

## Nucleation studies in supersaturated aqueous solutions of $\text{KH}_2\text{PO}_4$ doped with $\text{KBr}$ and $\text{K}_2\text{Cr}_2\text{O}_7$

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**Abstract.** Induction periods were measured for various supersaturated aqueous solutions of potassium dihydrogen orthophosphate doped separately with potassium bromide and potassium dichromate by the direct vision method. Various critical nucleation parameters were calculated based on the classical theory for homogeneous crystal nucleation and the results are reported and discussed. The critical nucleation parameters increased with increase in doping concentration for both the dopants considered.

**Keywords.** Nucleation parameters; doped KDP crystals.

### 1. Introduction

Potassium dihydrogen orthophosphate,  $\text{KH}_2\text{PO}_4$  (abbreviated as KDP), belongs to scalenohedral (twelve sided polyhedron) class of tetragonal crystal system with the tetramolecular unit cell having the dimensions (Wyckoff 1960) given as  $a = b = 7.448 \text{ \AA}$  and  $c = 6.977 \text{ \AA}$ . KDP is soluble in water and its solubilities at 0, 10, 20, 30, 40, 60, 80 and 90°C are 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, respectively (John 1979).

Nucleation process is the first and most important phenomenon in liquid–solid phase transition. The induction period ( $\tau$ ) can be measured (Shanmugham *et al* 1984; Mullin 1993; Ramesh and Mahadevan 1998) and used to calculate certain critical nucleation parameters like interfacial tension ( $\sigma$ ) of the solid relative to its solution, energy of formation ( $\Delta G$ ) of a critical nucleus, and radius of the nucleus ( $r$ ) in equilibrium with its solution, based on the classical theory for homogeneous crystal nucleation.

In the case of ammonium dihydrogen orthophosphate  $\text{NH}_4\text{H}_2\text{PO}_4$  (abbreviated as ADP), it was found (Premila Rachelin 1998; Rajesh and Mahadevan 1998; Ramesh and Mahadevan 1998) that the nucleation parameters increased with increase in impurity concentration for ADP added with impurities like  $\text{KCl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and decreased with increase in impurity concentration for ADP added with  $\text{NH}_4\text{Cl}$ . Premila Rachelin and Mahadevan (1998) attempted to explain this result qualitatively by considering the density values of ADP and impurities.

Nucleation studies on aqueous KDP solutions with and without some added impurities (impurity concentration in the range 100–500 ppm) have already been reported (Joshi and Antony 1979; Shanmugham *et al* 1984, 1985). In the present study we attempted to investigate the effect of the impurities (having higher densities than that for KDP and common cation  $\text{K}^+$  with KDP) like  $\text{KBr}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  (impurity concentration in the range 2000–10000 ppm) on the nucleation parameters of KDP crystals. KDP was added with  $\text{KBr}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  separately in solution each in six different KDP : impurity molecular ratios, viz. 1 : 0.0 (pure KDP), 1 : 0.002, 1 : 0.004, 1 : 0.006, 1 : 0.008 and 1 : 0.010. Induction periods were measured for various supersaturated solutions by the direct vision method. Various critical nucleation parameters have been calculated and the effect of supersaturation and concentration of doping on them is also reported and discussed.

### 2. Experimental

Analytical reagent grade (AR) samples of KDP,  $\text{KBr}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  along with double distilled water were used in the present study. Aqueous solutions of various supersaturated concentrations ( $x$ ) (2.1, 2.2, 2.3, 2.4 and 2.5 M) were prepared by dissolving the required amount of KDP and the impurity at a temperature slightly higher than the saturation temperature (32°C). Supersaturation was obtained by natural cooling.

Induction periods were measured and critical nucleation parameters were calculated following the procedures adopted by Ramesh and Mahadevan (1998). Several nucleation runs were carried out under controlled and unstirred conditions and reproducible results within an

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accuracy of  $\pm 2.5\%$  were obtained. The supersaturated concentration considered provided an induction period of at least 100 s.

The orange-reddish colouration of KDP crystal caused by the  $K_2Cr_2O_7$  impurity indicated that the impurities had entered into the lattice of KDP crystals. Moreover, it was observed (visually) that the intensity of the colour (though not estimated using proper methods) increased with the increase in impurity concentration of the aqueous solution of KDP.

### 3. Results and discussion

The measured induction periods are presented in table 1. For both the impurities considered in the present study, the value of  $\tau$  decreases and hence the nucleation rate increases as the supersaturation and concentration of impurity of the aqueous solution increase. This is similar to the results observed for the ADP added (in the same ratio considered in the present study) with  $NH_4Cl$ ,  $KCl$ ,  $(NH_4)_2SO_4$ ,  $K_2SO_4$  and  $(NH_4)_2C_2O_4 \cdot H_2O$  (Premila

Rachelin and Mahadevan 1998; Rajesh and Mahadevan 1998; Ramesh and Mahadevan 1998).

