Extension of modified classical theory to nucleation of NKAP from aqueous solutions

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Induction period was recorded for pure and 1mol% of Na^+ added KAP solutions at different supersaturation values at 45°C using visual observation method. A plot of $1/(\ln S)^2$ against $\ln \tau$ is determined. In order to reduce the effect of heterogeneous nucleation on the nucleation parameters, the interfacial energy was calculated from the slopes determined in the linear region of the line plots. Nucleation parameters like free energy change, rate of nucleation and critical radius were determined using the value of interfacial energy. The critical supersaturation ratio for the pure and 1mol% Na^+ doped KAP solutions at 45°C was evaluated to be 1.00473 and 1.003485 respectively. Correction was made to the interfacial energy based on the thermodynamical approach. An attempt has been made to calculate the nucleation parameters corresponding to the critical supersaturation ratio using the modified classical nucleation theory.

1. Introduction

The potassium acid phthalate (KAP) crystals are promising materials for the qualitative and quantitative x-ray spectral analysis of light elements Fe, Al, Mg, F, Si in a long wave spectral area and a good monochromator (Sassella et al 2001, Shujun et al 1993). This is a fine model material for studying the crystallization process especially the mechanism of spiral growth in crystals (Beck et al, 1995, Timpanaro et al 2001). The present study aimed at to predict the crystal growth mechanism and impact of additives such as sodium chloride with potassium hydrogen phthalate on the granulometric (crystal size distribution and external shape) of the grown crystals. So active research works are being carried out in understanding the fundamental growth and nucleation mechanism of these crystals. Theoretical modeling plays a key role in understanding the kinetics of growth mechanism. They are also essential to understand the growth phenomena and inorder to predict the growth rate and the thickness of the grown crystals.

In the present study, investigations have been made to evaluate the interfacial tension (γ) between the solid-liquid interfaces by measuring the induction period and hence to calculate Gibb's free energy (ΔG^*), the critical radius (r^*) and number of molecules in the formation of a critical nucleus of the pure and 1mol% Na^+ doped KAP crystals grown from aqueous solution using classical homogeneous nucleation theory. 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 KAP and NKAP solutions.

2. Nucleation kinetics

The extent to which of KAP and 1mol% Na^+ doped KAP (NKAP) in aqueous solution occurs is determined by the supersaturation of the KAP and NKAP molecules in aqueous solution. Thus, higher supersaturation produces more stable aggregates (due to higher probability of collision of diffusing molecules) and therefore increases the formation of stable nuclei. The time period that elapses between the attainment of supersaturation and appearance of a visible speck is defined as induction period (τ). In the present work, the induction period of KAP and NKAP in aqueous solution has been measured by the visual observation method.

2.1 Experimental procedure

There are several methods of measuring the induction period depending upon the solubility of the materials.(Zaistseva et al, 1995). In the present work, the visual observation method was followed. KAP and NKAP solutions at different supersaturation values were prepared. The experimental set up consists of small cells of identical volume placed in a constant temperature bath and the temperature was controlled to the accuracy of ±0.01°C. A powerful lamp was placed at the rear side of the bath, so that the cells can get illuminated. One of the cells was taken as a reference cell for the determination of accuracy of temperature. A sensitive thermometer was inserted into

this cell. Supersaturated solution of equal volume was taken in the cells at slightly higher temperature. As the temperature of the solution reaches the temperature of the bath, the time was recorded until the nucleation starts and a visible speck appear. The time period that elapses between the achievement of supersaturation and the appearance of visible nuclei is taken as the induction period (τ). Several trial runs were performed to minimize the error. Experiments were repeated for supersaturation (S) like 1.05, 1.06, 1.07, 1.08, 1.09 and 1.1 at 45ºC. From the results obtained, a plot of ln τ against $1/(\ln S)^2$ is drawn and is shown in Fig. 1. The interfacial tension was calculated (Ushasree et al, 2000) from the slope of the curve using the equation

