

# Nucleation studies in supersaturated aqueous solution of Potassium Acid Phthalate doped with Alkali Metal Ion Dopants

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Induction periods have been measured for various supersaturated aqueous solution of 1mol% of  $\text{Rb}_2\text{CO}_3$  doped potassium acid phthalate by direct vision method. Nucleation parameters such as radius of critical nucleus, Gibb's free energy change have also been investigated. The critical supersaturation ratio for the  $\text{Rb}_2\text{CO}_3$  doped KAP solutions at 45°C was evaluated to be 1.002615. Based on the thermodynamical approach correction was made to the interfacial energy. An attempt has been made to calculate the nucleation parameters corresponding to the critical supersaturation ratio using the modified classical nucleation theory.

(Received December 12, 2013; accepted September 11, 2014)

**Keywords:** Nucleation, Induction period, Interfacial tension, Gibb's free energy, Modified classical nucleation theory

## 1. Introduction

Investigations on the growth of good quality single crystals play an important role in the development of modern scientific world with advanced technology. Behind the development in every new solid state device and the explosion in solid state device, there stands a single crystal. Crystal growth is an important field of materials science, which involves controlled phase transformation. In the past few decades, there has been a growing interest in crystal growth process, particularly in view of the increasing demand for materials for technological applications [1]. In order to understand how a solid crystallizes from its supersaturated solution, various theories have been developed which consider the transfer of atoms or molecules from the liquid to the solid state. Nucleation is the forerunner of crystal growth and of the overall crystallization processes. Nucleation is defined as the spontaneous formation of cluster of solid molecules or atoms in the bulk of super saturated systems.

In the present study, investigations have been made to evaluate the interfacial tension ( $\gamma$ ) between  $\text{Rb}_2\text{CO}_3$  mixed potassium acid phthalate (RbKAP) and aqueous solution by measuring the induction period and hence to calculate the critical radius ( $r^*$ ), the classical rate of nucleation ( $J$ ) and Gibb's free energy ( $\Delta G^*$ ) for the formation of critical nucleus of RbKAP mixed crystal grown from aqueous solution. It has been noticed that the interfacial tension of curved surface differs from that of the planar surface only for very small drops and bubbles. Hence the classical

nucleation theory (CNT) is modified by incorporating the size factor for the interfacial tension and this modified classical theory (MCNT) is applied to the nucleation of potassium acid phthalate (KAP) and 1mol%  $\text{Rb}_2\text{CO}_3$  added KAP (RbKAP) solutions.

## 2. Experimental procedure

### 2.1 Induction period

As soon as the solution attains supersaturation, embryos are formed by single molecular addition starting from the monomer at the beginning. Thus it takes some time for the formation of critical nucleus from the monomers. The time taken between the achievement of supersaturation or supercooling and the appearance of crystal nucleus in a supersaturated solution is known as induction period.

In the present investigation, the direct vision observation method was employed to measure the induction period. The saturated solution was cooled to the desired temperature and maintained at that temperature and the time taken for the formation of the first speck was measured. The critical nucleus can be observed only after the nucleus reaches a sufficient size with time. The appearance of first visible speck of nucleus was noticed at the bottom of the container and hence the induction period was recorded. The consistency of the reading was verified by repeating the experiment three or four times.

### 3. Nucleation kinetics

The induction period has been frequently used as a measure of the nucleation rate. The induction period is devoted to nucleus formation and is inversely proportional to the steady state nucleation rate  $\tau \propto J^{-1}$ .

$$\ln \tau = \ln B + 16\pi\gamma^3 V^2 N / 3R^3 T^3 (\ln S)^2 \quad (1)$$

Where,  $\tau$  is the induction period of the solution at temperature  $T$ ,  $V$  is the molar volume of the crystal,  $\gamma$  is the interfacial tension,  $S$  is the supersaturation ratio ( $S = C/C^*$ ),  $N$  is the Avogadro's number and  $R$  is the gas constant.

Equation (1) suggests that the plot of  $\ln \tau$  against  $1/(\ln S)^2$  is straight line. It can be drawn with slope of

$$m = 16\pi\gamma^3 V^2 N / 3R^3 T^3 \quad (2)$$

The interfacial tension of the solid relative to its solution can be calculated as

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

#### 3.1 Nucleation parameters

The interfacial energy ( $\gamma$ ) determined by conducting nucleation experiments has been used for the kinetics study. The change in the Gibb's free energy ( $\Delta G$ ) between the crystalline phase and the surrounding mother liquor results in a driving force, which stimulates crystallization. The Gibb's free energy is represented as the sum of surface free energy and volume free energy.

