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Review Article

Phase Equilibria and Crystallization Behaviour of Succinonitrile - 8-Hydroxyquinoline Eutectic System

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Abstract

The phase diagram of the Succinonitrile (SCN) – 8-Hydroxyquinoline (8-HQ) system has been studied by the thaw melt method and the results showed the formation of a simple eutectic type phase diagram with eutectic composition at 0.9600 mole fraction of succinonitrile. The flexural strength of the pure components and the eutectic mixture were measured. Microstructural studies of eutectics have shown the formation of a regular structure which change on the additions of impurities. Computer simulation has shown the presence of H-bonding between the two components.

INTRODUCTION

A eutectic mixture is a composite material consisting of two or more solid phases, which are in equilibrium with a single liquid phase. Simple eutectic systems have been widely used as model system. In modern technology there is a great demand of low cost, superior quality and high- strength materials. In recent years, it is found that composite materials exhibit superior mechanical properties [1-12]. During the last few years, the phase diagram, solidification behaviour, undercooling, microstructures and other properties of binary organic systems forming eutectic mixtures have been studied. However, different systems under different conditions exhibit different properties. The properties of such materials depend on the evolution of their microstructures. In this paper phase diagram of Succinonitrile - 8-Hydroxyquinoline system showing the formation of simple eutectic mixture and microstructural behavior during crystallization have been discussed.

EXPERIMENTAL PROCEDURE

Purification of materials

Succinonitrile (*Alfa Aesar*)(SCN) was used without any further purification and the melting point was found to be 330.2 K (330.2 K literature value). 8-Hydroxyquinoline (*sd fine*) (8HQ) was purified by repeated crystallization from hot water. The purity of the compound was checked by determining the melting temperature. The melting point of purified 8-Hydroxyquinoline was found to be 348.7 K (345.7-349.2 K literature value).

Phase diagram studies

The phase diagram of the SCN + *8-HQ* system was studied by thaw-melt method [13]. Accurate amounts of SCN and *8-HQ* were weighed in glass tubes to make mixtures of different compositions. The glass tubes were sealed and heated in an oil bath at a temperature slightly higher than the melting temperatures of the components. The melts were shaken well and then chilled immediately in ice-cold water. To prepare homogeneous mixtures, the process of heating and chilling was repeated several times, and finally the tubes were broken. The solidified mass was crushed into fine powder. The melting points of the mixtures were determined with the help of a precision mercury thermometer which could read up to 0.1 °C. The melting points were plotted as a function of composition to obtain the phase diagram (Figure 1). The thaw points and the melting points of different mixtures are given in Table 1.

Undercooling measurements

Undercooling measurements of SCN- 8-HQ system was investigated in clean glass tubes. The glass tubes were sealed and immersed in liquid paraffin oil bath maintained at a temperature slightly above the melting temperatures of the mixtures to destroy any germ nuclei. The temperature at which the first crystallite appeared was noted. In favorable cases; the phase separation can be suppressed completely by increased cooling. The under cooling values of different mixture of SCN - 8-HQ systems were recorded (Table 1) and are also plotted in Figure 1.

Micro structural studies

Small quantity of fine powders of SCN, 8-HQ and Eutectic mixture were placed on separate glass slides which were then kept in an oven at a temperature slightly above their melting temperatures. The melts were crystallized by moving separate glass cover slips gently pressed over them in one direction. The microphotographs of the crystallized fronts were recorded with the help of digital camera attached to an optical microscope (Olympus Chi20). Effect of 0.1 wt% impurities on the microstructural behavior was also studied.

Mechanical strength

SCN, 8-HQ and Eutectic mixture were melted in uniform cylindrical glass tubes and then dropped vertically into ice bath maintained at ~0°C. After complete solidification of the sample, the glass tubes were slowly scrapped off to give solid cylindrical shaped samples. These cylindrical samples were placed on the stand. A small container was hung in the middle of the cylindrical sample with the help of a metallic wire. In these test, the rupture observations were made visually watching the fracture process. The modulus of rupture (σ_{fs}) of the materials was calculated using Eq. (1) [14];

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

Where F_f is the load at fracture; L is the distance between support points; and R is the specimen radius.

