



## **Impurities and Homogeneous Crystal Nucleation in Aqueous Solutions - An Overview**

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### **Abstract**

Nucleation process is the most important stage in the formation of a crystal and has attracted the attention of researchers due to its importance in many technological and biological contexts. As the presence of impurities affects the nucleation process significantly, several studies have been made in the past to understand it. In this article is presented an overview of various studies made to understand the effect of soluble impurities on the crystal nucleation parameters of certain important materials in aqueous solution focusing the results reported by the research group of the present author.



### **Article History**

Received: 17 November 2019

Accepted: 16 December 2019

### **Keywords:**

Aqueous Solutions, Crystal Growth from Solution, Crystal Nucleation, Nucleation Kinetics, Nucleation Parameters, Soluble Impurities.

### **Introduction**

There are two stages in arranging atoms or ions or molecules in a particular order in three dimension (crystal growth) which are: (I) crystallization (nucleation and growth of crystals); and (II) large size single crystal growth. Forming a crystal in the absence of a seed begins with nucleation (generation of minute specks of crystal nuclei) which is considered to be the most important stage in phase transition.

Nucleation and crystallization have attracted the researchers due to their widespread practical interest in many technological and biological contexts.<sup>1</sup> The understanding of the "two-step" mechanism in protein crystallization has brought this

attraction. Also, several reports are available on the complex pathways for many other systems which include calcium carbonate, potassium di-hydrogen orthophosphate, polyoxometalates, biomimetic polymers, etc.<sup>1-8</sup>

The first step in the formation of a new thermodynamic phase via self-assembly is called crystal nucleation. This is the process that determines the time required for the new phase to appear. Moreover, crystal nucleation is sensitive to the presence of impurities in the system which can control the nucleation rate. The primary nucleation time is the time required for the appearance of the first crystal. The primary nucleation describes the transition to a new phase that does not rely on the new phase already being

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Doi: <http://dx.doi.org/10.13005/msri/160302>

present. It is the very first minute crystal of that phase to form, or because the minute crystal forms far from and pre-existing piece of the new phase. Formation of a new minute crystal directly caused by pre-existing crystals is called the secondary nucleation.<sup>9</sup> So, it can be understood that primary nucleation occurs in systems that do not contain pre-existing crystals and secondary nucleation is that nuclei generated in the vicinity of crystals.

Formation of ice is a common crystallization process on Earth and many of the materials we make and use are crystalline. Nucleation of crystalline materials is widely used in chemical and semiconductor industries.<sup>10</sup> Moreover, crystal nucleation is much involved in bio-mineralization (processes spontaneously occurring in living beings). In a super-saturated or super-cooled system, when few atoms or molecules join together to form a cluster (nucleus) in a new phase, a change in free energy takes place. The kinetics of this phase change takes place in four steps, viz.<sup>11</sup>: (1) the development of super-saturated state arising due to chemical or photo-chemical reaction or the consequence of a change in temperature, pressure, tension or other chemical or physical condition; (2) the generation of minute specks or nuclei; (3) the growth of nuclei to form domains of the new phase or particles of macroscopic dimensions; and (4) the relaxation processes like agglomeration by which the new phase changes in texture.

The spontaneous formation of crystal nuclei in the interior of the bulk parent phase (super-saturated or super-cooled system) is called homogeneous crystal nucleation. Although homogeneous crystal nucleation in the bulk of a super-saturated system is comparatively a rare occurrence, its fundamental principles form the required background for the understanding of numerous processes in science and technology as well as in nature when phase transitions are involved. The crystal nucleation is called heterogeneous when the crystal nuclei form heterogeneously around impurity molecules, ions or on dust particles, on surfaces or at structural singularities like dislocations or other imperfections.<sup>11</sup>

Nucleation process is a rather complicated process and is the most controversial and less understood stage of crystallization. All the theories of

homogeneous crystal nucleation involve the concept of critical nucleus. Several attempts have been made to determine the typical sizes of these critical nuclei. Theoretical and experimental difficulties are encountered. The nucleation theories developed by Volmer and Weber, Becker and Döring, Turnbull and Fisher, etc. form the basis of modern approach to nucleation studies. Most of the modern nucleation theories are based on Gibbs' ideas and are known as "Classical approach". Nucleation in solutions has been the subject of extensive study in the past several decades.

