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The Phenanthrene/Anthracene–Picric Acid System

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The phase relations in the phenanthrene/anthracene–picric acid system have been determined by calorimetry and X-ray diffraction. Four series of solid solutions occur in this system: the terminal solid solutions P and A, which are based on the parent picrate lattices, and the I and II solutions, which are based on the incongruently-melting ternary compounds. A eutectic is observed at about 47 mol% anthracene and at 124 °C. Enantiotropic transitions appear at about 76, 103, and 120 °C in the I solid solution and at about 80, 103, and 120 °C in the II solid solution. The Gibbs energy of formation from the solid component compounds has been estimated as −2.04, −1.67, −1.21, and −0.68 kcal/mol for the stable forms at the room temperature of the phenanthrene picrate, the I solid solution (at 34.58 mol% anthracene), the II solid solution (at 58.96 mol%), and the anthracene picrate respectively. The two transitions in the phenanthrene picrate have been shown to be easily detectable by recording the electrical resistivity as a function of the temperature.

The mutual solid solubility in many pairs of molecular complexes has been examined by Rheinboldt and Senise and by Lower;[1,2] however, no determination of the phase boundaries in the solids has been reported except for phenanthrene/anthracene–*s*-trinitrobenzene. In connection with our finding of the marked effects of impurities on an enantiotropic transition at 77 °C in phenanthrene picrate,[3,4] we have determined the phase diagram of the phenanthrene/carbazole–picric acid system. As part of our general interest in the physical properties of solid molecular complexes, we decided to study further the phase diagram of a binary system with phenanthrene picrate as one component. The system chosen was phenanthrene/anthracene–picric acid because a comparison of it with the phenanthrene/anthracene–*s*-trinitrobenzene system studied by Lower seemed to be interesting.

Experimental

Materials. Phenanthrene, Eastman white label, was purified according to the method reported by Feldman *et al.*[5] and then zone-refined. Pure anthracene was obtained by the reduction of anthraquinone prepared starting from benzene and phthalic anhydride. Picric acid, Wako special reagent, was twice recrystallized from ethanol. The picrate of the former hydrocarbon was crystallized from methanol and that of the latter, from carbon tetrachloride, as has been described by Kofler.[6] They were mixed together in various ratios and then fused in a small test tube by heating in an oil-bath for a short time. The melt was well shaken and then rapidly cooled. Finally the samples were kept at room temperature for various periods of time. Over forty samples were prepared for the examinations.

Measurements. Calorimetric curves up to the thaw points were recorded on a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C, at a heating rate of 3 °C/min. The heats of transitions were estimated by comparing the peak areas with that for the transition in hexamethylbenzene, which is known to take place at 110.6 °C with ΔH=0.422 kcal/mol.[7] The melting points were visually measured with a magnifying lens and a polarizer. X-Ray measurements on powdered samples were made with a Toshiba recording diffractometer, Model ADG-301, with filtered copper radiation. In order to examine the powder pattern at various temperatures, the sample was mounted on an aluminum plate with a 20 W heater attached to the other side. The temperature of the plate was controlled with the aid of an autotransformer and was monitored by means of a copper-constantan thermocouple.

The approximate values of the Gibbs energy of formation at 25 °C from the solid-component compounds (ΔG_f, kcal/mol) were determined from the $\Delta G_f = RT\cdot\ln(c_2/c_1)$ relation, where c_1 (mol/l) is the concentration of undissociated picric acid in the saturated aqueous solution of picric acid and where c_2 is its concentration in equilibrium with a solid complex and solid hydrocarbon.[8] The assumption is made that the solutions are sufficiently dilute for the activities to be proportional to the concentrations. The total concentrations of picric acid (C, mol/l) in these solutions were measured by the spectrophotometric method and also by the gravimetric method.

The electrical resistivity of the hydrocarbon picrates was measured on pressed pellets by the two-probe method. The pellet and its holder were accommodated in a brass cylinder and were slowly heated with an electric furnace. During this process, the temperature of the holder was recorded on the X-axis of a Yokogawa X–Y recorder, Type 3078, and the current was amplified by a Keithley 3010 operational amplifier on the Y-axis.

