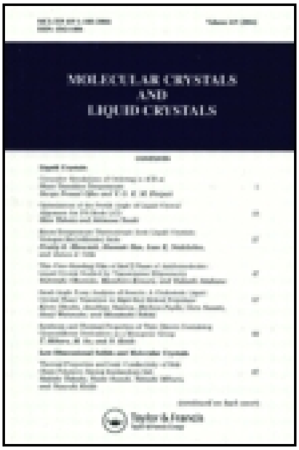

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Binary Phase Diagrams of Some Molecular Compounds—I

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Binary Phase Diagrams of Some Molecular Compounds—I

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Abstract—The naphthalene-anthracene and naphthalene-*d*-camphor phase diagrams have been determined by calorimetric measurements and optical microscopy in order to establish the extent of the terminal solid solutions. The manner in which the solid solubility is affected by the crystal symmetry and molecular volumes of the components is considered.

In the naphthalene-camphor system, in which the crystal symmetries and molecule volumes of the components are different, a eutectic is formed at 39 mole pct naphthalene and 304.5 K with terminal solid solubilities of 12.0 mole pct naphthalene in camphor and 6.0 mole pct camphor in naphthalene. In the naphthalene-anthracene system even though the crystal symmetries of the components are the same, the differences in molecular volumes results in a miscibility gap in the solid and the formation of a eutectic at 6.2 mole pct anthracene and 350.8 K. The terminal solid solubility is limited to 2.9 mole pct naphthalene in anthracene with practically no solid solubility in the reverse case. These experimental results are considered in conjunction with those for the anthracene-carbazole system, the phase diagram of which has been published previously.

1. Introduction

The factors influencing the formation of solid solutions in binary organic systems have been considered by Kitaigorodskii.[1,2] He concludes that extensive solid solubility will only occur if the molecules of the components are similar in size and shape (isomorphous). Even if this condition of molecular isomorphism is satisfied the existence of a complete range of solid solutions also requires the crystal symmetries of the two pure components to be identical (both for space group and number of molecules in the unit cell) since formally changes in symmetry are necessarily discontinuous. An apparent exception to this rule may occur if the molecules of one, and only one, of the components are enantiomorphic. These two considerations, molecular configuration and crystal symmetry, yield necessary, though not sufficient, conditions for complete solid solubility but do not indicate at all precisely the solid solubility to be expected in any particular case.

It was decided, therefore, as part of a general investigation of the physical properties of molecular compounds[3,4] to investigate further the alloying characteristics of some binary systems with either anthracene or naphthalene as one component. The systems chosen were anthracene-carbazole, the results for which have already been published,[5] naphthalene-camphor and naphthalene-anthracene. In the naphthalene-camphor system neither of the criteria for complete solid solubility are satisfied while in the naphthalene-anthracene system the crystal symmetries of the two components are the same but the molecular volumes are different. On the other hand, in the anthracene-carbazole system the crystal symmetries are different but the molecular volumes are similar. The extent of the terminal solid solutions in each of the two systems was measured by determining the binary phase diagrams by scanning calorimetry, with additional observations by optical microscopy.

2. Naphthalene-Anthracene System

(a) SAMPLE PREPARATION

Ingots of about 200 mg were made by weighing zone-refined materials into $\frac{1}{8}$ in. bore pyrex tubes. Anthracene was introduced first, pumped for some time to remove adsorbed oxygen, and then melted under nitrogen. The naphthalene was weighed in after cooling, and the whole sealed under nitrogen. Due allowance was made for evaporation of naphthalene during weighing. The contents of the tube were melted, mixed, quenched and annealed at 347 K for 1 week. Segregation during the quench proved troublesome, especially for alloys in the region of the terminal solid solution. This was overcome by separating the liquid into thin layers before cooling and thus increasing the effective rate of quenching. A strip of 0.001 in. aluminium foil was dimpled by rolling over glass paper, degreased and etched with 1% HNO_3 1% HF solution, and rolled up on a clean aluminium wire to $\frac{1}{8}$ in. diameter. This roll was put in a side-arm on the sealed-off tube containing the alloy and, after mixing, the liquid was run in to fill the spaces of the roll. The tube was then quenched and discs were cut from the solidified composite for calorimetry specimens.