$$\ln \tau = \ln B + 16\pi\gamma^3 V^2 N / 3RT \, (\ln S)^2 \qquad (1)$$

Where A is a constant related to the pre-exponential factor of the nucleation rate expression. V is the molar volume, N is the Avogadro number and R is the gas constant. The factor $16\pi/3$ in the above equation refers to the spherical nuclei. The interfacial tension between the crystal and the aqueous solution is calculated by measuring the slope value of the curve obtained at 45ºC. The values are given in Table 1. According to the Classical Homogeneous
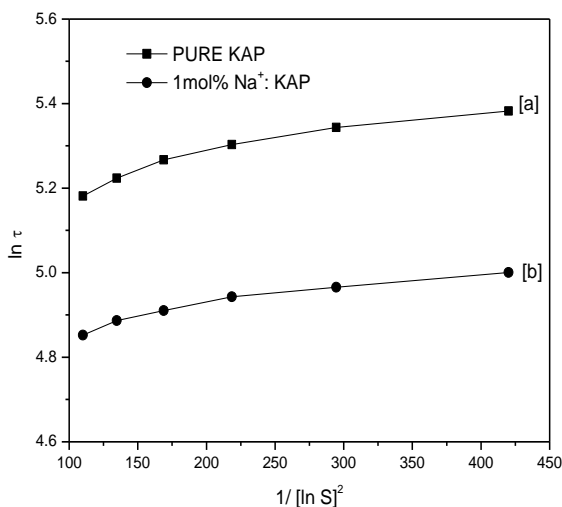

Fig. 1. Plot of ln τ vs $1/(\ln S)^2$.

Table 1. Interfacial tension of pure and NKAP solutions.

Sample	Interfacial Tension (mJ/m^2)
KAP solutions	0.5329
1mol% Na$^+$: KAP solutions	0.4348

Nucleation theory the free energy required to from a KAP and NKAP nucleus is given by

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

Where ΔG_v is the energy change per unit volume, r is the radius of the nucleus. At the critical state, the free energy of formation obeys the condition that

$$d(\Delta G)/dr = 0 \qquad (3)$$

Hence the radius of the critical nucleus is expressed as

$$r^* = -2 \, \gamma/\Delta G_v \qquad (4)$$

where

$$\Delta G_v = -kT\ln S/v \qquad (5)$$

where v is the molecular volume, S = C/C*, C – actual concentration and C* - equilibrium concentration. Hence

$$r^* = 2 \, \gamma v/kT\ln S \qquad (6)$$

The critical free energy is given by

$$\Delta G^* = 16\pi\gamma^3 v^2/3\Delta G_v^2 \qquad (7)$$

The nucleation rate is expressed as

$$J = A \exp(- \Delta G^*/kT) \qquad (8)$$

Using the interfacial tension value, calculated from the slope of the curves obtained experimentally the radius of the critical nuclei (r*), the free energy change for the formation of a critical nucleus (ΔG^*) and rate of nucleation were calculated at 45ºC and presented in Fig. 2, 3 and 4 respectively. It was noted that with the increase in supersaturation the free energy change decreases (ΔG^*) with radius (r*). This favours the easy formation of nucleation in aqueous solution at higher supersaturations.

2.2 Modified classical nucleation theory

The classical nucleation theory makes use of the capillarity approximation according to which, the physical properties of nucleus at micro level are assumed to be the same as those in the macro level. The application of the concept of surface tension to nucleation phenomena and the strong dependence of the nucleation rate, as derived in the classical nucleation theory on the value of the surface tension, led to a renewed interest in the problems. Since the interfacial energy plays an important role, a correction has to be applied and the classical theory was suitably modified to calculate the nucleation parameters of the critical nucleus. Some new results for the curvature dependence of droplets were also derived based on thermodynamical considerations.
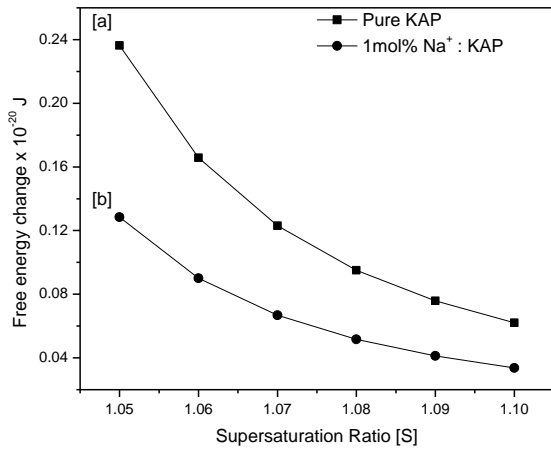
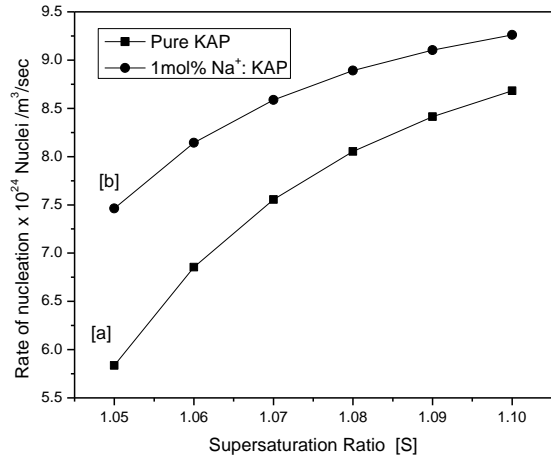*Fig. 2. Variation of free energy change with supersaturation ratio of (a) pure and (b) 1 mol% Na⁺ doped KAP solutions.*

