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Determination of Nucleation Temperature, meta stable zone width spectral analysis of sulphanilic acid grown from Ethanol-Water as growth medium

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Abstract

Sulphanilic acid, one of the organic crystals which has typical properties is grown by simple solution technique by adopting slow evaporation method using dilute ethyl alcohol as solvent at room temperature. The solubility of sulphanilic acid, in EtOH/H_2O was determined. The solution grown sulphanilic acid, was carefully harvested and subjected to various characterization studies *viz.* UV, FTIR, H^1 NMR. The results are suitably interpreted to know the application oriented properties of solution grown sulphanilic acid.

Key words : Sulphanilic acid**,** nucleation temperature, meta stable zone width Solution technique,

Introduction

It is evident that study of crystals is bound to throw light on the intrinsic nature of the solid state and hence the introduction of a new branch in physical chemistry, known as chemical crystallography or crystal chemistry. A crystal is defined as homogeneous (*i.e.*, of uniform chemical composition) portion of a solid substance, having a very regular structure *i.e.*, bonded by plane faces, making definite angles with each other, resulting in a typical and distinctive symmetry and geometric form. Organic molecular materials have emerged as a new class of promising nonlinear materials because of their superior qualities over inorganic materials, some of the advantages of the crystalline organic materials are large damage thresholds in laser beam & large birefringence.

Though organic materials have been known for their applications in semi-conductors superconductors and NLO devices, very little attention has been focused on the dielectric and polar properties of pure and binary organic materials future photonics technology is dependent on the design, synthesis and characterization of materials exhibiting, in particulars, second-order NLO properties.

Anbusrinivasan and Suganthi[1] reported the growth of high quality benzophenone crystals by simple solution technique. Benzophenone crystals grown by solution technique adopting slow evaporation method. The crystal was subjected to XRD studies, FTIR studies and Thermal studies and the results were suitably interpreted. Madhurambal and Anbusrinivasan[3], reported the growth of high quality anthracene crystals by simple solution technique.

Anbusrinivasan.*et.al.*,[4] reported the thermal studies and spectral characterization of "p-N,N Dimethyl aminobenzaldehyde (DAB) grown by solution technique using CCl_4 as growth medium-"

High quality benzophenone single crystals were grown by vertical Bridgman – Stockbarger Growth system. X– ray diffraction studies, FT-IR, TG-DTA and optical transmission studies were carried to determine the quality of grown crystals[2].

Materials and Method

Crystal growth of sulphanilic acid :

The analar sample of sulphanilic acid was further purified by repeated recrystallization. The extent of solubility of sulphanilic acid in various solvents viz $CHCl_3$, CCl_4, were determined. Finally sulphanilic acid was grown by solution technique using $EtOH/H_2O$ as growth medium. The saturated solution of sulphanilic acid was prepared in a beaker at room temperature. Then it was allowed for systematic slow evaporation. Well needle shaped crystals were obtained in 1-2 days. The solubility of sulphanilic acid in ethanol-water at various temperature ranges from 30°C to 50ºC was determined.

Metastable zone width determination :

After solubility determination, the metastable zone width of sulphanilic acid in ethanol-water was determined. Saturated solutions of sulphanilic acid in ethanol-water at different temperatures were allowed for systematic slow cooling. The temperature at which the first nucleation was observed which corresponds to their width of metastable zone. The solubility of sulphanilic acid in ethanol-water and the metastable zone width of sulphanilic acid in ethanol-water is shown in Figure 1.