The most common theoretical model used to quantitatively study the nucleation kinetics is the classical nucleation theory (CNT).<sup>11-14</sup> In many cases, liquids and solutions can be cooled down or concentrated up to conditions where the liquid or solution is significantly less thermodynamically stable than the crystal. Here, no crystals will form for minutes, hours, weeks or longer. A key achievement of CNT is that it explains and quantifies this immense variation.<sup>15</sup> Despite having many shortcomings, the CNT is a simple yet powerful theory which can explain at least qualitatively the thermodynamics and kinetics of nucleation for very different systems, from liquid metals to organic crystals. Also, it can be extended to include heterogeneous nucleation, and it can be easily modified to take into consideration multicomponent systems like binary mixtures as well.<sup>16-18</sup>

Often, crystal nucleation in liquids takes place within a small time (in nanoseconds) not to allow for a sequence of snapshots to be taken with high-spatial resolution instruments. In such cases, microscopic insights cannot be obtained, and more macroscopic measurements have to be performed. Experimental methods using optical microscopy can detect nucleation and the crystal formation but do not provide any microscopic detail. However, they have helped to shed light on issues like the role of impurities or solvent. Even though there are available a large number of powerful experimental techniques and new ones emerging, it is still challenging to obtain microscopic level insight into nucleation from experiments.<sup>18</sup>

It is well known that the presence of impurities in a system can affect the nucleation behavior

considerably. Presence of small amounts of colloidal substances like gelatin can suppress nucleation in aqueous solution, and surface active agents also exert a strong inhibiting effect. Formation of zinc chloride crystal by the free evaporation method requires some impurities to induce crystallization; single crystals could be formed with laboratory reagent (LR) grade precursor but not with the analytical reagent (AR) grade precursor.<sup>19</sup> Several studies have been made related to promotion and inhibition of bio-minerals.<sup>20</sup> The presence of soluble and insoluble impurities affects the nucleation time (called as the induction period) but it is virtually impossible to predict the effect in a proper way.<sup>21, 22</sup>

Literature available on crystal nucleation is numerous. All aspects of crystal nucleation is impossible to be accounted in a brief article like this. So, in this article (overview), we consider only the effect of soluble impurities on the crystal nucleation parameters of certain important materials in aqueous solution focusing the results reported by the research group of the present author.

### Homogeneous Crystal Nucleation

The free energy change associated with the process of homogeneous crystal nucleation may be considered as follows<sup>23</sup>: The overall excess free energy ( $\Delta G$ ) between a nucleus (nanoparticle or cluster or embryo) and solute in the solution is equal to the sum of the surface excess free energy ( $\Delta G_s$ ) and the volume excess free energy ( $\Delta G_v$ ) given by

$$\Delta G = \Delta G_s + \Delta G_v. \quad \dots (1)$$

Where  $\Delta G_v$  is given by

$$\Delta G_v = -(kT/v)\ln(S). \quad \dots (2)$$

Here  $k$  is the Boltzmann's constant,  $T$  is the absolute temperature,  $v$  is the volume per molecule in solid phase, and  $S$  is the super-saturation.

As  $\Delta G_s$  and  $\Delta G_v$  are always positive and negative respectively, it is possible that we can find a maximum free energy which a nucleus will pass through to form a stable nucleus by differentiating  $\Delta G$  with respect to the size parameter and setting it to zero which gives a critical free energy. The critical size corresponds to the maximum size at which the

crystal particle can survive in solution without being re-dissolved. The same is true for the particle's free energy where a critical excess free energy is required to obtain stable particles within solution.<sup>24</sup>

The present author<sup>23</sup> has studied the effect of critical nucleus shape on the nucleation parameters by deriving the required formulae and has shown that it would be better to consider the shape of the critical nucleus as cylindrical (illustrated with ammonium dihydrogen orthophosphate and urea nitrate crystals). Also, it was proposed that the following facts should be considered while assuming a shape for the critical nucleus.

