

Nucleation kinetics of various proportions of Urea-Thiourea mixed crystal in Water-Methanol

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ABSTRACT

The solubility, induction period and nucleation parameters of various proportions of urea-thiourea mixed crystals have been determined. Solubility study of various proportions of urea-thiourea mixed crystals were carried out at different temperatures in Water-methanol solvent. The induction period was measured at different super saturation level. The nucleation parameters like interfacial tension, radius of critical nucleus and number of molecules in the critical nucleus were calculated based on the classical theory of nucleation values of different parameters were found to be larger for 0.9 urea-thiourea mixed crystal than any other proportions of urea-thiourea mixed crystal.

Keywords: Induction Period, Solubility, Nucleation, Urea-Thiourea Mixed Crystal.

1. INTRODUCTION

Nonlinear optic (NLO) materials have recently attracted much attention because of their potential applications in emerging opto-electronic technologies. The search for new frequency conversion materials over the past decade has led to the discovery of many organic materials [1-4]. Though NLO crystals have high nonlinearity, fast responses and tailor made flexibility. Their applications are limited due to inherent poor chemical stability caused by pi conjugated system [5,6]. Many authors investigated various organic and organometallic compounds due to their very important roles in chemical, biological, electrical and environmental sciences and also examined their various properties [7-10]. Urea is representative of one class of materials which are applicable to photonics and served as a model compound and reference material in the diffusive mixing in organic solutions (DMOS) experiment in

microgravity carried out by NASA. Recently metal complexes of thiourea have been explored. Thiourea is an interesting inorganic modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds. Only few thiourea complexes, like zinc thiourea sulphate, bithiourea cadmium chloride, triallylthiourea mercury bromide, thiosemicarbazide crystallize in non-centro symmetric structure, show second harmonic generation (SHG) [11,12]. Motivated by these considerations urea-thiourea mixed crystals were grown by slow evaporation technique at different temperatures in Water-methanol.

2. EXPERIMENTAL

2.1 Nucleation Kinetics

The organic Mixed crystal was synthesized by the combination of urea (Merck, 99.5% pure), thiourea (Merck, 99.5% pure), along with water-methanol (AR grade) as solvent.

Homogeneous solutions were prepared by dissolving 1:9, 2.5:7.5, 5:5, 7.5:2.5 and 9:1 g of urea and thiourea in Water-methanol respectively.

Series 1 (0.1 urea-thiourea) 9g of urea, 1g of thiourea was dissolved in 5.6ml

of Water-methanol

Series 2 (0.25 urea-thiourea) 2.5g of urea, 7.5g of thiourea was dissolved in 6.7ml

of Water-methanol

Series 3 (0.5 urea-thiourea) 5g of urea, 5g of thiourea was dissolved in 13.6ml

of Water-methanol

Series 4 (0.66 urea-thiourea) 3.4g of urea, 6.6g of thiourea was dissolved in 23.5ml

of Water-methanol

Series 5 (0.75 urea-thiourea) 2.5g of urea, 7.5g of thiourea was dissolved in 27.6ml

of Water-methanol

Series 6 (0.9 urea-thiourea) 1g of urea, 9g of thiourea was dissolved in 41.7ml

of Water-methanol

The crystal growth solutions should be in equilibrium at room temperature (303 K) and should not contain any spurious nuclei. The procedure adopted can be explained by taking series 1, 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 5K. 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 performed.

The filtration of the solution was performed with the help of a Buckner funnel and filtration assembly. A filter paper of the size of Buckner funnel is taken and placed over the 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 2K above the saturation temperature (303 K); 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 adapted for Series 2 to 6. 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.

2.2. Solubility Studies

It is desirable to study the solubility of the material in a suitable solvent before proceeding for the crystal growth. In the present study different proportions of urea, thiourea (0.1, 0.25, 0.5, 0.66, 0.75 and 0.9; It was observed that the salt thiourea is less soluble. So the proportions of the crystals were expressed in terms of less soluble salt.) was determined in Water-methanol at different temperatures. The solutions of various proportions of urea-thiourea were kept at a constant temperature bath having an accuracy of $\pm 0.01^\circ\text{C}$ with constant stirring. 100ml of solution of each sample was taken to measure the dissolved solute. For this Water-methanol was used as a solvent throughout the experiment. Same process was repeated for different temperatures.

2.3. Determination of Induction period

The change in the Gibbs free energy (ΔG) between the crystalline phase and the surrounding mother liquor results in a driving force which stimulates crystallization.