Computer simulation

The computer simulation studies on SCN-8HQ system were carried out with the help of GAUSSIAN 03 suite of programs. The geometries of SCN-8HQ eutectic system, SCN and 8HQ were optimized by density functional theory (DFT) using DFT (B3LYP/6-31 G(d)+ZPVE (B3LYP/6-31 G(d)) functions.

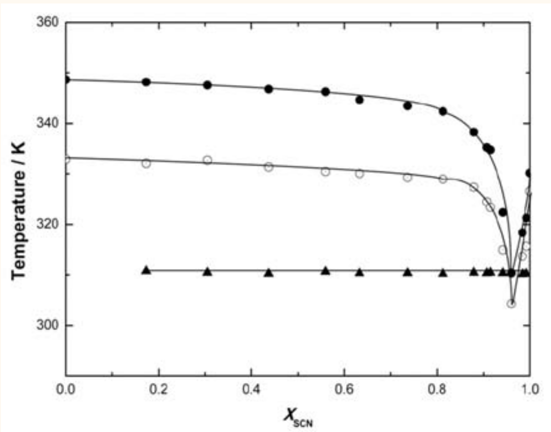

Figure 1 Temperature-composition diagram for SCN-8HQ Eutectic system: thaw melting; ▲, solidus temperature; ●, liquidus temperature; ○.

Table 1: Temperature- composition data for SCN-8HQ system.

X_{SCN}	Solidus Tempera-ture (T_S) (K)	Liquidus tempera-ture (T_L) (K)	Temperature at first nuclei appear (T) (K)	$\Delta T = T_L - T$ (K ± 0.0)
0.0000	--	348.65	332.85	15.8
0.1733	310.75	348.15	332.05	16.1
0.3049	310.45	347.55	332.65	14.9
0.4368	310.25	346.75	331.35	15.4
0.5591	310.65	346.25	330.45	15.8
0.6327	310.35	344.65	330.05	14.6
0.7358	310.35	343.45	329.25	14.2
0.8125	310.25	342.35	328.95	13.4
0.8793	310.45	338.25	327.35	10.9
0.9068	310.35	335.25	324.45	10.8
0.9421	310.35	322.35	314.95	7.4
0.9600[a]	--	310.35	304.25	6.1
0.9839	310.15	318.35	313.65	4.7
0.9919	310.25	321.25	315.65	5.6
1.0000	--	330.15	326.55	3.6

[a] Eutectic

RESULT AND DISCUSSION

Phase diagram

The phase diagram of the SCN - 8-HQ system has been studied by thaw melt method and represented in the form of a temperature composition curve in Figure 1. The curve shows the formation of eutectic type phase diagram. The Eutectic mixture is formed at 0.9600 mole fraction of Succinonitrile and melts at 310.4 K. Since in the eutectic mixture, SCN is in larger proportion, the formation of eutectic can be represented by Figure 2.

At eutectic point two solids (SCN and 8-HQ) are in equilibrium which can be considered as a eutectic reaction as given below.

$$Eutectic \xrightarrow{Cooling} \text{SCN + 8-HQ}$$

Undercooling temperatures for pure components and all the compositions are also given in the Table 1.

Microstructural studies

Various physical properties of the eutectic mixtures depend on their microstructures and the crystallization behaviour could be explained in a better way with the help of their microstructure. A prediction of microstructure of eutectics can be made from Spengler's equation [15]

$$\theta = \frac{T_1 - T_E}{T_2 - T_E}$$

where, T_1 and T_2 are the melting temperature of low melting and high melting components, respectively; and T_E is the eutectic temperature. The normal eutectics are formed when θ lies between 0.1 and 1.0 but if it lies between 0.01 to 0.1 anomalous structures are obtained and when it has values less than 0.01, divorced structures are formed. In the present case the value of θ is 0.52 and hence the eutectic is expected to have normal structure. Microstructures of SCN, 8-HQ and Eutectic in the presence and absence of impurities are shown in Figure 3. Microstructure of SCN (Figure 3 (a)) shows fractal type structure

