interactions are sufficient at this stage of embryonic development to overcome solvation forces.

2.3-b Homogeneous nucleation

The stability of an established and extended solid phase AY in an electrolyte solution AX + BY of the described type is governed by the molar Gibbs free energy of dissolution

$$G(\text{diss}) = R \cdot T \cdot \ln K_{AY} / K_{AY(s)}$$

as already described in section 2.1-a. The formation of previously non-existing AY is not yet contained in this picture. It involves an interfacial energy term, too. Thus, $G(\text{diss}) > 0$ is not a sufficient condition for AY formation yet. The Gibbs free energy of formation of a AY nucleus with radius r reads

$$G(r) = -(4/3) \pi r^3 (\rho/M) \cdot RT \cdot \ln K_{AY}/K_{AY(\infty)} + 4\pi \cdot r^2 \cdot \sigma$$

with ρ = density, M = molar mass, σ = interfacial tension between precipitated solid AY and solution in the respective gel. For $K_{AY}/K_{AY(\infty)}$, $G(r)$ displays the well-known nucleation curve (see Fig.2.6) with an energy threshold

$$E_A = (16\pi/3) \cdot (\sigma^3 \cdot M^2) / [\rho^2 \cdot (RT)^2 \cdot \ln^2 K_{AY}/K_{AY(\infty)}]$$

at the critical radius

$$r = r_c = (2 \cdot \sigma \cdot M) / [\rho \cdot RT \cdot \ln K_{AY}/K_{AY(\infty)}]$$

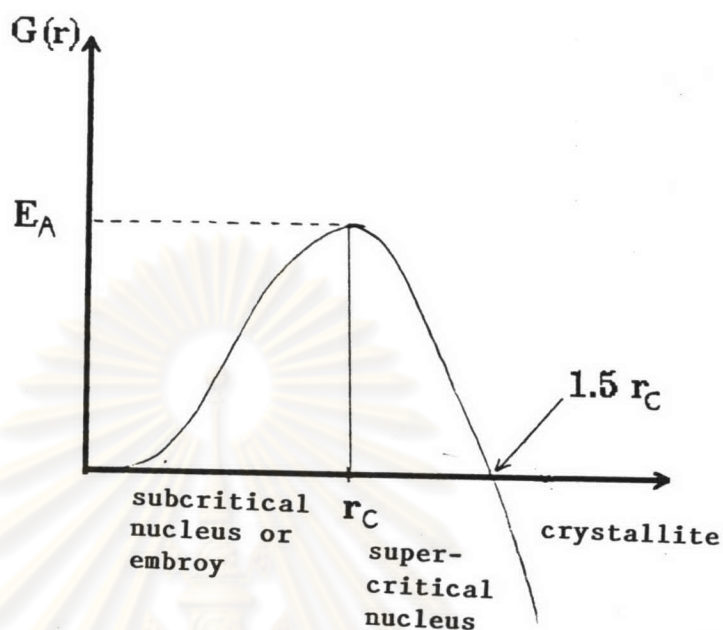


Fig.2.6 Nucleation curve

Fig. 2.6 shows that, in the range $r < r_c$, the cluster gains stability by decay (subcritical nucleus or embryo). In the range $r > r_c$, the cluster gains stability by further growth (supercritical nucleus). Finally, for $r > 1.5 r_c$, the cluster is statically stable with respect to its environment already and may be called a crystallite.