As per the classical theory for homogeneous crystal nucleation, we expect a linear relationship between  $\ln \tau$  and  $1/\ln^2(x/x_0)$ , where  $x_0$  is the saturated concentration;  $x_0$  for KDP at  $32^\circ C$  is 1.348 M. However, we observed significant deviations from linearity at lower supersaturation levels (figures 1 and 2) of  $\ln \tau$  and  $1/\ln^2(x/x_0)$ . Such deviations from linearity have been reported earlier also (Nagalingam *et al* 1980; Shanmugham *et al* 1984, 1985; Backiyam *et al* 1991; Premila Rachelin and Mahadevan 1998; Rajesh and Mahadevan 1998). Freeda *et al* (1997) explained this non-linearity not due to the difficulties in induction period measurements but due to the heterogeneous nucleation caused by the unwanted impurity particles naturally present in the solvent.

Although the experiments were conducted at controlled conditions, the practical difficulties (such as having the solvent free from natural impurities) in maintaining the nucleation strictly homogeneous led to deviations from the classical theory for homogeneous nucleation especially at lower supersaturations. For higher supersaturated solutions, the effect of the natural impurity particles present in the solvent is dominated by the presence of greater amount of solute. Hence, we expect a

Table 1. Results of induction period measurements.

Impurity ratio	$x$ (M)	$\tau$ (sec) for	
		KBr added KDP	$K_2Cr_2O_7$ added KDP
Pure KDP	2.1	15120	15120
	2.2	12240	12240
	2.3	3720	3720
	2.4	2220	2220
	2.5	1020	1020
1 : 0.002	2.1	6000	14436
	2.2	4560	9000
	2.3	2400	3199
	2.4	1200	1620
	2.5	600	900
1 : 0.004	2.1	4860	12600
	2.2	4020	6974
	2.3	2280	2300
	2.4	1020	1440
	2.5	480	780
1 : 0.006	2.1	4500	8100
	2.2	3900	5184
	2.3	1200	1500
	2.4	540	1000
	2.5	300	600
1 : 0.008	2.1	4320	6300
	2.2	3600	4176
	2.3	1080	1140
	2.4	420	578
	2.5	240	300
1 : 0.010	2.1	3720	4900
	2.2	2400	3240
	2.3	900	840
	2.4	360	240
	2.5	120	120

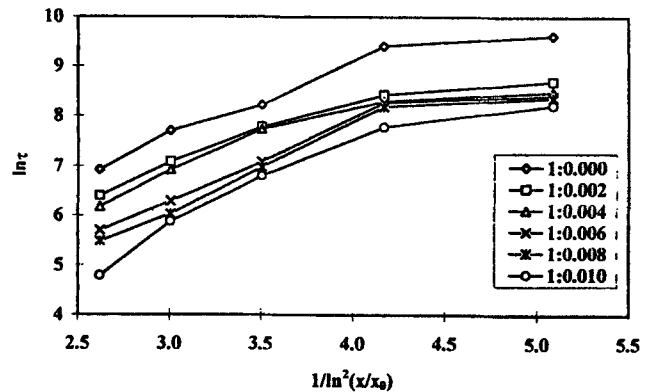


Figure 1. Plots of  $\ln \tau$  against  $1/\ln^2(x/x_0)$  for KBr doped KDP.

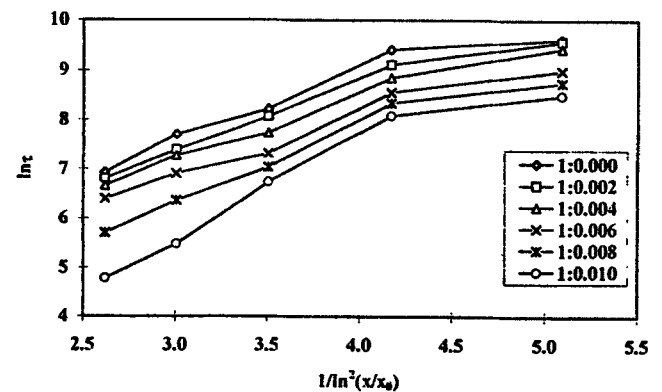


Figure 2. Plots of  $\ln \tau$  against  $1/\ln^2(x/x_0)$  for  $K_2Cr_2O_7$  doped KDP.

linear relationship at higher supersaturations. Also, the linear dependence is greater when the solubility of the substance is greater. The higher solubility component may dominate over the unwanted natural impurities present in the solvent more effectively than a substance with lower solubility as it was observed with  $FeSO_4 \cdot 7H_2O$  (lower solubility and lower linear dependence) and  $ZnSO_4 \cdot 7H_2O$  (higher solubility and greater linear dependence) (Backiyam *et al* 1991).

