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SOLID–LIQUID EQUILIBRIUM OF THE PHENANTHRENE–FLUORENE SYSTEM

IRENA KOTULA, and A. RABCZUK

Department of Physical Chemistry, Pedagogical University of Częstochowa, Poland

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The solid-liquid equilibrium of the phenanthrene-fluorene system was investigated by differential thermal analysis. Supplementary measurements were applied too: crystal decay temperature examination and melting point examination with a Boetius microscope. The investigated system forms a stable solution with a minimum at 58 mole% of phenanthrene and a temperature of 95.5°.

The discovery of a testing mixture which forms stable solutions for fractional crystallization or zone melting within the whole concentration range was this object of our investigations. There are few organic substances which form the type of system and fulfil other indispensable conditions for testing mixtures: low activity, lack of toxicity, accessibility, and easily obtainable in pure form.

The phenanthrene-fluorene system, investigated by Krawczenko [1], who found the existence of a stable solution within the whole concentration range and by Klochko and Jovnir [2], who found a simple eutectic system, fulfils these conditions. According to data given by Lipławk [3], this system forms a stable solution with a minimum point (only the liquidus was presented). Because of the divergence of the literature data shown in Figs 1a, b, c, a new investigation of this system was considered necessary.

Experimental

Materials

Chemically pure phenanthrene (POCh – Gliwice), crystallized from a toluene -methanol mixture (1 : 1) and next from ethanol; m.p. 101°; purity 98.9% examined by gas chromatography. Pure fluorene (POCh – Gliwice), purified by zone melting during 200 zone transitions: m.p. 117°, purity 99.74% examined by gas chromatography.

Apparatus and procedure

For determination of solid-liquid equilibria, a Paulik–Paulik–Erdey model OD 102 derivatograph (Hungary) was used.

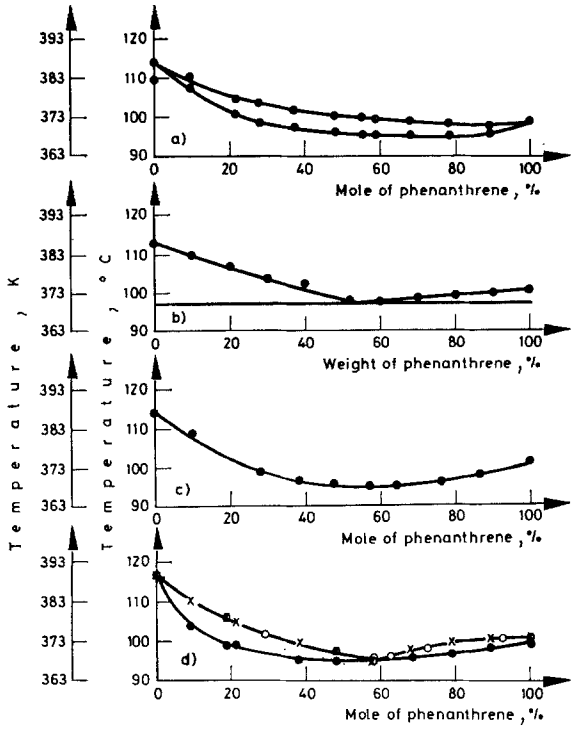

Fig. 1. Phase system of phenanthrene-fluorene. (a) by Krawczenko; (b) by Klacho-Jovnir; (c) by Lipławk; (d) examinated phase system of phenanthrene-fluorene. • T_1 solidus-DTA; × T_2 liquidus — Boetius microscope; ○ T_3 liquidus — crystal decay temperature

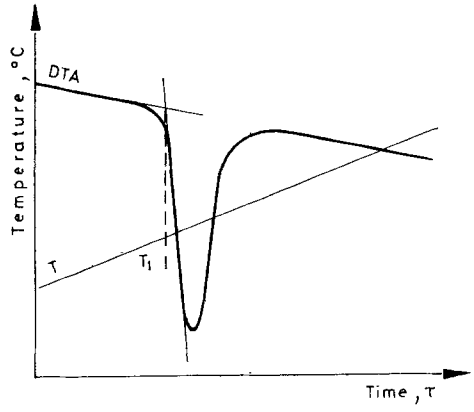

Fig. 2. Interpretation of DTA curve

Supplementary measurements were applied: crystal decay temperature examination, by the method of Hill [4] as modified by Swierczek [5], and melting point examination with a Boetius microscope with heating stage.

