

# Investigation on Nucleation Kinetics of Urea-Thiourea Mixed Crystal in Methanol

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## ABSTRACT

The induction period of various proportion of urea-thiourea mixed crystal in methanol, absolute alcohol has been measured experimentally by the visual observation method. The induction period, which is inversely proportional to the nucleation rate, has been used to estimate the interfacial tension between the urea-thiourea mixed crystal and methanol, hence the nucleation parameters like critical radius ( $r^*$ ), number of molecules in the radius ( $r^*$ ) and Gibbs free energy change for the formation of a critical nucleus ( $\Delta G^*$ ) have been calculated.

**Keywords:** Solubility, induction period, interfacial tension, critical radius, critical nucleus.

## 1. INTRODUCTION

Urea crystal is a promising organic crystal that found practical applications in nonlinear optics (NLO) to date, because it is transparent down to 200 nm and has fairly large birefringence, so that phase matching for second harmonic and frequency mixing processes can be achieved well into the UV region<sup>1-4</sup>. Urea is representative of one class of materials which are applicable to photonics and served as a model compound and reference material in the DMOS (Diffusive Mixing of Organic Solutions) experiment in microgravity carried out by NASA<sup>5-9</sup>. So active research works are being carried out by in understanding the fundamental growth and nucleation mechanism of these crystals. There are several reports available on bulk growth of urea crystals from alcohol based solutions<sup>10,11</sup>. But there are no reports available in the literature on the nucleation of urea-thiourea mixed crystals. In the present study, investigations have been made to evaluate the interfacial tension ( $\gamma$ ) between urea-thiourea mixed crystal and methanol, absolute alcohol by measuring the induction period and hence to calculate the critical radius ( $r^*$ ), number of molecules in the in the critical nucleus ( $i^*$ ) and Gibb's free energy ( $\Delta G^*$ ) for the formation of critical nucleus of urea-thiourea mixed crystals grown from methanol.

## 2. EXPERIMENTAL

There are several methods of measuring the induction period depending upon the solubility of materials. In the present work, the visual

observation method was followed. Solutions at different saturation 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 an accuracy of plus or minus 0.01° C. A sensitive thermometer was inserted into this cell. As the temperature of solution reaches the temperature of the bath, the time was recorded until the nucleation starts and a visible speck appears. The time period that elapses between achievement of super saturation and appearance of visible nuclei is taken the induction period ( $\tau$ ). Several trial runs were performed to minimise the error. From the results obtained, a plot of  $\ln \tau$  against  $1/(\ln S)^2$  is drawn. From the slope of the curves interfacial tension was calculated by using the equation

$$\ln \tau = \ln A + 16\pi\gamma^3 V^2 N / 3RT (\ln S)^2 \text{ ----- (1)}$$

where A is a constant related to the pre-exponential factor of the nucleation rate expression, V is the molar volume, N is the Avagadro 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 urea-thiourea mixed crystal nucleus and methanol was calculated by measuring the slope value of the curve obtained at these three different temperatures. The values are given in table 1. According to the classical homogeneous nucleation theory the free energy required to form a nucleus is given by

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

where  $\Delta G^*$  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  $d(\Delta G)/dr = 0$ . Hence the radius of the critical nucleus is expressed as  $r^* = -2\gamma/\Delta G_v$ , where  $\Delta G_v = -kT \ln S/v$ , where  $v$  is molecular volume.

Hence  $r^* = 2\gamma/kT \ln S$ . The critical free energy is given by  $\Delta G^* = 16\pi\gamma^3 v^2 / \Delta G_v^2$ . The number of molecules in the critical nucleus is expressed as  $i^* = 4\pi(r^*)^3 / 3v$ . Using the interfacial tension, 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 ( $\Delta G^*$ ) and number of molecules in the critical nucleus ( $i^*$ ) were calculated at three different temperatures and presented in table 5 and 6. It was noted that with the increase in super saturation the free energy change decreases ( $\Delta G^*$ ) with radius ( $r^*$ ). This favours the easy formation of nucleation in 0.5 urea-thiourea mixed crystal when compared to other proportions.

