International Journal of Engineering & Applied Sciences (IJEAS)
Vol.6, Issue 1(2014)53-59

EXTENSION OF MODIFIED CLASSICAL THEORY TO NUCLEATION OF LKAP FROM AQUEOUS SOLUTION

S.K. Geetha 1 [a*] *and G. Chandrasekar 2* [b]

[a] *Department of Physics, Government Arts College, Nandanam, Chennai – 600 035, India*
[b] *Department of Chemistry, M.P.B. Government Girls Higher Secondary School, Tambaram East, Chennai – 600 059, India*
[*] *E-mail address*: yeskgeetha@gmail.com

Abstract

The dependence of the induction period of crystallization on super cooling was determined for the system lithium chloride—potassium acid phthalate (KAP) over the composition of 1mole % $LiCl_2$. This dependence can be described by $1/(\ln S)^2$ against $\ln \tau$ curve. 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. Correction was made to the interfacial energy based on the thermodynamically approach. An attempt has been made to calculate the nucleation parameters corresponding to the critical super saturation ratio using the modified classical nucleation theory.

Keywords: Nonlinear optical materials; induction period; interfacial energy; nucleation parameters

1. Introduction

Super cooling of liquids is a phenomenon the nature of which is not yet fully understood. The existence of a liquid in thermodynamically unstable state at the temperature lower than is its equilibrium temperature of solid—liquid transition can be explained by an anomalous slow-down of nucleation of crystals. A quantitative measure of super cooling is the induction period of crystallization [1]. This induction period corresponds to the time at which the first observable crystal forms in the liquid at given super cooling. Generally it holds that the induction period shortens when super cooling increases. At the critical temperature of super cooling it reaches its minimum value, the so-called critical induction period of crystallization. If the temperature is further decreased the induction period of crystallization starts to increase as a result of increasing viscosity of the liquid.

Ability of some salt solutions for super cooling has been studied by several authors [1—3]. It has been found that salt solutions are suitable model systems for investigation of the influence of salts on super cooling. The aim of this work is to present the results of investigation of the influence of composition on the induction period of crystallization in the system potassium acid phthalate — lithium chloride. The interfacial tension (σ) between the solid-liquid interfaces is evaluated by measuring the induction period. 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% LiCl doped potassium acid phthalate 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 the system potassium acid phthalate –lithium chloride (LKAP) solutions.

2. Experimental procedure

2.1 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 [4]. 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 of LKAP

The change in the Gibbs free energy (ΔG) between the crystalline phase and the surrounding mother liquor results in a driving force which stimulates crystallization. For rapid crystallization, $\Delta G < 0$; “The energy required to form LKAP nuclei is given by Eq. (1)”.

$$\Delta G = (4/3)\pi r^3 \Delta G_v + 4\pi r^2 \gamma \qquad (1)$$

Where ΔG_v is the energy change per unit volume, γ is the interfacial tension and r is the radius of the nucleus. The first term expresses the formation of new surface and the second term expresses the difference in chemical potential between the crystalline phase (μ) and the mother liquor (μ_0). At the critical state, the free energy formation obeys $d(\Delta G)/dr = 0$; Hence "the critical nucleus is expressed as Eq. (2)".

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

Where $\Delta G_v = -\,\Delta\mu\, /\, v$, $\Delta\mu = (-kT/v) \ln S$, $S = C/C^*$, C – actual concentration C* – equilibrium concentration. Hence "the radius of the critical nucleus is expressed as Eq. (3)".

$$r^* = 2\, v\gamma \,/\, \Delta\mu \qquad (3)$$

"The critical free energy barrier is expressed as Eq. (4)".

$$\Delta G^* = 16\pi\gamma^3 v^2 \,/\, 3\, (\Delta\mu)^2 \qquad (4)$$

"The number of molecules in the critical nucleus is expressed as Eq. (5)".

$$i^* = 4\pi\, (r^*)^3 \,/\, 3v \qquad (5)$$

3.1 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 [5]. 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 thermodynamically considerations. The "interfacial energy of a spherical shaped nucleus of size 'r' can be written as Eq. (6)",

$$\gamma = \gamma_0 - (\, d\gamma /dr)\, r \qquad (6)$$

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 "interfacial energy of the spherical shaped nucleus is given as Eq. (7)".

$$\gamma = \gamma_0\, (1 - (\delta/r) \qquad (7)$$

Thus when $r = \infty$, the “value of the interfacial energy is determined as in Eq. (8)”.

$$\gamma = \gamma_0 \quad (8)$$

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 the Eq. (9)”.