AY formation requires the accidental formation of an AY nucleus with $r \geq r_c$ first. Nucleation probability W thus takes the form

$$W = \exp -E_A/RT = f(T) \cdot \exp -1/[\ln^2 K_{AY(c)}/K_{AY(s)}] ,$$

where $f(T)$ summarizes all influences other than solubility. If we adopt, for reasons of demonstration, a set of realistic values,

$$\sigma \approx 0.07 \text{ N/m} ,$$

$$M \approx 60 \text{ g/mol} ,$$

$$\rho \approx 3 \text{ g/cm}^3 ,$$

$$T \approx 300 \text{ K} ,$$

then the relation for r_c yields, in turn, a critical super saturation $K_{AY(c)}/K_{AY(s)}$ with

$$\begin{aligned} K_{AY(c)}/K_{AY(s)} &\approx \exp (1.2 \text{ nm}/r_c) \approx 11 \quad \text{for } r_c = 0.5 \text{ nm} , \\ &\approx 5.6 \quad \text{for } r_c = 0.7 \text{ nm} , \\ &\approx 3.3 \quad \text{for } r_c = 1 \text{ nm} , \\ &\approx 1.3 \quad \text{for } r_c = 5 \text{ nm} , \\ &= 1 \quad \text{for } r_c \rightarrow \infty . \end{aligned}$$

So, in typical aqueous electrolyte systems, super-saturation of 5 to 10 may be required before (homogeneous) nucleation and hence spontaneous precipitation will occur (see graphs in figure 2.7). This is a quantification to Ostwald's concept of supersaturation as explained in section 2.1-c before.

