imates experimental errors of vibrating tube densimeters.

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Registry No. NaCl, 7647-14-5; $MgCl_2$, 7786-30-3; KCl, 7447-40-7; NaBr, 7647-15-6; LiCl, 7447-41-8; $CaCl_2$, 10043-52-4.

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Structure of Melts in Binary Organic Eutectics and Molecular Complexes. Phenanthrene–Picric Acid and Anthracene–Picric Acid Systems

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Phenanthrene–picric acid and anthracene–picric acid systems were chosen for detailed thermochemical measurements. Phase-diagram studies confirmed that a maximum is surrounded by two eutectics, and a molecular complex of 1:1 stoichiometry with congruent melting is formed in both systems. Enthalpy of fusion values do not obey the mixture law. The exothermic mixing confirms the compound formation in both systems. The values of enthalpy of mixing for the eutectics show the tendency of ordering in the melts.

Introduction

There has been a great deal of discussion (*1–3*) concerning the nature of liquid eutectics. Three types of structures have been suggested depending on the sign and magnitude of the enthalpy of mixing. Strong interactions between unlike molecules are expected when the enthalpy of mixing is negative. Quasieutectic structures are suggested for the positive enthalpy of mixing. The small departure from the mixture law shows the formation of simple molecular solution. Various types of studies such as viscosity measurements, X-ray scattering, centrifuge, and other structure-related properties have given (*4*, *5*) diverse views. Recently, Singh and Singh (*3*) have measured the heats of fusion for various simple eutectics and found that clustering of parent components is very likely in the eutectic melts. Phenanthrene and anthracene are very similar in structure and both form congruent types of eutectics with picric acid. We carried out detailed experimentation to determine the phase diagram and heats of fusion to throw light on the nature of liquid eutectics and 1:1 molecular complexes.

Table I. Values of Enthalpy of Mixing for Anthracene–Picric Acid and Phenanthrene–Picric Acid Systems

	enthalpy of mixing, kJ mol^{-1}		
system	eutectic 1	eutectic 2	1:1 molecular complex
anthracene–picric acid	−3.98	−1.81	−14.14
phenanthrene–picric acid	−0.54	−2.63	−7.63

Experimental Section

The purification process has been reported in ref *6*. The details of phase-diagram studies are also given in the same paper.

Enthalpy of fusion measurements were carried out on a Perkin-Elmer DSC-2 with a computer-aided data acquisition and

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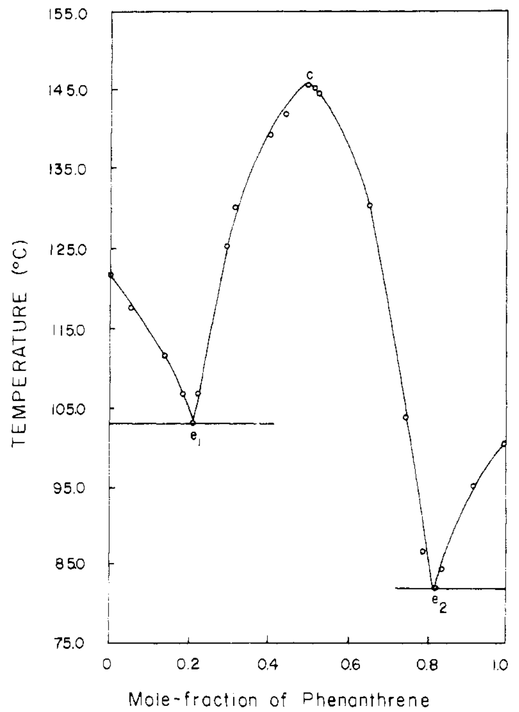

Figure 1. Phase diagram for the phenanthrene-picric acid system.

analysis system. The measurements were made in hermetically sealed Al pans. DSC was calibrated by taking indium as temperature standard. All runs were performed with the heating range of 2 mcal s^{-1} and chart speed of 2 mm min^{-1}.

Results and Discussion

Phase diagrams are given in Figure 1 for the phenanthrene-picric acid and in ref *6* for the anthracene-picric acid system. The eutectics (designated as e_1 and e_2) have the compositions 0.102 and 0.625 mole fraction of anthracene in anthracene-picric acid and 0.231 and 0.818 mole fraction of picric acid in phenanthrene-picric acid, respectively. Phase diagrams indicate the formation of 1:1 molecular compounds, capable of existing as solid compounds in equilibrium with liquids of the same composition.

The values for the enthalpy of mixing are given in Table I. Analysis shows that the mixture law is not obeyed for the eutectics as well as the molecular complexes. The enthalpy of mixing was calculated by the equation

$$(\Delta_{fus}H)_M = (\Delta_{fus}H)_{exptl} - \sum x_i \Delta_{fus}H_i^\circ \quad (1)$$

where $(\Delta_{fus}H)_{exptl}$ is the experimental enthalpy of fusion, and x_i and $\Delta_{fus}H_i^\circ$ are the mole fraction and enthalpy of fusion, respectively, for the component *i*. As shown in the Table I, both complexes have very high exothermic enthalpies of mixing. Anthracene-anthracene, phenanthrene-phenanthrene, or picric acid-picric acid interactions are very weak in comparison to anthracene-picric acid or phenanthrene-picric acid interactions. Situations for the eutectics are more complex. In the anthracene-picric acid system, picric acid and the 1:1 molecular complex act as the parent components for eutectic 1, while the 1:1 molecular complex and anthracene do so for eutectic 2. Similarly, in the phenanthrene-picric acid system, eutectics 1 and 2 have phenanthrene and 1:1 complex, and picric acid and 1:1 complex as the parent phases, respectively. The enthalpies of mixing for all the eutectics are positive. These values are very low in comparison to the values of complexes. This shows very weak interactions at the eutectic compositions. It is also very interesting that one of the eutectics in each system has very low enthalpy of mixing, and one might argue for the possibility of simple molecular solutions instead of weak interactions. These results are quite different from those of simple eutectic systems[2] where merely ordering of the parent phases has been suggested in the melts. It seems there is considerable enhancement in the interactions due to the presence of 1:1 molecular complex in the eutectic melts.

Registry No. Phenanthrene, 85-01-8; anthracene, 120-12-7; picric acid, 88-89-1.

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