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Maria Radomska [a] , Ryszard Radomski [a c] & Krzysztof Pigoń [b d]

[a] Institute of Chemistry Pedagogical College, Opole
[b] Institute of Organic and Physical Chemistry Technical University, Wroclaw
[c] Oleska 48, Opole, Poland
[d] Wybrzeze Wyspiańskiego 27, Wroclaw, Poland

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Phase Diagram and Growth of Single Crystals in the Anthracene–Acridine Binary System

MARIA RADOMSKA and RYSZARD RADOMSKI†
Institute of Chemistry
Pedagogical College
Opole

and

KRZYSZTOF PIGOŃ‡
Institute of Organic and Physical Chemistry
Technical University
Wrocław

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Abstract—The revision of the phase diagram of the anthracene–acridine system by thermal analysis revealed the compositions of terminal solid solutions amounting to 2 and 88 mole % of anthracene respectively, and a eutectic at 8% of anthracene and 384.4°K. Relatively stable binary single crystals of composition ranging from 0 to 45 mole % of acridine in anthracene and from 2 to 10 mole % of anthracene in acridine have been obtained by the vapour growth technique. The lattice constants of the mixed crystals have been determined.

In the course of study of electric conductivity in binary organic single crystals attention was focused on the anthracene–acridine system. After Myasnikova and Kitaigorodskii(1) the system belongs to the Roozeboom's V-type with a eutectic at 7 w. % of anthracene and the miscibility gap extending from 4 to 28 w. % of anthracene. A wide range of miscibility reported in the anthracene–acridine system inclined us to choose the system as the object for the study of electric conductivity in mixed organic crystals. The range of miscibility found for single crystals grown by us from the vapour phase disagreed, however, with the results of the paper.(1) To check the phase diagram of the system thermal analysis of high-purity samples was performed.

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† Address: Oleska 48, Opole, Poland.
‡ Address: Wybrzeże Wyspiańskiego 27, Wrocław, Poland.

1. Materials

Coal-tar anthracene (Chemical Works Hajduki, p.a. grade) and acridine (Reanal, purissimum) were recrystallized from benzene and methanole, vacuum-sublimed and eventually zone refined. Three zones of approx. 1.5 cm in length and being approx. 10 cm apart were moved at the speed of 2 cm p.h. along the charge of 50 cm in length. After ca. 200 zones passed the material from the ends of the tube was rejected and the zone melting process was repeated. Mixtures for thermal analysis were prepared by weighing up appropriate amounts of components (every 10 mole % of anthracene in the whole composition range and every 1.5 mole % of anthracene between 0 and 10 mole % of anthracene, the total charge being approx. 5 g) into glass ampoules. The ampoules were then sealed under the vacuum of 10^{-5} Torr, their content was melted, vigorously stirred, rapidly cooled to room temperature and eventually annealed at 333 °K for two months. Samples of approx. 60 mg in weight were taken for thermal analysis from the above material.

2. Single Crystal Growth from the Vapour

The design of the apparatus for growing single crystals based on the paper by Vitovskii *et al.*(2) is shown in Fig. 1. A glass ampoule with the sample sealed under vacuum (10^{-5} Torr) was placed in the inner tube and pulled upwards at the approximate rate of 1 cm per week. The evaporation of the starting material and the growth of the crystal occurred at nearly the same temperature (353–372 °K depending on composition). As the pulling rate was adjusted to the linear rate of the crystal growth, the level of the evaporating material as well as the surface of the growing crystal were kept in the same positions in relation to the heater. Thus the same conditions of the sublimation and the crystallization were maintained during the whole process. The essential advantage of the method when applied to grow mixed crystals is the lack of the concentration gradient within the bulk. The uniform composition of the crystals has been confirmed within the limits of experimental error (ca. 2%) by elemental analysis (nitrogen determination), as well as by the evaluation of lattice constants. The crystals obtained were about 1.5 cm in diameter and about 1.5 cm in length.

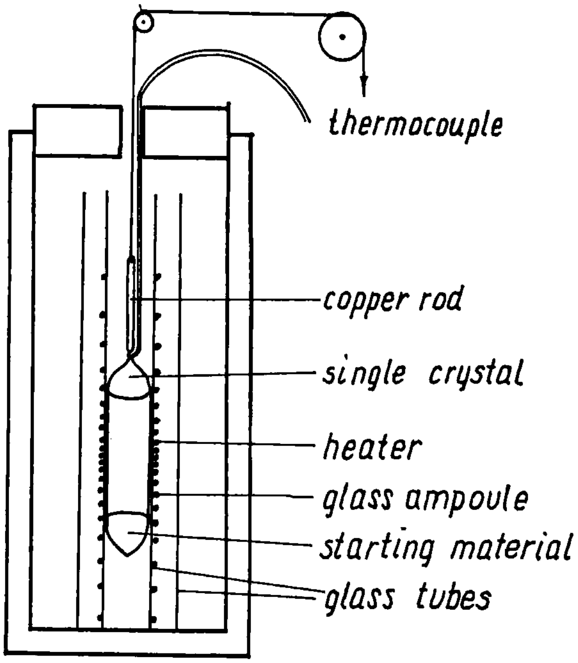

Figure 1. Apparatus for growing crystals from vapour.