## 2.1 SOLUBILITY

The literature survey indicates the organic urea, thiourea salts as nonlinear optic materials. The salts used for the experiments are Analar Merck grade. The salts were recrystallised by using water. It is essential to increase purity to a respectable level before proceeding further. Considerably recrystallization will produce material which is pure for crystal growth. Urea, thiourea salts

are recrystallized with distilled water. Saturated solutions of urea, thiourea was prepared at 40°C. The solutions were filtered to avoid any insoluble impurities by using heated apparatus to prevent nucleation. The solutions were cooled down to room temperature in order obtain maximum yield. The resulted crystals were recrystallized further. The fine powdered crystals were filtered off by suction and were air dried at room temperature. The purity was then checked by standard method analysis like melting point. Doubly distilled water was used in all experiments. First of all the solubility of the salts were determined. The experimental procedure adopted was as follows:

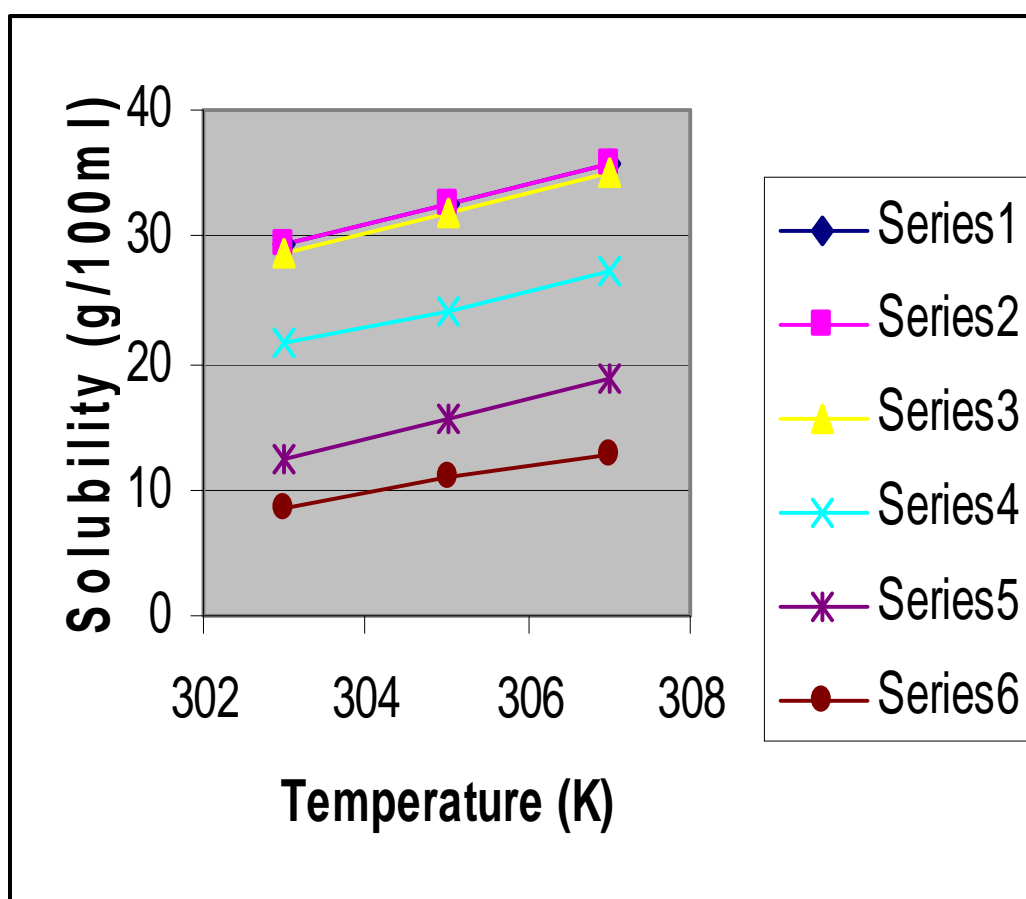
The saturated urea, thiourea and solutions of A to L are prepared individually. Then the empty weight of silica crucible was weighed. 5ml of saturated solution was taken in a crucible and it was also weighted. From this the solubility of urea in 100ml of water was found as 108.09 g and that of thiourea was 10.58 g. Similarly the solubility of 0.1, 0.25, 0.5, 0.66, 0.75 and 0.9 urea thiourea mixed crystals in methanol, absolute alcohol were tabulated in table 1 and table 2. It was observed that the salt thiourea is less soluble so the proportions of the crystals were expressed in terms of less soluble salt. From the figure 1, 2 it was clearly shown that the solubility of urea-thiourea mixed crystal in absolute alcohol was lower than that of urea-thiourea mixed crystal in methanol.