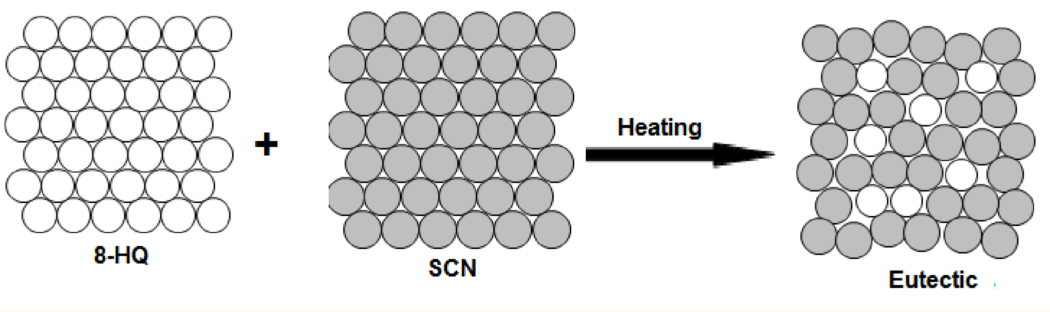

Figure 2 Representation of formation of eutectic.

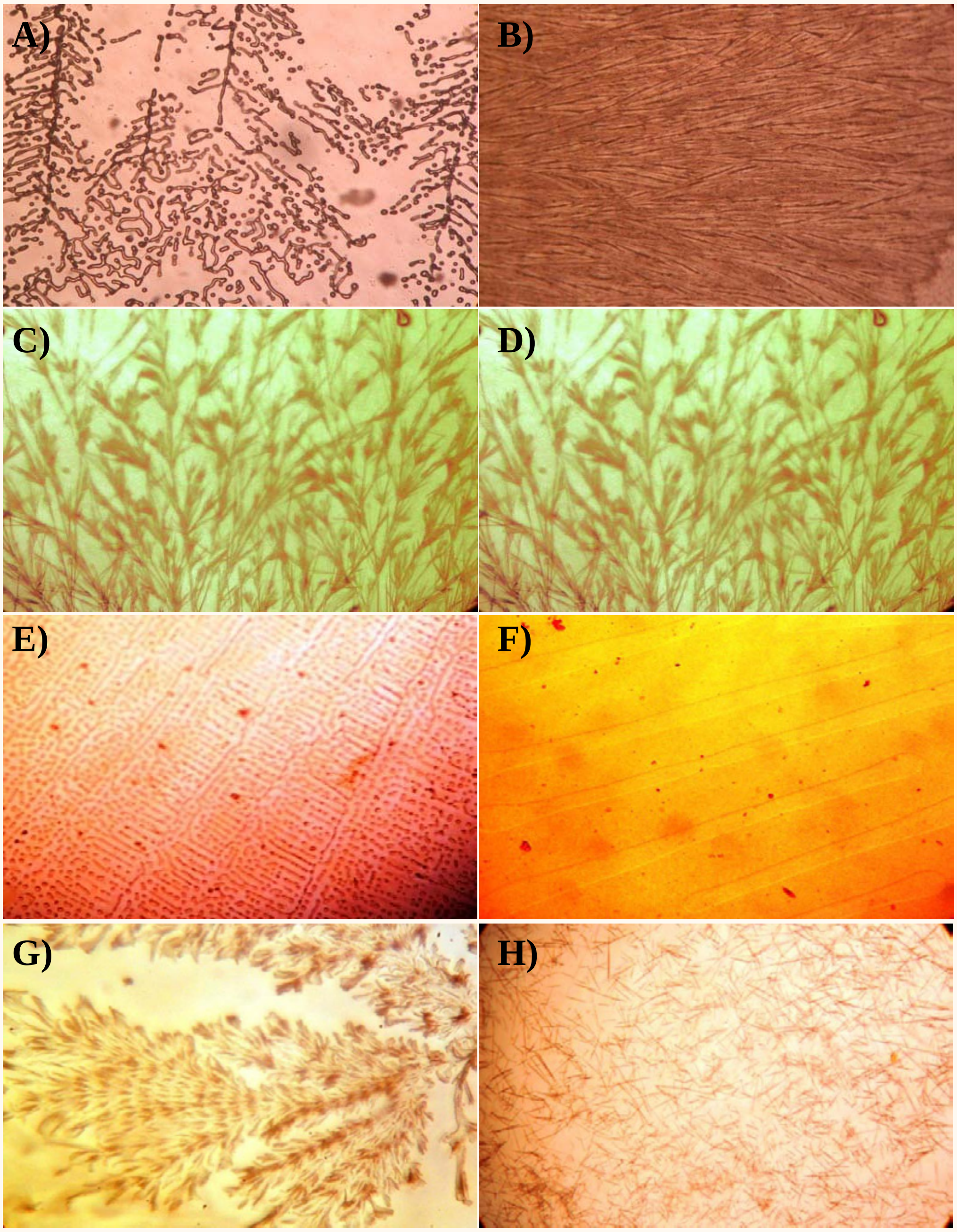

Figure 3 Microstructures: (a) SCN, (b) 8-HQ, (c) Eutectic, (d) Eutectic + Phenothiazene, (e) Eutectic + Chlorobenzoic acid, (f) Eutectic + 2-Amino Pyridine, (g) Euetctic + Benzoic acid, (h) Euetctic + 8-hydroquinone.

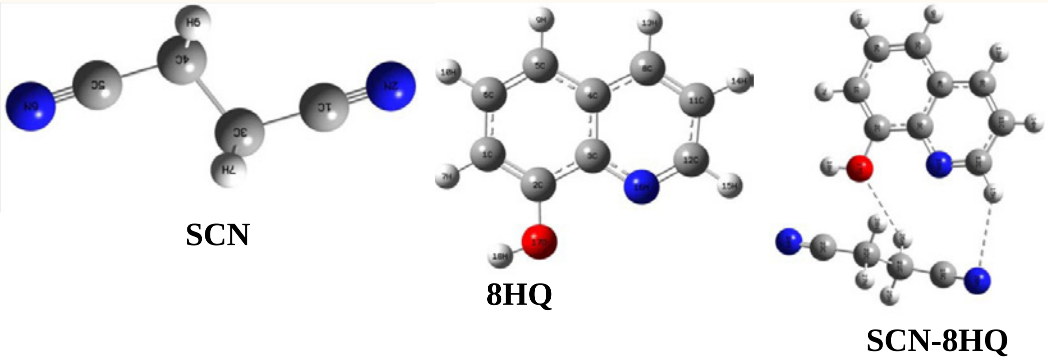

Figure 4 Optimized Geometries.

whereas the microstructure of 8-HQ (Figure 3 (b)) shows fibrous structure. Microstructure of Eutectic is shown in (Figure 3 (c)). The microstructure of eutectic is entirely different than that of pure components. It has a regular structure. In the presence of Phenothiazene as an impurity in Eutectic (Figure 3d), the microstructure is changed to mosaic structure. Chlorobenzoic acid as an impurity modifies the microstructure of the eutectic into a very regular structure (Figure 3e). In presence of 2-aminopyridine as an impurity the microstructure of the eutectic changed to a lamellar structure (Figure 3f). Benzoic acid and 8-HQ (Figures. 3g & 3h) alters the microstructure of the eutectic. It seems that the kind of interaction in the system influences the formation of critical nuclei which in turn determines the microstructure. Impurities alter the interactions and hence change the microstructures.

Strength measurements

Mechanical strength measurements of SCN, 8HQ and Eutectic are given in Table 2, and the value for Eutectic is higher than that of pure components. This shows that the eutectic of SCN and 8-HQ is more aligned leading to better flexural strength.

Optimized geometry

The computer simulation studies performed at the DFT level show the formation of H-bond between the two components via O------H and N-------H. The interaction energy between the two components was found to be 38.71kJ/mol showing the existence of the hydrogen bond. The optimized geometries of the components and the mixture are shown in Figure 4.

CONCLUSION

Phase equilibria of SCN - 8-HQ system have shown the formation of eutectic mixture. Microstructural investigations have indicated that the microstructures change from system to system and modified in the presence of impurities. Flexural strength of eutectic is found higher than those of the components.

Table 2: Values of modulus of rupture of SCN-8HQ system.

Components	Modulus of Rupture M Pa
SCN	0.5344 ± 0.08
8HQ	2.0611 ± 0.05
Eutectic	2.8001 ± 0.04

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