For rapid crystallization, $\Delta G < 0$; the energy required to form UTMC nuclei is given by

$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma \quad (1)$$

where ΔG_v is the energy per unit volume, γ is the interfacial tension and r is the radius of the nucleus. The first term expresses the formation of new surfaces and the second term expresses the difference in chemical potential between crystalline phase (μ) and surrounding mother liquor (μ^0). At the critical state, the free energy of formation obeys the condition $d(\Delta G)/dr = 0$; Hence the radius of the critical nucleus is expressed as

$$r^* = -2\gamma / \Delta G_v \quad (2)$$

where $\Delta G_v = -\Delta\mu/v$, $\Delta G_v = -k_v T \ln S$, S solubility

$$\text{Hence } r^* = 2\omega / \Delta\mu \quad (3)$$

$$\Delta G^* = 16\pi v^3 \gamma^2 / 3 (\Delta\mu)^2 \quad (4)$$

The number of molecules in the critical nucleus is expressed as

$$i^* = 4\pi r^{*3} / 3v \quad (5)$$

In the present study, in order to estimate the critical nucleation parameters, the interfacial tension has been calculated using the

experimentally measured induction period values by the relation

$$\ln \tau = \ln A + 16\pi\gamma^3 V^2 N / 3RT (\ln S)^2 \quad (6)$$

where r^* -radius of critical nucleus, i^* -number of molecules in the critical nucleus, τ - induction period, γ - interfacial tension, V - molar volume, N - Avogadro number.

3. RESULTS AND DISCUSSIONS

Figure 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 Water-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 2.7679 to 4.5333 mj/m² in Water-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 τ was measured by the most commonly used method (visual observation method). Based on nucleation theory interfacial tension was calculated from Eq 1.

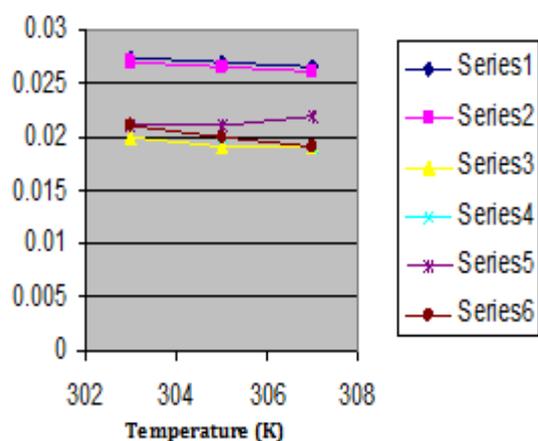


Figure - 1: Relation between the free energy change (ΔG^*) and temperature for urea-thiourea mixed crystal in Water-methanol.

Series 1-0.1 urea-thiourea; Series 2-0.25 urea-thiourea; Series 3-0.5 urea-thiourea

Series 4-0.66 urea-thiourea; Series 5-0.75 urea-thiourea; Series 6-0.9 urea-thiourea

The free energy change as a function of temperature is given in Figure 1. 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 Water-methanol.

3.1. Solubility Curves

The solubility curves for various proportions of urea-thiourea are shown in Figure. 2. It is observed that the solubility of various proportions of urea-thiourea decreases with increase in thiourea proportions. That is, the solubility of different samples of solution was found in the following order; 0.1 urea-thiourea > 0.25 urea-thiourea > 0.5 urea-thiourea > 0.66 urea-thiourea > 0.75 urea-thiourea > 0.9 urea-thiourea.

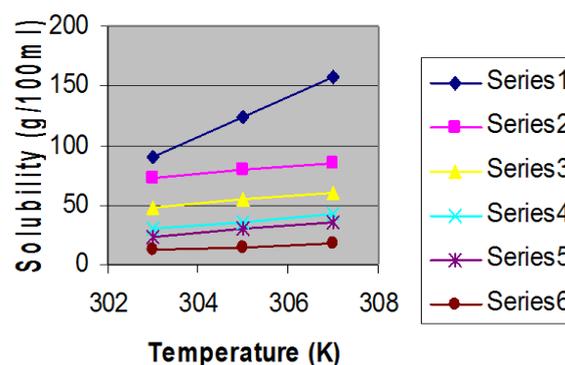


Figure - 2: Solubility of various proportions of urea-thiourea mixed crystal in Water-methanol.

Series 1-0.1 urea-thiourea; Series 2-0.25 urea-thiourea; Series 3-0.5 urea-thiourea

Series 4-0.66 urea-thiourea; Series 5-0.75 urea-thiourea; Series 6-0.9 urea-thiourea

Table - 1: Nucleation parameters of urea-thiourea mixed crystal in Water-methanol.