**Table 1: Effect of temperature on solubility and interfacial tension in methanol solvent**

Proportions	Solvent	Temperature (K)	Solubility	Interfacial tension (10 <sup>-8</sup> KJ/mj)
0.1	Methanol	303	29.4	3.2947
		305	32.6	3.4576
		307	35.9	3.5078
0.25	Methanol	303	29.4	3.4163
		305	32.6	3.4748
		307	35.9	3.5269
0.5	Methanol	303	28.5	3.2052
		305	31.7	3.2647
		307	34.9	3.3209
0.66	Methanol	303	21.7	3.0822
		305	24.2	3.1529
		307	27.4	3.2291
0.75	Methanol	303	12.5	2.7155
		305	15.4	2.8342
		307	18.7	2.9430
0.9	Methanol	303	8.5	2.4732
		305	10.9	2.6501
		307	12.7	2.7615

**Table 2: Effect of temperature on  $\ln \tau$  and  $1/(\ln S)^2$  in methanol**

Proportions	Solvent	Temperature (K)	$\ln \tau$	$1/(\ln S)^2$
0.1	Methanol	303	7.7007	0.0875
		305	7.5758	0.0824
		307	7.4413	0.0780
0.25	Methanol	303	7.6862	0.0875
		305	7.5653	0.0824
		307	7.4413	0.0780
0.5	Methanol	303	6.2916	0.0891
		305	6.02046	0.0837
		307	6.1420	0.0792
0.66	Methanol	303	6.5147	0.1056
		305	6.4615	0.0985
		307	6.3886	0.0913
0.75	Methanol	303	6.5482	0.1568
		305	6.3099	0.1338
		307	6.1203	0.1166
0.9	Methanol	303	6.7452	0.2174
		305	6.6464	0.1752
		307	6.5999	0.1548

**Fig. 1: Solubility of various proportions of urea-thiourea mixed crystal in methanol****Nucleation Kinetics**

**Solution A** (0.1 thiourea) 9g of urea, 1g of thiourea was dissolved in 15ml of methanol

**Solution B** (0.25 thiourea) 2.5g of urea, 7.5g of thiourea was dissolved in 15ml of methanol

**Solution C** (0.5 thiourea) 5g of urea, 5g of thiourea was dissolved in 30ml of methanol

**Solution D** (0.66 thiourea) 3.4g of urea, 6.6g of thiourea was dissolved in 46ml of methanol

**Solution E** (0.75 thiourea) 2.5g of urea, 7.5g of thiourea was dissolved in 60ml of methanol

**Solution F** (0.9 thiourea) 1g of urea, 9g of thiourea was dissolved in 74ml of methanol

The crystal growth solutions should be in equilibrium at room temperature (303K) and should not contain any spurious nuclei. The procedure adopted can be explained by taking solution A, a saturated solution at a temperature slightly higher than initially required was prepared and filtered through a hot sintered glass flask. The solution was stirred by using magnetic stirrer for about 6 hours. The undissolved material collected at the bottom of the same flask and the clean solution was transferred to another flask and it is slightly heated above 5°K. So that the undissolved material gets completely dissolved. After dissolving, filtration of the solution which plays a vital role (i.e. chemical purity of the solution) during growth is preformed. The filtration of the solution was preformed with the help of a Buckner funnel and filtration assembly. A filter paper of the size of Buckner funnel is taken and placed over it perforated disc. It is then fitted in a filtration flask connected to suction pump. The rate of filtration through conical flask