(b) CALORIMETRY-HEATING CURVES

The solidus and liquidus in the binary system were determined by heating samples at rates of 1 to 4 K per minute in a Perkin-Elmer DSC-1B scanning calorimeter: this calorimeter measures the difference in power needed to heat the sample and a standard, at a constant rate, as a function of temperature. The temperature scale was calibrated by determining the melting points of high-purity mercury,[6] gallium,[6] naphthalene,[7] indium,[6] camphor,[8] and tin.[6]

A typical melting curve for a hypo- or hyper-eutectic alloy is shown in Fig. 1. The sharp peak corresponds to melting of the eutectic and the subsequent slow rise to melting of the pro-eutectic component. The temperature of the solidus and liquidus are taken as the points of departure and return to base heat capacity line respectively (Fig. 1). At least eight determinations were carried out of the solidus and liquidus temperature of each alloy. The overall reproducibility of results varied somewhat from alloy to alloy because of slight segregation in some ingots but the standard deviation from arithmetic mean of determinations from any one ingot was generally better than 0.3 K for the solidus and 1.2 K for the liquidus.

The naphthalene-anthracene phase diagram is shown in Fig. 2. A eutectic point occurred at 6.2 mole pct anthracene and 350.8 K, compared with earlier reported values of 350 K and 8.9 mole pct anthracene.[9] The limit of solid solubility of naphthalene in

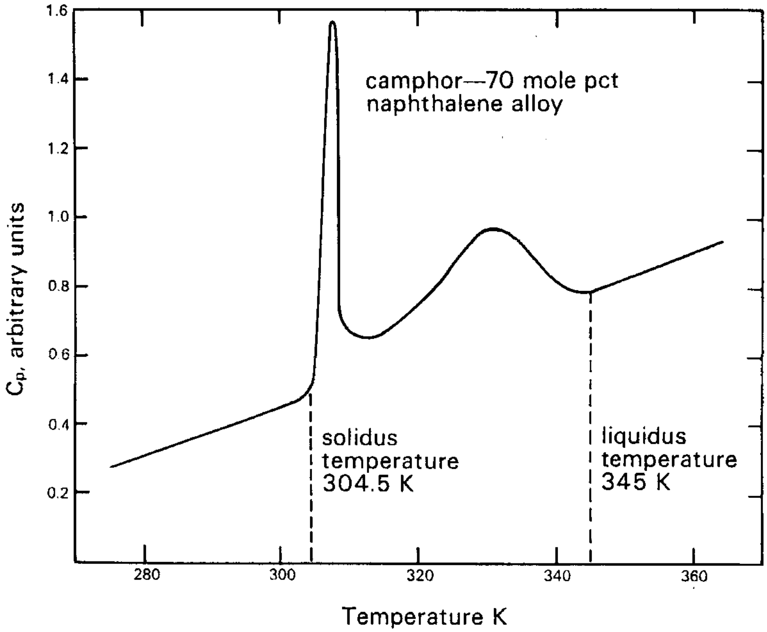

Figure 1. Typical melting curve for a hypo- or hyper-eutectic alloy showing the method adopted for determining the position of the solidus and liquidus.

anthracene was 2.9 mole pct at 350.8 K. The limit of solubility of anthracene in naphthalene could not be determined because of the limit of sensitivity of the calorimeter. Nevertheless, an alloy of composition 0.045 mole pct anthracene was certainly two-phase, and there is evidence that this terminal solid solution is about 10^{-4} mole pct anthracene.[10]

(c) Calorimetry-Enthalpy of Fusion of Eutectic

The limit of solid solubility of naphthalene in anthracene is difficult to determine unambiguously from the heating curves alone. However, a further indication of the solubility may be obtained by measuring the relative amounts of eutectic in a number of alloys. In Fig. 3 the enthalpy of fusion of the eutectic portion of the alloys, which is directly proportional to the amount of eutectic present is plotted against composition. The line of least squares through the experimental points indicates that no eutectic is detectable in the 97.1 mole pct anthracene alloy and that this is, therefore, the limit of solid solubility. The enthalpy of melting of the eutectic alloy was 19.22 kJ mole^{-1} and that of the 97.1 mole pct anthracene alloy was 30.80 kJ mole^{-1} (ΔH_M, pure anthracene = 27.90 kJ mole^{-1})^5.

