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Chemistry of Organic Eutectics and Molecular Complexes: Naphthalene-Picric Acid and Anthracene-Picric Acid Systems.

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Crystallization behavior and nature of complexation have been studied for the napthalene-picric acid and anthracene-picric acid systems. Phase diagrams were determined experimentally to get the exact compositions of eutectics and molecular complexes. Data on crystallization velocity obey the relation $V = u(\Delta T)^n$ where ΔT is undercooling, u and n are constant. Experimental values of heats of fusion do not go in subordination with mixture law. Infra-red and ultraviolet-visible spectral studies indicate the charge transfer interactions in both systems.

1. INTRODUCTION

The chemistry of eutectics has been a field of active investigation[1–3] during the recent past due to unusual physical properties of eutectics not normally shown by the parent components. The metallic eutectics constitute an interesting area of research in metallurgy, where as nonmetallics particularly organic eutectics have been of interest to a

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number of research groups[4-6] due to low transformation temperature and transparency. Most of the systems studied in the past were simple type, however, there are other cases of phase-diagram in which two components form a molecular compound with congruent and incongruent melting points. The formation of such molecular compounds had been established on the basis of phase diagrams which exhibit a characteristic maximum surrounded by two eutectics (clear maximum in the case of congruent melting compounds but apparent maximum in the case of incongruent melting compounds) corresponding to the stoichiometry of the molecular compounds formed. While simple eutectics may be considered as mechanical mixtures, the systems with molecular compounds may definitely not be so, owing to the molecular interactions, which impart them directional characteristics in solid-state. With a view to throw the light on crystallization mechanism, and nature of interactions we have chosen naphthalene-picric acid and anthracene-picric acid systems. Phase diagrams, crystallization rates, heats of fusion, and spectral studies were made for these two systems.

2. EXPERIMENTALS

2.1. Materials and purification: Naphthalene (BDH, Analar), anthracene (BDH, Analar), and picric acid (BDH, L.R.) were further purified by fractional crystallization and sublimation. Naphthalene was recrystallized from cyclohexane and anthracene from ethanol and benzene. Picric acid was purified by fractional crystallization from ethanol. The melting points of pure naphthalene, anthracene, and picric acid were 80.2, 216.5 °C respectively.

2.2 Phase-diagram study: Various compositions of naphthalene-picric acid and anthracene-picric acid covering the entire range of concentration in molefraction were prepared by weighing the appropriate amounts of the two components. The weighed components were thoroughly mixed and subjected to a number of melting and chilling in ice in a sealed glass test tube. The samples were taken out by breaking the tube and were homogenized by grinding in a mortar with a care to avoid moisture and any contamination at every step. The melting and thaw temperatures were determined by the method described in reference 6.

2.3 Determination of linear velocity of crystallization: The linear velocities of crystallization of parent components, eutectics and molec-

ular complexes were determined by following the procedure of Rastogi, *et al.*[7]

2.4 Heats of fusion measurements: The heats of fusion of pure components, eutectics, and 1 : 1 complexes were determined by a differential thermal analyser.

2.5 Spectral Studies: UV visible spectra of pure components, eutectics and 1 : 1 complexes were recorded on Cary-spectrophotometer in nujol mull. The infrared spectra of these systems were recorded in the region 4000–250 cm^{-1} on a Perkin-Elmer 621 instrument.

3. RESULTS AND DISCUSSION

3.1 Phase-diagram and thermochemistry; solid-liquid equilibrium data are plotted in Figures 1 and 2 for naphthalene-picric acid and anthracene-picric acid system. It is evident that in both cases a maximum is surrounded by two eutectics and a molecular complex of 1 : 1 stoichiometry with congruent melting is formed. The two eutectics (first being marked as E_1 and the second E_2) in case of naphthalene-

