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# Phase Diagrams in Binary Systems of Octafluoronaphthalene and Polynuclear Aromatic Compounds

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**Synopsis.** Solid-liquid phase diagrams were obtained for binary mixtures of octafluoronaphthalene with six polynuclear aromatic compounds, pyrene, phenanthrene, naphthalene, 1,5-naphthylenediamine, anthracene, and phenothiazine, and for mixtures of naphthalene and pyrene. The first four systems all formed well-defined 1:1 molecular complexes with congruent melting points.

In the course of our experiments on the photochemical reaction of octafluoronaphthalene (OFN) with pyrene, we observed that a solid was formed on mixing these two substances in methanol. The solid had a surprisingly high melting point compared with OFN and pyrene. Experimental evidence has indicated that hexafluorobenzene,[1—10] pentafluorobenzene,[4] pentafluorobenzonitrile,[9,11] and decafluorobiphenyl[5] form complexes with aromatic hydrocarbons. OFN has not been reported to produce complexes with the aromatic hydrocarbons except for benzene.[5] On the intermolecular force resulting in formation of such complex, opinions have differed.[5,6] Our attention is being paid to whether perfluoro-aromatic compounds always form molecular complexes with the aromatic hydrocarbons or not, and what kind of force acts between them. As the first step, the phase diagrams of binary mixtures of OFN and several polynuclear compounds were examined.

## Experimental

OFN (guaranteed reagent, Tokyo Chemical Industry) was recrystallized from methanol and sublimed *in vacuo.* Pyrene (Katayama Chemicals) was of analytical grade, phenanthrene (Tokyo Chemical Industry) was zone-refined material, and anthracene (Wako Pure Chemical Industries) was a standard reagent. Naphthalene (Katayama Chemicals), 1,5-naphthylenediamine (Wako Pure Chemical Industries), and phenothiazine (Nakarai Chemicals), respectively, were reagent grade.

A mixture of a known composition of OFN and one of the other compounds was made up by weight and dissolved in diethyl ether. After the ether was evaporated at room temperature and atmospheric pressure, a part of the mixture (about 5 mg) was sealed in an aluminum vessel (15 mm$^3$). Calorimetric experiments were done on a differential scanning calorimeter (Daini-Seikosha DSC-560S).[12] The scanning rate was 5 K min$^{-1}$. Repeated heating produced lowering of the transition temperatures in the systems except for the naphthalene-pyrene system.

## Results and Discussion

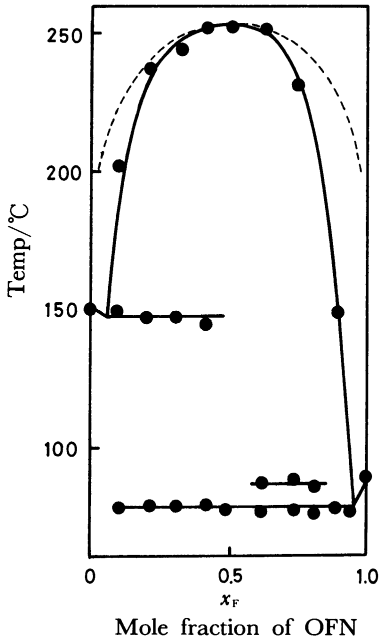

Fig. 1. Phase diagram of the OFN-pyrene system. The dotted curve is the calculated values from Eq. 2.

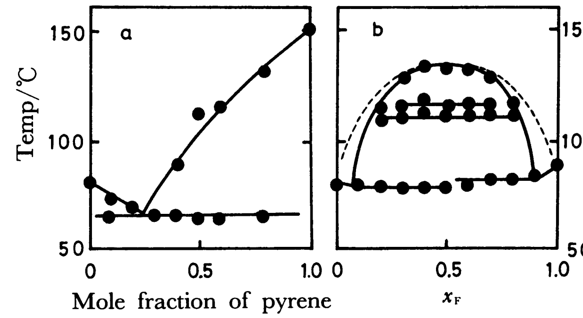

Fig. 2. Phase diagram of the naphthalene-pyrene system(a); the solid curves were calculated from Eq. 1, and that of the OFN-naphthalene system(b); the dotted curve was calculated from Eq. 2.

