

Nucleation studies in supersaturated aqueous solutions of urea and thiourea doped with inorganic dopants

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Abstract. Induction periods were measured for various supersaturated aqueous solutions of urea doped separately with NH_4NO_3 and NaNO_3 and thiourea doped separately with NaCl and KCl by the direct vision method. Based on classical theory for homogeneous crystal nucleation various critical nucleation parameters were calculated and the results are reported and discussed. In all the cases, the critical nucleation parameters increased with increase in doping concentration.

Keywords. Nucleation parameters; doped urea; thiourea crystals.

1. Introduction

Nucleation process is the initial and most important phenomenon in liquid–solid phase transition. Based on the classical theory for homogeneous crystal nucleation certain critical nucleation parameters like interfacial tension (σ) of the solid relative to its solution, energy of formation (ΔG) of a critical nucleus, and radius of the nucleus (r) in equilibrium with its solution can be calculated using the induction period (τ) which can be measured (Shanmugham *et al* 1984; Mullin 1993; Ramesh and Mahadevan 1998).

Urea ($\text{NH}_2\text{—CO—NH}_2$) belongs to the tetragonal crystal system. The unit cell has the dimensions given as $a = b = 5.645 \text{ \AA}$ and $c = 4.704 \text{ \AA}$ and two molecules (ASTM file). Urea is highly soluble in water and its solubility at 17°C is 100 parts by weight per 100 parts by weight of water. Its molecular weight and density are 60.06 and 1.335 g/cc respectively (John 1979).

Thiourea ($\text{NH}_2\text{—CS—NH}_2$) belongs to the orthorhombic crystal system. The unit cell has the dimensions given as $a = 5.50$, $b = 7.68$ and $c = 8.57 \text{ \AA}$ and four molecules (ASTM file). Thiourea is soluble in water and its solubility at 13°C is 9.2 parts by weight per 100 parts by weight of water. Its molecular weight and density are 76.12 and 1.405 g/cc respectively (John 1979).

An attempt has been made in the present study to determine the nucleation parameters of pure urea and thiourea crystals and also to investigate the effect of some inorganic substances as added impurities (impurity concentration in the range 2000–10000 ppm) on the nucleation parameters of these crystals.

Urea was doped with ammonium nitrate (NH_4NO_3) and sodium nitrate (NaNO_3) (both are denser than urea) separately each in six different urea : dopant molecular ratios, viz. 1 : 0.0, 1 : 0.002, 1 : 0.004, 1 : 0.006, 1 : 0.008 and 1 : 0.010. Similarly, thiourea was doped with sodium chloride (NaCl) and potassium chloride (KCl) (both are denser than thiourea) separately each in six different thiourea : dopant molecular ratios, viz. 1 : 0.0 (pure thiourea), 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 urea, thiourea, NH_4NO_3 , NaNO_3 , NaCl and KCl along with double-distilled water were used in the present study. Aqueous solutions of various supersaturations (S) (1.225, 1.250, 1.275, 1.300, 1.325, etc for urea and 1.45, 1.50, 1.55, 1.60, 1.65, etc for thiourea) were prepared by dissolving the required amount of urea or thiourea and the dopant at a temperature slightly higher than the saturation temperature (35°C). Supersaturation was obtained by natural cooling.

Induction periods were measured and the critical nucleation parameters were calculated following the procedures adopted by Ramesh and Mahadevan (1998). The experimental set-up used by us for induction period (τ) measurement consists of two identical nucleation cells (100 ml beakers of corning glass) kept at a constant temperature of 35°C (controlled to an accuracy of

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$\pm 0.1^\circ\text{C}$). 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 aqueous solutions of equal volume (20 ml in the present work) were taken in the cells at a slightly higher temperature. A sensitive thermometer (accuracy $\pm 0.1^\circ\text{C}$) was placed in the dummy cell. As the cell attained experimental temperature (i.e. 35°C), the time was noted. Once 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. Several nucleation runs were carried out under controlled and unstirred conditions and reproducible results within an accuracy of $\pm 2.5\%$ were obtained.

Table 1. Results of induction period measurements for pure and doped urea.