Single crystals of several organic compounds, single mixed crystals of other binary systems, and single crystals of the molecular complexes of 1,3,5-trinitrobenzene with some aromatic hydrocarbons were also grown by the same procedure.

The crystals of the anthracene-rich phase containing up to 45 mole % of acridine have been grown. They are transparent, of uniform pale-yellow colour and do not undergo any visible changes for a period of one year. The crystals of acridine as well as those of acridine with a small amount of anthracene (up to 2 mole %) have been grown, but they disintegrate on cooling, presumably due to phase transformation. The crystals containing from 2 to 8 mole % of anthracene are full yellow, exhibit intensive green fluorescence and are stable for at least one year. Those containing 8 to 10 mole % of anthracene are pale yellow, do not fluoresce and disintegrate into yellow powder within several days. Attempts to grow crystals containing between 45 and 90% of acridine have failed.

The lattice constants of the stable crystals have been determined by the oscillating-crystal technique. The crystals containing up to 45 mole % of acridine have the anthracene lattice and reveal the (001) cleavage plane, and those containing 92 to 98 mole % of acridine have the acridine II lattice and cleave along (010) plane. The dependence of the lattice constants on the composition is shown in Fig. 2. The general feature of the relationship is similar

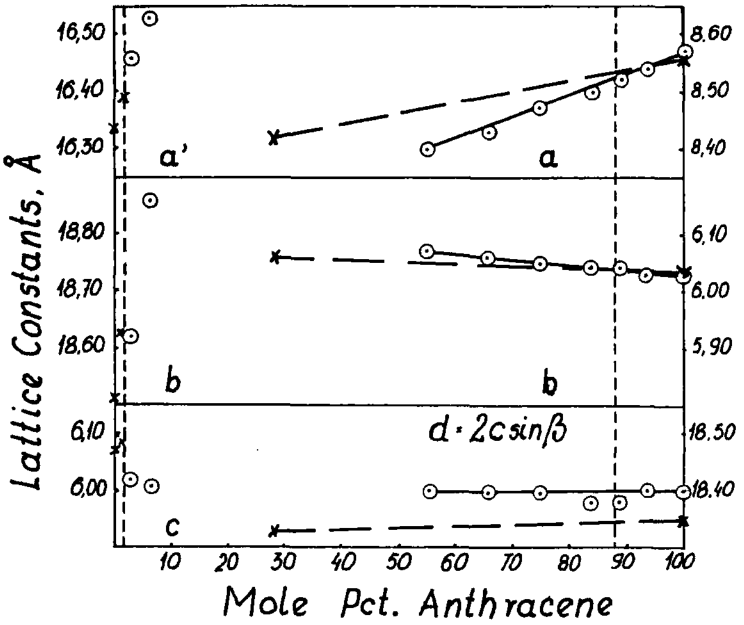

Figure 2. Dependence of the lattice constants on mole % of anthracene in the anthracene–acridine system. The constant a' of the acridine phase equals a·sin β. Miscibility gap indicated by broken lines. ○—this work, ×—Ref. 1

to that found by Myasnikova and Kitaigorodskii,⁽¹⁾ the effect differing however somewhat in magnitude. The data relating to the structure of pure components have been taken from the papers by Mathieson⁽³⁾ and Lowde.⁽⁴⁾

3. Phase Diagram

The position of the liquidus line was determined from the temperature-time curves recorded at the constant heating rate (0.5 deg/min approx.) assured by the constant temperature difference between the heater and the sample. Temperature was measured with the accuracy of 0.1° by teflon-insulated copper–constantan thermocouple. The samples were held in argon atmosphere. The phase diagram constructed from the heating curves is shown in Fig. 3, together with the data reported by Myasnikova and Kitaigorodskii (Ref. 1). The compositions of the terminal solutions as

