Bull. Mater. Sci., Vol. 21, No. 4, August 1998, pp. 287–290. © Indian Academy of Sciences.

Nucleation studies in supersaturated aqueous solutions of $(NH_4)H_2PO_4$ doped with $(NH_4)_2C_2O_4 \cdot H_2O$

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MS received 24 April 1998

Abstract. Induction periods were measured for various supersaturated aqueous solutions of ammonium dihydrogen orthophosphate doped with ammonium oxalate monohydrate by the direct vision method. Various critical nucleation parameters were calculated based on classical theory for homogeneous crystal nucleation and the results reported and discussed. The critical nucleation parameters increased with increase in doping concentration.

Keywords. Nucleation parameters; doped ADP crystals.

1. Introduction

Ammonium dihydrogen orthophosphate, $(NH_4)H_2PO_4$ (abbreviated as ADP), belongs to scalenohedral class of tetragonal crystal system. It has the tetramolecular unit cell having the dimensions (Wyckoff 1960) given as $a = b = 7{\cdot}510$ Å and $c = 7{\cdot}564$ Å. ADP is soluble in water and its solubilities at 0, 10, 20, 30, 40, 60, 80 and 100°C are 22·7, 29·5, 37·4, 46·4, 56·7, 82·5, 118 and 173 parts by weight of water, respectively (John 1979).

Nucleation process is the initial and important phenomenon in liquid–solid phase transition. Nagalingam *et al* (1980, 1981) have reported nucleation studies in supersaturated aqueous ADP solutions with and without some added impurities (doping concentration, 100 ppm only). An attempt has been made in the present work to investigate the effect of ammonium oxalate monohydrate $[(NH_4)_2C_2O_4 \cdot H_2O]$ as impurity added heavily (impurity concentration in the range 2000–10000 ppm) on the nucleation parameters of ADP crystals.

ADP was doped with $(NH_4)_2C_2O_4 \cdot H_2O$ in six different molecular ratios, viz. 1 : 0·0 (Pure ADP), 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 were calculated based on classical theory for homogeneous crystal nucleation.

2. Experimental

AnalaR grade samples of ADP and $(NH_4)_2C_2O_4 \cdot H_2O$ along with double distilled water were used in the present study. Aqueous solutions of various supersaturated concentrations were prepared by dissolving the required amount of ADP and $(NH_4)_2C_2O_4 \cdot H_2O$ at a temperature slightly higher than the saturation temperature. Supersaturation was obtained by natural cooling.

The experimental setup used for induction period (τ) measurement consisted of two identical nucleation cells (100 ml beakers of corning glass) kept at a constant temperature of 33°C (controlled to an accuracy of ±0·1°C). One of the cells was used as dummy (As insertion of thermometer in the experimental cell may disturb the system, this dummy cell was used for keeping the sensitive thermometer). Using a powerful lamp, the cells were illuminated. Supersaturated solutions of equal volume (20 ml in the present work) were taken in the cells at a slightly higher temperature. A sensitive thermometer (accuracy, ±0·1°C) was placed in the dummy cell. As the temperature of the cell reached the experimental temperature (i.e. 33°C), the time was noted. Once the nucleation occurred, it grew quickly and a bright sparkling particle was seen. The time of observation of the sparkling particle in the undisturbed nucleation cell from the time at which the nucleation cell reached the experimental temperature gave the induction period. It was measured in seconds.

Experiments were performed with five selected supersaturations, viz. 1·200, 1·225, 1·250, 1·275 and 1·300. Volume of the solutions taken in the nucleation cell was maintained at 20 ml in all the experiments in the present work. Several nucleation runs were carried out under controlled and unstirred conditions. Reproducible results within an accuracy of ±2·5% were obtained.

The direct vision method is not very accurate and does not involve rigorous methodology to study nuclea-

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tion. The nuclei are non-observable even by microscopy; at the observable level, they are already at the growth stage. It is assumed that the time required for the critical nucleus to grow to an observable level is very small when compared to the induction period, and is negligible. Despite all these problems, this method was considered for the present study for the reason that no other better method is available to study nucleation in supersaturated solutions of highly soluble substances. Moreover, in order to reduce the inaccuracy, it was taken care that the supersaturated concentration considered should provide the induction period more than 5 s at least. The effect of heterogeneous nucleation by dust particles from air was reduced by carrying out the experiment in a relatively dust free space. Also, the effect of heterogeneous nucleation by scratching on the inner wall of the nucleation cell (glass beaker) was reduced by properly choosing the glass beaker without scratches (tested with a microscope).