Doping ratio	*S	τ (sec) for	
		NH_4NO_3 -doped urea	NaNO_3 -doped urea
Pure urea	1.225	4200	4200
	1.250	2830	2830
	1.275	1631	1631
	1.300	1015	1015
	1.325	600	600
1 : 0.002	1.225	3310	3780
	1.250	2400	2603
	1.275	1255	1365
	1.300	810	830
	1.325	495	425
1 : 0.004	1.225	2820	3435
	1.250	1680	2280
	1.275	900	1104
	1.300	600	616
	1.325	385	315
1 : 0.006	1.225	2425	3060
	1.250	1200	1740
	1.275	720	923
	1.300	410	525
	1.325	240	238
1 : 0.008	1.225	1740	2412
	1.250	785	1500
	1.275	440	774
	1.300	343	423
	1.325	120	180
1 : 0.010	1.225	1145	1875
	1.250	630	1200
	1.275	315	476
	1.300	120	280
	1.325	50	100

*Saturated concentration for urea is 9.0489 M.

The direct vision method is not very accurate and does not involve rigorous methodology to study nucleation. 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 as no other better method is available to study nucleation in supersaturated solutions of highly soluble substances. Moreover, to reduce inaccuracy, the supersaturated concentration considered was ensured to provide the induction period more than 50 sec at least. The effect of heterogeneous nucleation by dust particles from air was reduced by carrying out the experiments in a relatively dust-free space. Also, the effect of heterogeneous nucleation by scratchings on

Table 2. Results of induction period measurements for pure and doped thiourea.

Doping ratio	*S	τ (sec) for	
		NaCl -doped thiourea	KCl -doped thiourea
Pure thiourea	1.45	1720	1720
	1.50	1574	1574
	1.55	1380	1380
	1.60	1155	1155
	1.65	915	915
1 : 0.002	1.45	1150	1090
	1.50	1110	1040
	1.55	1040	950
	1.60	950	810
	1.65	780	650
1 : 0.004	1.45	1020	995
	1.50	980	920
	1.55	900	820
	1.60	810	685
	1.65	670	540
1 : 0.006	1.45	930	900
	1.50	875	820
	1.55	790	715
	1.60	700	570
	1.65	567	460
1 : 0.008	1.45	860	822
	1.50	797	720
	1.55	706	623
	1.60	603	483
	1.65	470	350
1 : 0.010	1.45	780	715
	1.50	712	630
	1.55	624	514
	1.60	516	370
	1.65	402	278

*Saturated concentration for thiourea is 1.7285 M.

the inner wall of the nucleation cell (glass beaker) was reduced by properly choosing the glass beaker without scratches (tested with a microscope).

3. Results and discussion

The measured induction periods are presented in tables 1 and 2. For all systems considered in the present study, the value of τ decreases and hence the nucleation rate increases as the supersaturation and concentration of doping of the aqueous solution increase. This is similar to the results observed for the ammonium dihydrogen orthophosphate (ADP) doped (in the same ratio considered in the present study) with some inorganic dopants (Premila Rachelin and Mahadevan 1998; Rajesh and Mahadevan 1998; Ramesh and Mahadevan 1998).

Plots of $\ln \tau$ vs $1/\ln^2(S)$ are presented in figures 1–4. In the case of NH_4NO_3 -doped urea, these plots are nearly linear satisfactorily explaining the classical theory for homogeneous nucleation (supposed to be linear according to theory). In the case of NaNO_3 -doped urea, the plots are again 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. This is similar to that observed for $(\text{NH}_4)_2 \text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ doped ADP (Ramesh and Mahadevan 1998). A possible explanation to this result is the occurrence of heterogeneous nucleation caused by the added impurity, NaNO_3 .

In the case of thiourea, plots of $\ln \tau$ vs $1/\ln^2(S)$ are not linear at lower supersaturation levels. Such deviations from linearity have also been reported earlier (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 nonlinearity as not due to difficulties in the induction period measurements but due to the heterogeneous nucleation caused by unwanted impurity particles naturally present in the solvent. There are normally between 10^6 and 10^8 unwanted impurity particles present per ml of aqueous solution, whatever precautions are taken in performing the experiment

