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Note

A RE-EXAMINATION OF THE PHASE DIAGRAM OF THE BINARY SYSTEM PYRENE—PICRYL CHLORIDE

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One of the methods of investigating phase equilibria and the stoichiometry of organic compounds is thermal analysis, in particular, differential scanning calorimetry (DSC). To obtain a correct phase diagram by this method one has to ascertain not only an adequate precision of calorimetric measurements but also a sufficient degree of purity of starting materials, accurate knowledge of the mole ratio of the components in the sample and, last but not least, the attainment of thermodynamic equilibrium by the sample.

If a sample lacks equilibrium and a metastable phase is present, thermal effects which appear in the sample during heating are spurious and interpretation of results is either impossible or leads to incorrect conclusions. The situation was observed by us in the system anthracene—trinitrofluoren-9-one [1]. For unannealed samples irregularities in the plots of heats of eutectic and peritectic melting vs. sample composition were observed and the value of eutectic temperature scattered within a 4 K range. Moreover, the eutectic melting was observed in all samples containing 0—50 mole% of anthracene, behaviour inconsistent with the existence of an incongruently melting DA_2 complex revealed by the presence of peritectic melting at higher temperatures. On the contrary, samples annealed for 12 days at temperatures close to eutectic temperature revealed perfectly "normal" behaviour — eutectic melting reproducible within 0.6 K with anthracene content between 0 and 33.3 mole%, peritectic melting in those containing ca. 22—50 mole% of anthracene, the thermal effects fulfilling the Tammannś-triangle criterion [2].

Recently, the phase diagram of the pyrene—picryl chloride system has been published by Bando and Matsunaga [3]. Its quite intricate features (e.g. the extension of the eutectic line beyond the region of existence of an appropriate phase) resembles the behaviour of non-equilibrated samples in other systems studied by us. Thus, the re-examination of this system (especially in the pyrene-rich range) with emphasis on attainment of thermodynamic equilibrium in the material seemed interesting.

EXPERIMENTAL

Pyrene (Fluka) was crystallized from benzene, sublimed and then purified by zone melting. The melting temperature of the purified material (T_m) is 425 K.

Picryl chloride (Fluka) was crystallized several times from chloroform and eventually purified by vacuum sublimation, $T_m = 356$ K. The purity of these materials was checked by DSC.

Appropriate amounts of each component were weighed in glass ampoules and sealed under inert gas. The samples were then melted and shaken vigorously. After rapid cooling the samples were held at ca. 333 K, i.e. 20 K below the temperature of phase transition, in the 1 : 1 complex for 2 weeks in order to attain the phase equilibrium in the system. Material from the ampoules was ground in an agate mortar and used in DSC and microscopic observations.

Perkin-Elmer DSC-1B and Böetius hot-stage microscope were used in the experiments. Thermal effects were registered starting at room temperature up to the temperature of melting of the whole material.

RESULTS

Figure 1 shows the experimental data obtained as compared with those obtained by Bando and Matsunaga [3]. The following effects were observed in our experiments:

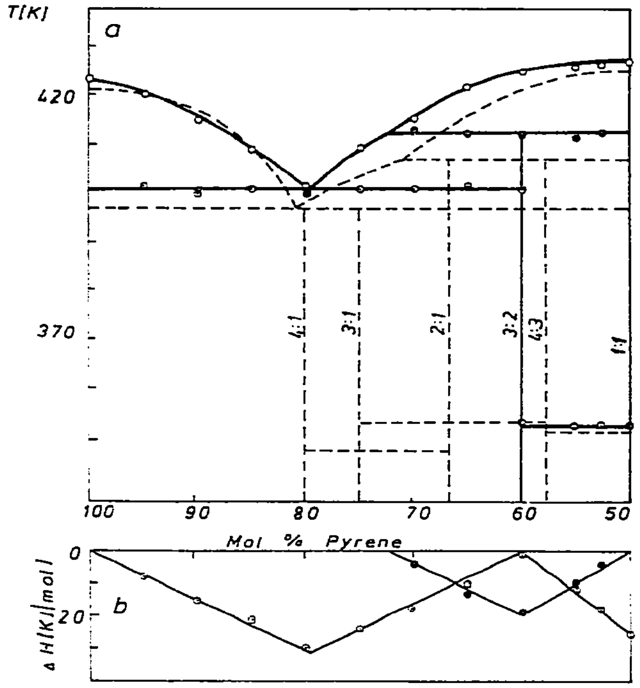

Fig. 1. Fragment of the phase diagram of the pyrene—picryl chloride system (in the region 50—100 mole% of pyrene). (a) — — —, According to Bando and Matsunaga [3]; ⊙——⊙, eutectic line; ●——●, peritectic line; ◑——◑, phase transition line; ○——○, liquidus line (this work). (b) Molar heat of eutectic, peritectic melting and phase transition vs. composition (this work).

(1) the endothermic peak appearing at 355 K (354 K [3]) in samples containing less than 60 mole% of pyrene was attributed to a solid phase transition in the 1 : 1 complex (ΔH_t = 26.0 kJ mole^{-1}) in accordance with a linear dependence of the peak area on the complex content [see Fig. 1 (a), (b)];

(2) the endothermic peak at 403 K (399 K [3], 398 K [4]) in samples containing more than 60 mole% of pyrene was ascribed to the melting of a eutectic formed by pyrene and D_3A_2 complex [see in Fig. 1 (a), (b)];

(3) the endothermic peak at 414.5 K connected with peritectic melting of the D_3A_2 compound [$\Delta H_{p.m.}$ = 19.1 kJ mole^{-1}; see Fig. 1 (a), (b)].

(4) the pure 1 : 1 complex melts at 429 K (427 K [3], 426.5 K [4]), the heat of melting amounting to 45.2 kJ mole^{-1}.

DISCUSSION

Under equilibrium conditions the pyrene—picryl chloride system reveals quite a simple phase diagram with two molecular compounds only, i.e. congruently melting DA and incongruently melting D_3A_2 complexes. Due to decomposition of the latter, samples which are heated above 414.5 K and are not annealed afterwards actually contain, as well as D_3A_2 complex, both DA complex and pyrene. It is the presence of a metastable phase (viz. pyrene in picryl chloride-rich samples or DA complex in pyrene-rich ones) which causes both effects mentioned in points (1) and (2) to be observed beyond the true region of existence of an appropriate phase. Moreover, samples containing nominally 60 mole% of pyrene show, besides the "normal" endothermic effect at 414.5 K connected with decomposition of a 3 : 2 compound, a feeble thermal effect of solid phase transition and an even insignificant effect of eutectic melting. Samples of this composition were synthesized several times and held at constant temperature (333 K); however, DSC curves reveal the same behaviour for all samples. We suppose that a slight temperature difference over the length of an ampoule (probably ca. 0.5 K), which is difficult to avoid during prolonged annealing, brings about partial segregation of the sample and formation of a small quantity of the metastable phase.

In a related system, pyrene—picryl bromide, the existence of two molecular compounds of the same DA and D_3A_2 stoichiometry has been found by Herbstein and Kaftory [5]. It is interesting to note that the two systems differ with respect to the relative stability of the complexes: pyrene$_3$ · (picryl bromide)$_2$ melts congruently and pyrene · picryl bromide decomposes prior to melting, whereas the reverse situation was found in the pyrene—picryl chloride system.

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