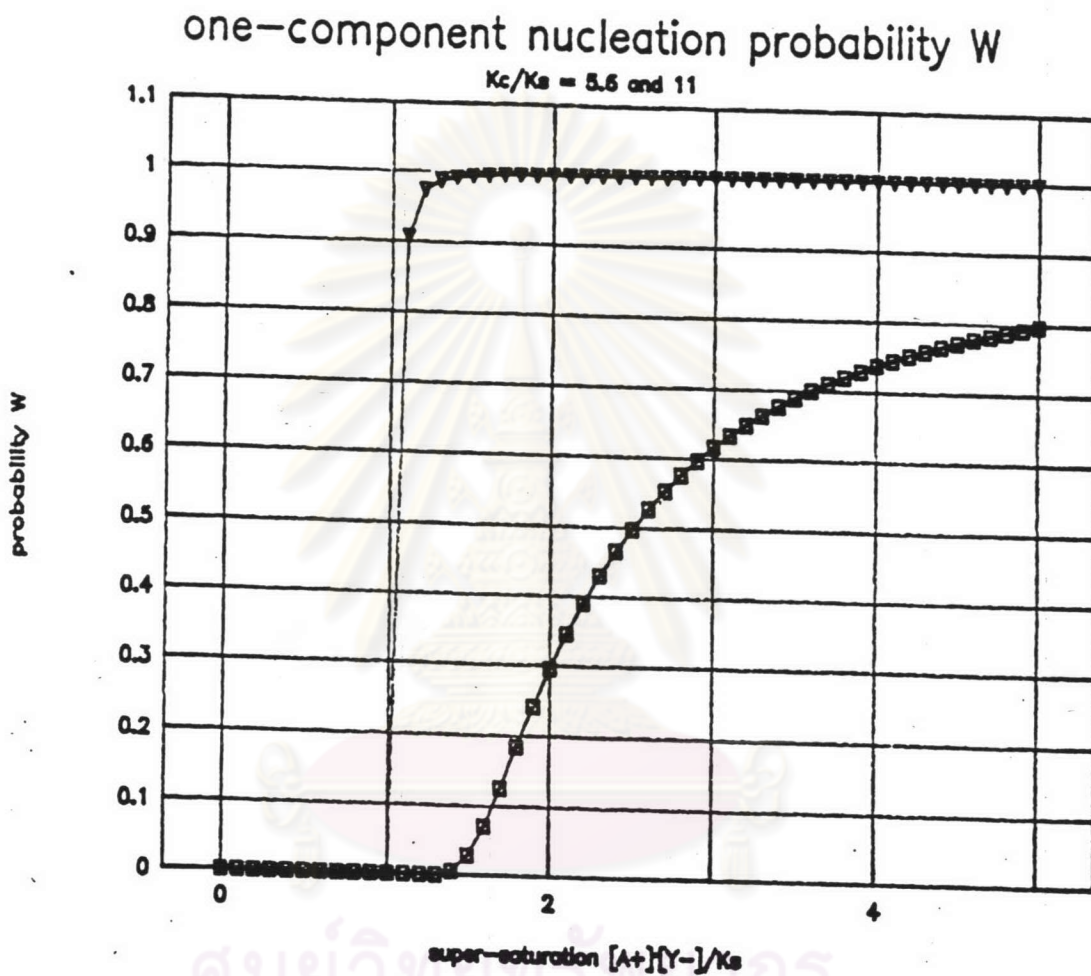


Fig.2.7 Nucleation probability W as a function of actual saturation $K/K_{(s)}$, and critical super-saturation $K_{(c)}/K_{(s)}$

2.3-C Heterogeneous nucleation in gels

A real aqueous system always contains a certain amount of alien solid phases (such as dust particles) which may serve as heterogeneous nuclei. And even in perfect absence of such phases, there are always the container walls which may induce the formation of a precipitate. In the case of gels containing dispersed glass grains, it is all the more important to study such effects. Precipitation in such a system may be regarded as precipitation on a substrate rather than as volume precipitation. The Gibbs free energy function $G(r)$ maintains its general shape, however, involves several additional terms(20):

$$G(r) = V(r) \cdot [(\rho/M) RT \ln K_{AY}/K_{AY(s)} + E (a_g - a_p)/a_p] \\ + A(r) (\delta_{p1} + \delta_{px} + \delta_{x1}) + f_{edge} ;$$

E = elasticity modulus of the nucleus; a = lattice or interatomic distance parameter for the substrate (g) or the precipitating phase AY (p); $V(r)$ and $A(r)$ are the volume and surface area of the nucleus, respectively; δ = interfacial energy; index 1 denotes the aqueous phase. The term containing E allows for a lattice mismatch between precipitate and substrate, and the term f_{edge} allows for edge energies (not yet included in the interfacial quantities).

In almost every case, the influence of the substrate is to lower the energy barrier to nucleation and hence to catalyze the nucleation process. The question whether or not heterogeneous nucleation becomes the predominant factor, largely depends on the wetting angle between aqueous phase and substrate. If the system can be managed in such a way that no wetting occurs, then the substrate cannot initiate nucleation. This will become a major part of the experimental strategy. It will be demonstrated how hydrophobation of the glass grains suppresses the mechanism of heterogeneous nucleation.

The colloidal dimension d of the substrate plays a significant role, too. For very small d , the local effect of the substrate remains minor (probably due to the strongly convex interface between substrate and solution). On the other hand, large materials do not offer enough overall interface area; so the overall effect remains minor in spite of an enhanced local effect. It is reported(20) that substrate effects are considerable in a range of $d \approx 100$ to 1000 nm only. Beyond this, the substrate effect can be neglected. The highly disperse silicas A200 and A300 have mean diameters smaller than 20 nm and a very narrow particle size distribution. Thus substrate effects will be small. By contrast, the product OX50 with a considerable amount of particles assuming sizes $>$

100 μm , a strong substrate effect occurs. For glass grains significantly larger than 1000 nm, the effect is expected to be small. However, the edges and corners of the particles may reach critical dimensions. That is why a step is taken into consideration to remove surface roughness by etching in hydrofluoric acid.

2.3-d Conditions for periodic precipitation

By its very nature, a diffusion process in a system of length L has a characteristic time scale $t_d = (L/2)^2/D$ already. The above elaboration on nucleation probability does not provide an equivalent scale for AY formation yet. Therefore, when discussing simultaneous diffusion and nucleation, a condition for nucleus growth velocity is needed. Otherwise, the periodic phenomenon cannot be understood. It is precisely this point which reconciles the super-saturation and coagulation hypotheses. Nuclei formed already, but not able to undergo significant further growth under local conditions shall be interpreted and identified as the metastable colloids put forward by the coagulation hypothesis.