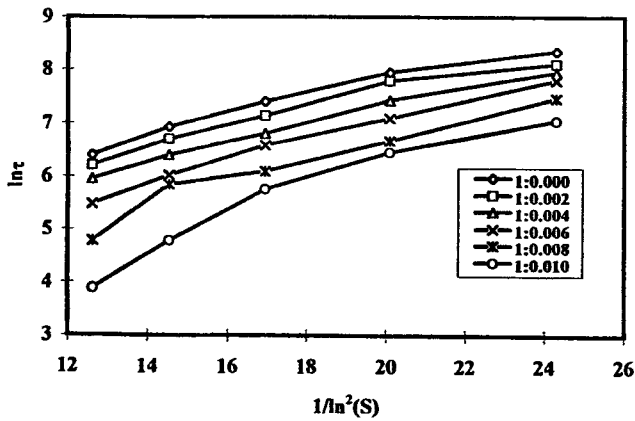


Figure 1. Plots of $\ln \tau$ against $1/\ln^2(S)$ for NH_4NO_3 -doped urea.

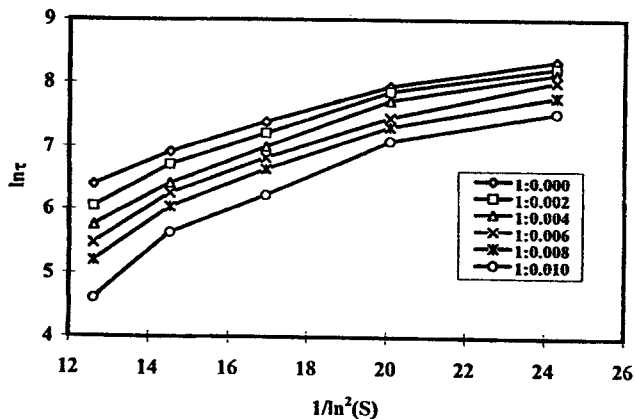


Figure 2. Plots of $\ln \tau$ against $1/\ln^2(S)$ for NaNO_3 -doped urea.

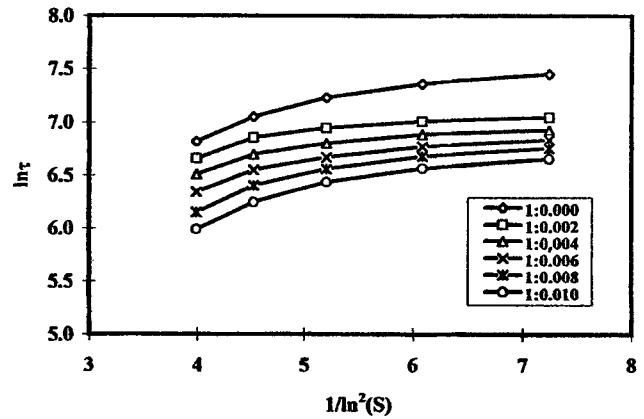


Figure 3. Plots of $\ln \tau$ against $1/\ln^2(S)$ for NaCl -doped thiourea.

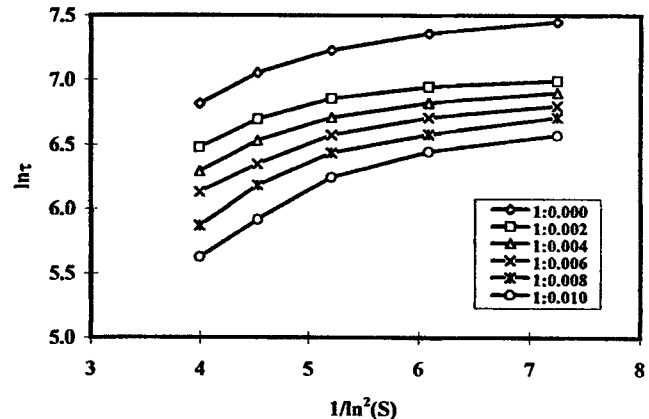


Figure 4. Plots of $\ln \tau$ against $1/\ln^2(S)$ for KCl -doped thiourea.