considerably increased using a perforated filter paper. Thus purified solution has prepared. While transferring the solution, temperature of the growth chamber was brought down to 2°K above the saturation temperature (305K); doing so the seed crystal may dissolve slightly as the solution was under saturated. Since periphery of the crystals dissolve in this case clear and clean, seed will be remaining. The temperature of the solution was adjusted to saturation temperature (303K), the seed dissolution stops. After that the flask was covered with polyethylene sheets, in which small holes were bored to allow slow evaporation. Similar procedure was adopted for Solution B, C, D, E, F. As the temperature of the bath, the time was recorded until the nucleation starts and appearance of visible nuclei was taken as the induction period. It was observed that for all the mixed crystals, the induction period was decreased from 0.1 to 0.5 and then slightly increased from 0.66 to 0.9.

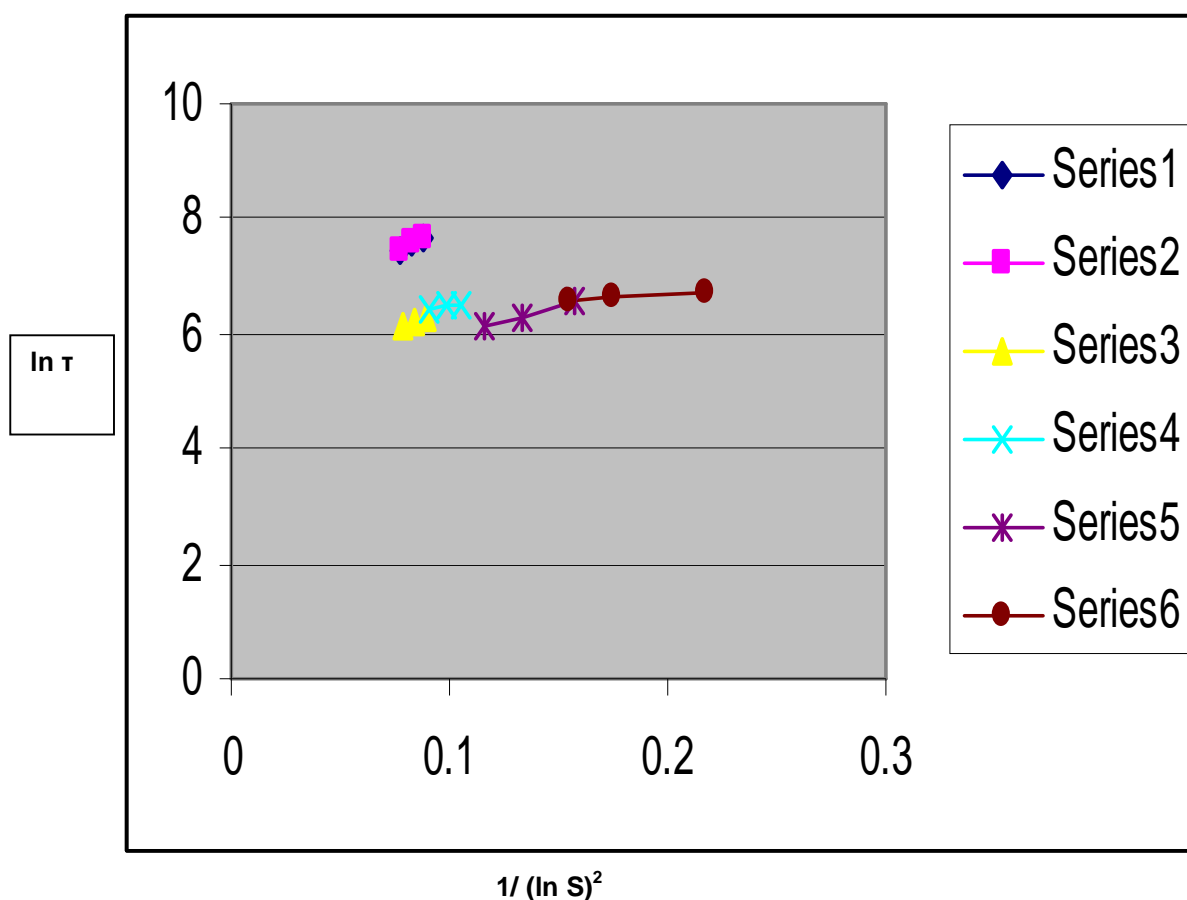


Fig. 2: A plot of  $\ln \tau$  vs  $1/(\ln S)^2$  in methanol

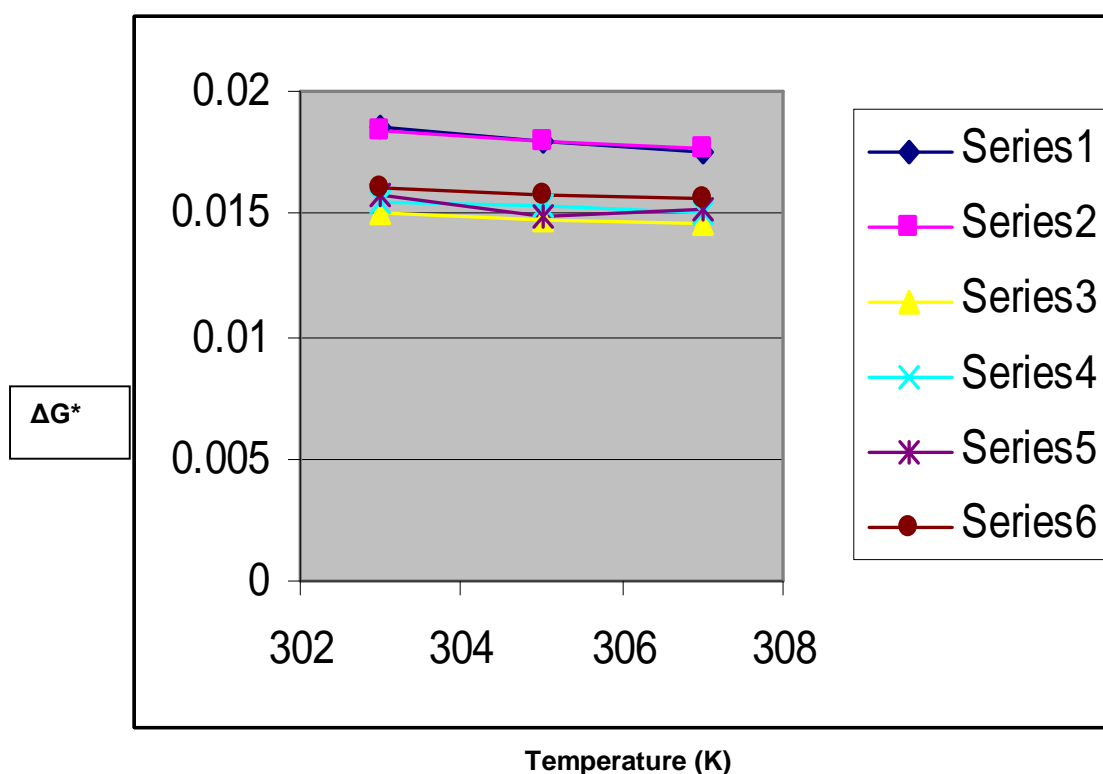
## RESULTS AND DISCUSSION

The solubility of various proportions of urea-thiourea mixed crystals was determined as a function of temperature is shown in Fig. 1 and 2. Here the solubility of mixed crystal decreases with increase in proportions of thiourea. It was clearly shown that the solubility of 0.9 urea-thiourea mixed crystals in was lower than that of all other proportions. Fig. 2 shows the induction period as function of various temperatures. In the present study, the