Research Article

Microhardness studies of various proportions in urea thiourea mixed crystals in water, 10%, 20% and 30% methanol

G Madhurambal[1], M Mariappan[2] and G. Selvarajan[2]

[1]Department of Chemistry, ADM College for Women, Nagapattinam 611 00, Tamil Nadu, India.
[2]Department of Chemistry, Thiru.Vi.Ka. Government Arts College, Tiruvarur-610 003, Tamil Nadu, India.

ABSTRACT
Various proportions of urea-thiourea mixed crystal (UTMC) via solution growth by using urea, thiourea and deionised water is starting materials. The functional groups and vibrational frequencies were identified using FTIR spectral analysis. Microhardness studies of various proportions of urea thiourea mixed crystal was determined by using Vicker's method.

Keywords: Urea thiourea mixed crystal, Solution growth, FTIR, Microhardness.

1. INTRODUCTION

Nonlinear optical materials play an important role in electro-optical modulators, high density optical memories, colour displays in the realization of signal processing devices involving the generation of new frequencies, signal processing devices involving the generation of new frequencies, signal amplifications, emission or oscillation etc.[1-6]. In recent years, some organic NLO materials are attracting a great deal of attention for possible use in optical devices such as switches, optical bitable devices and electro-optical devices because organic NLO materials have large optical susceptibilities, short cut-off wavelength, short response time and high thresholds for laser power compared with inorganic materials[7-12]. This works reports the microhardness of an organic NLO UTMC in water, 10%, 20% and 30% methanol. UTMC shows one of the largest power SHG signals observed which suggest this material may be of potential interest for frequency doubling of laser diodes.

Methods of hardness tests

Hardness measurements can be carried out by various methods,
In general there are two types,
a. static indentation tests
b. dynamic indentation tests
In addition to scratch tests, plough tests, rebound tests, damping tests, cutting tests, abrasion tests are also there.

Static indendation tests

A steady load is applied to an indenter which may be a ball or diamond core of diamond pyramid and the hardness is calculated from the area or depth of the indentation produced. The variables are the type of the indenter and load. The indenter is made of very hard material to prevent its deformation by the test piece so that it can cover materials over a wide range of hardness. For this reason either hardness steel sphere on a diamond pyramid indenter is preferred. In this static indentation test the indenter is pressed perpendicularly into the surface of a sample by means of an applied load then by measuring the cross sectional area or the depth of the indentation and knowing the applied load an empirical hardness number may be calculated. This procedure is followed in Brinell, Meyu, Vickers, Knoop and Rockwell tests. But Vickers's hardness test is adopted to study the microhardness of UTMC of varying compositions.

Vicker's test

Among the various methods of hardness measurements, the most commonly used and reliable method is Vickers's hardness test. In this method micro indentation is made on the surface of the crystal with the help of a diamond pyramid indenters are said to be best suited for hardness tests due to two reasons namely

i. The contact pressure for a pyramid indenter is independent of indent size.
ii. The pyramid indenters are less affected by elastic release than other indenters

The base of the Vickers's pyramid is a square and the depth of indentation corresponds 17th of the indentation diagonal. Hardness is generally defined as the ratio of the load applied to the surface area of the indentation. The Vickers's hardness test, a square based diamond pyramid is used and the Vickers's hardness number Hv or DPN (Diamond Pyramid Number) is defined as

$$Hv = \frac{2W \sin \alpha/2}{d^2}$$

Where α is the apex angle of the indenter (α = 136º)
The Vickers's hardness number is therefore calculated from the relation

Hv =W/pyramid area =1.8544 X W/Kg/mm^2

In microhardness tests, load in the range 1-25g are used and the impression is only microns (10^{-3} mm) across requiring a more powerful microscope for measurement.