(Shanmugham *et al* 1984). Linear relationship may be expected at higher supersaturations because the effect of the natural impurity particles present in the solvent is dominated by the presence of a greater amount of solute. Also, for the substance with higher solubility, the higher solubility component may dominate over the unwanted natural impurities present in the solvent more effectively than a substance with lower solubilities. This was observed with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (lower solubility and lower linear dependence) and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (higher solubility and greater linear dependence) (Backiyam *et al* 1991). The present study also shows this. Linear dependence is

greater with urea (higher solubility) than with thiourea (lower solubility). The maximum practical limit for the measurement of induction period does not allow the supersaturation to exceed 1.65 in the case of thiourea. Nucleation occurs before the attainment of supersaturation if it is beyond this value. Hence, in order to reduce the effect of these difficulties on the nucleation parameters, the results were obtained using slopes determined in the linear region of the plots of $\ln \tau$ vs $1/\ln^2(S)$.

The nucleation parameters are presented in tables 3 and 4. The values of ΔG and r at various supersaturations

Table 3. Nucleation parameters of pure and doped urea crystals.

Doping ratio	For NH_4NO_3 -doped urea			For NaNO_3 -doped urea		
	σ (mJ m^{-2})	$^*\Delta G$ (kJ/mole)	*r (nm)	σ (mJ m^{-2})	$^*\Delta G$ (kJ/mole)	*r (nm)
Pure urea	5.326	5.985	0.667	5.326	5.985	0.667
1 : 0.002	5.252	5.740	0.658	5.553	6.784	0.696
1 : 0.004	5.293	5.875	0.663	5.723	7.424	0.717
1 : 0.006	5.556	6.794	0.696	5.856	7.958	0.734
1 : 0.008	5.854	8.035	0.733	5.918	8.210	0.741
1 : 0.010	6.370	10.241	0.798	6.168	9.296	0.773

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

Table 4. Nucleation parameters of pure and doped thiourea crystals.

Doping ratio	For NaCl -doped thiourea			For KCl -doped thiourea		
	σ (mJ m^{-2})	$^*\Delta G$ (kJ/mole)	*r (nm)	σ (mJ m^{-2})	$^*\Delta G$ (kJ/mole)	*r (nm)
Pure thiourea	5.405	2.968	0.467	5.405	2.968	0.467
1 : 0.002	4.805	2.085	0.415	5.249	2.720	0.453
1 : 0.004	4.907	2.221	0.424	5.370	2.912	0.464
1 : 0.006	5.053	2.425	0.436	5.479	3.093	0.473
1 : 0.008	5.486	3.104	0.474	5.931	3.922	0.512
1 : 0.010	5.705	3.491	0.493	6.182	4.441	0.534

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

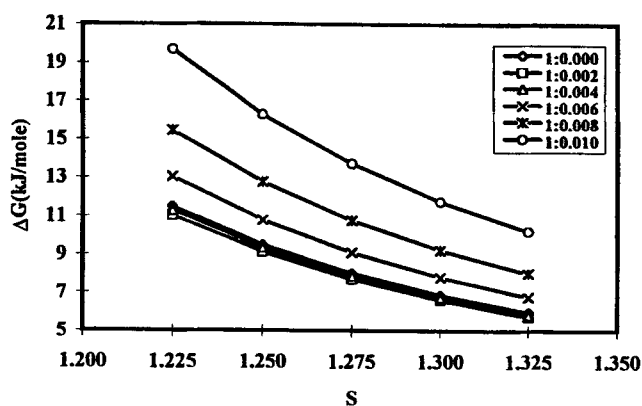


Figure 5. Dependence of energy of formation of critical nucleus on supersaturation for NH_4NO_3 -doped urea.

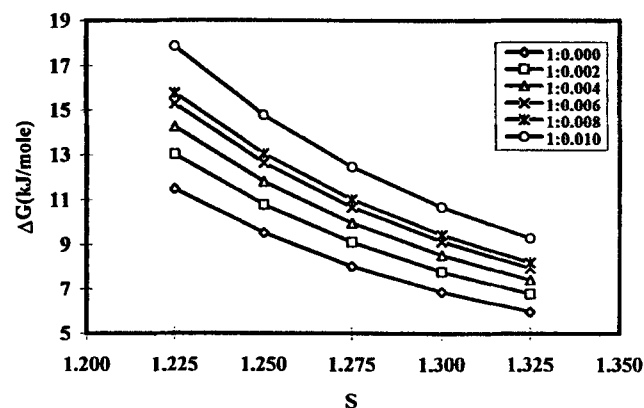


Figure 6. Dependence of energy of formation of critical nucleus on supersaturation for NaNO_3 -doped urea.

