

## Effect of Solvent on the Growth of Various Proportion of Organic Mixed Crystal

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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 ( $\Delta G^*$ ) have been calculated.

**Key Words:** Induction period, Interfacial tension, Critical radius, Critical nucleus.

### INTRODUCTION

Urea 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 process 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>4,7</sup>. Thiourea, urea possesses a large dipole moment which are potentially useful material for frequency doubling of near IR laser radiation. Single crystals of laser damage threshold<sup>8-12</sup>. It is also significant impact on laser technology, optical communication and optical data storage<sup>13,14</sup>. Motivated by these considerations urea-thiourea mixed crystals were synthesized in methanol and absolute alcohol by slow evaporation technique.

Thus, the active research works are being carried out in understanding the fundamental growth and nucleation mechanism of these crystals. There are several reports available on bulk growth of urea single crystals from alcohol based solution. But there are no reports available in the literature on the nucleation kinetics of urea-thiourea mixed crystals from water solvent.

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In the present studies, investigation have been made to evaluate the interfacial tension ( $\gamma$ ) between urea-thiourea mixed crystal and water by measuring the induction period and hence to calculate the critical nucleus ( $r^*$ ), number of molecules in the critical nucleus ( $i^*$ ) and Gibbs free energy for the formation of urea-thiourea mixed crystal.

### EXPERIMENTAL

The extent to which nucleation of urea-thiourea mixed crystal in water is determined by the super saturation produces more stable aggregates (due to higher probability of collision of diffusion molecules) and therefore increases the formation of stable nuclei. The time period that elapses between the attainment of super saturation and appearance of visible speck is defined as induction period ( $\tau$ ). In the present work, the induction period of urea-thiourea mixed crystal in water had been measured by the visual observation method.

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  $\pm 0.01^\circ\text{C}$ . 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

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

where  $A$  is a constant related to the pre-exponential factor of the nucleation rate expression,  $V$  is the molar volume,  $N$  is the Avogadro 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 two 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.

TABLE-1  
EFFECT OF TEMPERATURE ON SOLUBILITY AND  
INTERFACIAL TENSION

Proportions	Solvent	Temperature (K)	Solubility	Interfacial tension ( $\gamma$ )
0.10	Water	303	91.0	4.2080
0.10	Water	305	125.0	4.3965
0.25	Water	303	73.3	4.0931
0.25	Water	305	79.5	4.1412
0.50	Water	303	48.6	3.5877
0.50	Water	305	55.2	3.6266
0.66	Water	303	30.3	3.3477
0.66	Water	305	36.2	3.4277
0.75	Water	303	24.4	3.2156
0.75	Water	305	30.1	3.3189
0.90	Water	303	12.8	2.8167
0.90	Water	305	15.5	2.9339

Hence  $r^* = 2v\gamma/kT \ln S$ . The critical free energy is given by  $\Delta G^* = 16\pi\gamma^{3/2}/\Delta Gv^2$ . 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 ( $\Delta G^*$ ) and number of molecules in the critical nucleus ( $i^*$ ) were calculated at two different temperatures and presented in Table-2. It was noted that with the increase in super saturation the free energy change decreases ( $\Delta G^*$ ) with radius ( $r^*$ ).

TABLE-2  
NUCLEATION PARAMETERS OF UREA-THIOUREA  
MIXED CRYSTAL IN WATER

Proportions	Solvent	Temperature	$r^*$	$\Delta G^*$	$i^*$
0.10	Water	303	3.3361	1.9599	20.7854
0.10	Water	305	3.2346	1.9234	18.9438
0.25	Water	303	3.3802	1.9580	21.7946
0.25	Water	305	3.3343	1.9270	20.9213
0.50	Water	303	3.2319	1.5750	28.9695
0.50	Water	305	3.1422	1.5000	26.6504
0.66	Water	303	3.3992	1.6170	22.6684
0.66	Water	305	3.4975	1.5470	20.6678
0.75	Water	303	3.4734	1.6240	24.3061
0.75	Water	305	3.3419	1.5514	21.6479
0.90	Water	303	3.7803	1.6829	31.6219
0.90	Water	305	3.6389	1.6242	28.2039

This favours the easy formation of nucleation in 0.5 urea-thiourea mixed crystal when compared other proportions.

Urea-thiourea mixed crystal has got high solubility of 125 g/100 mL in 0.1 proportion and less soluble in 12.8 g/100 mL in 0.9 proportion of urea-thiourea mixed crystal in water (at 303K) be chosen as the solvent for crystal growth. The crystals were grown by slow evaporation technique. Saturation solution of urea-thiourea mixed crystal at different proportions was prepared. The solution was filtered through hot sintered glass funnel into the beaker and was kept open for prevent evaporation. The beaker was kept in the constant temperature bath controled to an accuracy of  $\pm 0.001^\circ\text{C}$ .

## RESULTS AND DISCUSSION

In the present study, the nucleation kinetics of urea-thiourea mixed crystals from various porportions 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 two 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, 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.

### Conclusion

The value of interfacial tension of urea-thiourea mixed crystal in 0.1, 0.25 and 0.5 proportions has much higher value than 0.66, 0.75 and 0.9 proportion of urea-thiourea mixed crystals. From the induction period measurements the interfacial tension has been calculated. Also the values of nucleation parameters like critical radius ( $r^*$ ), the fre energy of formation of critical nucleus and the number of molecules in the nucleus ( $i^*$ ) have been calculated. 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 when compared to all other proportions predict the easy formation of nucleation in water.

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