nucleation kinetics of urea-thiourea mixed crystals from various proportions has been carried out to calculate the interfacial tension between the crystal and methanol. The interfacial tension can be calculated at various temperatures from the graph drawn between  $\ln \tau$  and  $1/(\ln S)^2$ . The measured interfacial tensions various from 2.4732 to 3.5269  $\text{mj/m}^2$  in methanol. The value of interfacial tension of urea-thiourea mixed crystal in 0.1, 0.25, 0.5 proportion has much higher value compared to

0.66, 0.75 and 0.9. In our experiments the induction period  $\tau$  was measured by the most commonly used method (visual observation method). Based on nucleation theory interfacial tension was calculated from Eq 1. The free energy change as a function of temperature is given in Fig. 3. It is clear that the free energy exponentially decreases with increase in temperature. The values of critical radius, number of molecules in the critical nucleus was decreased and small values of free energy of activation in 0.5 proportion of urea-thiourea mixed crystal when compared to all other proportions predict the easy formation of nucleation in methanol. From the Fig. 3 shows that the value of  $\Delta G^*$  as a function of various temperatures. It was clearly shown that the  $\Delta G^*$  of 05 urea-thiourea mixed crystal in methanol was lower than that of all other proportions predict the easy formation of nucleation in methanol.

**Table 3: Nucleation parameters of urea-thiourea mixed crystal in methanol**

Proportions	$r^*$	$\Delta G^*$ (303K)	$i^*$	$r^*$	$\Delta G^*$ (305K)	$i^*$	$r^*$	$\Delta G^*$ (307K)	$i^*$
