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# Solidification and thermodynamic parameters of binary faceted organic alloys: Picric acid–Resorcinol system

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## ABSTRACT

With increasing interest in low power high speed microelectronic devices, organic based neutron detectors to replace helium and design of low power controlled explosives, thermodynamic and crystal growth parameters of single and binary organic materials have attracted attention significantly. We have studied Solid–liquid phase equilibrium for Picric acid–Resorcinol system, undercooling, crystallization velocity as function of undercooling, and thermodynamic parameters. The phase diagram shows 1:1 congruent melting compound melting at 374.9 K along with two eutectics which melt at 360.4 and 369.3 K. The linear velocity of crystallizations at different undercoolings followed the  $v=k(\Delta T)^n$  equation, where  $v$  is the crystallization velocity,  $\Delta T$ , is the undercooling,  $k$  and  $n$  are constant. To understand the nature of molten liquid, excess Gibbs free energy, excess entropy, and excess enthalpy have been calculated from the measured values of heat of fusion and specific heat. FT-IR spectral studies indicated the formation of H-bond in the eutectic mixtures. The eutectics and congruent melting compound were investigated by X-ray diffraction technique and scanning electron microscopy. Microstructural studies were made in the presence and absence of impurities.

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## 1. Introduction

Organic crystals have been studied since past half century [1–4] as the model materials to test the validity of several diffusion model solidification theories for eutectics and dendrites. Due to low melting temperature and transparency, these systems have played very important roles in enhancing the faceted and non-faceted materials. Recently faceted organics have attracted interest as potential nonlinear optical materials for frequency conversion and have high, electro-optic coefficient. In addition, because of high cost Helium based detectors; organics has been suggested as an excellent alternatives. In spite of great interest in applications, single crystals of faceted and nonlinear organics have been of great challenge due to lack of solidification and thermodynamic parameters and availability of high purity source materials. Solid–liquid equilibrium (SLE) and thermodynamic parameters provide valuable information about casting, modelling of crystal growth and fabrication, crystal growth and design. Synthesis and characterization of the binary and multinary materials with special features having low cost and high performing devices require more attention for light emitting diodes (LEDs) and fluorescent probe type applications [5–14]. Transparency of these organic

substances and their alloys helps in identifying defects and hence performance generated during growth and fabrication. A direct relationship between microstructure and performance of material can be established and parameters can be changed to achieve better material and hence devices. Further organic alloys and compounds can be prepared through green routes [15,16].

In the present paper the phase diagram study of Picric acid (P) and Resorcinol (R) system have been studied, where congruent melting compound (CMC) with two eutectics are formed. Thermal behaviour of the eutectics has been studied by DSC measurements. Excess thermodynamic functions such as  $G^E$ ,  $S^E$  and  $H^E$  have been calculated from the heat of fusion determined by DSC studies. Linear velocity of crystallization, mechanical properties and microscopic studies have also been made.

## 2. Experimental procedure

### 2.1. Materials and purification

As supplied Picric acid (P) (MERCK) with assay 98.0–99.0% and Resorcinol(R) (RANKEM) with assay 98.0% were further purified by repeated crystallization using distilled water and purity of both the compounds was checked by determining their melting points. The melting points of P and R were found to be 394.3 K (395.2 K

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literature value) [17] and 382.25 K (383.2 K literature value) [18] respectively.

## 2.2. Phase diagram studies

Phase diagram of Picric acid–Resorcinol binary system was determined by preparing the mixtures of different compositions and measuring melting temperatures as described earlier [19]. In this method, mixtures of different compositions were prepared by weighing the two components. About 1.0 g of each mixture was taken in a glass test tube. The tube was sealed in order to prevent the evaporation of the components on heating. The tube was kept in an oil bath maintained at a temperature slightly higher than the melting temperature of the components in order to ensure complete melting of the components. The melt was taken out from the oil bath, shaken well and chilled in ice-cold water. The heating and quenching process was repeated four times. Finally, the tube was broken and the solid mass was crushed in to a fine powder in an agate mortar. This process was adopted for each sample differing in composition. The thaw and true melting temperatures of mixtures of different mole fractions were recorded with the help of a precision thermometer within the accuracy of  $\pm 0.1$  °C. Each temperature was measured three times. The melting points of different mixtures with mean deviations are recorded in Table 1. In the same table thaw points are also given.

## 2.3. Measurements of under-cooling temperature

The under-cooling temperatures of different mixtures were determined by the method similar to that described by Rastogi and Verma [20]. 0.2–1 g mass of the pure components and their mixtures of different composition were taken in clean glass tubes. Glass-tubes were sealed and immersed in liquid paraffin oil bath maintained at a temperature slightly above their melting temperatures. After complete melting of the material, the oil bath temperature was allowed to cool slowly but at a constant rate. The formation of first nuclei was noticed with the help of a magnifying glass and the temperature was noted. Each experiment was repeated at least 3 to 4 times. The difference between the true melting temperature and this temperature gave the under-cooling temperature. The under-cooling values of different mixtures of Picric acid–Resorcinol system are also recorded in Table 1.

## 2.4. Determination of linear velocity of crystallization

Linear velocity of crystallizations of the pure components, the addition compound and the two eutectics, were determined at different under-cooling temperatures employing the method as described earlier [21]. The measurements were made in a cleaned U-shaped Pyrex glass-tube of length 10–11 cm and diameter 0.5 cm. The tube was filled with the solid components (powder) and kept in an oil thermostat maintained at a temperature slightly higher than the melting temperature of the individual component. A seed crystal was added from one side of the tube. On adding the seed crystal, crystallization started. The time required for crystallization for a definite length in the tube was recorded. Each measurement was repeated three times and performed for the pure components and all the mixtures.