The phase diagrams for OFN+pyrene, OFN+phenanthrene, OFN+naphthalene, and OFN+1,5-naphthylenediamine, respectively, indicated clearly the formation of a 1:1 molecular complex between OFN and the other component (Figs. 1—4). The system naphthalene+pyrene was studied in comparison with the system OFN+pyrene. It is seen from Fig. 2-a that naphtalene and pyrene form a simple eutectic. For such a binary mixture the thermodynamic equation relating the melting point of one component of the mixture to the composition of the solution is

$$\ln x = (\Delta H_1/R)(1/T_1 - 1/T), \quad (1)$$

where $x$ is the mole fraction of the first component, and $\Delta H_1$ and $T_1$ are the enthalpy of fusion and melting temperature of pure 1. The solid curve in Fig. 2-a

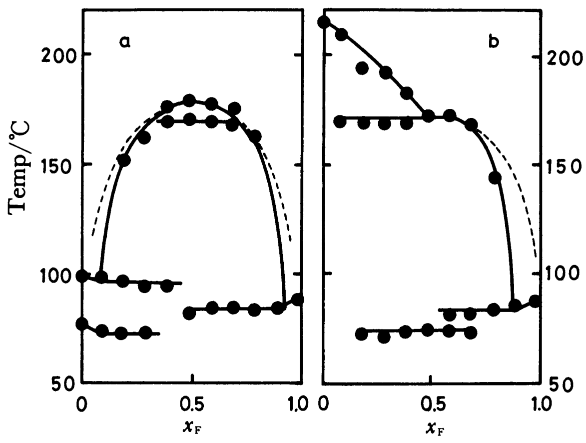

Fig. 3. Phase diagrams of the OFN-phenanthrene system(a) and the OFN-anthracene system(b). The dotted curves were calculated from Eq. 2.

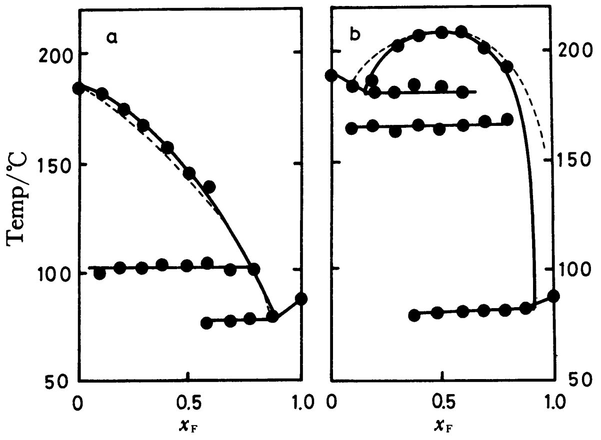

Fig. 4. Phase diagram of the OFN-phenothiazine system(a), the dotted curve was calculated from Eq. 1, and that of the OFN-1,5-naphthylenediamine system(b), the dotted curve was calculated from Eq. 2.

represents the melting temperatures calculated from Eq. 1 and is in good agreement with the experimental points. This evidence means that formation of the complex between OFN and pyrene results from the presence of fluorine atoms in OFN. Although in the system OFN+anthracene the compound molecule may be made from one OFN and one anthracene molecules, its melting temperature was lower than that of anthracene. The system OFN+phenothiazine did not give a congruent melting temperature.

The dotted curves in Figs. 1—4 represent the values calculated from Eqs. 1 or 2.[13]

$$-\ln x(1-x)+\ln 0.25=\Delta H_c/R(1/T-1/T_c), \qquad (2)$$

here $T_c$ is the melting temperature of the compound, and $\Delta H_c$ is its enthalpy of fusion. The equations assume ideal mixing in solution and for $\Delta H$ to be independent of temperature. The systems with congruent melting points exhibited negative deviation from Eq. 2, while the phase diagram for the system OFN+phenothiazine deviated positively from Eq. 1. The system OFN+phenothiazine seems to interact differently than the other systems. The other transition points, which were indicated in Figs. 1—4, were detected. Although some of these points may correspond to the phase transition of the molecular complexes, further investigation is required.

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12) The points in Figs. 1—4 are the temperatures at the intersection of the base line of a DSC curve with the tangent of the peaks. The tangent of a curve on a lower temperature side of the peak was used for the first peak, while for the subsequent peak the tangent on its higher temperature side was used.

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