3. Naphthalene-Camphor System

(a) SAMPLE PREPARATION

Naphthalene-Camphor. Ingots weighing approximately 200 mg were prepared from zone-refined naphthalene and *d*-camphor, containing less than 30 ppm total impurities, by melting under

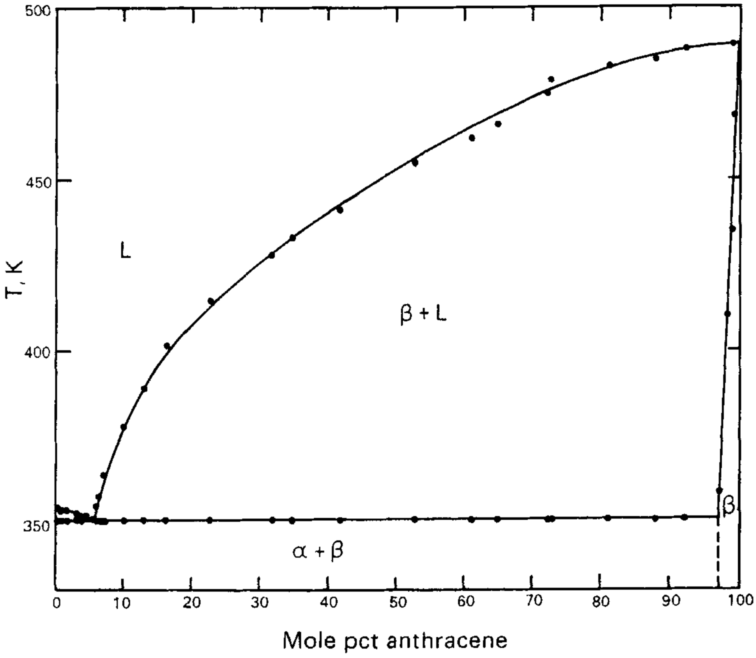

Figure 2. The naphthlaane-anthracene phase diagram.

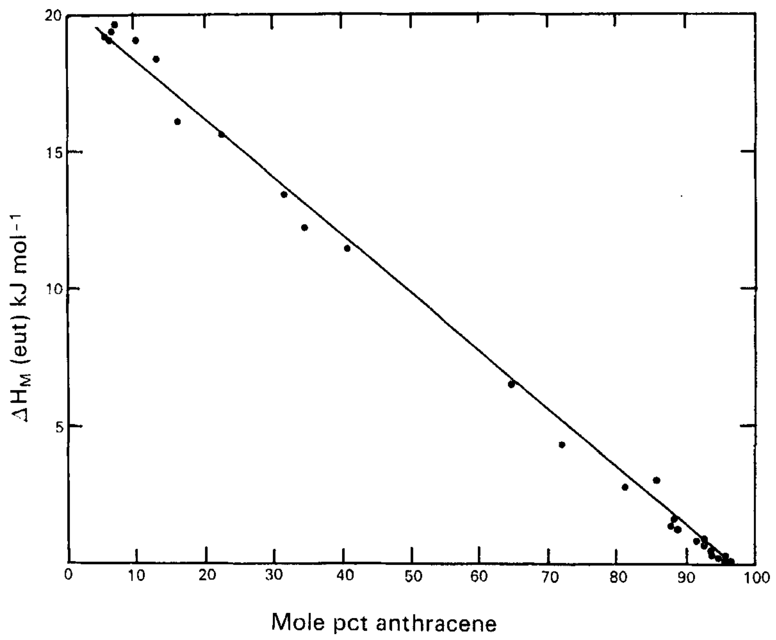

Figure 3. The enthalpy of fusion of the eutectic portion of naphthalene-anthracene alloys as a function of composition.

nitrogen in sealed $\frac{1}{8}$ in. bore pyrex capsules. The melts were agitated for approximately one hour and then quenched into a mixture of dry ice and acetone. Finally the alloys were held at temperatures just below the solidus for 3–4 days in order to eliminate any inhomogeneities. To check for any subsequent changes in the alloys, melting curves were determined after various times at room temperature (generally $> 0.9\,T_M$) for periods of up to five months. Samples were taken from four positions along the length of the ingot with at least two specimens being taken from each sample.

(b) Calorimetry

The solidus and liquidus were determined from the heating curves as described previously, the resulting phase diagram being shown in Fig. 4. A eutectic point occurs at 39 mole pct naphthalene and 304.5 K and the terminal solid solubilities are 12.0 mole pct of naphthalene in camphor and 6.0 mole pct of camphor in naphthalene. Earlier work of Grechnyi[11] indicated that the eutectic point occured at approximately 40 mole pct naphthalene and 304 K but gave no indication of the degree of solid solubility.