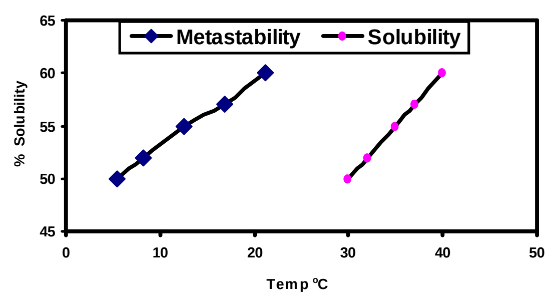

Figure 1. Metastable zone width of sulphanilic acid in ethanol-water

Experimental determination of induction period, interfacial energies and nucleation parameters

There are several methods of measuring the induction period depending upon the solubility of the materials. Here the visual observation method was followed. Solutions of sulphanilic acid in ethanol-water at different supersaturation values were prepared and subjected to systematic slow evaporation. The time period that elapses between the achievement of supersaturation and appearance of visible nuclei is taken as the induction period [τ]. Several trial runs were performed to minimize the error. Experiments were repeated for supersaturation (S) like 1.10,1.15,1.20 at two different temperatures. From the results obtained, a plot of ln τ against $1/(\ln S)^2$ is drawn and is shown in Figure 2. The interfacial tension was calculated from the slope of the curves using the equation

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

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 function ln A weakly depends on temperature and hence there is a linear dependence between ln τ and $1/(\ln S)^2$ at constant temperature. The factor 16π/3 in the above equation refers to the spherical nuclei.

According to the classical homogenous nucleation theory, the free energy required to form sulphanilic acid in ethanol-water nucleus is given by

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

Where ΔGv is the energy change per unit volume, r is radius of the nucleus.
At the critical state, the free energy of formation obeys the condition
d (ΔG) / dr = 0. Hence the radius of the critical nucleus is expressed as

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

Where

$$\Delta G_v = -KT \ln S / V \qquad (3)$$

Where V is the molar volume, and S = C/C*,
C- actual concentration
and C* - equilibrium concentration
Hence

$$r^* = 2V\gamma / KT \ln S \qquad (4)$$

The critical free energy is given by

$$\Delta G^* = 16\,\gamma\pi^3\,V^2 / \Delta G2v \qquad (5)$$

The number of molecules in the critical nucleus is expressed as

$$i^* = 4\,\pi\,(\gamma^*)^3 \,/\, 3V \qquad (6)$$

The interfacial tension values between the sulphanilic acid in ethanol-water is calculated as 1.218 and 1.237 mJ/m^2 at 303 and 308 K respectively.

There fore using the interfacial tension value, the radius of the critical nuclei (r^*), the free energy change for the formation of a critical nucleus (ΔG^*) and the number of molecules in the critical nucleus (i^*) were calculated at two different temperatures for sulphanilic acid in ethanol-water.

It was noted that with the increase in supersaturation, the free energy change for the formation of a critical nucleus (ΔG^*) decreases with radius (r^*). This favours the easy formation of nucleation in CCl_4 solutions at higher supersaturations

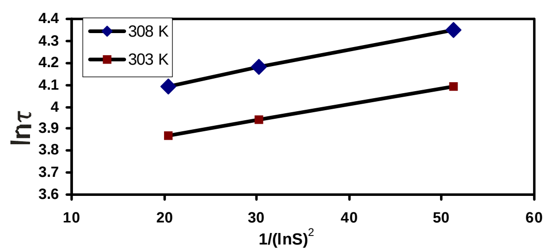

Figure 2. A plot of ln τ Vs $1/(\ln S)^2$ for sulphanilic acid in ethanol-water

Table 3. Nucleation parameters of sulphanilic acid in ethanol-water

Super Saturation ratio S = C/C*	303 K			308 K		
	r*/m	(ΔG*) /10^{-15}kJ	i* 10^{-10}	r*/m	(ΔG*) /10^{-15}kJ	i* 10^{-10}
1.10	13.82	4.938	4.937	13.89	5.105	5.012
1.15	9.43	2.301	1.568	9.48	2.38	1.593
1.20	7.22	1.349	0.704	7.26	1.394	0.715

Results and Discussion

FT-IR spectral analysis

The absorption of IR-radiation causes the various bands in a molecule to stretch and bend with respect to one another. The range 4000-400 cm^{-1} is of prime importance for the study of an organic compound by spectral analysis. Infrared spectrum is an important record, which gives sufficient information about the structure of a compound. In this technique almost all functional groups in a molecule absorb characteristically within a definite range of frequency.