P_a	r^* ($10^{-10}m$)	ΔG^* mj/m ² (303K)	i^*	r^* ($10^{-10}m$)	ΔG^* mj/m ² (305K)	i^*	r^* ($10^{-10}m$)	ΔG^* mj/m ² (307K)	i^*
0.1	3.3337	0.0274	18.6617	3.2349	0.0269	18.1084	3.1599	0.0265	17.6802
0.25	3.3787	0.0269	19.0681	3.3355	0.265	18.8243	3.2917	0.0261	18.5745
0.5	3.1881	0.0200	18.2392	3.1185	0.0190	17.8411	3.0586	0.0190	17.4984
0.66	3.3743	0.0210	19.4748	3.2829	0.0200	18.9474	3.01895	0.0190	18.4083
0.75	3.4506	0.0211	20.0157	3.4280	0.0210	19.8835	3.4057	0.0220	19.7541
0.9	3.07618	0.0212	22.0040	3.6362	0.0200	21.2693	3.1993	0.0191	20.4686

a- Proportions

Table - 2: Effect of temperature on solubility and interfacial tension in Water-methanol.

Proportions	Solvent	Temperature (K)	Solubility	Interfacial Tension (v) (10 ⁻⁸ Kj/mj)
0.1	Water-methanol	303	90.6	4.2017
		305	124	4.3899
		307	158	4.5333
0.25	Water-methanol	303	73.0	4.0875
		305	78.9	4.1355
		307	85.2	4.1801
0.5	Water-methanol	303	48.0	3.5277
		305	54.1	3.5808
		307	60.2	3.6298
0.66	Water-methanol	303	29.4	3.2897
		305	35.5	3.4014
		307	41.9	3.4766
0.75	Water-methanol	303	23.8	3.1678
		305	29.7	3.2986
		307	36.2	3.4219
0.9	Water-methanol	303	12.4	2.7679
		305	14.8	2.8844
		307	18.5	3.0233

Table - 3: Effect of temperature on ln τ and 1/(ln S)² in Water-methanol.

Proportions	Solvent	Temperature (K)	ln τ	1/(ln S) ²
0.1	Water-methanol	303	8.1817	0.0492
		305	8.1017	0.0430
		307	8.0359	0.0390
0.25	Water-methanol	303	8.1761	0.0543
		305	8.1152	0.0524
		307	8.0408	0.0506
0.5	Water-methanol	303	6.2823	0.0667
		305	6.1420	0.0628
		307	6.0282	0.0596
0.66	Water-methanol	303	6.5624	0.0875
		305	6.4052	0.0785
		307	6.2623	0.0717
0.75	Water-methanol	303	6.6012	0.0995
		305	6.4693	0.0870
		307	6.4052	0.0777
0.9	Water-methanol	303	6.8628	0.1578
		305	6.7214	0.1377
		307	6.5723	0.1175

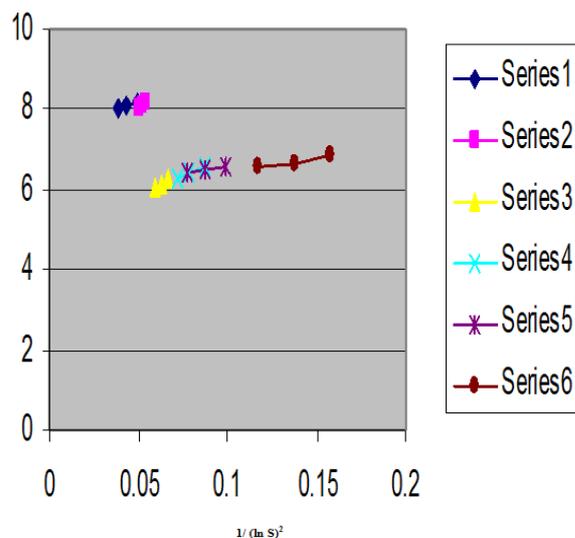


Figure - 3: A plot of $\ln \tau$ vs $1/(\ln S)^2$ in Water-methanol.

4. CONCLUSION

It was clearly shown that the solubility of urea-thiourea mixed crystal in 0.9 proportions were lower than that of all other proportions. 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. 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 2.7679 to 4.5333 mj/m^2 in Water-methanol. The values of critical radius, number of molecules in the critical nucleus were decreased and small values of free energy of activation in 0.5 urea- thiourea mixed crystal when compared to all other proportions predict the easy formation of nucleation in Water-methanol.

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