Results and Discussion

Phase Diagram. If only the thaw-point-melting-point method of Rheinboldt was employed,[9] one would conclude that this system is of the V type in the Roozeboom classification of two-component solid solutions,[10] as are the phenanthrene/anthracene–*s*-trinitrobenzene and phenanthrene/carbazole–picric acid systems.[2,4] The eutectic is located at about 47 mol% anthracene and at 124 °C. Actually, the phase relations in this "immiscibility region", extending from about 20 to 80 mol% anthracene, are not at all simple. The appearance of two solid solutions is shown by X-ray diffraction patterns distinctly different from those of the terminal solid solutions. Although peritectics cannot be located in Fig. 1, these two solid solutions based on new ternary molecular complexes appear to melt incongruently. Therefore, the whole diagram is a combination of two diagrams of the IV type and

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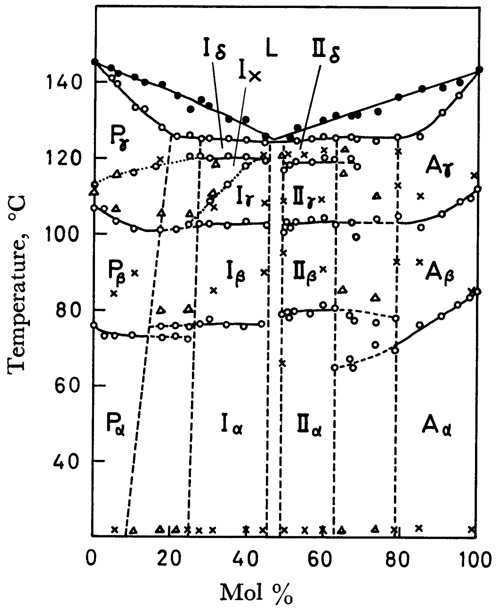

Fig. 1. The phenanthrene/anthracene–picric acid phase diagram: × single phase by X-ray diffraction, △ two phases by X-ray diffraction.

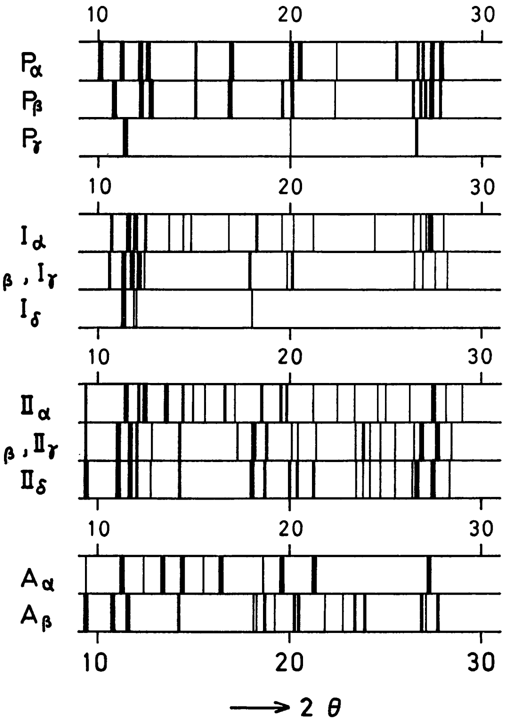

Fig. 2. X-Ray diffraction patterns of the phenanthrene/anthracene–picric acid system: the solid solution I at 31.18 mol % anthracene, the solid solution II at 58.86 mol %.

one of the V type in the Roozeboom classification. The solid solutions, I and II, may be regarded as non-stoichiometric compounds.

As was described in our earlier notes,[3,4] two enantiotropic transitions are observed in the P solid solution. The three phases, denoted as P_α, P_β, and P_γ in Fig. 1, can be well distinguished from each other by the X-ray method (see Fig. 2). It must be noted that the pattern given by the P_γ phase is very simple. The change from P_β to P_α is slow, and it becomes slower upon the addition of anthracene picrate;[3] therefore, the P_α phase can be observed up to only 4 mol% with the samples annealed for one week instead of 9 mol%, as is indicated in Fig. 1. After the same period of storage, the samples in the composition range from 4 to 6.5 mol% were shown by X-ray examination to be mixtures of P_α and P_β and only the P_β phase was found between 6.5 and 12 mol%. These observations are in reasonable agreement with the results of calorimetry reported previously.[3] The anthracene-rich solid solution P is metastable. The samples in the composition range from 9 to 12 mol% became mixtures of the P_α and I_α phases upon standing for five months. The P_β phase is gradually transformed into P_γ upon heating when the anthracene picrate is added. The dotted curve indicates the upper limit of the temperature range given by the point of return to the base line of the calorimetric curve. The temperature-dependence of the X-ray diffraction pattern also shows the coexistence of the P_β and P_γ phases over a wide temperature range.