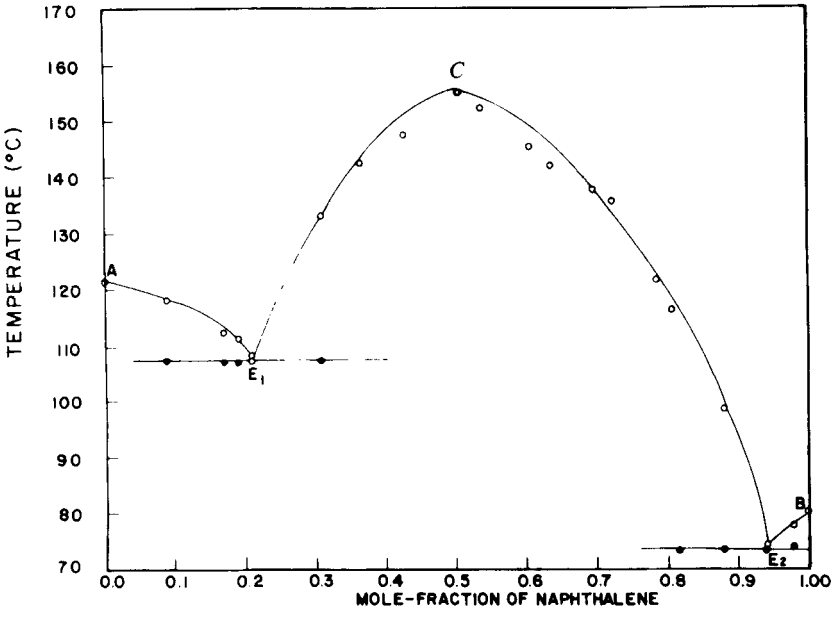

FIGURE 1 Phase-diagram for naphthalene-picric acid system. ○ Melting temperature ● Thaw temperature.

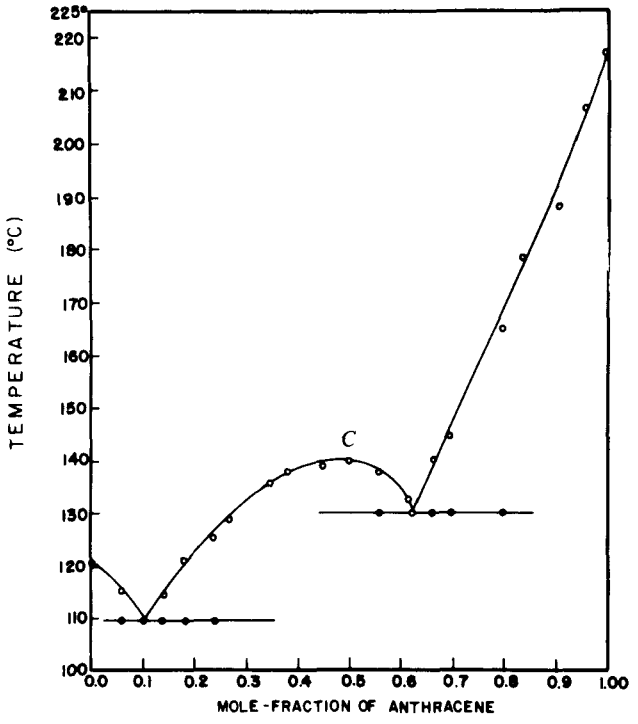

FIGURE 2 Phase-diagram for anthracene-picric acid system. ○ Melting temperature ● Thaw temperature.

picric acid system have compositions 0.2132 and 0.9405 in model-fractions of naphthalene, whereas the corresponding compositions in the case of anthracene-picric acid system are found to be 0.1017 and 0.6250 in mole-fractions of anthracene respectively. Thaw temperatures to E_1 and E_2 in the case of naphthalene-picric acid system are 107.5°C, 73.5°C, whereas, the corresponding eutectics in the case of anthracene-picric acid system have thaw temperatures 109.5°C and 130.°C. The melting points of the resulting complexes in the case of naphthalene-picric acid system and anthracene-picric system are found to be 155.0°C and 140.°C respectively. From the phase diagrams it can be inferred that both the systems have molecular compounds capable of existing as a solid compound in equilibrium with a liquid of same composition. From the first eutectic point E_1, onwards, on addition of the second component, the melting point again rises, attains a maximum at C, where the composition of liquid and solid phases are identical. This maximum temperature corresponds to this

congruent melting point of the addition compound. A maximum point on the liquids, a sharp meeting point of solidus and liquidus, a good length of a middle branch of the curve, and existence of an eutectic point on either side of the maximum provides an information about the large stability of the resulting molecular compound.

