Investigation on Nucleation Kinetics of Urea-Thiourea Mixed Crystal in Water Solvent

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ABSTRACT

The induction period of various proportion of urea-thiourea mixed crystal in water 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 water, 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 (ΔG^*) have been calculated.

KEY WORDS: Solubility, induction period, interfacial tension, critical radius, critical nucleus

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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 (1-4). 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 (5-9). 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 (10-12). 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 (γ) between urea-thiourea mixed crystal and water 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 (ΔG^*) for the formation of critical nucleus of urea-thiourea mixed crystals grown from water.

2. EXPERIMENTAL PROCEDURE

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 (τ). Several trial runs were performed to minimise the error. From the results obtained, a plot of ln τ against $1/(\ln S)^2$ is drawn. From the slope of the curves interfacial tension was calculated by using the equation

$$\ln \tau = \ln A + 16\pi\gamma^3 \, V^2 N / 3RT \, (\ln S)^2 \qquad (1)$$

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 water 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

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

where ΔG^* 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 $r^* = 2v\gamma/kT\ln S$. The critical free energy is given by $\Delta G^* = 16\pi\gamma^3 \; v^2 {}^/\Delta Gv^2$. 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 (ΔG^*) and number of molecules in the critical nucleus (i^*) were calculated at three different temperatures and presented in table 2. It was noted that with the increase in super saturation the free energy change decreases (ΔG^*) with radius (r^*). This favours the easy formation of nucleation in 0.5 urea-thiourea mixed crystal when compared other proportions.

3   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 F 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 was tabulated in table 1. 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, it was clearly shown that the solubility decreases with increase in thiourea proportions.

Table 1: Effect of temperature on solubility and interfacial tension

| Proportions	Solvent	Temperature (K)	Solubility (g/100ml)	Interfacial Tension(γ)
				(10^{-8} Kj/mj)
0.1	Water	303	91	4.2080
0.1	Water	305	125	4.3965
0.1	Water	307	160	4.5444
0.25	Water	303	73.3	4.0931
0.25	Water	305	79.5	4.1412
0.25	Water	307	85.7	4.1865
0.5	Water	303	48.6	3.5877
0.5	Water	305	55.2	3.6266
0.5	Water	307	61.4	3.6599
0.66	Water	303	30.3	3.3437
0.66	Water	305	36.2	3.4277
0.66	Water	307	42.4	3.4975
0.75	Water	303	24.4	3.2156
0.75	Water	305	30.1	3.3189
0.75	Water	307	36.4	3.4117
0.9	Water	303	12.8	2.8167
0.9	Water	305	15.5	2.9339
0.9	Water	307	18.7	3.0420
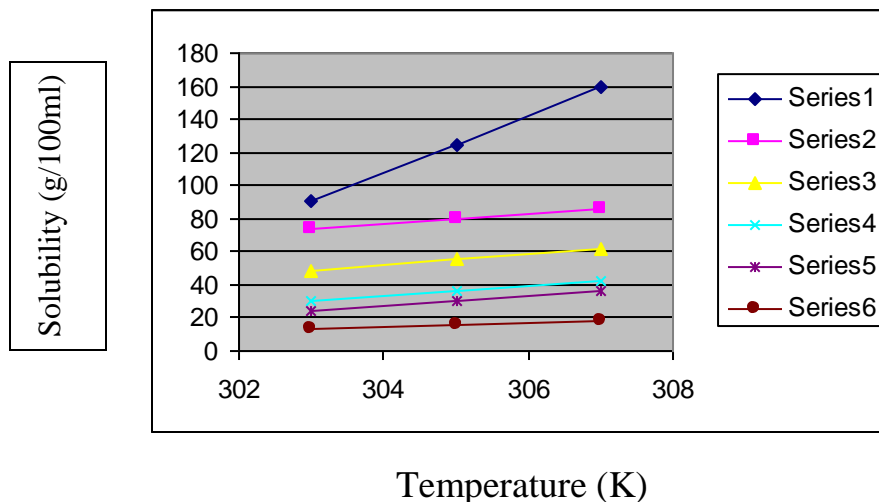
Fig. 1 Solubility of various proportions of urea-thiourea mixed crystal in water

4   NUCLEATION KINETICS

Solution A (0.1 thiourea) 9g of urea, 1g of thiourea was dissolved in 15ml of distilled water.

Solution B (0.25 thiourea) 2.5g of urea, 7.5g of thiourea was dissolved in 18ml of distilled water.

Solution C (0.5 thiourea) 5g of urea, 5g of thiourea was dissolved in 24ml of distilled water.

Solution D (0.66 thiourea) 3.4g of urea, 6.6g of thiourea was dissolved in 34ml of distilled water.

Solution E (0.75 thiourea) 2.5g of urea, 7.5g of thiourea was dissolved in 41ml of distilled water.

Solution F (0.5 thiourea) 1g of urea, 9g of thiourea was dissolved in 45ml of distilled water.

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 ten 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 (32°C); 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 and 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 decreased from 0.1 to 0.5 and then slightly increased from 0.66 to 0.9.