The effect of solvent impurities cannot be reduced by increasing the supersaturation because the maximum practical limit for the measurement of induction period does not allow the supersaturated concentration to exceed 2.5 M. If the concentration is beyond this practical limit, then nucleation occurs before the attainment of supersaturation (that is before cooling to the experimental temperature). Hence, in order to reduce the effect of these practical difficulties on the nucleation parameters, the results were obtained in the present study using the slopes determined in the linear region of the plots of  $\ln \tau$  against  $1/\ln^2 (x/x_0)$ .

The nucleation parameters are presented in table 2. The values of  $\Delta G$  and  $r$  at various supersaturated concentrations have also been calculated for all the crystals and the results are presented in figures 3–6.

In the present study, it was observed that, for both the impurities, the values of  $\Delta G$  and  $r$  decrease with increase in supersaturated concentration which is similar to the results observed for pure and impurity added ADP (Nagalingam *et al* 1980, 1981; Premila Rachelin and Mahadevan 1998; Rajesh and Mahadevan 1998; Ramesh and Mahadevan 1998), pure and impurity added KDP (Shanmugham *et al* 1984, 1985) and  $FeSO_4 \cdot 7H_2O$  and  $ZnSO_4 \cdot 7H_2O$  (Backiyam *et al* 1991).

It was seen that the values of  $\sigma$ ,  $\Delta G$  and  $r$  increased with the increase in concentration of impurities in the KDP solution (table 2 and figures 3–6). Similar results have been observed for the impurities KCl,  $(NH_4)_2SO_4$ ,  $K_2SO_4$  and  $(NH_4)_2C_2O_4 \cdot H_2O$  in the case of ADP (Premila Rachelin and Mahadevan 1998; Rajesh and Mahadevan 1998; Ramesh and Mahadevan 1998). However, Premila Rachelin and Mahadevan (1998) have found that for  $NH_4Cl$  added ADP the nucleation parameters decrease with increasing impurity concentration. They attempted to explain qualitatively this result by considering the densities of impurities. The nucleation parameters increase with increase in impurity concentration for the impurities having higher density values and decrease with the increase in impurity concentration for the impurities having lower density values than ADP. The densities

Table 2. Nucleation parameters.

Impurity ratio	For KBr added KDP			For $K_2Cr_2O_7$ added KDP		
	$\sigma$ (mJ/m <sup>2</sup> )	* $\Delta G$ (kJ/mole)	* $r$ (nm)	$\sigma$ (mJ/m <sup>2</sup> )	* $\Delta G$ (kJ/mole)	* $r$ (nm)
Pure KDP	8.790	9.484	0.654	8.790	9.484	0.654
1 : 0.002	9.081	10.459	0.676	9.047	10.341	0.673
1 : 0.004	9.104	10.537	0.677	9.325	11.323	0.694
1 : 0.006	9.115	10.575	0.678	9.612	12.401	0.715
1 : 0.008	9.267	11.114	0.690	9.760	12.983	0.726
1 : 0.010	9.549	12.158	0.711	9.888	13.499	0.736

\* $\Delta G$  and  $r$  values were calculated at the maximum supersaturation.

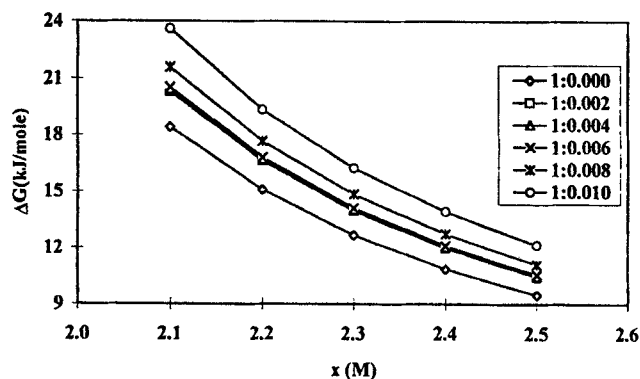


Figure 3. Dependence of energy of formation of critical nucleus on supersaturated concentration for KBr doped KDP.