The eutectic composition is somewhat difficult to establish precisely from the heating curves. However, additional evidence of its position may be found by determining the relative amounts of eutectic in the various alloys. The enthalpy of fusion of the eutectic portion of the alloys, which is directly proportional to the amount of eutectic present, is plotted against composition in Fig. 5. The enthalpy of fusion of the eutectic present can also be calculated from the enthalpy of fusion of the terminal solid

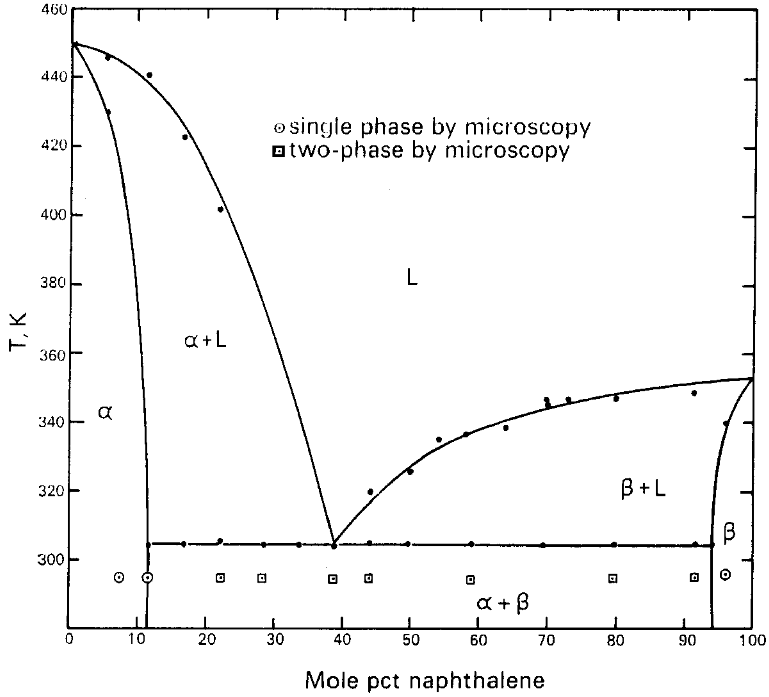

Figure 4. The naphthalene-*d*-camphor phase diagram.

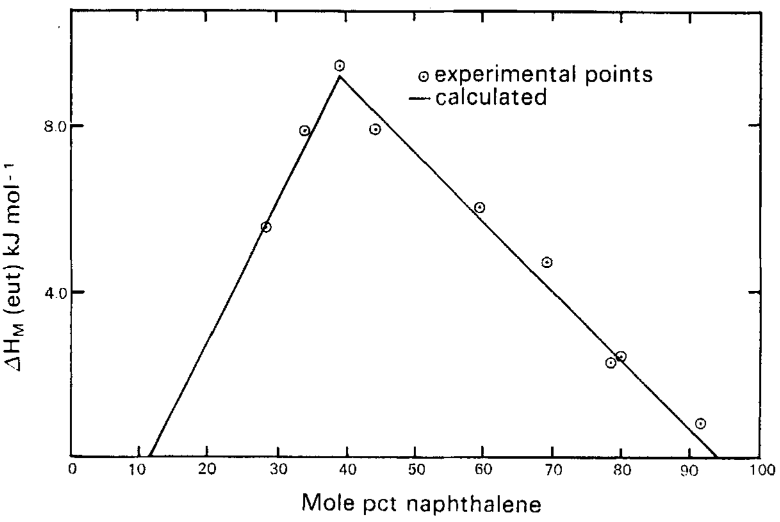

Figure 5. The enthalpy of fusion of the eutectic portion of naphthalene-camphor alloys as a function of composition.

solutions using the eutectic composition and limits of solid solubility given in Fig. 4. The solid line in Fig. 5 was calculated using the experimentally determined enthalpies of fusion of the 12.0 and 94.0 mole pct naphthalene alloys of 5.81 and 16.1 kJ mole^{-1} respectively. The maximum experimentally determined enthalpy of fusion occurred at 39 mole pct naphthalene (Fig. 5) and this, together with the close agreement between the other experimental points and the calculated line, confirms the eutectic composition and the limits of solid solubility determined from the heating curves.

(c) OPTICAL MICROSCOPY

Samples for optical microscopy were prepared by melting specimens of the alloys between a microscope slide and a cover slip. The different optical properties of camphor and naphthalene enabled the camphor-rich and naphthalene-rich phases in the eutectic alloy to be distinguished in polarized transmitted light. The microstructures of alloys containing 0 to 100 pct naphthalene confirmed that the limits of solid solubility were approximately 12 mole pct naphthalene in camphor and approximately 6 mole pct camphor in naphthalene (see, for example, Fig. 6a and b).