- Atoms are not strictly spherical in shape regardless of the minimum energy consideration;
- Molecules are not spherical in shape – wide variation available;
- Crystal lattices are not spherical in shape;
- Grown crystals which are of spherical in shape are very rare;
- Needle (cylindrically shaped) crystals are quite commonly found;
- Crystals with many flat faces are quite commonly found;
- In the case of melt growth, liquid (melted substance) solidifies. But, in the case of slow evaporation or slow cooling process, only the excess of solute in the solution solidifies and not the solvent;
- Using the conventional experiment for determining the induction period (the direct vision method) and classical theory for homogeneous crystal nucleation, we obtain only one value for the energy of formation of the critical nucleus (independent of the shape) for a particular super-saturation; etc.

After preparing the super-saturated solution, there is often a period where no phase change can be observed, the induction period (the time of formation of the first nucleus); then minute nuclei appear and grow into visible crystals. The induction period ( $\tau$ ) can be measured for several super-saturated aqueous solutions of the material by the direct vision method<sup>21,23</sup> and used to calculate certain nucleation parameters like interfacial tension ( $\sigma$ ) of the solid relative to its solution, energy of formation ( $\Delta G$ ) of

the critical nucleus, and size of the nucleus (critical nucleus) in equilibrium with its solution, based on the classical theory of homogeneous crystal nucleation. The induction period is considerably influenced by the level of super-saturation, state of agitation, presence of impurities, viscosity, etc. Existence of induction period is contrary to expectations of classical theory of homogeneous crystal nucleation. Theory assumes steady-state conditions and predicts immediate nucleation once super-saturation is achieved. The induction period, may be written as:

$$\tau = t_r + t_n + t_g$$

$t_r$  = Relaxation time required for the system to achieve a quasi-steady-state distribution of molecular clusters

$t_n$  = Time required for the formation of a stable nucleus

$t_g$  = Time required for the nucleus to grow to a detectable size

Both theoretical and experimental difficulties are encountered during the study of nucleation. The major theoretical difficulty arises from the fact that the size of the nucleus is too small to be treated by the thermodynamic theories and too large to be dealt with the atomistic concepts. As the critical nuclei are so small (nano-sized), accurate measurements are not really feasible and calculated values depend very much on assumptions made, many of which cannot as yet be independently tested. So, the inferences drawn from observations are indirect.<sup>25</sup>

Induction periods are often measured visually, but a different result can be recorded if new crystalline matter in the system is detected by more sensitive means, Eg, by laser light scattering or electric zone sensing methods. The variability serves to emphasize the fact that an experimentally determined  $\tau$  is not, by itself, a fundamental characteristic of a crystallizing system. However, in practice, determination of  $\tau$  by conventional methods presents less problem so long as it exceeds about 10 s.<sup>21</sup> So, a practical limit is proposed in selecting the maximum and minimum super-saturated concentrations of the solutions considered for the induction period measurement.

The maximum super-saturated concentration to be considered should have an induction period of at least few seconds so that the nucleation should not occur before the attainment of super-saturation (that is before cooling to the experimental temperature). The minimum super-saturated concentration to be considered should have a practically measurable induction period of within few hours.

The direct vision method, used in the study of homogeneous crystal nucleation in aqueous solutions by several researchers<sup>21-23,25-47</sup> is not very accurate and does not involve rigorous methodology. The critical nuclei are not visible even by microscopes as they are nano-sized. At the observable level, they are already at the growth stage. It is normally assumed that the time required for the critical nucleus to grow to an observable level is very small and negligible when compared to the induction period. Despite the above problems, the direct vision method has been considered for the reason that no other better method is available to study nucleation kinetics in super-saturated solutions of highly soluble substances. In order to reduce the inaccuracy, care has been taken by the researchers so that the super-saturated concentration considered provides an induction period of around 10 s or more. The effect of heterogeneous nucleation due to dust particles from air has been reduced by carrying out the measurement in a relatively dust-free zone. Further, the effect of heterogeneous nucleation due to scratching on the inner wall of the nucleation cell (glass beaker) has been reduced by choosing glass beakers without scratches (tested with optical microscopes).