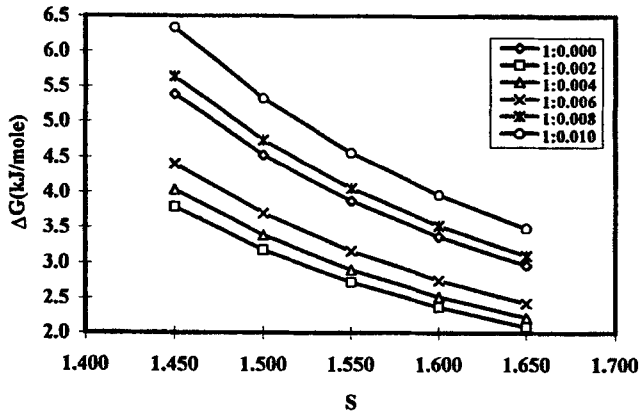


Figure 7. Dependence of energy of formation of critical nucleus on supersaturation for NaCl-doped thiourea.

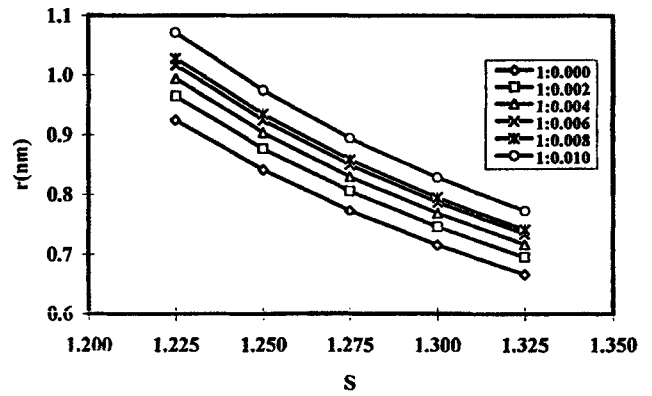


Figure 10. Dependence of radius of critical nucleus on supersaturation for NaNO₃-doped urea.

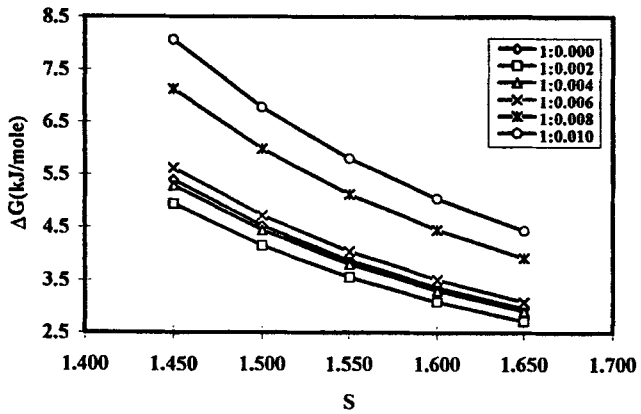


Figure 8. Dependence of energy of formation of critical nucleus on supersaturation for KCl-doped thiourea.

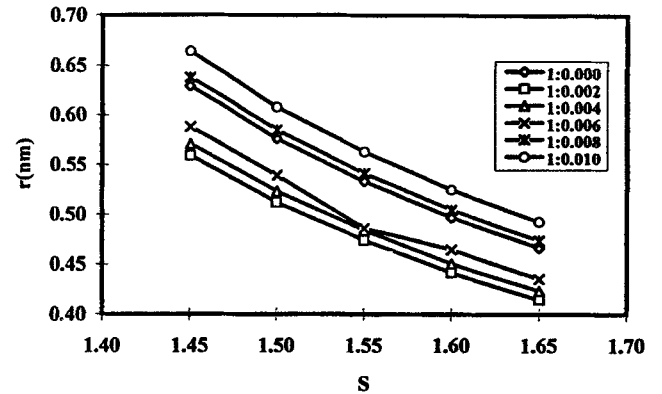


Figure 11. Dependence of radius of critical nucleus on supersaturation for NaCl-doped thiourea.