The solution grown sulphanilic acid in ethanol-water was subjected FTIR spectral analysis using PERKIN ELMER Spectrophotometer using KBr pelleting technique in the 400-4000 cm^{-1} range. The FTIR – Spectrum of sulphanilic acid grown by solution technique adopting slow evaporation method using Ethyl alcohol and water as growth medium is shown in figure 3.

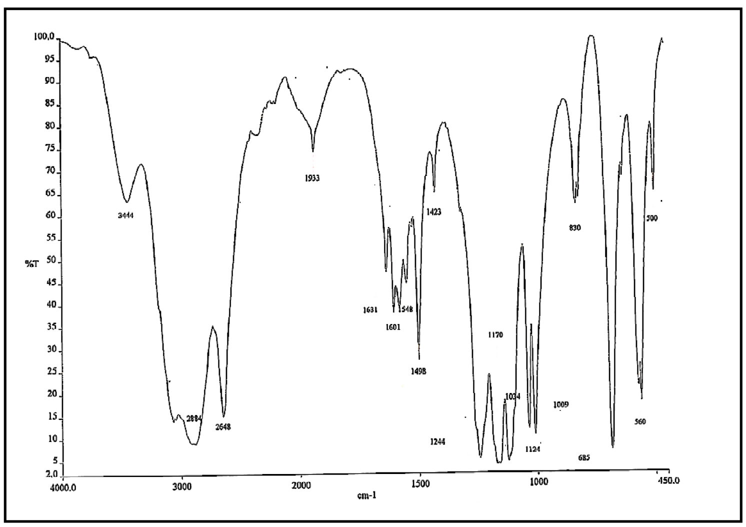

Figure 3. FTIR Spectrum of Solution grown sulphanilic acid

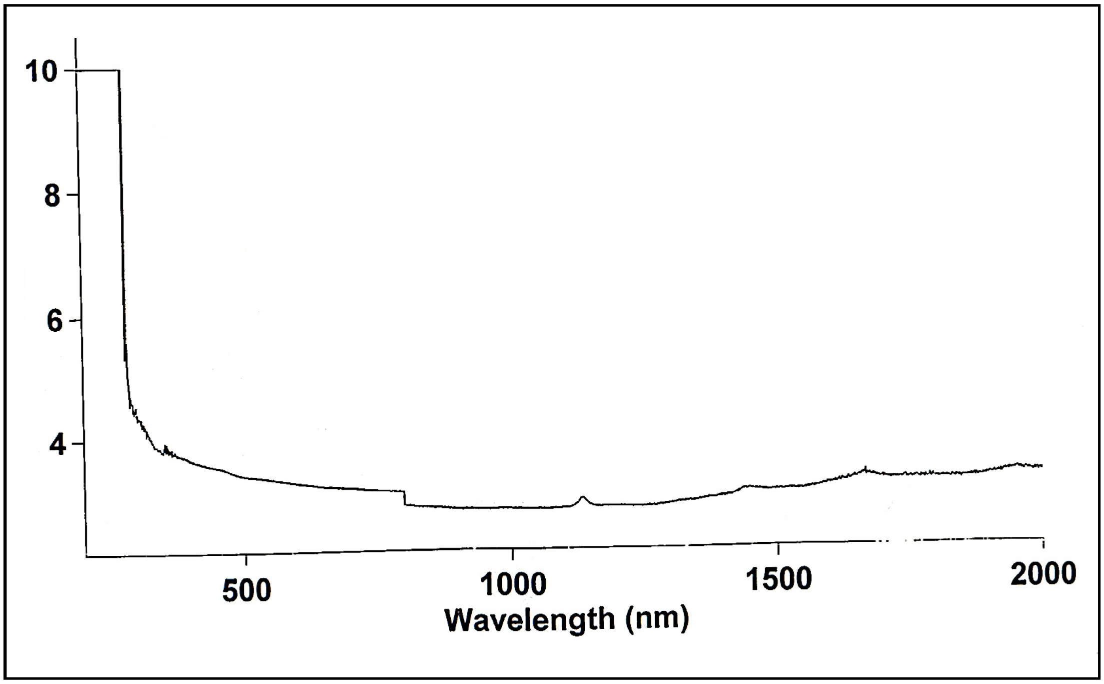

Figure 4. UV – VIS – Spectrum of solution grown sulphanilic acid

In the FTIR Spectrum of solution grown sulphanilic acid the peak at 3444 cm^{-1} is observed and is assigned to $-NH_2$ in aromatic amines[5,6]. The peak at 2884 cm^{-1} is due to –CH- stretching attached to Nitrogen. The peak at 3050 cm^{-1} is due to = CH in aromatic compounds. The amino group in sulphanilic acid in ethanol-water is observed at 1601 cm^{-1} and 1631 cm^{-1}. The peak at 1498 cm^{-1} is the characteristic of benzene ring. The peaks observed from 1009-1244cm^{-1} is the characteristic of sulphonic acid group. The peak observed at 830 cm^{-1} is due to C-H out of plane deformation in para di subsitituted benzene. The peak at 685cm^{-1} is assigned to C-S Stretching

U.V.-Visible spectral analysis :

The solution grown sulphanilic acid was subjected to UV-VIS-Spectral analysts to know its transparency. The UV-VIS Spectrum of solution grown sulphanilic acid was recorded in CARY 5E VARIAN SPECTRO PHOTOMETER. The recorded spectrum is shown in fig. 4. This spectrum shows the characteristic absorption around 200-280 nm which is assigned to a substituted benzene with $–NH_2$ group and $–SO_3H$ group[5,6]. This spectrum also confirms the aromatic nature of grown