A typical experimental set up used for the measurement of induction period consists of two identical nucleation cells (100 ml corning glass beakers) kept at a constant (near ambient) temperature (controlled to an accuracy of at least  $\pm 0.1^\circ\text{C}$ ). One of the cells is used as dummy (as insertion of thermometer in the experimental cell may disturb the system). The cells can be illuminated using a powerful lamp. Super-saturated (saturated at a required higher temperature) aqueous solutions (prepared with double distilled water as the solvent) of equal volume are taken in the cells. A sensitive thermometer (accurate up to at least  $0.1^\circ\text{C}$ ) is placed in the dummy cell. As the temperature of

the cell reaches the experimental temperature, the time is noted. Once the nucleation occurs, it grows quickly and a bright sparkling particle is seen. The time of observation of the sparkling particle in the undisturbed nucleation cell from the time at which the solution reached the experimental temperature is measured as the induction period<sup>25</sup> If the effect of any added impurity on the nucleation parameters has to be studied, then the material is doped with the impurity material in different Material (Host) : Dopant molecular ratios and the induction period measurement is carried out as above.

The nucleation parameters can be determined by using the relations given below:<sup>23</sup>

Assuming spherical nucleus:

$$\tau = RT[3m/(16\pi V^2N)]^{1/3} \quad \dots(3)$$

$$\Delta G = RTm/\ln^2(S) \quad \dots(4)$$

$$r = 2\sigma V/[RT \ln(S)] \quad \dots(5)$$

$V \rightarrow$  molar volume of crystal

$N \rightarrow$  Avogadro number

$R \rightarrow$  gas constant

$T \rightarrow$  temperature

$S \rightarrow$  super-saturation

$m \rightarrow$  slope of the line plot of  $\ln(\tau)$  versus  $1/\ln^2(S)$

Assuming cylindrical nucleus:

$$\sigma_o = RT[m/(18\pi V^2N)]^{1/3} \text{ (for flat surface)} \quad \dots (6)$$

$$\sigma_c = (RT/\sqrt{\pi})[m/(4V^2N)]^{1/3} \text{ (for curved surface)} \quad \dots(7)$$

$$\Delta G = RTm/\ln^2(S) \text{ (same as for spherical)} \quad \dots(8)$$

$$r_c = 2\sigma_c V/[RT \ln(S)] \quad \dots(9)$$

$$h = 4\sigma_o V/[RT \ln(S)] \quad \dots(10)$$

### Effect of Natural Impurities

The plots of  $\ln(\tau)$  versus  $1/\ln^2(S)$  are supposed to be linear as per the CNT for homogeneous crystal nucleation. However, non-linearity has been observed for most of the systems studied. In this situation, the slope ( $m$ ) of the line plot of  $\ln(\tau)$  versus  $1/\ln^2(S)$  is normally determined in the most linear part of it to remove the heterogeneous effect due to

natural impurities present in the solute and solvent of the solution.

Studies made by Freeda *et al.*,<sup>45,47</sup> with ammonium di-hydrogen orthophosphate showed that this nonlinearity is not due to difficulties in induction period measurements but due to heterogeneous nucleation caused by natural impurity particles present in the solvent. High purity of the solvent leads to less heterogeneous effect. Natural impurities present in the solute substance causes negligible heterogeneous effect. Moreover, the linear dependence is found to be more when the solubility of the solute substance is more.

Premila Rachelin and Mahadevan<sup>33,45</sup> and some others have also shown that the linear dependence is more when the solubility of the salt material (substance) is more. This is because the substance molecules in the case of substance with higher solubility may dominate over the unwanted (natural) impurity molecules present in the solvent in a better way than the substance molecules in the case of substance with lower solubility. It is better to consider a solvent in which the solute has a solubility between 10 to 60 %.