0.1	3.4842	0.0168	23.6774	3.5247	0.0180	24.5127	3.4570	0.0175	23.1272
0.25	3.5836	0.0184	25.9727	3.5269	0.0179	24.4802	3.4476	0.0176	23.1264
0.5	3.3473	0.0150	32.1848	3.2828	0.0147	30.3599	3.2248	0.0146	24.8119
0.66	3.4734	0.0155	36.2783	3.4089	0.0153	34.2945	3.3385	0.0151	32.3124
0.75	3.7090	0.0157	29.5950	3.5530	0.0149	26.0158	3.4070	0.0152	22.9387
0.9	3.9437	0.0161	53.8158	3.7712	0.0158	47.0600	3.6694	0.0156	43.3484



**Fig. 3: Relation between the free energy change ( $\Delta G^*$ ) and temperature for urea-thiourea mixed crystal in methanol**

**CONCLUSIONS**

1. It was clearly shown that the solubility of 0.9urea-thiourea mixed crystal was lower than that all other proportions in methanol.
2. It was observed that for all the mixed crystals, the induction period decreased from 0.1 to 0.5 and then slightly increased from 0.66 to 0.9.
3. The interfacial tension can be calculated at various temperatures from the graph drawn between  $\ln \tau$  and  $1/(\ln S)^2$ . The measured interfacial tensions various from 2.4732 to 3.5269  $\text{mJ/m}^2$  in methanol.
4. The values of critical radius, number of molecules in the critical nucleus was decreased and small values of free energy of activation in 0.5 proportion of urea-thiourea mixed crystal when compared to all other proportions predict the easy formation of nucleation in methanol.
5. It was clearly shown that the  $\Delta G^*$  of 0.5urea-thiourea mixed crystal in methanol was lower than that of all other proportions in methanol.

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