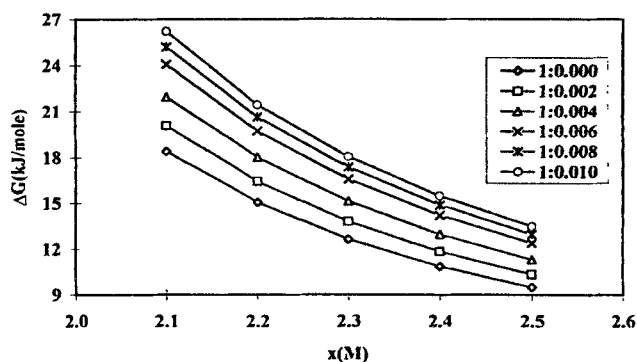
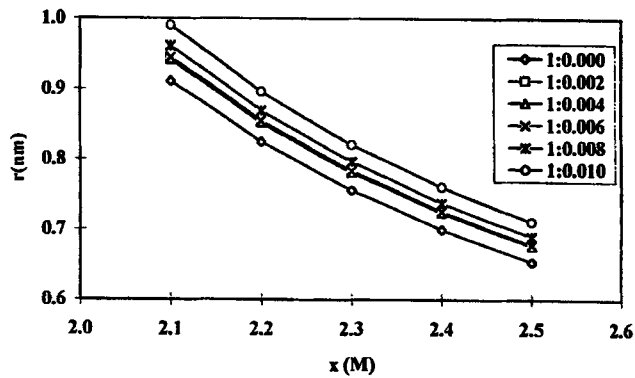


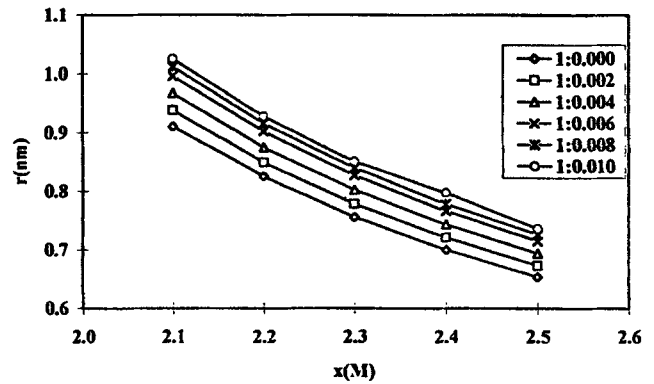
Figure 4. Dependence of energy of formation of critical nucleus on supersaturated concentration for  $K_2Cr_2O_7$  doped KDP.



**Figure 5.** Dependence of radius of critical nucleus on supersaturated concentration for KBr doped KDP.

(Mullin 1993) of  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ , ADP, KCl, KDP,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and KBr are, respectively 1.50, 1.53, 1.77, 1.80, 1.99, 2.34, 2.66, 2.68 and 2.75 g/cc. All the impurities except  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{SO}_4$  in the case of ADP hold this density rule. The impurities considered in the present study in the case of KDP also hold this density rule. High molecular weight cations may act as structure breakers in the solution phase (Mullin 1993).  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  have high molecular weight cations than the ADP. Hence, it may be attempted to say that, for an inorganic substance like ADP and KDP the nucleation parameters increase with increase in impurity concentration for the impurities having higher density values and high or equal (molecular) weight cations and decrease with the increase in impurity concentration for the impurities having lower density values and low or equal (molecular) weight cations.

The interfacial tension calculated for pure KDP and ADP by various authors differ very much. The value obtained for KDP in the present study ( $8.790 \text{ mJ/m}^2$ ) is less than that obtained by Söhnel *et al* (1977) ( $13 \text{ mJ/m}^2$ ) and Söhnel (1978) ( $15 \text{ mJ/m}^2$ ) but more than that obtained by Shanmugham *et al* (1984) ( $5.915 \text{ mJ/m}^2$ ) and Joshi and Antony (1979) ( $2.434 \text{ mJ/m}^2$ ). Similarly, the value obtained for ADP by Ramesh and Mahadevan (1998) ( $3.985 \text{ mJ/m}^2$ ) is larger than reported as  $2.668 \text{ mJ/m}^2$  (Premila Rachelin and Mahadevan 1998) and slightly smaller than reported as  $4.014 \text{ mJ/m}^2$  (Rajesh and Mahadevan 1998) and  $4.304 \text{ mJ/m}^2$  (Nagalingam *et al* 1981) by other workers. This means that a considerable variation has occurred in the  $\sigma$  values. The interfacial tension of KDP determined for a macro crystal will be higher than that of a microcrystal discussed in nucleation experiments (Shanmugham *et al* 1984). Also, the interfacial tension determined for a microcrystal will be different for different experimental temperatures and humidity conditions which make the evaporation rate different. This could be the reason for obtaining different values of interfacial tension for pure KDP and ADP by different workers though the estimation has been on microcrystals.



**Figure 6.** Dependence of radius of critical nucleus on supersaturated concentration for  $\text{K}_2\text{Cr}_2\text{O}_7$  doped KDP.

#### 4. Conclusions

Induction period measurements were done on KDP solutions added with KBr and  $\text{K}_2\text{Cr}_2\text{O}_7$  as impurities separately by the direct vision method at  $32^\circ\text{C}$  with five selected supersaturations. The present study indicates that the induction period decreases with increase in impurity concentration in the aqueous solution of KDP. The nucleation parameters calculated based on the classical theory for homogeneous crystal nucleation increase with increase in impurity concentration.

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