The I solid solution, examined within one week after melting, exhibits only an enantiotropic transition near 120 °C. After the samples have been left at room temperature for three months, the I_α phase, extending from about 25 to 45 mol% anthracene, appears. Upon heating, two more well-separated endothermic peaks are observed at about 76 and 103 °C (see Fig. 1). Although the enthalpy changes at these transitions are comparable, the I_γ phase cannot be distinguished from I_β by X-ray diffraction. In addition, one or two extra peak(s) partially overlapped with the one near 120 °C are detectable below 40 mol% anthracene. The dotted curve in this composition range was drawn on the basis of the point of departure from the base line of the calorimetric curve. The X-ray diffraction also shows that the solid solution above this boundary is heterogeneous. The phase(s) appearing in this region could not be clarified; therefore, the region is denoted as I_x in the diagram. The absence of the transitions from I_α to I_β and from I_β to I_γ, the temperatures of which are close to those of the transitions from P_α to P_β and from P_β to P_γ, in newly-prepared samples can be considered as additional evidence of the appearance of the I solid solution. The range of the solid solution embraces such simple compositions as 2: 5, 1: 2, 2: 3, and 3: 4. For the present, there is no *a priori* reason for preferring any one of the possible compositions.

The II solid solution extends from about 49 to 63 mol% anthracene after storage for several months. Upon heating, three transitions, the temperatures of which are essentially the same as those in the I solid solution, are observed by the calorimetric method. The enthalpy change at the transition from II_β to II_γ is small, and these two phases are not distinguishable from each other by X-ray diffraction. Nevertheless, the recovery of the II_β phase from the II_γ phase is so slow that II_γ and II_δ are the only phases observable if the sample is examined within a day after melting. Qualitatively speaking, the behavior of the II solid

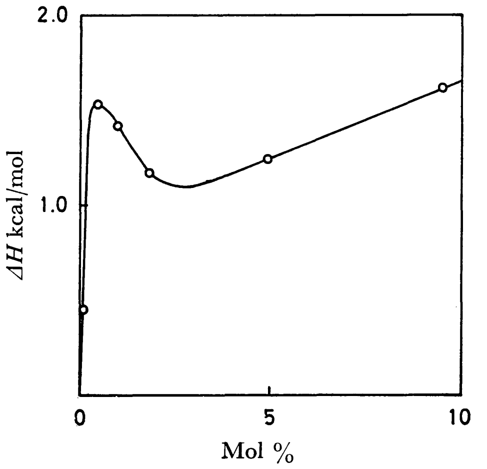

Fig. 3. Heat of the transition from A_β to A_γ plotted against the amount of added phenanthrene picrate.

solution is similar to that of the I solid solution. However, it must be noted that the diffraction patterns observed with the former solid solution are more complicated than those observed with the latter. Possible simple compositions included in the range of solid solution are 1: 1, 5: 4, 4: 4, 3: 2, and so forth.

The limit of the solubility of phenanthrene picrate into anthracene picrate is about 20 mol%. Although only one transition (at 85 °C) is seen in pure anthracene picrate, an additional transition detectable only by the calorimetric method appears in this terminal solid solution. Even the addition of as little as 0.1 mol% of phenanthrene picrate is enough to induce a sizable peak. The amount of the heat of this new transition is plotted against the composition in Fig. 3. The enthalpy and entropy of the transition both reach their maximum values at 0.5 mol% phenanthrene, and then reach their shallow minima around 3 mol%. The transition temperature and the amount of the enthalpy and entropy changes for representative samples of the four series of solid solutions are summarized in Table 1.