The term periodic precipitation may be misleading anyway. Precipitation from an initially homogeneous or continuous system will always result in spatially



distributed inhomogeneities, i.e., will always be "periodic". As concluded from (14), we may however distinguish between apparently homogeneous and periodic precipitation. The former case is established when the nucleus density is constant or varies steadily within the system. The latter case is established only if

- nucleus density varies periodically within the system (periodic length X),
- the nucleus/nucleus distance d within the ranges of high nucleus density is much smaller than X :
 $d \ll X$.

Kahlweit(14) points out that the condition $d \ll X$ is a matter of the diffusion flow and crystallite growth velocities. If crystallite growth itself is a diffusion-controlled step, then d and X will be of the same order of magnitude, i.e., the condition $d \ll X$ is never reached. The result is a continuous precipitation zone. If, by contrast, crystallite growth is a surface-controlled step, then it will occur rapidly in a narrow range where (under somewhat simplified conditions) the stoichiometric condition $[A^+] = [Y^-]$ is satisfied. Intermediate space with $[A^+]/[Y^-]$ very different from unity remains void even if

$K_{AY}/K_{AY(=)} > K_{AY(c)}/K_{AY(=)}$. When diffusion proceeds, the equality condition $[A^+] = [Y^-]$ will soon be satisfied again some place downwards the column, and a new ring of precipitation is formed. It is worth mentioning that the ratio $[A^+]/[Y^-]$ plays a key role in the coagulation hypothesis, too.

Based on mere probabilistic arguments, Henisch and co-workers also derived the equality condition. In this theory, the equality condition is a second condition for nucleation at all. Precipitation is observed when

$$K_{(c)}/K_{(=)} > 1$$

and when

$$[A^+]/[Y^-] = 1 \pm \varepsilon$$

The more stringent application of these conditions simplifies the algorithm. Nucleation probability is just modified by the additional term W'

$$W' = \exp -([A^+]/[Y^-] - 1)^2/4\varepsilon^2$$

The parameter ε is nothing but a mathematical tool to control the "fatness" of the probability curve for W' .

Figure 2.8 illustrates the result.