Fig. 3. Variation of Rate of nucleation with Supersaturation Ratio of (a) pure and (b) 1 mol% Na⁺ doped KAP solutions.

The interfacial energy of a spherical shaped nucleus of size 'r' can be written as,

$$\gamma = \gamma_0 - (\,d\gamma\,/dr)\,r \qquad (9)$$

where, γ be the interfacial energy of the spherical shaped nucleus when the size is 'r', γ_0 is interfacial energy of the macro level and $d\gamma/dr$ is the surface energy gradient. 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, $\gamma = 0$. At this condition

$$\gamma = \gamma_0 \,(1 - (\delta/r) \qquad (10)$$

Thus when $r = \infty$,

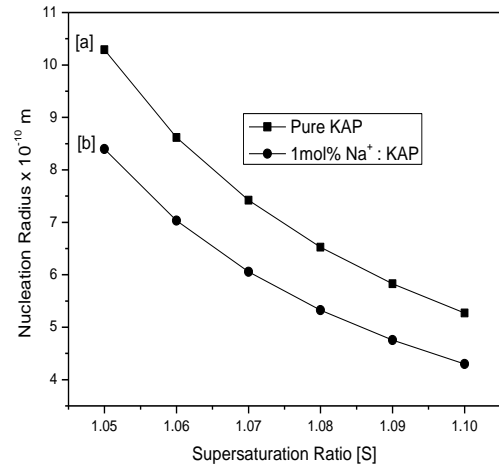$$\gamma = \gamma_0 \qquad (11)$$

Fig. 4. Variation of Nucleation radius with Supersaturation Ratio of (a) pure and (b) 1 mol% Na⁺ doped KAP solutions.

When the crystal nucleus just forms, there is no formation of interface between the crystal and the solution and hence the interfacial energy is zero. When the crystal nucleus attains considerably large size the interfacial energy becomes equal to the bulk value. This condition implies that interfacial energy depends on the size of the nucleus. The critical radius was given by,

$$r^* = (\gamma_0/\Delta G_v)\,(1 + (1 - (\Delta G_v \delta\,/\,\gamma_0)^{\tfrac{1}{2}}) \qquad (12)$$

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

$$\Delta G^* = 4r^*\pi\,(\gamma_0\,(r^* - \delta) - (1/3)r^{*2}\Delta G_v) \qquad (13)$$

Now, the rate of nucleation is

$$J = A\,\exp\,(-\Delta G^*/kT) \qquad (14)$$

2.3 Theoretical determination of critical supersaturation of KAP and NKAP

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°C using the experimentally evaluated interfacial energy for pure and 1 mol% Na⁺ doped KAP solutions. The classical nucleation parameters like critical free energy change, critical nucleation rate and critical radius of pure and Na⁺doped KAP solutions were calculated for different supersaturation ratios were calculated using the equations

$$r^* = 2\gamma_0/\Delta G_v \qquad (15)$$

$$\Delta G_v^* = 16\pi\,\gamma_0 3/3\Delta G_v^{\,2} \qquad (16)$$

and

$$J = z\beta_i n_1\,\exp\,(\,-\Delta G_v^*\,/kT) \qquad (17)$$

respectively where z is the Zeldovich factor, β_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} (Paul et al, 2000). The classical theory was modified by incorporating

correction to the capillarity approximation and the modified values of nucleation parameters were calculated using the equations 12 - 14. Tables 2 and 3 present the calculated basic growth parameters of pure and doped KAP solutions using the theoretical models.

Table 2. Critical Nucleation parameters of Pure KAP solution (T=318K and γ_0 = 0.5329 mJ/m^2).