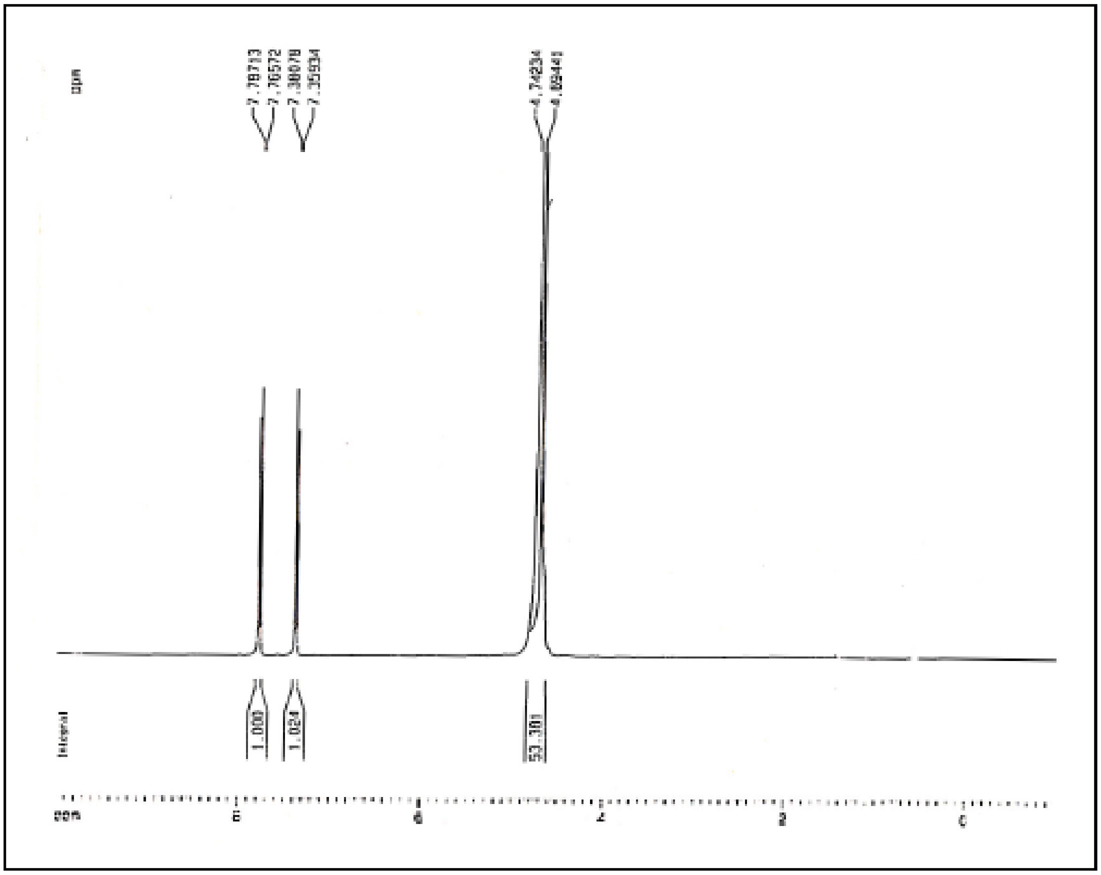

Figure 5. H^1 NMR Spectrum of solution grown sulphanilic acid

crystal. The recorded spectrum is in accordance with the theoretical values . The spectrum also gives on idea about the highly transparent nature of the solution grown sulphanilic acid which is an important requirement for the optical materials.

H^1 NMR Spectral study :

NMR Spectral analysis is used to determine the molecular structure based on the chemical environment of the magnetic nuclei like H^1, C^{13} *etc.*, even at low concentrations. The H^1 NMR Spectrum of sulphanilic acid grown by solution technique, was recorded using a JEOL GSX-400 Spectrometer using D_2O as solvent. The recorded NMR Spectrum of solution grown sulphanilic acid in ethanol-water is shown in figure 5.

In the spectrum the doublet signal at 7.7 ppm is assigned to phenyl protons which are present in ortho – position to sulphonic acid group. The doublet signal at 7.3 ppm is assigned to phenyl protons which are present in ortho-position to amino group. The solvent D_2O peak is merged with the protons of $–NH_2$ and $–SO_3H$ groups. So this peak is highly intense[5,7]. These three distinct peaks clearly reveals that the solution grown sulphanilic acid is para substituted. And it further confirms the purity of solution grown sulphanilic acid.

Conclusion

As it is a compound with non-centre of symmetry, sulphanilic acid has an importance in crystal growth. The solubility of sulphanilic acid in various solvents was determined and finally ethyl alcohol-water was chosen as growth medium. The solubility determination of sulphanilic acid in EtOH – H_2O was carried out. This clearly shows that there is a linear relationship between solubility and temperature.

By knowing the saturation temperature and nucleation temperature, the metastable zone width was determined. The induction period was calculated by repeating the experiments for 1.10, 1.15 and 1.20 supersaturation values at two different temperatures 303 and 308 K . From the calculated induction period value, the interfacial tension was calculated. Using the interfacial tension value, the radius of the critical nuclei (r^*), the free energy change for the formation of a critical nucleus (ΔG^*) and the number of molecules in the critical nucleus (i^*) were calculated at two different temperatures for sulphanilic acid in EtOH – H_2O.

After the determination of solubility of sulphanilic acid in Ethyl alcohol – water mixture it was grown by solution technique adopting slow evaporation method at room temperature. The growth period of sulphanilic acid in EtOH - H_2O is around 15 days. Well defined crystals are collected. To know the transparency of sulphanilic acid, it was subjected to UV-VIS Spectral analysis and found that it is transparent for a wide range. The presence of functional groups $–NH_2$ and $–SO_3H$ in para positions of phenyl ring is confirmed by FTIR Spectral analysis. The purity of grown crystal in also supported by the H^1 NMR Spectral analysis. As sulphanilic acid is transparent for a wide range, it may have several application oriented properties.

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