The method of interpretation of DTA curves and plotting of data was in accordance with that of Gaumann [6]. No data were found concerning interpretation of DTA curves for organic compound systems.

DTA curve analysis of phase systems of organic compounds which form stable solutions shows the possibility of accurate designation of the solidus curve (within the limit of thermal measurement error), whereas the liquidus curve designation by this method was not equivalent in meaning.

For investigations with derivatograph a 2 g sample of mixture was prepared. This was ground to uniform particle size. Analysis of mixtures was done under stable condition for each sample. A 250 mg weighed portion was placed in a platinum crucible and the heating programme was set from 20° to 300°. The heating rate was 1.65 $\pm$ 0.05°/min Al_2O_3 calcined at 900° was used as the reference material. DTA curves with one endothermic effect, and different peak widths depending on the mixture composition, were obtained. The temperature of the start of melting for the stable solution was determined through the point of deviation of the DTA curve from the base line.

An interpretation of a DTA curve is presented in Fig. 2.

Supplementary measurements, described above, allowed accurate identification of characteristic points in the DTA curve. The start and the end of melting were determined with a Boetius microscope. This method was used in particular for designation of the liquidus curve, because the final melting temperature, determined from the DTA curve, appeared not to be too characteristic.

The heating rate near the melting point was 1.6°/min on the Boetius microscope.

To verify if the points which lie on the liquidus curve are determined accurately, an additional method of designation of the crystal decay temperature was applied. 4 g samples which differed in composition by weight in steps of 20% were used. The heating rate near the melting point was 1.5°/min. Temperature was measured with an Anschütz thermometer, graduated in 0.05°.

The points of the liquidus curve determined by this method and with the Boetius microscope were exactly the same.

Results and discussion

In Fig. 1d, the examined phase system of phenanthrene-fluorene is presented. The solidus curve was determined on the basis of the start of melting in the DTA curve. The liquidus curve was obtained with a Boetius microscope, and the crystal decay temperature was measured.

The phenanthrene-fluorene system was found to have a minimum at 58 mole% phenanthrene and a temperature of 95.5°.

This mixture can be applied to test mixtures in fractional crystallization and in zone melting, which contain less than 50 and more than 60 mole% phenanthrene.

References

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RÉSUMÉ — L'équilibre solide-liquide du système phénanthrène-fluorène a été étudié par analyse thermique différentielle. Des essais complémentaires ont également été effectués: détermination de la température de disparition des cristaux et détermination du point de fusion au microscope suivant Boetius. Le système étudié forme une solution stable avec un minimum à 58 mol% de phénanthrène et une température de 95.5°.

ZUSAMMENFASSUNG — Das fest-flüssig-Gleichgewicht des Systems Phenantren-Fluoren wurde durch die Differentialthermoanalyse untersucht. Als ergänzende Messungen wurden eingesetzt: die Untersuchung der Kristallzerfallstemperatur und die Prüfung des Schmelzpunktes mit dem Mikroskop nach Boetius. Das untersuchte System bildet eine stabile Lösung mit einem Minimum bei 59 Mol% Phenantren und einer Temperatur von 95.5°C.

Резюме — С помощью дифференциального термического анализа было исследовано ыавновесие твердое состояние-жидкость в системе фенентрен-флуорен. Дополнительно рбло проведено измерение температуры разрушения кристалла и точки плавления с помощью микроскопа Ботиуса. Исследованная система образует стабильный раствор с минимумом при 58 мол.% фенантрена и температуре 95.5°C.