2. EXPERIMENTAL

In the present work, Vickers's pyramid indenter has been used to study the microhardness of UTMC. Sample preparation is very important for microhardness studies, hence great care must be taken to ensure that the microhardness recorded is a representative of the sample. Smooth polished surface if the crystals were subjected to static indentation tests in all at room temperature (30ºC) using a Wetzler's hardness tester fitted with a Vickers's diamond pyramidal indenter attached to a microscope. Loads varying from 5-25g are applied over a fixed interval of time (in seconds).
The crystals were indented with increasing load. Several indentations with each load are indented on the sample. From the average values if the indentation diagonal, the ratio of load to area of the permanent indentation and the microhardness value is estimated from the relation.

$$Hv = 1.8544 \text{ X } p/ D^2 \text{ Kg/mm}^2 \qquad (1)$$

where Hv is the Vickers's hardness number, P is the applied load and d is the average diagonal length of the indentation impression (mm). The relation between load P and the indentation length d is represented by

$$P = K_1 d^n \qquad (2)$$

Where P is the load applied (g), d is the observed length of the indentation (mm) and K_1 (standard hardness) and n (logarithmic exponent) are constants. The values are given in the table. The values of n represent the capacity of work hardening
From the microhardness number, the field strength can be calculated using the equation

$$\sigma_v = Hv \left[1-(n-2) \frac{\{12.5(n-2)\}^{n-2}}{1-(n-2)}\right] \qquad (3)$$

Where σ_v is the yield strength, Hv is the hardness and n is the logarithmic exponent, as the hardness value and the logarithmic exponent are known, the yield strength of UTMC of varying compositions can be calculated. The values are given in the table and the graphs also be presented.

Correlation of microhardness with other properties

The hardness properties are related to the crystal structure of the material, hence wide applications in the study of deformation during indentations is not clearly understood, micro indentation study provides useful information concerning the mechanical behavior of the brittle materials. Several investigations have used indentation techniques to study deformation, anisotropy, cracks, grain boundary hardening impurity distribution in the system, solid solution formation, irradiation and environment dislocation mobility of various crystals and in the choice of ceramics for abrasives, tar bits and bearings Vickers's micro indentation values can be correlated with the strength of inter atomic binding of some of the cubic crystals. According to them the shorter the inter atomic distances, stronger is binding and hence the greater is the hardness value.

RESULTS AND DISCUSSION

In all the crystals, the indentation impression was square and their size increased with the increase of applied load. In all cases the loads are applied up to 100gms. Beyond 50gms the crystal begins to show multiple cracks around the indentation mark, hence microhardness measurements are restricted up to 50gms of load, even 25gms of load in certain cases. The results discussed are conferred to microhardness corresponding to the range of loads. From the tables and the graph, it is observed that for all the mixed crystals, microhardness decreases with increase of load and this shows that there is dislocation in the crystal. The validity of Mayer's law is tested by its constancy for the mixed crystals indicate that the slopes for all

the composition are lesser than 2. This supports the concept that if n<2 the microhardness value decrease as the load increased.

The work hardening co-efficient decreases from 0.5 to 0.9 in 10%, 20% and 30% methanol due to hardening effect of thiourea to a précised extent. But in the case of water the work hardening co-efficient increases from 0.5 to 0.9 and this may due to structural dislocations. Thus water solvent enhances the incorporation of thiourea in UTMC and makes the lattice tightly packed and so work hardening co-efficient increases from 0.5 to 0.9.

Table 1: Micro hardness of urea thiourea mixed crystal in water

P	Solvent	P	d	Log P	log d	Hv	n
0.5	Water	5	3.3403	0.6989	0.5240	8.31	0.7143
		10	5.6489	1.0000	0.7520	5.81	
		20	9.5689	1.3010	0.9808	4.05	
0.66	Water	5	3.1902	0.6989	0.5038	9.11	0.8333
		10	5.3429	1.0000	0.7263	6.54	
		20	9.2019	1.3010	0.9639	4.38	
0.75	Water	5	2.9787	0.6989	0.4740	10.45	0.8333
		10	5.1955	1.0000	0.7156	6.87	
		20	9.0583	1.3010	0.9571	4.52	
0.9	Water	5	2.9702	0.6989	0.4728	10.51	0.8652
		10	4.9527	1.0000	0.6948	7.56	
		20	8.1601	1.3010	0.9117	5.57	