Gibbs Energy of Formation. The concentration of picric acid (C) in equilibrium with the solid hydrocarbon picrates and the Gibbs energies of formation (ΔG_f) from their parent solids are collected in Table 2. As naphthalene picrate is the only hydrocarbon picrate for which the Gibbs energy of formation is available in the literature, this picrate was included in our measurements for the sake of comparison. The concentrations given here were spectrophotometrically measured and were in reasonable agreement with those obtained by the evaporation of the solutions to dryness—*e.g.*, 0.0572 mol/l for picric acid and 0.0173 mol/l for the II solid solution. The dissociation constant of picric acid in an aqueous solution is required in order to calculate the concentration of undissociated acid. Four values ranging from 0.196 to 0.60, have been compiled by Kortüm *et al.*[11] Of these, the compilers have considered the value of 0.381 by Halban and Seiler to be most reliable.[12] However, the Gibbs energy of the formation of naphthalene picrate calculated with this constant, −2.44 kcal/mol, is appreciably larger than the value of −2.05 kcal/mol at 20 °C reported by Brönsted,[8] the value of −2.08 kcal/mol at 3 °C reported by Brown from cryoscopic measurements in nitrobenzene,[13] and also the value of −2.07 kcal/mol at 25 °C reported by Bell and Fendley from direct electrometric measurements.[14] On the other hand, the constant determined by Dippy *et al.* gives a value of 2.10 kcal/mol, which is in fair agreement with the above-mentioned literature values. Consequently, the energies in Table 2 were calculated using the latter value, that is, 0.196.[15]

TABLE 1. TRANSITION TEMPERATURES AND ENTHALPY AND ENTROPY CHANGES OF THE REPRESENTATIVE SAMPLES IN THE PHENANTHRENE/ANTHRACENE–PICRIC ACID SYSTEM

Sample		Transitions		
		$\alpha \to \beta$	$\beta \to \gamma$	$\gamma \to \delta$
Phenanthrene picrate	T (°C)	77	106	—
	ΔH(kcal/mol)	1.10	3.10	—
	ΔS(e.u.)	3.1	8.2	—
Solid solution I	T (°C)	76	103	120
(at 31.18 mol%)	ΔH(kcal/mol)	0.66	0.76	0.88
	ΔS(e.u.)	1.9	2.0	2.3
Solid solution II	T (°C)	80	103	119
(at 59.86 mol%)	ΔH(kcal/mol)	2.39	0.06	0.72
	ΔS(e.u.)	6.8	0.16	1.8
Anthracene picrate	T (°C)	85	112[a)]	—
	ΔH(kcal/mol)	3.50	1.53[a)]	—
	ΔS(e.u.)	9.8	4.4[a)]	—

a) With 0.5 mol% of phenanthrene picrate.

TABLE 2. STABILITIES OF SOLID HYDROCARBON PICRATES AT 25°C

Compound	C(mol/l)	$-\Delta G_f$ (kcal/mol)	
		This work	Literature[a)]
Naphthalene picrate	0.00656	2.10	2.05,[8)] 2.08[13)] 2.07,[14)] (2.08)[16)]
Phenanthrene picrate	0.00797	2.04	(2.41)[16)]
Phase I_α (at 34.58 mol%)	0.0116	1.67	—
Phase II_α (at 58.96 mol%)	0.0174	1.21	—
Anthracene picrate	0.0283	0.68	(0.84)[16)]
Picric acid	0.0573	—	—

a) The values in parentheses are for the corresponding *s*-trinitrobenzene complexes.

Hammick and Hutchison have determined the Gibbs energies of formation for ten hydrocarbon-*s*-trinitrobenzene complexes and have noted that the value for the naphthalene complex is very close to that of the corresponding picrate.[16] On the basis of the data of this pair only, they have concluded that there is no very great difference in the stabilities of the solid picrates and the corresponding *s*-trinitrobenzene complexes. Our results are in accordance with their conclusion. However, it may be noted that the relative stabilities are not parallel in these two series. Such an inversion of the relative stabilities of naphthalene and phenanthrene has also been found in the *s*-trinitrobenzene and the trinitrotoluene complexes studied by Hammick and Hutchison.