$$\Delta G = \Delta G_s + \Delta G_v \quad (4)$$

For a spherical nucleus

$$\Delta G = 4\pi r^2 \gamma + (4/3) \pi r^3 \Delta G_v \quad (5)$$

Where,  $r$  is the radius of nucleus,  $\gamma$  is the interfacial energy and  $G_v$  is the free energy change per unit volume. The free energy formation obeys the condition  $d(\Delta G)/dr = 0$ . Hence the radius of the critical nucleus is expressed as

$$r^* = -2 \gamma / \Delta G_v \quad (6)$$

and the interfacial energy [2]

$$\gamma = (kT/d^2) [0.174 - 0.247 \ln S] \quad (7)$$

Where,  $k$  is the Boltzmann's constant ( $1.38 \times 10^{-23}$  J/ K),  $d$  is the interionic distance. The value of  $d$  is estimated using the expression  $d = (abc)^{1/3}$ , where  $a$ ,  $b$  and  $c$  are lattice parameters of the crystal. The bulk energy change per unit volume is represented as

$$\Delta G_v = - (kT \ln S) / V \quad (8)$$

The corresponding free energy barrier is

$$\Delta G^* = 16 \pi \gamma^3 / 3 \Delta G_v^2 \quad (9)$$

The number of molecules in the critical nucleus is given as

$$i^* = 4\pi(r^*)^3 / 3V \quad (10)$$

The nucleation rate is given as

$$J = A \exp(- \Delta G^* / kT) \quad (11)$$

### 4. Modified classical nucleation theory

The classical nucleation theory makes use of capillarity approximation. According to this approximation the physical properties of the nucleus at the micro level are assumed to be the same as those in the macro level. A microclustre in a supersaturated system in the liquid phase possesses a structure which is different from that of a bulk condensed phase. Therefore the concept of constant interfacial tension [3] in the micro system and macro system is not valid. A correction has to be applied and hence the classical nucleation theory is suitably modified. The nucleation parameters are evaluated based on this concept.

Let  $\gamma$  be the interfacial energy of the spherical shaped nucleus when the size is  $r$ . The interfacial energy at the micro level will be less than that at the macro level. If the interfacial energy of a spherical shaped nucleus of size [3] can be written as

$$\gamma = \gamma_0 - (d\gamma/dr) r \quad (12)$$

Where  $d\gamma/dr$  is the surface energy gradient.

$$d\gamma / (\gamma_0 - \gamma) = dr/r \quad (13)$$

Integrating,

$$-\ln(\gamma_0 - \gamma) = \ln r + c \quad (14)$$

Where  $c$  is the constant of integration. The constant  $c$  is evaluated from the initial condition. When the size of the nucleus is equal to the size of the single monomer there is no interface at all. It means when  $r = \delta$ , the size of the single monomer,  $\gamma = 0$ . Applying this initial condition an expression for  $\gamma$  as a function of the size of the cluster obtained.

$$\gamma = \gamma_0 (1 - \delta/r) \quad (15)$$

When  $r = \delta$ ,  $\gamma = 0$  (the new phase just forms)

When  $r = \infty$ ,  $\gamma = \gamma_0$  (the nucleus attains microlevel)

When the crystal nucleus just forms, there is no formation of interface between the crystal and the solution and hence the interfacial energy is 0. When the crystal nucleus attains considerably larger size, the interfacial energy becomes equal to the bulk value. This condition implies that interfacial energy depends on size of the nucleus.

The critical radius is given as

$$r^* = (\gamma_0/\Delta G_v) (1 + (1 - (\Delta G_v \delta / \gamma_0)^{1/2})) \quad (16)$$

The free energy change associated with the critical nucleus is obtained as,

$$\Delta G^* = 4\pi r^* (\gamma_0 (r^* - \delta) - (1/3)r^{*2}\Delta G_v) \quad (17)$$

the rate of nucleation is

$$J = A \exp(-\Delta G^*/kT) \quad (18)$$

## 5. Results and discussion

The effect of supersaturation on induction period experiments were conducted for various level of supersaturation ( $S = 1.05$  to  $1.1$ ) at  $45^\circ\text{C}$ . The variations of induction period with supersaturation measured at  $45^\circ\text{C}$  for KAP and RbKAP samples are presented in Fig. 1. The induction period is found to

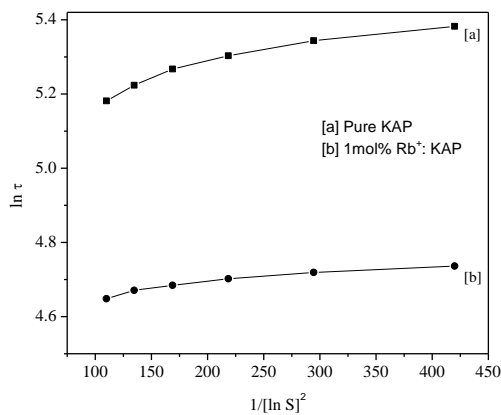


Fig.1. Plot of  $\ln \tau$  vs  $1/(\ln S)^2$ .

decrease with increase in supersaturation, which indicates the increase in the nucleation rate [4]. Thus the level of supersaturation plays a major role in controlling the nucleation rate. It can be noticed that the induction period decreases with the addition of 1mol% of  $\text{Rb}_2\text{CO}_3$ .