Table 2: Micro hardness of urea thiourea mixed crystal in 10%methanol

P	Solvent	P	d	Log P	log d	Hv	n
0.5	10% Methanol	5	2.8569	0.6989	0.4559	11.36	1.0000
		10	5.0298	1.0000	0.7016	7.33	
		20	8.6559	1.3010	0.9378	4.95	
0.66	10% Methanol	5	2.8080	0.6989	0.4480	11.76	0.8333
		10	4.8511	1.0000	0.6858	7.88	
		20	8.2798	1.3010	0.9180	5.41	
0.75	10% Methanol	5	2.7658	0.6989	0.4498	12.12	0.7500
		10	4.6062	1.0000	0.6633	8.74	
		20	7.5888	1.3010	0.8802	6.44	
0.9	10% Methanol	5	2.7512	0.6989	0.4395	12.25	0.6429
		10	4.4799	1.0000	0.6513	9.24	
		20	7.0321	1.3010	0.8471	7.50	

Table 3: Micro hardness of urea thiourea mixed crystal in 20%methanol

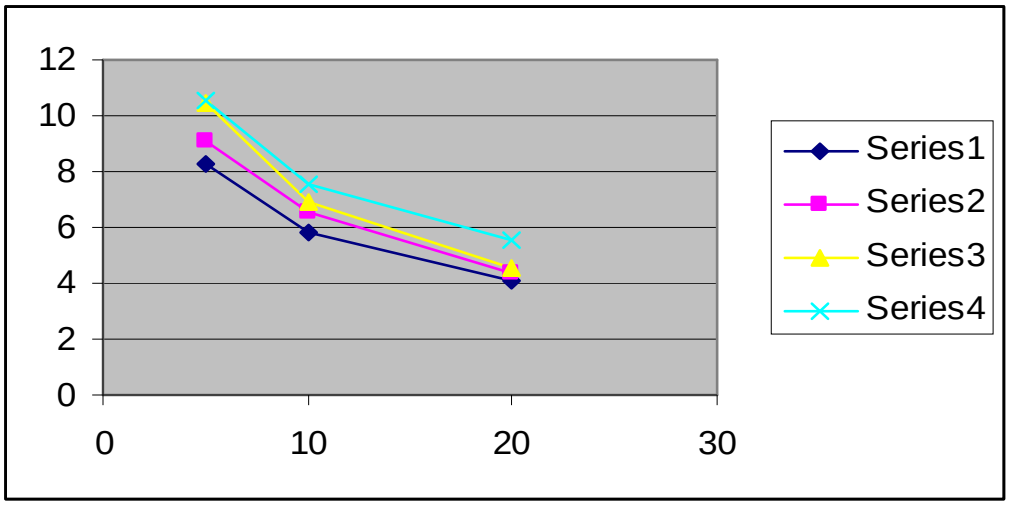
P	Solvent	P	d	Log P	log d	Hv	n
0.5	20% Methanol	5	2.5898	0.6989	0.4751	10.40	0.6250
		10	4.7555	1.0000	0.6772	8.20	
		20	7.5479	1.3010	0.8778	6.51	
0.66	20% Methanol	5	2.8941	0.6989	0.4615	11.07	0.5000
		10	4.6245	1.0000	0.6654	8.66	
		20	7.2686	1.3010	0.8615	7.02	
0.75	20% Methanol	5	2.8333	0.6989	0.4523	11.55	0.6250
		10	4.3974	1.0000	0.6432	9.59	
		20	6.8561	1.3010	0.8308	7.89	
0.9	20% Methanol	5	2.6967	0.6989	0.4308	12.75	0.5500
		10	4.0156	1.0000	0.6038	11.50	
		20	6.1771	1.3010	0.7908	9.72	