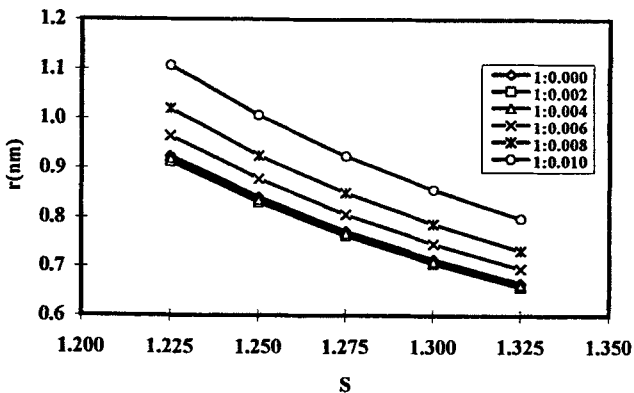


Figure 9. Dependence of radius of critical nucleus on supersaturation for NH₄NO₃-doped urea.

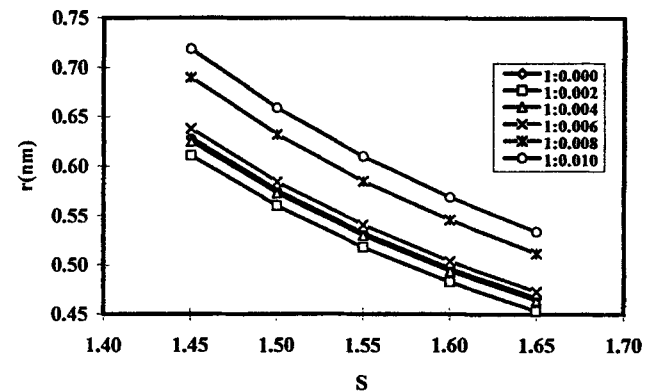


Figure 12. Dependence of radius of critical nucleus on supersaturation for KCl-doped thiourea.

have also been calculated for all crystals and the results are presented in figures 5 to 12. It was observed that the values of ΔG and r decreased when supersaturation increased. This result is similar to that observed by previous authors for their systems.

For all systems considered in the present study, the nucleation parameters (σ , ΔG and r) increased with increase in concentration of doping in the aqueous solution (tables 3 and 4 and figures 5–12). However, the nucleation parameters observed for systems having urea : NH_4NO_3 ratios 1 : 0.002 and 1 : 0.004 are less than that observed for pure urea. Similarly, the nucleation parameters observed for systems having thiourea : NaCl ratios 1 : 0.002, 1 : 0.004, and 1 : 0.006 and thiourea : KCl ratios 1 : 0.002 and 1 : 0.004 are less than that observed for pure thiourea. While this cannot be due to an experimental error we may attribute this to the unpredictable situation caused by inorganic impurities. However, the exact reason is still to be understood.

4. Conclusions

Induction period was measured for urea doped separately with NH_4NO_3 and NaNO_3 and thiourea doped separately with NaCl and KCl by the direct vision method at 35°C with five selected supersaturations. The induction period decreased with increase in supersaturation and doping

concentration. The present study indicates that nucleation parameters calculated based on classical theory for homogeneous crystal nucleation 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 $1/\ln^2(S)$.

References

- Backiyam M, Anitha R Nair and Mahadevan C 1991 *Indian J. Pure Appl. Phys.* **29** 455
- Freedra T H, Rajesh N P and Mahadevan C 1997 *Recent developments in crystal growth* (Karaikudi: Alagappa University) Vol. 1, p. 68
- John A D (ed.) 1979 *Lange's handbook of chemistry* (New York: McGraw Hill) 12th ed.
- Mullin J W 1993 *Crystallization* (Oxford: Butterworth-Heinemann)
- Nagalingam S, Vasudevan S, Ramasamy P and Laddha G S 1980 *Kristall. Tech.* **15** 1151
- Premila Rachelin Y and Mahadevan C 1998 *Indian J. Pure Appl. Phys.* **36** 38
- Rajesh N P and Mahadevan C 1998 *J. Indian Chem. Soc.* **75** 307
- Ramesh R and Mahadevan C 1998 *Bull. Mater. Sci.* **21** 287
- Shanmugham M, Gnanam F D and Ramasamy P 1984 *J. Mater. Sci.* **19** 2837
- Shanmugham M, Gnanam F D and Ramasamy P 1985 *J. Mater. Sci. Lett.* **4** 746