The interfacial tension between the crystal and the aqueous solution is calculated by measuring the slope value of the curve obtained at  $45^\circ\text{C}$ . Using equation (3), the value of the interfacial tension is calculated and presented in Table 1. The smaller interfacial energy value

Table 1. Interfacial tension of RbKAP solutions.

Sample	Interfacial Tension (mJ/m <sup>2</sup> )
1mol% Rb <sup>+</sup> : KAP solutions	0.3591

suggest that this dopant would have a greater tendency to nucleate faster than the pure [5]. Since the interfacial energy are indeed related to the solubilities, the lower

interfacial energy values are consistent with the higher solubilities of solid phases and their rapid dissolution [6] Also decrease in interfacial energy of the  $\text{Rb}_2\text{CO}_3$  doped KAP aqueous solution indicates the increase in the nucleation rate [7]. The number of critical nuclei formed will be increased. The study of induction period against supersaturation was used to grow good quality single crystals.

The free energy change for the formation of a critical nucleus ( $\Delta G^*$ ) and number of molecules in the critical nucleus ( $i^*$ ) were calculated at  $45^\circ\text{C}$  and presented in Figs. 2-4.

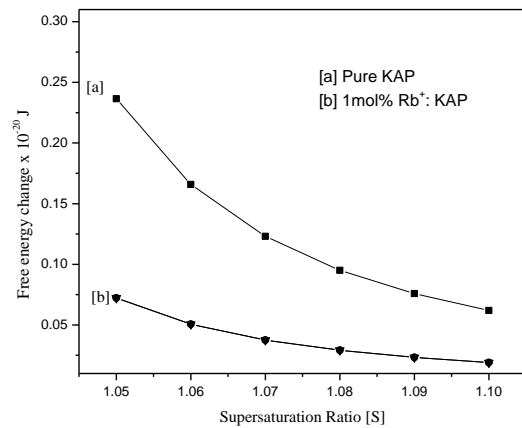


Fig. 2. Variation of free energy change with supersaturation ratio.

It was noted that with the increase in supersaturation the free energy change decreases ( $\Delta G^*$ ) with radius ( $r^*$ ). This clearly indicates that the radius of critical nucleus decreases as the supersaturation increase. Contrary to this, an increase in energy of formation was observed with corresponding rise in the supersaturation. This favours the easy formation of nucleation in aqueous solution at higher supersaturations.

### 5.1 Theoretical determination of critical supersaturation ratio of KAP and RbKAP

The main idea of calculating the nucleation parameters was to find the critical supersaturation ratio required to grow one nucleus per unit volume in one second. Hence an attempt was made to calculate the critical supersaturation ratio at  $45^\circ\text{C}$  using the experimentally evaluated interfacial energy for pure and 1 mol%  $\text{Rb}_2\text{CO}_3$  doped KAP solutions. The classical nucleation parameters like critical free energy change, critical nucleation rate and critical radius of pure and  $\text{Rb}^+$  doped KAP solutions were calculated for different supersaturation ratios using the equations

$$r^* = 2\gamma_0/\Delta G_v \quad (19)$$

$$\Delta G_v^* = 16\pi \gamma_0^3/3\Delta G_v^2 \quad (20)$$

and

$$J = z\beta i n_1 \exp(-\Delta G_v^*/kT) \quad (21)$$

respectively where  $\beta_i$  is the Zeldovich factor [8]  $\beta_i$  is the impingement term and  $n_1$  is the concentration of the atoms or molecules in the parent phase. In the case of nucleation from solution the pre-exponential factor is  $10^{25}$  [9]. The classical theory was modified by incorporating correction to the capillarity approximation and the modified values of nucleation parameters were calculated using the equations 16 – 18. Table 2 presents the calculated basic growth parameters of pure and doped KAP solutions using the theoretical models.

The critical supersaturation ratio for the 1mol%  $\text{Rb}_2\text{CO}_3$  doped KAP at  $45^\circ\text{C}$  was evaluated to be 1.002615. Since the classical nucleation theory was based on capillarity approximation a correction was made to the interfacial energy based on the thermodynamical approach. The values of nucleation parameters corresponding to the critical supersaturation ratio were also calculated using the modified classical nucleation theory.