Table 4: Micro hardness of urea thiourea mixed crystal in 30%methanol

P	Solvent	P	d	Log P	log d	Hv	n
0.5	30% Methanol	5	2.8091	0.6989	0.4486	11.75	0.8333
		10	4.5621	1.0000	0.6592	8.91	
		20	7.0415	1.3010	0.8477	7.48	
0.66	30% Methanol	5	2.8032	0.6989	0.4477	11.80	0.6000
		10	4.3499	1.0000	0.6385	9.80	
		20	6.7212	1.3010	0.8275	8.21	
0.75	30% Methanol	5	2.7434	0.6989	0.4383	12.32	0.6000
		10	4.2639	1.0000	0.6298	10.20	
		20	6.5292	1.3010	0.8149	8.70	
0.9	30% Methanol	5	2.6453	0.6989	0.4225	13.25	0.6666
		10	3.9311	1.0000	0.5945	12.00	
		20	5.9123	1.3010	0.7718	10.61	

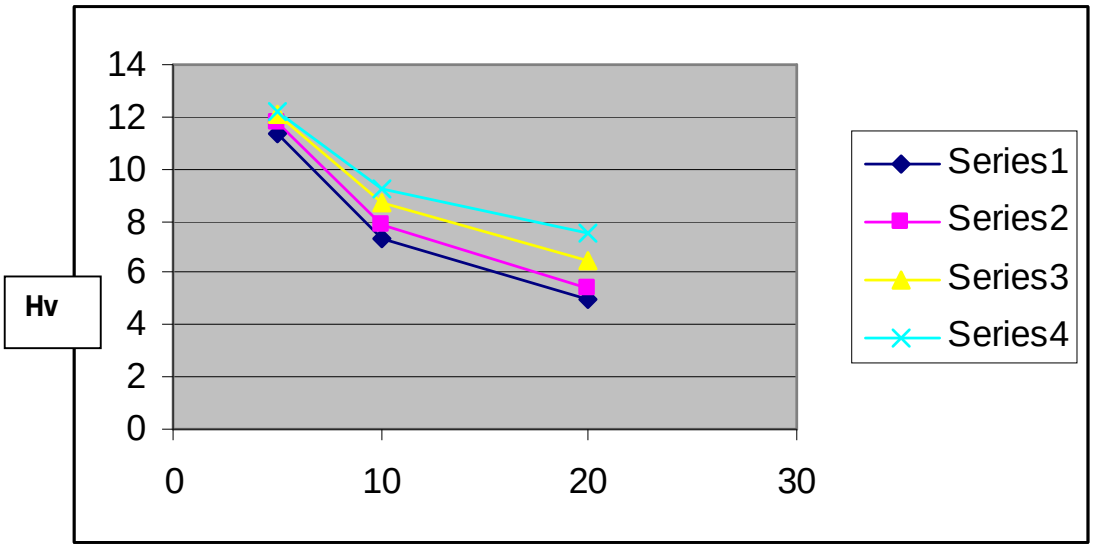
Table 5: Yieldstrength of urea thiourea mixed crystal in Water, 10%methanol, 20%methanol and 30%methanol

Proportions	Solvent	Yield strength
0.5	Water	27.4272
0.66	Water	39.3963
0.75	Water	36.6105
0.9	Water	49.2645
0.5	10%Methanol	39.3904
0.66	10%Methanol	49.2698
0.75	10%Methanol	57.8547
0.9	10%Methanol	67.1859
0.5	20%Methanol	59.0315
0.66	20%Methanol	87.1808
0.75	20%Methanol	68.2479
0.9	20%Methanol	84.2879
0.5	30%Methanol	55.3476
0.66	30%Methanol	71.4749
0.75	30%Methanol	74.8565
0.9	30%Methanol	81.5244