### Effect of Added Impurities

Homogeneous crystal nucleation in super-saturated aqueous solutions and the effect of soluble impurities on the crystal nucleation parameters have been the object of many investigations. Often there appears to be a 'threshold' concentration of impurity above which the inhibiting or promoting effect may actually diminish.<sup>48</sup> High molecular weight substances may have their main action on the hetero-nuclei rendering them inactive by adsorbing on their surfaces.<sup>21, 22</sup> Moreover, doping a crystal lattice during crystal formation leads to replacement of ions or occupation of the interstitials available. If the probability of occupation of an interstices is  $f$ , then the probability of finding a vacant neighbor site is  $(1-f)$ . Even for very high concentrations, of the order of  $10^{20} \text{ cm}^{-3}$ ,  $f$  does not exceed  $10^{-2}$  so that in real cases with concentration of interstitials of the order of  $10^{15}$  to  $10^{20} \text{ cm}^{-3}$ ,  $(1-f) \ll 1$ .<sup>49</sup>

Several investigations have been carried out (by the present author and his group) to understand the effect of added impurities (soluble in water) on the

nucleation parameters of certain important materials like potassium di-hydrogen orthophosphate (KDP), ammonium di-hydrogen orthophosphate (ADP),  $\text{MSO}_4 \cdot 7\text{H}_2\text{O}$  ( $\text{M} = \text{Mg, Ni, etc.}$ ), urea, thiourea, urea nitrate, etc. These investigations lead to several useful results.

Potassium di-hydrogen orthophosphate ( $\text{KH}_2\text{PO}_4$ , abbreviated as KDP) belongs to scalenohedral (twelve sided polyhedron) class of tetragonal crystal system with the tetra-molecular unit cell having the dimensions<sup>39,44,50</sup> given as  $a = b = 7.448$  and  $c = 6.977$  Å. KDP is soluble in water and its solubility at 0, 10, 20, 30, 40, 60, 80 and 90 °C are respectively 14.8, 18.3, 22.6, 28.0, 33.5, 50.2, 70.4 and 83.5 parts by weight per 100 parts by weight of water.<sup>39,51</sup>

Joshi and Antony<sup>27</sup> have (first) studied systematically the nucleation kinetics of pure KDP crystal in aqueous solution. Shanmugham *et al.*,<sup>30,31</sup> have studied the nucleation kinetics in supersaturated aqueous KDP solutions without and with some added impurities (impurity concentration is 100 ppm only with  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{C}_2\text{O}_4$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{KIO}_4$ , and  $\text{KMnO}_4$  and 100 to 600 ppm with  $\text{KClO}_4$ ). Later, the present author along with his co-workers<sup>37,39,41,43,44</sup> have studied the effect of various types of soluble inorganic impurities (having and not having any common ion with KDP) and some small molecular organic impurities (added in the solution with impurity concentration in the range of 2000 to 10000 ppm, i.e. 0.2 to 1.0 mole %) on the nucleation parameters of KDP.

Ammonium di-hydrogen orthophosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ , abbreviated as ADP) is isomorphous with KDP and has the tetra-molecular unit cell having dimensions given as  $a = b = 7.510$  and  $c = 7.564$  Å.<sup>33,34,50</sup> ADP is soluble in water and its solubility at 0, 10, 20, 30, 40, 60 and 80°C are respectively 22.7, 29.5, 37.4, 46.4, 56.7, 82.5 and 118 parts by weight per 100 parts by weight of water.<sup>34,51</sup>

Nagalingam *et al.*,<sup>28,29</sup> have studied the nucleation kinetics in super-saturated aqueous ADP solutions without and with some added impurities (doping concentration is 100 ppm only with  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{I}$ ,  $\text{NH}_4\text{NO}_3$ , KDP and  $\text{NaH}_2\text{PO}_4$ ). Later, the present author along with his co-workers<sup>25,33-36</sup> have

investigated the effect of various types of soluble inorganic impurities (having and not having any common ion with ADP added in the solution with impurity concentration ranging from 2000 to 10000 ppm) on the nucleation parameters of ADP.

Magnesium sulphate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , abbreviated as MSH and mineralogically known as epsomite) crystal has an orthorhombic crystal system with a tetra-molecular unit cell of dimensions  $a = 11.86$ ,  $b = 11.99$  and  $c = 6.858$  Å.<sup>45,50</sup> Nickel sulphate heptahydrate ( $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , abbreviated as NSH and mineralogically known as morenosite) crystal is isomorphous with MSH (and also with  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) and has a tetra-molecular unit cell of dimensions  $a = 11.86$ ,  $b = 12.08$  and  $c = 6.81$  Å.<sup>38,50</sup>

Backiyam *et al.*,<sup>32</sup> have studied (first) the nucleation kinetics of pure  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  crystals in super-saturated aqueous solutions. Later, the present author and his co-workers<sup>38,45</sup> have investigated the effect of different soluble impurities (added in the solution with impurity concentration ranging from 2000 to 10000 ppm) on the nucleation parameters of MSH and NSH.