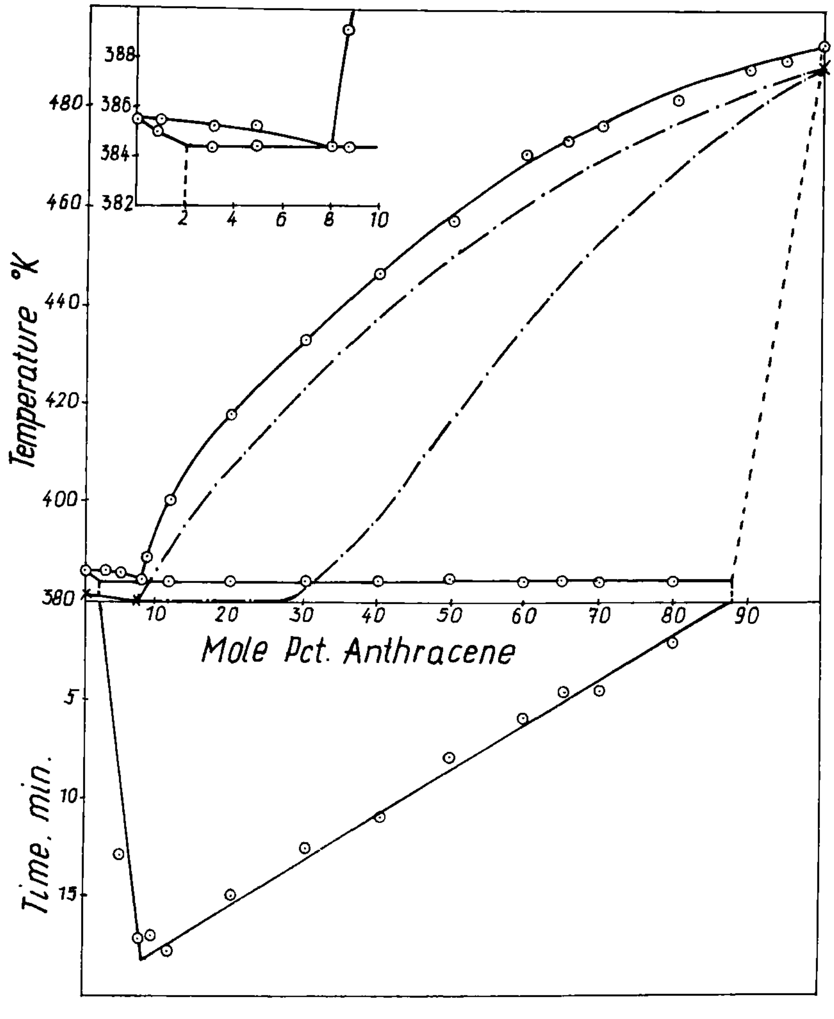

Figure 3. Phase diagram of the anthracene–acridine system. ○, ———, – – –, —this work, ×, —·—·–, —Ref. 1. In the lower part of the diagram the time of eutectic arrest has been shown.

well as the composition of the eutectic mixture have been evaluated from the duration of eutectic arrest. The miscibility gap extends from 2 to 88 mole % of anthracene with the eutectic at 8 mole %. The melting points of the eutectic, acridine, and anthracene amount to 384.4, 385.5, and 492.7 °K respectively. The composition of the eutectic mixture was additionally checked by elemental analysis of a eutectic sample subjected to repeated zone refining. The results of thermal analysis were also confirmed by microscopic observations of melting points of the samples sealed in capillary tubes in the atmosphere of argon.

4. Discussion

Considerable differences in the range of miscibility reported for the anthracene–acridine system are probably due to the different methods of construction of the phase diagram. In the paper(1) the positions of the liquidus and solidus lines were deduced from the compositions of the melt and of the crystals grown from it at the temperature 0.1–0.3° lower than the melting temperature. The experiments were carried out on materials of inferior purity to those used in this study and no care was taken to avoid oxidation during the experiments.

Thermal analysis carried out in this study on annealed samples of high purity indicates that the thermodynamically stable anthracene-rich phase does not contain more than 12% of acridine. Thus the crystals grown by us, containing up to 45 mole % of acridine, as well as those grown by Myasnikova and Kitaigorodskii, containing up to 72 mole % of acridine, were a metastable form of the anthracene-rich phase. Similarly the acridine-rich phase extends by 8 mole % of anthracene beyond the region of stability.

The metastable forms were also observed in the samples prepared for thermal analysis. Immediately after freezing the samples were pale-yellow. In the course of annealing the terminal solutions separated and the colour changed to full yellow, the colour being characteristic of the stable acridine-rich phase.

The electric conductivity of the annealed samples increased by 2 to 3 orders of magnitude at 384.4 °K because of the onset of melting. Similar effect was observed when the metastable crystals were heated for the first time not until the temperature exceeded 400 to 410 °K, in the next runs, however, the rise in conductivity occurred already at eutectic temperature. The detailed results of the measurement of electric conductivity will be published elsewhere.

The linear dependence of the lattice constants on the mole fraction of the solute indicates that only one anthracene-rich phase exists beyond the region of the thermodynamical stability.

The " coefficient of packing " defined as the ratio of the sum of the volumes of molecules in one unit cell to the volume of the unit cell, was proposed by Kitaigorodskii(5) as an index of stability of the crystalline phase. The smallest value of the coefficient of packing permitted by condition of stability amounts, after Kitaigorodskii, to 0.6. The values found by us for the crystals of metastable anthracene-rich and acridine-rich phases amounted to 0.714 and 0.683 respectively. It is possible that the fulfilment of geometrical requirements for lattice formation is sometimes sufficient for the formation of a relatively stable phase although its components have not attained thermodynamic equilibrium.

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