Table 2: Effect of temperature on solubility and interfacial tension

| Proportions	Solvent	Temperature (K)	$\ln \tau$	$1/(\ln S)^2$
0.1	Water	303	8.20	0.049
0.1	Water	305	8.11	0.043
0.1	Water	307	8.05	0.039
0.25	Water	303	8.19	0.054
0.25	Water	305	8.12	0.052
0.25	Water	307	8.06	0.051
0.5	Water	303	6.57	0.066
0.5	Water	305	6.32	0.062
0.5	Water	307	6.12	0.059
0.66	Water	303	6.77	0.086
0.66	Water	305	6.54	0.078
0.66	Water	307	6.34	0.071
0.75	Water	303	6.80	0.098
0.75	Water	305	6.54	0.086
0.75	Water	307	6.33	0.077
0.9	Water	303	7.05	0.154
0.9	Water	305	6.85	0.133
0.9	Water	307	6.68	0.112

$1/(\ln S)^2$
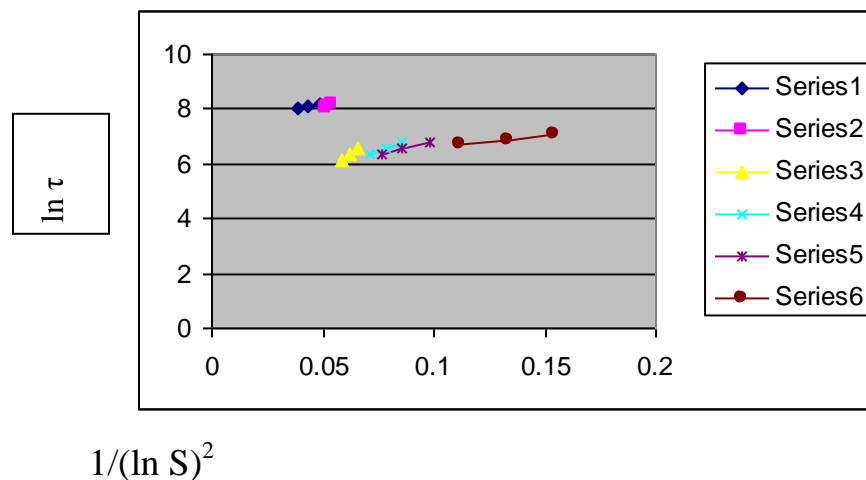
Fig. 2 A plot of ln τ vs 1/(ln S)^2

5.   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. Here the solubility of mixed crystal decreases with increase in proportions of thiourea. Fig. 2 shows the induction period as function of various temperatures. The interfacial tension can be calculated at various temperatures from the graph drawn between ln τ and 1/(ln S)$^{2.}$ The measured interfacial tensions various from 2.82 to 4.54 mj/m^2. In our experiments the induction period τ 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. 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 water. The induction period of urea-thiourea mixed crystal in water was determined at three different temperatures. 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. 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 water.
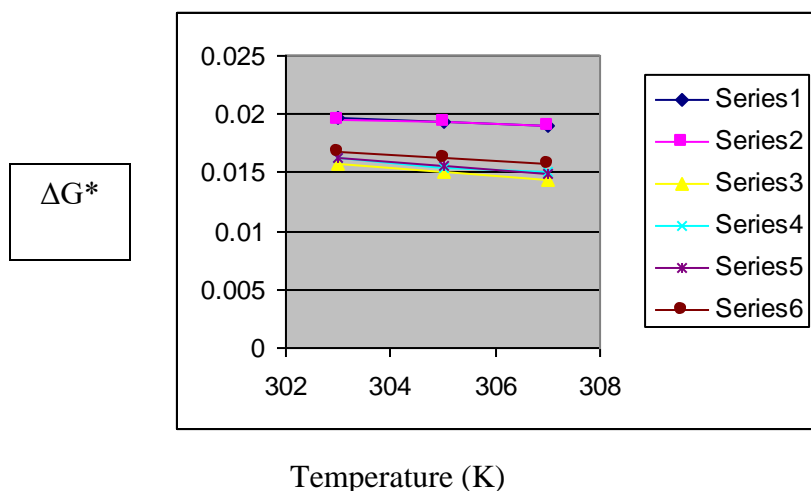
Fig. 3 Relation between the free energy change (ΔG*) and temperature for urea-thiourea mixed crystal

Table 2: Nucleation parameters of urea-thiourea mixed crystal in water

Proportions	r*	ΔG*	i*	r*	ΔG*	i*	r*	ΔG*	i*
	(303K)			(305K)			(307K)		
0.1	3.336	0.0197	20.785	3.235	0.0193	18.944	3.159	0.0190	17.6612
0.25	3.3805	0.0196	21.7946	3.3343	0.0193	20.9213	3.2924	0.0190	20.1417
0.5	3.2319	0.0158	28.9695	3.1433	0.0150	26.6504	3.0692	0.0144	24.8119
0.66	3.3992	0.0162	22.6684	3.4975	0.0154	26.6678	3.0692	0.0150	18.8201
0.75	3.4734	0.0163	24.3061	3.3419	0.0155	21.6479	3.2325	0.0149	19.5915
0.9	3.7803	0.0168	31.6219	3.6389	0.0168	28.2039	3.5138	0.0157	25.3953

6.   CONCLUSIONS

(1) It was clearly shown form the Fig. 1 that the solubility decreases with increase in thiourea proportions.

(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 2.82 to 4.54 mj/m^2.

(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 water.

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