$$r^* = (\gamma_0/\Delta G_v)\ (1+ (1- (\Delta G_v\delta / \gamma_0)^{½}) \quad (9)$$

“The critical free energy change associated with the critical nucleus was obtained as in Eq. (10)”,

$$\Delta G^* = 4r^*\pi\ (\gamma_0\,(r^* - \delta) - (1/3)r^{*2}\Delta G_v) \quad (10)$$

Now, “the rate of nucleation is given as Eq. (11)”

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

4. Results and Discussions

The crucial parameter involved between a growing crystal and the super cooling mother liquor is the interfacial tension ‘γ’ [6]. This complex parameter has been determined by conducting the nucleation experiments on saturated solution of pure potassium acid phthalate (KAP) and LKAP under stirred condition. Plots of ln (τ) against $1 / [\ln S]^2$ is given in the “Fig. 1” are nearly linear [7]. It is inferred from our experiments that the interfacial tension for LKAP solution is 0.4729mJ/m^2.

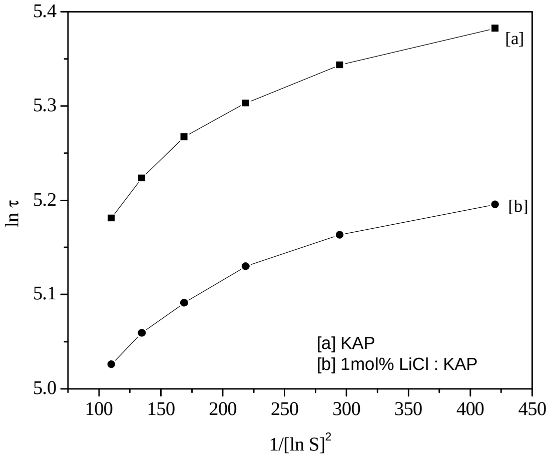

Figure 1: Plot of ln τ vs $1/(\ln S)^2$

In the present study, in order to estimate the criticial nucleation parameters, the interfacial tension has been calculated using the experimentally measured induction period values by the relation Eq. (12) [8].

$$\ln \tau = -\ln B + 16\pi\gamma^3 v^2 N_A / 3 R^3 T^3 (\ln S)^2 \qquad (12)$$

The free energy change as a function of supersaturation ratio (S) for KAP and LKAP solutions are given in “Fig. 2”.

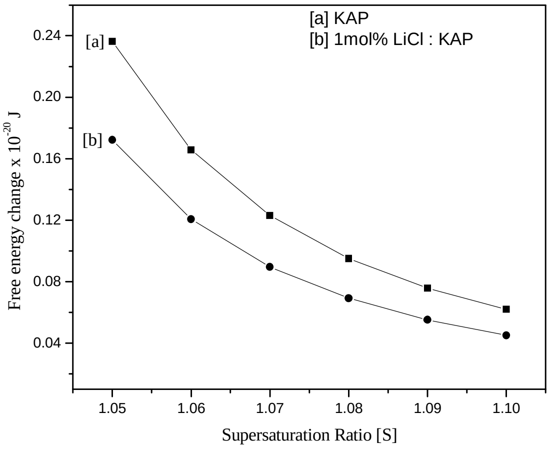

Figure 2: Variation of free energy change with supersaturation ratio of (a) pure and (b) 1mol% LiCl doped KAP solutions

The evaluated radius of critical nucleus and rate of nucleation as a function of supersaturation ratio (S) is shown in “Fig. 3” and “Fig. 4” respectively.

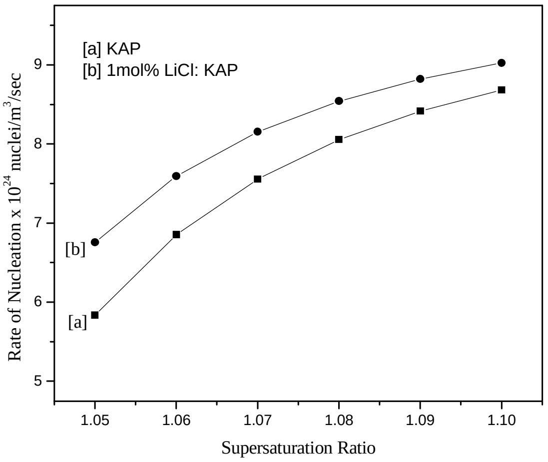

Figure. 3: Variation of Rate of nucleation with Supersaturation Ratio of (a) pure and (b) 1mol% LiCl doped KAP solutions