Various critical nucleation parameters have been calculated using the expressions (Mullin 1993; Shanmugam *et al* 1984)

$$\sigma = RT\,[3m/(16\Pi V^2 N)]^{1/3},$$

$$\Delta G = RTm/\ln^2(S),$$

$$r = 2\sigma V/[RT \ln (S)],$$

where V, N, R, T, S and m are respectively the molar volume of crystal, Avogadro's number, gas constant, temperature, supersaturation and slope of the line plot of $\ln \tau$ against $1/\ln^2(S)$. σ is the interfacial tension of the solid relative to the solution, ΔG the energy of formation of the critical nucleus and r the radius of the nucleus in equilibrium with its solution.

3. Results and discussion

Results of induction period measurements and calculations of nucleation parameters are presented in table 1. Plots of $\ln \tau$ vs $1/\ln^2(S)$ are presented in figure 1.

The value of τ decreases and hence the nucleation rate increases as the supersaturated concentration of the

Table 1. Induction periods and nucleation parameters of pure and $(NH_4)_2C_2O_4 \cdot H_2O$ doped $NH_4H_2PO_4$ crystals.

System (ADP : Dopant)	*S	τ (sec)	σ (mJm^{-2})	ΔG (kJ/mole)	r (nm)
Pure ADP	1·200	15480	3·985	12·246	1·104
	1·225	8280		9·880	0·992
	1·250	3480		8·175	0·902
	1·275	2160		6·897	0·828
	1·300	1020		5·914	0·767
1 : 0·002	1·200	14340	4·372	16·173	1·211
	1·225	4740		13·053	1·088
	1·250	1866		10·797	0·989
	1·275	947		9·108	0·909
	1·300	590		7·810	0·841
1 : 0·004	1·200	6125	4·559	18·339	1·263
	1·225	3185		14·802	1·134
	1·250	1542		12·243	1·032
	1·275	830		10·328	0·948
	1·300	420		8·856	0·877
1 : 0·006	1·200	4675	4·760	20·872	1·318
	1·225	2376		16·846	1·184
	1·250	816		13·934	1·077
	1·275	349		11·755	0·989
	1·300	118		10·079	0·916
1 : 0·008	1·200	3060	4·976	23·834	1·378
	1·225	1083		19·237	1·238
	1·250	331		15·911	1·126
	1·275	75		13·423	1·034
	1·300	15		11·510	0·958
1 : 0·010	1·200	2876	5·260	28·166	1·457
	1·225	910		22·733	1·309
	1·250	263		18·803	1·190
	1·275	66		15·863	1·093
	1·300	7		13·602	1·012

*Saturated concentration for ADP is 2·7337 M.

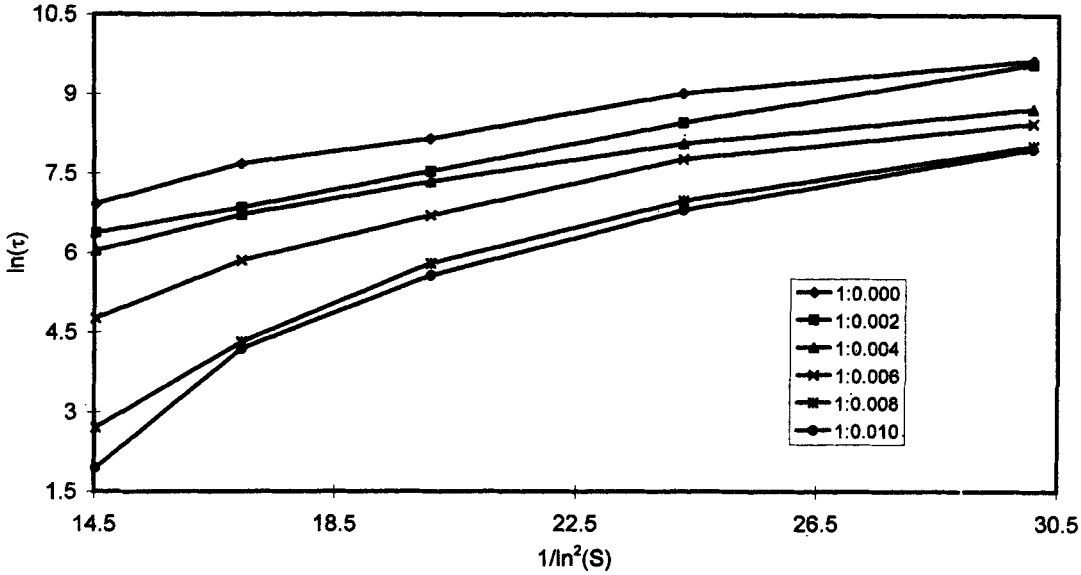

Figure 1. Plots of $\ln \tau$ against $1/\ln^2(S)$ for $(NH_4)_2C_2O_4 \cdot H_2O$ doped ADP.