Urea ( $\text{NH}_2\text{-CO-NH}_2$ ) crystal belongs to the tetragonal crystal system having the unit cell dimensions  $a = b = 5.645$  and  $c = 4.704$  Å.<sup>40</sup> Thiourea ( $\text{NH}_2\text{-CS-NH}_2$ ) crystal belongs to the orthorhombic crystal system having the unit cell dimensions  $a = 5.50$ ,  $b = 7.68$  and  $c = 8.57$  Å.<sup>40</sup> Urea nitrate ( $\text{CH}_4\text{N}_2\text{HNO}_3$ ) crystal belongs to the monoclinic crystal system having the unit cell dimensions  $a = 9.50$ ,  $b = 8.20$  and  $c = 7.54$  Å;  $\beta = 124^\circ$ .<sup>22</sup> The present author and his co-workers<sup>22,40,42</sup> have studied systematically the effect of different soluble impurities (added in the solution with impurity concentration ranging from 2000 to 10000 ppm) on the nucleation parameters of urea (added with  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ , urea nitrate and urea oxalate), thiourea (added with  $\text{NaCl}$ ,  $\text{KCl}$ , urea and urea nitrate) and urea nitrate (added with thiourea and urea oxalate).

In all the above-mentioned studies, it has been found that the values of induction period decreased and hence the nucleation rate increased as the super-saturated concentration of the aqueous solution increased. Also, the nucleation parameters

decreased when the super saturation increased. This is in line with the classical theory for homogeneous crystal nucleation.

Plots of  $\ln(\tau)$  versus  $1/\ln^2(S)$  have been found to be nearly linear for many of the systems studied. However, significant deviations from linearity have also been reported for several other systems. In general, significant deviations from linearity have been observed at lower super-saturation levels. Nagalingam *et al.*,<sup>28,29</sup> have observed non-linearity for pure ADP at lower super-saturation levels at temperatures higher than 25°C. However, they have not observed any non-linearity at 30°C for ADP added with  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{I}$ ,  $\text{NH}_4\text{NO}_3$ , KDP and  $\text{NaH}_2\text{PO}_4$  (impurity concentration is 100 ppm). Backiyam *et al.*,<sup>32</sup> also have observed non-linearity at lower super-saturation levels for  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . In the case of  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  added ADP, Ramesh and Mahadevan<sup>34</sup> have observed significant deviations from the linearity for the higher impurity concentrations at higher super-saturation levels. The authors stated that the deviation from linearity at higher super-saturation levels increased with impurity concentration and became significant at higher impurity concentrations. They explained this result as due to the occurrence of heterogeneous nucleation caused by the added impurity  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .

In all the impurity added KDP and ADP systems (except KCl,  $\text{KNO}_3$  and KSCN added KDP) studied and reported, the induction period is found to decrease with the increase in impurity concentration which may be due to the promotion of the chemical activity of the metal ions present in the solutions. In the case of KSCN added KDP,<sup>46</sup> the induction period increases with the increase in impurity concentration in the solution which may be due to the suppression of chemical activity of the metal ions present in the KDP solution. In the case of KCl or  $\text{KNO}_3$  added KDP, the induction period does not vary in a particular order with the concentration of added impurities in the solution which may be attributed to the unpredictable situation caused by the added impurities.<sup>41</sup> So, it would be unwise to attempt a general explanation of the phenomenon of nucleation promotion or suppression by added impurities with so little quantitative evidence yet available.

The presence of impurities (soluble or insoluble) in a system can affect nucleation behaviour considerably. The presence of soluble impurities affects the induction period but it is virtually impossible to predict the effect in a proper way with the available data. The effects of soluble impurities may be caused by changing the equilibrium solubility or the solution structure, by adsorption or chemisorption on nuclei or hetero-nuclei, by chemical reaction or complex formation in the solution and so on. The effects of insoluble impurities are unpredictable.<sup>21,43</sup> The presence of soluble impurities has been found to affect the nucleation parameters (the interfacial tension, the energy of formation, and size of the critical nucleus and the number of molecules in the critical nucleus) very significantly.