P

Fig. 1: Plot of P Vs Hv in water solvent



P

Fig. 2: Plot of P Vs Hv in 10% methanol

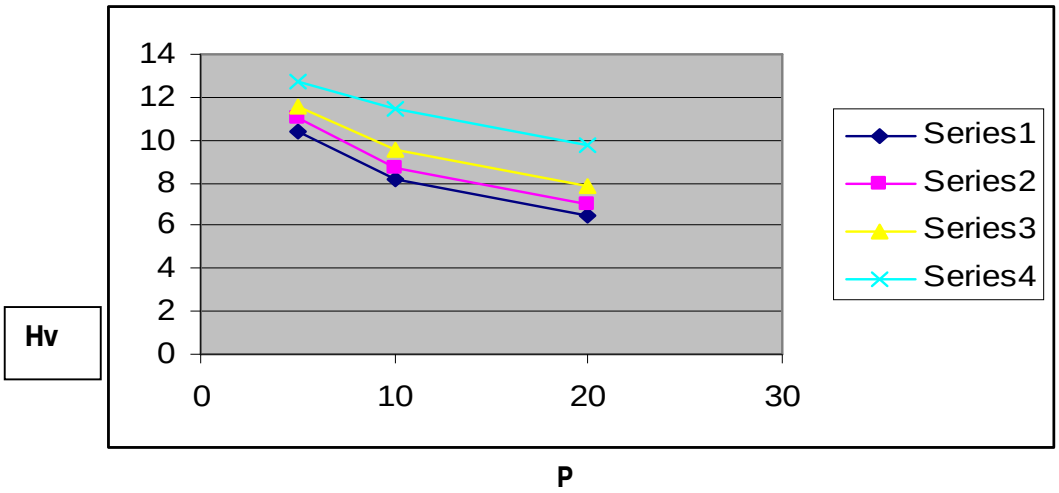


Fig. 3: Plot of P Vs Hv in 20% methanol

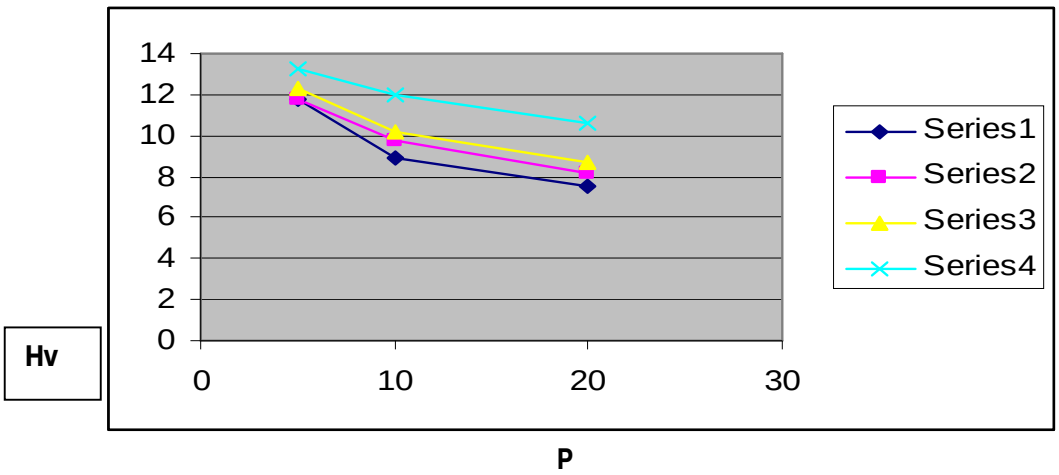


Fig. 4: Plot of P Vs Hv in 30% methanol

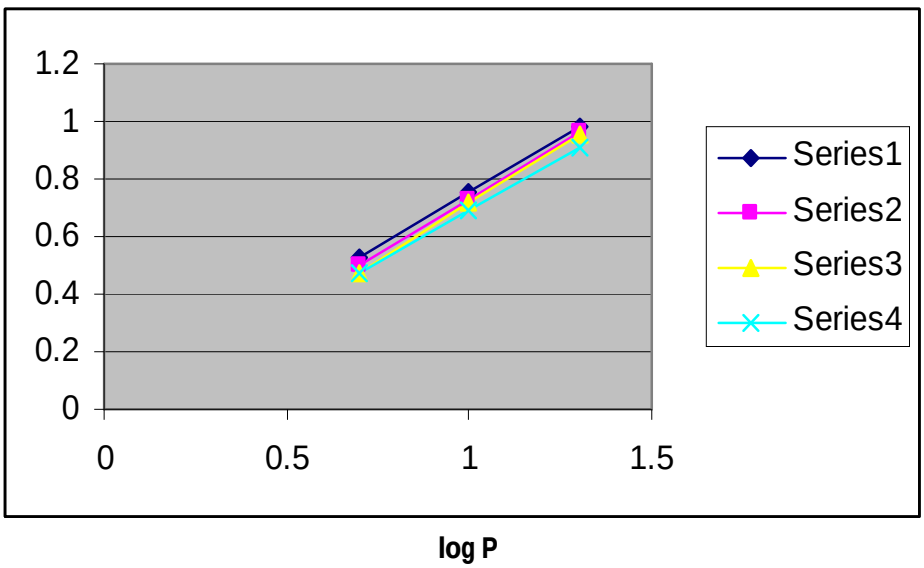


Fig. 5: Plot of log P Vs log d in water

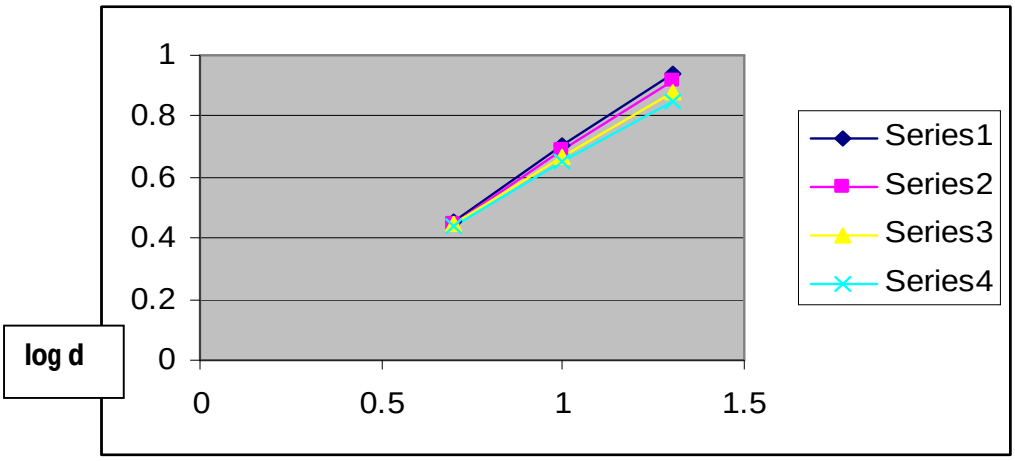


Fig. 6: Plot of log P Vs log d in 10% methanol

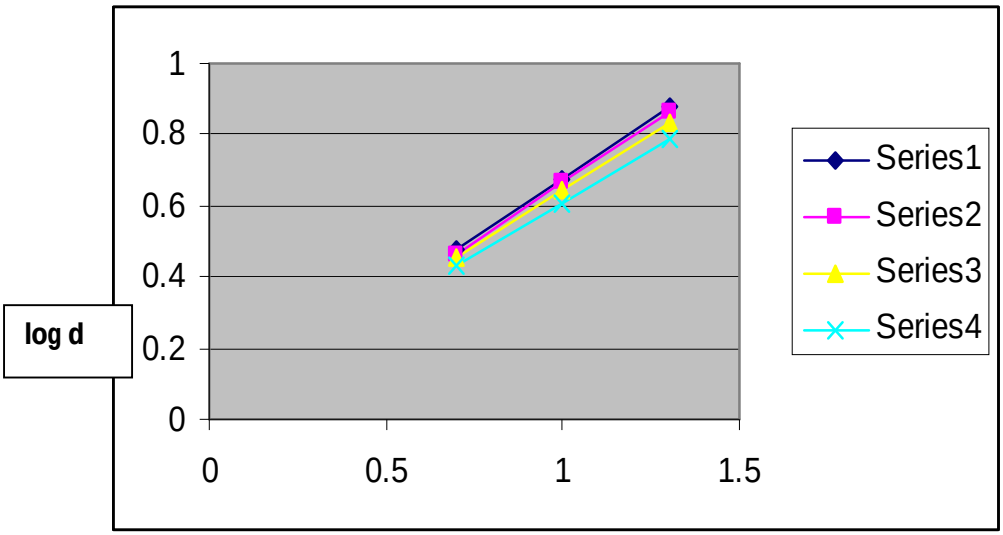


Fig. 7: Plot of log p Vs log d in 20% methanol

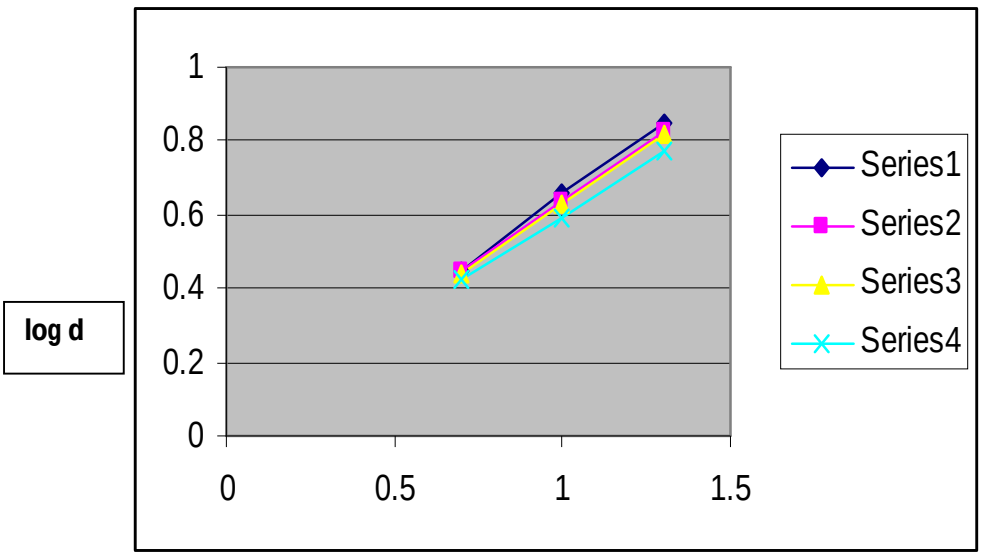


Fig. 8: Plot of log p Vs log d in 30% methanol