The values of the Gibbs energy of formation listed in Table 2 indicate that the I_α phase is more stable by 0.10 kcal/mol, while the II_α phase is less stable by 0.03 kcal/mol, than mixtures of the parent picrates. Although the latter difference is within the limits of our experimental error, strictly speaking, the comparison must be made with mixtures of the P_α phase containing about 9 mol% anthracene and the A_α phase containing about 20 mol% phenanthrene. As these solid solutions are, to some extent, more stable than the pure picrates, it is almost certain that the II_α phase is metastable. So far, though, we have not succeeded in the crystallization of the I and II solid solutions from solutions. The possibility that the I solid solution disappears if the samples are stored for a sufficiently long time cannot be completely eliminated.

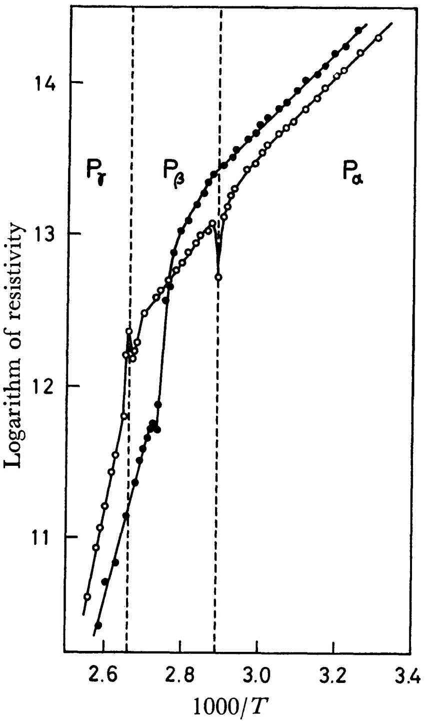

Fig. 4. Electrical resistivity of compressed phenanthrene picrate: ○ ascending temperature, ●: descending temperature.

Electrical Resistivity. The logarithm of the resistivity of the phenanthrene picrate, recorded at ascending and descending temperatures, is plotted against the reciprocal temperature in Fig. 4. In the former process, not only the changes in the slope but also the minima were observed at the transition temperatures. The minimum at the transition from P_α to P_β is deep and sharp, while that from P_β to P_γ is shallow and broad. The activation energy for semiconduction tends to be large in the high-temperature phase. The resistivity at 25 °C is in the order of 10^{14} ohm cm. This value is appreciably smaller than that reported for the corresponding *s*-trinitrobenzene complex. Kuroda *et al.* have measured the temperature-dependence of the resistivity of the *s*-trinitrobenzene complex in a range from room temperature to a little below the melting point; they obtained 7×10^{18} ohm cm for the resistivity at 15 °C and 1.24 eV for the activation energy.[17] The latter quantity in the picrate is smaller by a factor of approximately two in the P_α and P_β phases and larger almost by the same factor in the P_γ phase. The presence of an enantiotropic transition located 15 °C below the melting point has been reported in the phenanthrene–*s*-trinitrobenzene complex by Kofler.[6] Nevertheless, no anomaly in the resistivity due to this transition has been noted by Kuroda *et al.* The appearance of a sharp resistivity minimum at the transition point has been found in Würster's blue perchlorate by Pott and Kommandeur.[18] Contrary to our case, this phenomenon could be observed only on crystals, not in compressed polycrystalline samples. As is shown in Fig. 4, there is a large hysteresis in the high-temperature region. A delayed transition from P_γ to P_β could be detected by the resistivity measurements. Moreover, the activation energies observed in the cooling process are little smaller than those observed in the heating process.

Although a gradual change in slope in the resistivity curves was observed near the transition temperature(s) in the anthracene picrate and in that doped with phenanthrene picrate (1 mol%) upon an increase in the temperature, no resistivity minimum at the transition temperature(s) was detected with these samples. Again, the resistivity at 25 °C is in the order of 10^{14} ohm cm, which is about one-hundredth of the resistivity of the anthracene–*s*-trinitrobenzene reported by Kuroda *et al.* Such a large difference is in marked contrast to the observations made by Labes *et al.* that the resistivity of coronene–picric acid is of the order of 10^{12} ohm cm, while that of the corresponding *s*-trinitrobenzene complex is 10^{13} ohm cm at room temperature.[19]

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