aqueous solution increases. This is similar to the results obtained by previous workers for their systems (Joshi and Antony 1979; Nagalingam *et al* 1980, 1981; Shanmugham *et al* 1984, 1985; Backiyam *et al* 1991).

Plots of $\ln \tau$ vs $1/\ln^2(S)$ are nearly linear. However, significant deviations from the linearity have been observed for the highest doping concentration at higher supersaturation levels. So, it may be stated that the deviation from linearity at higher supersaturation levels increases with doping concentration and becomes significant at higher doping concentrations.

Nagalingam *et al* (1980) observed non-linearity for pure ADP at lower supersaturation levels at temperatures higher than 25°C. However, they did not observe any non-linearity at 30°C for ADP doped with NH_4Cl, $(NH_4)_2SO_4$, NH_4I, NH_4NO_3, KDP and NaH_2PO_4 (doping concentration, 100 ppm) (Nagalingam *et al* 1981). Shanmugham *et al* (1984, 1985) observed non-linearity at lower supersaturation levels for pure and doped KDP (potassium dihydrogen orthophosphate). Backiyam *et al* (1991) also observed nonlinearity at lower supersaturation levels for $FeSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 7H_2O$.

The previous authors have explained this non-linearity (supposed to be linear as per the classical theory for homogeneous crystal nucleation), not due to the difficulties in the induction period measurements but due to the heterogeneous nucleation caused by the unwanted impurity particles present in the aqueous solution. Also, it has been observed that the linear dependence is more so that the substance molecules in the case of substance with higher solubility may dominate over the unwanted impurities present in the solvent in a better way than that in the case of substance with lower solubility.

In the present system, the deviation caused by the unwanted impurity particles is negligible, because we have observed significant deviation only at higher supersaturation levels and that too only at higher doping concentrations. Hence, a possible explanation to the result observed in the present study is the occurrence of heterogeneous nucleation caused by the added impurity, $(NH_4)_2C_2O_4 \cdot H_2O$.

Considering the principles of homogeneous and heterogeneous nucleation theories, the free energy of formation of a nucleus under heterogeneous nucleation is less than that of a homogeneous condition (Mullin 1993).

In order to reduce the effect of heterogeneous nucleation on the nucleation parameters, the results were obtained using the slopes determined in the linear region of the line plots of $\ln \tau$ against $1/\ln^2(S)$.

It can be noticed that the induction period decreases with the increase in doping concentration (table 1). The presence of impurities in a system can affect nucleation behaviour very considerably. The presence of soluble impurities can also affect the induction period but it is virtually impossible to predict the effect (Mullin 1993). For all the XO_4 impurities, it was found that the presence of impurity in the KDP solution decreased the induction period. The increase in the concentration of impurity further decreased the induction time (Shanmugham *et al* 1985). The effects of soluble impurities may be caused by changing the equilibrium solubility or the solution structure, by adsorption or chemisorption on nuclei or heteronuclei, by chemical reaction or complex formation in the solution, and so on. The effects of insoluble impurities are unpredictable (Mullin 1993).

It was observed that the values of r and ΔG decreased when the supersaturation increased. This result is similar to that observed by previous authors for their systems.

It can be seen from the table that the values of σ, r and ΔG increase with increase in doping concentration. High molecular weight cations may act as structure breakers in the solution phase (Mullin 1993). $(NH_4)_2C_2O_4 \cdot H_2O$ has high molecular weight cation than the ADP. This may be the reason for the nucleation parameters to increase with the increase in doping concentration.

4. Conclusions

Induction period measurements were done for ADP doped with $(NH_4)_2C_2O_4 \cdot H_2O$ by the direct vision method at 33°C with five selected supersaturations. The induction period decreased with increase in doping concentration in the aqueous solution of ADP. The nucleation parameters calculated based on the classical theory for homogeneous crystal nucleation were found to increase with increase in doping concentration. The classical theory for homogeneous crystal nucleation is well explained by the experimentally observed linear relationship between $\ln \tau$ and $1/\ln^2(S)$.

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