CONCLUSION

In the case of water the work hardening co-efficient increases from 0.5 to 0.9 and this may due to structural dislocations. Thus water solvent enhances the incorporation of thiourea in UTMC and makes the lattice tightly packed and so work hardening co-efficient increases from 0.5 to 0.9.

REFERENCES

1. Jayarama A & Dharmaprakash S M, Indian J Pure & Appl Physics, 44 (2006) 461-467.
2. Kurtz S K & Pery T T, J Appl Phys, 39 (1968) 3798-3805.
3. Malyajdas S, Prasad R & Sen P, Indian J Pure & Appl Physics, 44 (2006) 555-561.
4. Boomadevi S, Dhanasekaran R & Ramasamy P, Cryst Res Technol, 37(2002)159-164.
5. Kumar K & Ramamurthy K, Cryst Res Technol, 41(2006)217-225.
6. Rajasekaran R & Rajendran KV, Mater Chem & Phys, 82(2003)273-281.
7. Angelimary PA, Dhanuskodi S, Cryst Res Technol, 36(2001)1231-1239.
8. Qui J & Lan L, Mater Sci: B, 133 (2006) 191-199.
9. Sing P, Babbar V K, Razdon A, Goel T C & Srivastsava S I, Indian J Appl Phys, 42 (2004) 221-228.
10. Krishnan H, Justin C & Jerome S, J Cryst Growth,310(2008)3313-3321.
11. Madhurambal G, Mojumdar SC, Hariharan S & Ramasamy P, J Therm Anal Cal, 78(2004)125-133.
12. Ravindran B, Madhurambal G, Mariappan M and Mojumdar S C, J Thermal Anal Calorim, 104 (2011) 893-899.