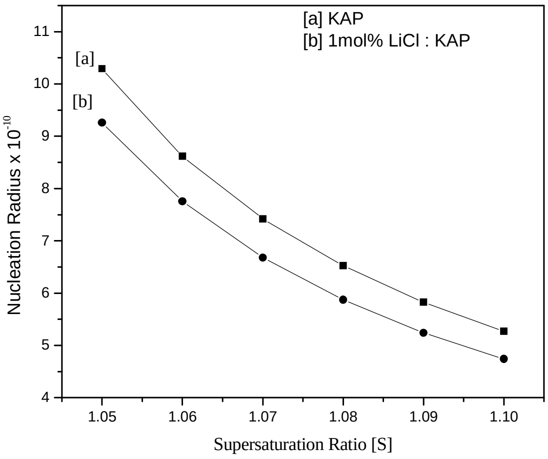

Figure 4: Variation of Nucleation radius with Supersaturation Ratio of (a) pure and (b) 1mol% LiCl doped KAP solutions

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 LKAP at 45˚C was evaluated to be 1.003954. 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.

Table 1: Critical Nucleation parameters of LKAP solution (T=318K and γ_0 = 0.4729 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
1.003951	8.3693	113.0083	112.5060	2.5298	2.4627	0.9205	4.270
1.003952	8.3714	112.9800	112.4777	2.5285	2.4615	0.8482	4.3649
1.003953	8.3735	112.9516	11.2.4493	2.5272	2.4602	0.9767	4.4960
1.003954	8.3757	112.9219	112.4197	2.5259	2.4589	1.0061	4.6312
1.003955	8.3778	112.8936	112.3914	2.5246	2.4577	1.0363	4.7596
1.003956	8.3799	112.8653	112.3631	2.5233	2.4565	1.0675	4.8915

A comprehensive data was prepared for the better understanding of the growth kinetics for the successful growth of LKAP single crystals from aqueous solution and presented in the “Table 1”.

5. Conclusions

Induction period was recorded for pure and 1mol% lithium chloride doped potassium acid phthalate solutions at different supersaturation values. A linear graph was obtained between 1/[ln S]^2 and ln τ for pure and doped solutions. The interfacial energy was calculated from the slopes of the graphs. The calculated values of the interfacial energy decrease for the LKAP solutions.

The nucleation parameters such as free energy change, rate of nucleation and nucleation radius for pure and doped solutions were calculated and represented graphically at 45ºC 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 solutions. The rate of nucleation increases by the addition of alkali metal ions to the potassium acid solutions. The radius of the nucleus decreases for alkali metal ions added solutions.

The critical supersaturation ratio for the pure and $_{\text{doped}}$ solution at 45˚C was calculated by applying homogeneous classical theory. The critical supersaturation ratio decreases for the LKAP solution. The variation in the nucleation parameter based on the modified classical theory also calculated.

References

[1] Pacák, P., Horsák, L, and Sláma, L, *Krist. Tech*. 14, 741 (1979).

[2] Pacák, P. and Sláma, L, *Collect. Czechoslov. Chem. Commun.* 46, 1629 (1981).

[3] Pacák, P. and Sláma, L, *J. Solution Chem.* 8, 529 (1979).

[4] Mohan Kumar R., Gopalakrishnan N., Jayavel R, and Ramasamy P., Investigations on the Nucleation Kinetics of L-Arginine Phosphate single crystals, *Cryst. Res. Technol.*, 34, 1265-1268 (1999).

[5] Chenthamarai S., Jayaraman D., Ushasree P.M., Meera K., Subramanian C. and Ramasamy P., 1999, Experimental determination of induction period and interfacial energies of pure and nitro doped 4-hydroxyacetophenone single crystals, *Mat. Chem. Phys.,* 8617, 1-5 (1999).

[6] Paul D.P., Jayavel R., Subramanian C. and Ramasamy P., Investigations on nucleation thermodynamical parameters of $NdBa_2Cu_3O_{7-\delta}$ (Nd123) crystallization by high temperature solution growth, *Bull. Mater. Sci.,* 23, 79-82 (2000).

[7] Rajesh N.P., Kannan V., Santhana Raghavan P., Ramasamy P. and Lan C.W., Nucleation studies and crystal growth of $(NH_4)H_2PO_4$ doped with thiourea in supersaturated aqueous solutions, *Mat. Chem. Phys*., 76,181-186 (2002).

[8] Zaitseva N.P., Rashkovich L.N. and Bogatyreva S.V. (1995), Stability of KH_2PO_4 and $K(H,D)_2PO_4$ solutions at fast crystal growth rates, *J. Crystal Growth*, 148, 276-282 (1995).