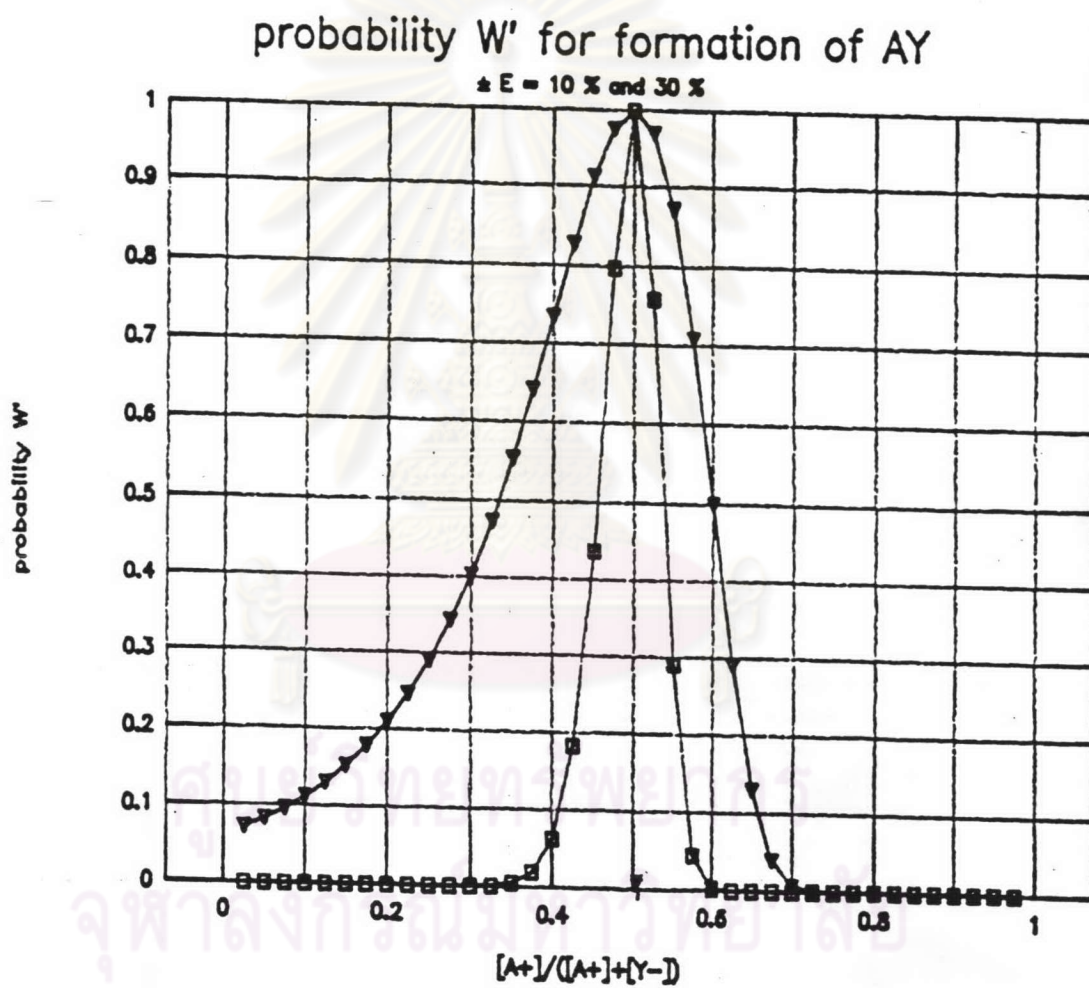
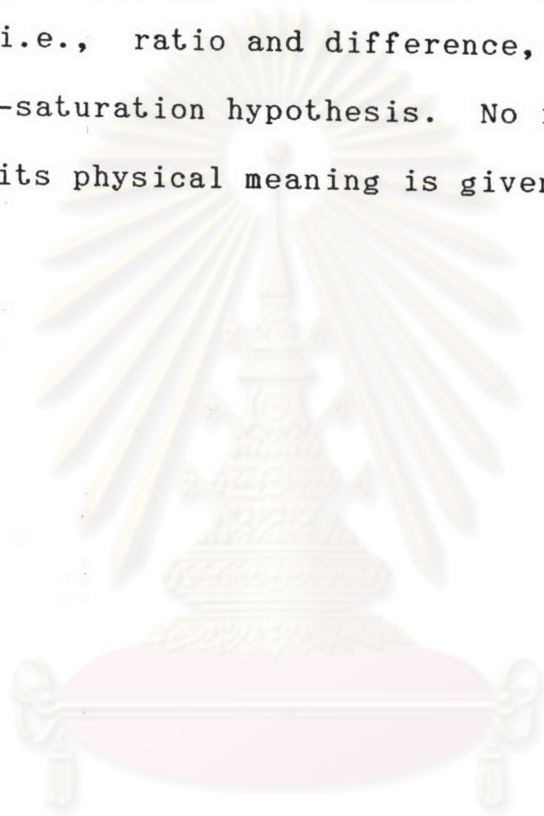


Fig.2.8 Probability of formation of AY as a function of the local stoichiometry

The probability w' has a more or less sharp maximum for $[A^+] = [Y^-]$. The argument of the exponential contains the ratio $[A^+]/[Y^-]$ and, rearranging $[A^+]/[Y^-] - 1 = ([A^+] - [Y^-])/[Y^-]$, the difference $[A^+] - [Y^-]$. It is worth mentioning that now both key parameters of the coagulation hypothesis, i.e., ratio and difference, are incorporated in the super-saturation hypothesis. No interpretation of it in terms of its physical meaning is given.



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