The results of heats of fusion measurements will be discussed in detail in reference 8. Preliminary analysis shows that mixture law is not obeyed for the eutectics as well as complex. The roughness parameter ($\Delta S_f/R$) is much greater than 2 for naphthalene, anthracene and picric acid. This indicates that these systems belong to faceted-faceted class.

3.2 Crystallization kinetics: The experimental data are plotted in the form of $\ln V$ vs $\ln \Delta T$ in Figures 3 and 4 for the pure components, eutectics and 1 : 1 complexes. Straight lines were obtained indicating

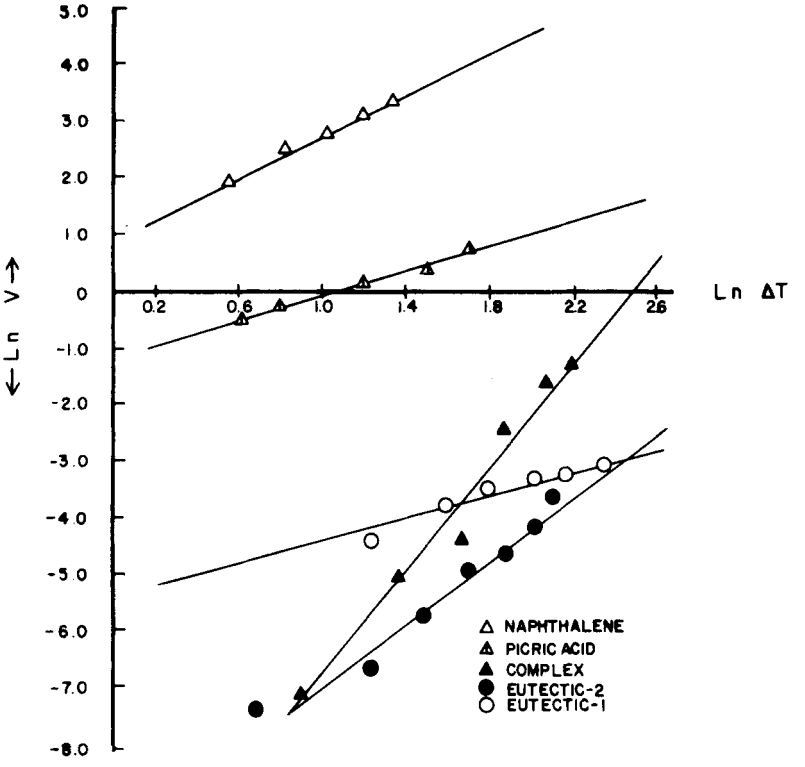

FIGURE 3 Plot of $\ln V$ vs ΔT for naphthalene-picric acid system.