A comprehensive data was prepared for the better understanding of the growth kinetics for the successful growth of pure and  $\text{Rb}_2\text{CO}_3$  added KAP single crystals from aqueous solution.

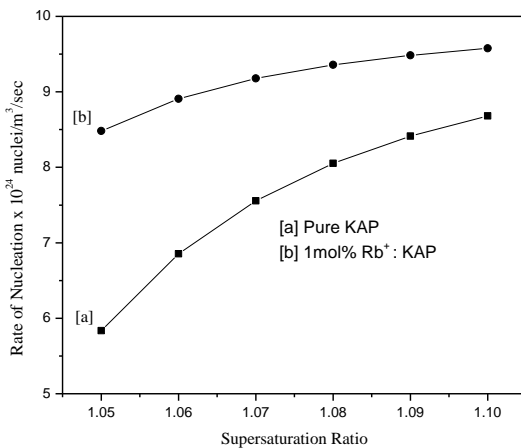


Fig. 3. Variation of rate of nucleation with supersaturation ratio.

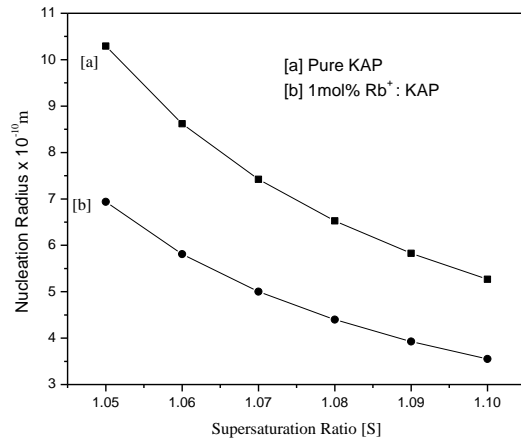


Fig. 4. Variation of nucleation radius with supersaturation ratio.

6. Conclusions

Induction period was measured for pure and 1mol%  $\text{Rb}_2\text{CO}_3$  doped KAP solutions at different supersaturation values. A linear graph was obtained between  $1/[\ln S]^2$  and  $\ln \tau$  for pure and doped KAP solutions. The interfacial energy was calculated from the slopes of the graphs. The calculated values of the interfacial energy decrease for the RbKAP solutions.

The nucleation parameters such as free energy change, rate of nucleation and nucleation radius for pure and 1 mol%  $\text{Rb}_2\text{CO}_3$  KAP solutions were calculated and represented graphically at  $45^\circ\text{C}$  using the classical homogeneous nucleation theory. The free energy change was found to be reduced for the large value of the supersaturation ratio. The value of free energy change decreases for the doped KAP solutions. The rate of nucleation increases by the addition of  $\text{Rb}_2\text{CO}_3$  to the KAP solutions. The radius of the nucleus decreases for RbKAP solutions.

Table 2. Critical nucleation parameters of 1mol%  $\text{Rb}_2\text{CO}_3$  doped KAP solution ( $T=318\text{K}$  and  $\gamma_0 = 0.3591 \text{ mJ/m}^2$ ).

S	$-\Delta G_v \times 10^4 \text{ J/m}^3$	$r^* (\text{Å})$		$\Delta G^* \times 10^{-12} \text{ J}$		J (nuclei/m <sup>3</sup> /sec)	
		CNT	MCNT	CNT	MCNT	CNT	MCNT
1.002613	5.5388	129.6671	129.1651	2.5291	2.4707	0.9353	3.5393
1.002614	5.5409	129.6179	129.1160	2.5272	2.4687	0.9757	3.7043
1.002615	5.5430	129.5688	129.0669	2.5253	2.4669	1.0199	3.8594
1.002616	5.5451	129.5198	129.0178	2.5233	2.4650	1.0675	4.0302
1.002617	5.5472	129.4707	128.9688	2.5214	2.4632	1.1147	4.1989
1.002618	5.5493	129.4217	128.9198	2.5195	2.4612	1.1640	4.3947

The critical supersaturation ratio for the pure and 1mol%  $\text{Rb}_2\text{CO}_3$  doped KAP solution at  $45^\circ\text{C}$  was calculated by applying homogeneous classical theory.

The critical supersaturation ratio decreases for the RbKAP solution. The variation in the nucleation parameter based on the modified classical theory also calculated.

### Acknowledgements

The author would like to thank Dr. D. Jayaraman, Department of physics, Presidency College, Chennai – 600 005, India for the useful discussions we had with him.

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