The nucleation parameters are found to increase with the increase in impurity concentration in the KDP solution added with  $\text{K}_2\text{CrO}_4$ , KBr,  $\text{K}_2\text{Cr}_2\text{O}_7$ , glycine, thiourea,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , etc. and in the ADP solution added with KCl,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , NaCl,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , urea, thiourea, glycine, etc. The nucleation parameters are found to decrease with the increase in impurity concentration in the KDP solution added with KCl, and  $\text{KNO}_3$  and in the ADP solution added with  $\text{NH}_4\text{Cl}$ .

The nucleation parameters are found to decrease with the increase in concentration of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  addition and increase with the increase in concentration of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  addition in the  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  solution. The nucleation parameters are found to increase with the increase in the impurity concentration in the  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  solution added with KCl,  $\text{KNO}_3$ , urea and thiourea.

The nucleation parameters are found to decrease with the increase in concentration of urea oxalate addition in the urea nitrate solution. They are found to increase with the increase in concentration of urea nitrate and urea oxalate additions in the urea solution and thiourea addition in the urea nitrate solution.

Premila Rachelin and Mahadevan<sup>33</sup> have (first) attempted to explain qualitatively the variation of nucleation parameters with impurity concentration in the case of ADP by considering the density of the impurities. It was stated that the nucleation

parameters increase with the increase in impurity concentration for the denser impurities and decrease with the increase in impurity concentration for the rarer impurities. However, later, this was found not to hold in the case of  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{SO}_4$  added ADP solutions. Then, in order to account this, the above statement was updated and stated as: For an inorganic substance like ADP and KDP, the nucleation parameters increase with the increase in impurity concentration for the impurities having higher density and high or equal (molecular) weight cation and decrease with the increase in impurity concentration for the impurities having lower density and low or equal (molecular) weight cation.

There arose further problems in the explanation of the variation of crystal nucleation parameters with the added impurity concentration in the solutions of inorganic substances. The effects of impurities having no common ion, isomorphous impurities and organic impurities could not be accounted. The present author,<sup>44</sup> with the available data on inorganic and organic impurities in the KDP solutions, updated the earlier statements for the KDP solution<sup>43</sup> as three empirical rules. Also, explanation is required for the variation of the nucleation parameters in the case of small molecular organic substances added with both organic and inorganic impurities (even though limited data are available). Now, with all the available data for the materials (inorganic and organic) considered, four empirical rules can be formulated (also by updating the earlier ones<sup>43-45</sup>) as:

- For inorganic materials like KDP and ADP added with impurities having common cation, the crystal nucleation parameters increase with the increase in impurity concentration for impurities having higher density and high or equal (molecular) weight cation and decrease with the increase in impurity concentration for impurities having lower density and low or equal (molecular) weight cation.

- For inorganic materials like KDP and ADP added with isomorphous impurities, the crystal nucleation parameters increase with the increase in impurity concentration for impurity with larger lattice and decrease with the increase in impurity concentration for impurity with smaller lattice.
- For inorganic materials like KDP and ADP added with impurities having no common ion and organic impurities, the crystal nucleation parameters increase with the increase in impurity concentration regardless of density or molecular weight or lattice size of the impurity.
- For organic materials, the crystal nucleation parameters do not vary systematically with the impurity concentration.

### Conclusion

In inorganic substances, variation of crystal nucleation parameters with added impurity concentration is understood by considering density, molecular weight, lattice volume, etc. of the impurity substances. However, unpredictable situation is evidenced in organic systems. Four empirical rules have been formulated with the available data. However, several more studies are required to be done for the full understanding of the effect of soluble impurities at least on the crystal nucleation parameters of organic systems.

### Acknowledgement

The support by the Council of Scientific and Industrial Research, New Delhi, India under the Emeritus Scientist Scheme (CSIR-ES Scheme No.: 21(1083)/19/EMR-II) is hereby gratefully acknowledged.

### Funding

This research received no specific grant from any funding agency.

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