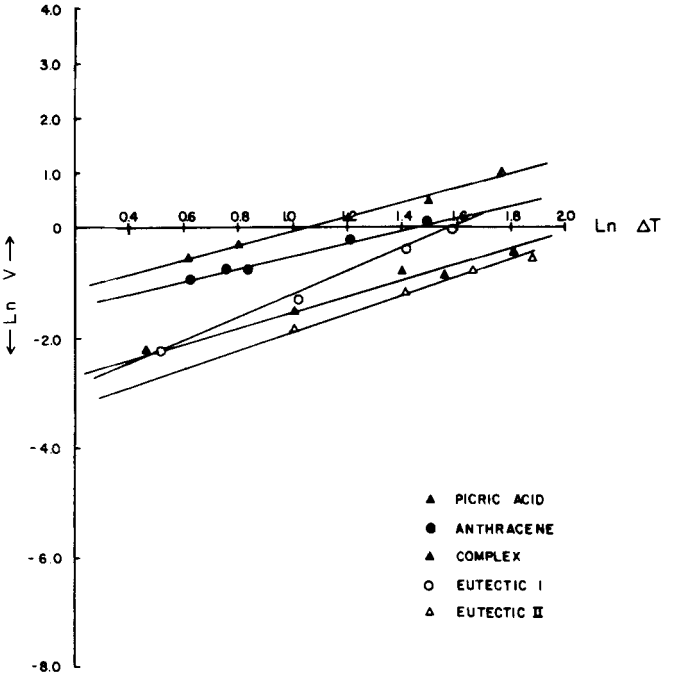

FIGURE 4 Plot of $\ln V$ vs $n\Delta T$ for anthracene-picric acid system.

the validity of relationships;

$$V = u(\Delta T)^n \tag{1}$$

where u and n are constant. The experimental values of these constants are given in Table I. The crystallization velocities of parent components are always higher than eutectics as well as 1 : 1 complex. In naphthalene-picric acid systems, parent components eutectics as well as 1 : 1 complex. In naphthalene-picric acid systems, parent components eutectics and complex have approximately the same under cooling value. For eutectic E_1 (0.213 mole-fraction of naphthalene), crystallization starts with the nucleation of 1 : 1 complex. This continues until the surrounding liquid becomes rich in picric acid and it starts nucleating. Similarly, for eutectic E_2 (0.940 mole-fraction of naphthalene), 1 : 1 complex, and naphthalene act like parent components. Naphthalene melts at very low temperature in comparison to 1 : 1 complex, again there is possibility of nucleation of 1 : 1 complex first, followed by nucleation of naphthalene. This mechanism of alternate nucleation explains the lower velocity of eutectics than parent components and 1 : 1 complex. In anthracene-picric acid sys-

TABLE I

Values of n and u

Material	n	u (mm/sec deg)
Naphthalene	1.88	1.514
Picric Acid	1.56	0.273
Anthracene	1.39	0.235
Naphthalene-picric acid Eutectic I	1.37	0.005
Naphthalene-picric acid Eutectic II	2.42	0.00005
Naphthalene-picric acid complex	3.75	0.00002
Anthracene-picric acid Eutectic I	2.15	0.058
Anthracene-picric acid Eutectic II	1.71	0.039
Anthracene-picric acid complex	1.55	0.064

tem, eutectic E_1 (0.102 mole-fraction of anthracene) follows the same trend. When eutectic melt undercools 1 : 1 complex usually nucleates on picric acid. The phases grow side-by-side and the velocity of eutectic lies between picric acid and 1 : 1 complex. The second eutectic (0.625 mole-fraction of anthracene) crystallizes with the nucleation of anthracene followed by 1 : 1 complex. The possibility of alternate nucleation is very low due to the large differences in melting temperatures of anthracene and 1 : 1 complex. This explains why the linear velocity of crystallization is lower for E_2 than those of anthracene and 1 : 1 complex.

3.3 Spectral Studies: Eutectic-1 of naphthalene-picric acid has no peak around 650 nm while eutectic-2 has a distinct band at 650 nm. In 400–300 nm range eutectic-1 has a distinct peak at 395 nm and 360 nm and shoulders at 345 and 375 nm while eutectic-2 has a diffused broad band in the region. This may be due to higher complex concentration in the second eutectic region than the first eutectic and due to the blue shift on the high energy side of the pure component band. Similarly, for anthracene-picric acid system, eutectic-1 has a shoulder at 500 nm while eutectic-2 has the same at 510 nm. Anthracene-picric acid complex has two shoulders at 510 nm and 450 nm. Also, there is significant intensity variation on the low energy peaks of the pure components between 300–400 nm region. This is due to the substantial effect of complexation on these transitions.

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