## 2.5. Powder X-ray diffraction

Powder X-ray diffraction patterns for the pure components, addition compound and the eutectics were recorded using a computerized X-ray diffractometer (Bruker AXS D8 Advance).

**Table 1**  
Temperature–composition data for the P–R congruent system.

$X_p$	Solidus temperature ( $T_s$ ) (K)	Liquids temperature ( $T_L$ ) (K)	Temperature at which first nuclei appear (T) (K)	$\Delta T_{ij} = T_L - T$ (K)
0.0000	–	382.25 $\pm$ 0.0	368.35 $\pm$ 0.0	13.9
0.0465	360.45 $\pm$ 0.0	379.95 $\pm$ 0.0	362.85 $\pm$ 0.0	17.1
0.1098	360.35 $\pm$ 0.0	376.15 $\pm$ 0.0	359.35 $\pm$ 0.0	16.8
0.1688	360.45 $\pm$ 0.0	372.35 $\pm$ 0.0	352.15 $\pm$ 0.0	20.2
0.2466	360.35 $\pm$ 0.0	367.15 $\pm$ 0.0	347.45 $\pm$ 0.0	19.7
0.2639	360.35 $\pm$ 0.0	364.75 $\pm$ 0.0	343.65 $\pm$ 0.0	21.1
0.2857 <sup>a</sup>	–	<b>360.35 <math>\pm</math> 0.0</b>	338.25 $\pm$ 0.0	22.1
0.3043	360.35 $\pm$ 0.0	364.55 $\pm$ 0.0	342.25 $\pm$ 0.0	22.3
0.3188	360.35 $\pm$ 0.0	368.15 $\pm$ 0.0	347.55 $\pm$ 0.0	20.6
0.4127	360.45 $\pm$ 0.0	373.25 $\pm$ 0.0	356.75 $\pm$ 0.0	16.5
0.5000 <sup>b</sup>	–	<b>374.95 <math>\pm</math> 0.0</b>	361.45 $\pm$ 0.0	13.5
0.5254	369.25 $\pm$ 0.0	374.55 $\pm$ 0.0	358.85 $\pm$ 0.0	15.7
0.5517	369.25 $\pm$ 0.0	374.15 $\pm$ 0.0	359.25 $\pm$ 0.0	14.9
0.5893	369.35 $\pm$ 0.0	373.65 $\pm$ 0.0	357.15 $\pm$ 0.0	16.5
0.6296	369.25 $\pm$ 0.0	372.15 $\pm$ 0.0	356.55 $\pm$ 0.0	15.6
0.6604	369.25 $\pm$ 0.0	370.35 $\pm$ 0.0	352.25 $\pm$ 0.0	18.1
0.6792 <sup>c</sup>	–	<b>369.25 <math>\pm</math> 0.0</b>	349.75 $\pm$ 0.0	19.5
0.8125	369.45 $\pm$ 0.0	379.15 $\pm$ 0.0	362.15 $\pm$ 0.0	17.0
0.8936	369.25 $\pm$ 0.0	384.95 $\pm$ 0.0	371.65 $\pm$ 0.0	13.3
1.0000	–	394.35 $\pm$ 0.0	382.55 $\pm$ 0.0	11.8

<sup>a</sup>  $E_1$ .

<sup>b</sup> Addition compound composition.

<sup>c</sup>  $E_2$ .

## 2.6. FT-IR spectral studies

Fourier transform infrared spectra of the pure components, addition compound and the eutectics were recorded in the spectral region of 400–4000  $\text{cm}^{-1}$  in KBr phase with the help of Thermo Nicolet, Avatar 370 instrument.

## 2.7. Determination of heat of fusion

The heat of fusion of the pure components, eutectics and the addition compound were determined by differential scanning calorimeter (METTLER STAR<sup>®</sup> SW 8.10) under nitrogen atmosphere. A sample of about 5 mg was taken in an aluminium pan and heated at a rate of 5 °C/min up to a temperature of 250 °C.

## 2.8. Mechanical properties

In order to determine the mechanical strength of the components and the eutectics, samples were prepared by a method described earlier [7]. The samples were melted in uniform cylindrical glass-tubes in paraffin oil bath. Once the sample was completely melted, the glass tube was taken out from the oil bath and the same was placed vertically in an ice bath. After complete solidification of the sample, the glass-tube was taken out from the ice bath and glass was slowly scrapped off to give a solid cylindrical shaped sample. The cylindrical sample was then placed horizontally supported by iron stand at the ends. A small pan was hung in the middle of the cylindrical sample with the help of a metallic wire. A known weight was kept in the pan. The weight was slowly increased by additional weights in the pan. The weight at which the sample broke in the middle was recorded. The experiment was repeated for a minimum of three to four times for each individual sample taken during the present investigation. The modulus of rupture ( $\sigma_{fs}$ ) of the materials was computed by using Eq. (1) [22].

$$\sigma_{fs} = (F_f L / \pi R^3) \dots \quad (1)$$

where,  $F_f$  is the load at fracture,  $L$  is the length of the cylindrical sample and  $R$  is the radius of the sample.

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