S	$-\Delta G_v \times 10^4$ J/m^3	r^* (Å)		$\Delta G^* \times 10^{-12}$J		J (nuclei/m^3/sec)	
		CNT	MCNT	CNT	MCNT	CNT	MCNT
1.00471	9.9733	106.8653	106.3630	2.5509	2.4778	0.5691	3.0106
1.00472	9.9944	106.6397	106.1374	2.5407	2.4673	0.7181	3.8244
1.00473	10.0156	106.4140	105.9116	2.5255	2.4566	1.0153	4.8804
1.00474	10.0367	106.1903	105.6879	2.5155	2.4462	1.2751	6.1855
1.00475	10.0578	15.9675	105.4651	2.5055	2.4357	1.6015	7.8576
1.00476	10.0789	105.7457	105.2433	2.4955	2.4254	2.0113	9.9363

Table 3. Critical Nucleation parameters of 1mol% Na$^+$ KAP solution (T=318K and γ_0 = 0.4348 mJ/m^2).

S	$-\Delta G_v \times 10^4$ J/m^3	r^* (Å)		$\Delta G^* \times 10^{-12}$J		J (nuclei/m^3/sec)	
		CNT	MCNT	CNT	MCNT	CNT	MCNT
1.003483	7.3797	117.8368	117.3346	2.5289	2.4647	0.9396	4.0578
1.003484	7.3818	117.8032	117.3011	2.5275	2.4633	0.9701	4.1894
1.003485	7.3839	117.7697	117.2673	2.5261	2.4618	1.0015	4.3350
1.003486	7.3860	117.7363	117.2341	2.5246	2.4605	1.0363	4.4654
1.003487	7.3881	117.7028	117.2007	2.5232	2.4590	1.0699	4.6206
1.003488	7.3903	117.6678	117.1656	2.5217	2.4579	1.1071	4.7704

3. Results and discussions

The induction period for the pure and 1mol% Na$^+$ KAP doped solution were measured by visual observation method. Plots of ln (τ) against 1 / [ln S] ^{2} (Fig. 1) are nearly linear. The value of 'τ' decreases as the supersaturated concentration of the aqueous solution is increased (Mohan Kumar et al 1999, Chenthamarai et al 1999, Rajesh et al 2002, Rajasekaran et al 2003). Considering the principles of homogenous and heterogeneous nucleation theories, the free energy of formation of a nucleus under heterogeneous nucleation was less than that of homogenous condition (Rajesh et al 2002).

It can be noticed that the induction period decreases with the addition of Na$^+$ with KAP. The smaller interfacial energy values between the alkali metal ions doped aqueous media and mother phase suggest that this dopant would have a greater tendency to nucleate faster than the pure. 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. Also decrease in interfacial energy of the alkali metal ion doped KAP aqueous solution indicates the increase in the nucleation rate. 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 nucleation parameters like free energy change, rate of nucleation and critical radius were calculated for

pure and 1mol% of Na$^+$ doped KAP solutions at different values of supersaturation ratio of 1.05, 1.06, 1.07, 1.08, 1.09 and 1.1 using the classical homogeneous nucleation theory with the experimentally evaluated interfacial energy at 45˚C. The critical radius and critical free energy decreases gradually with the increase in supersaturation (Fig. 2 and 4). But the nucleation rate, which is an important parameter needed to have a controlled growth rate, increases with the increase of the supersaturation (Fig. 3). The calculated values of rate of nucleation for pure and Na$^+$ doped KAP solutions range from 5 to 9 $\times$ 10^{24} nuclei/m^3/ sec. When the nucleation rate is unity, the growth rate was controlled and good quality crystal can be grown. Hence an attempt was made to calculate the supersaturation ratio required to grow one nucleus per unit volume in one second (i.e) the critical supersaturation, using the classical nucleation theories at 45˚C. The critical supersaturation ratio for the pure and 1mol% Na at 45˚C was evaluated to be 1.00473 and 1.003485 respectively. 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 Na$^+$ added KAP single crystals from aqueous solution.

4. Conclusion

Induction period was recorded for pure and 1mol% sodium 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 Na$^+$ doped KAP solutions.

The nucleation parameters such as free energy change, rate of nucleation and nucleation radius for pure and 1 mol% Na$^+$ doped KAP solutions were calculated and represented graphically at 45°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 alkali metal ions to the KAP solutions. The radius of the nucleus decreases for alkali metal ions added KAP solutions.

The critical supersaturation ratio for the pure and 1mol% Na$^+$ doped KAP solution at 45°C was calculated by applying homogeneous classical theory. The critical supersaturation ratio decreases for the Na$^+$ doped KAP solution. The variation in the nucleation parameter based on the modified classical theory also calculated.

Acknowledgements

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