In the hypo-eutectic alloys the pro-eutectic naphthalene-rich phase precipitated from the liquid as plates with a prominent (001) basal plane and with edges parallel to the [010], [110] and $[1\bar{1}0]$ directions. The eutectic mixture then solidified between the plates (Fig. 6c.) The eutectic was a lamellar structure of the naphthalene-rich and camphor-rich phases, the lamellar spacing depending on the rate of cooling from the melt. In the hyper-eutectic alloys the pro-eutectic camphor-rich phase precipitated initially as six-armed stars (Fig. 6d and e), their symmetry suggesting that the arms lay in [110] directions in a (111) plane. At the higher camphor concentrations the growth of the pro-eutectic phase was dendritic in the latter stages of precipitation (Fig. 6f and e).

(d) ROTATIONAL TRANSFORMATION IN CAMPHOR ALLOYS

In *d*-camphor the rotational transformation occurred at 243 K, with an associated heat effect of 10.65 kJ mole^{-1}. This compares with quoted values of 244.6 K and 11.50 kJ mole^{-1}.[12] The transformation could be detected calorimetrically in all camphor-naphthalene alloys, and the transformation temperature was almost independent of composition, indicating that above about 243 K the camphor molecules are free to rotate even when they are substituents in the naphthalene lattice.

The variation of the enthalpy of transformation with composition provided a further check on the limits of solid solubility. As naphthalene was added to camphor, or vice versa, the enthalpy of transformation per mole of camphor increased until the limit of solid solubility was reached. When the two phase region was entered, there was a sharp change of slope in the curve of enthalpy versus composition, the enthalpy in the two phase region being the weighted mean of the values for the two saturated solutions (Fig. 7).

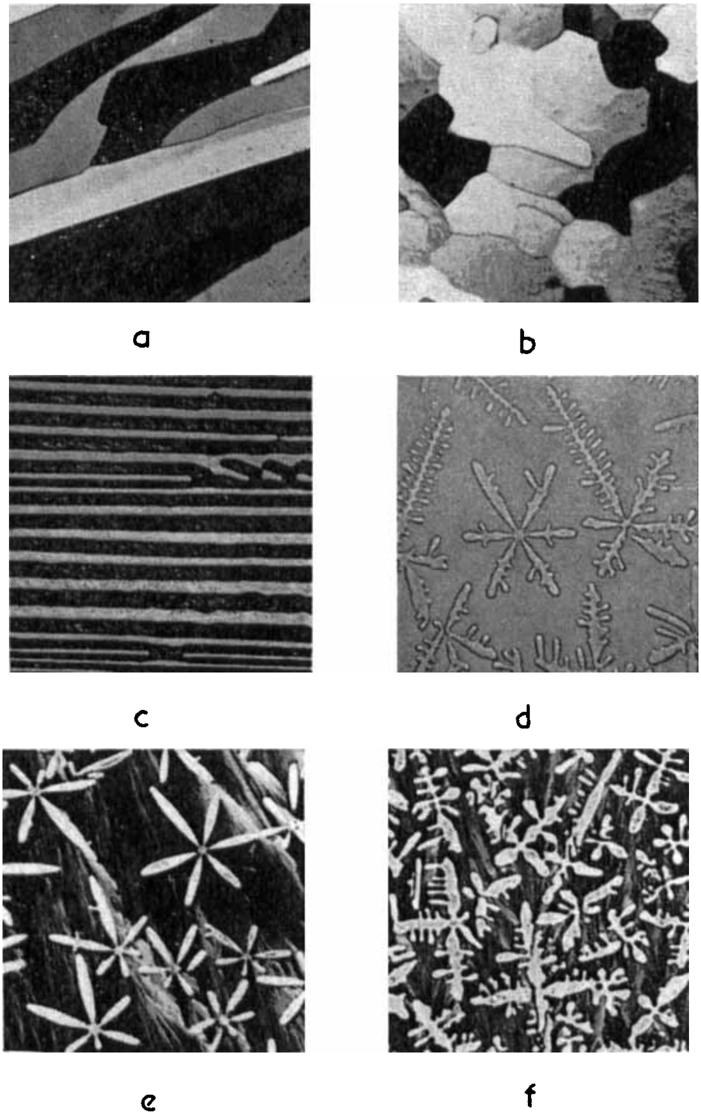

Figure 6. Microstructures of naphthalene-camphor alloys. (a) 96.0 mole pct naphthalene alloy; β single-phase. × 85; (b) 7.5 mole pct naphthalene alloy; α single-phase. × 85; (c) 59.0 mole pct naphthalene alloy; plates of pro-eutectic β phase (naphthalene-rich) plus eutectic. × 85; (d) 22.0 mole pct naphthalene alloy; pro-eutectic α phase (camphor-rich) in matrix of liquid eutectic. × 85; (e) 22.0 mole pct naphthalene alloy; pro-eutectic α phase plus solidified eutectic. × 85; (f) 28.0 mole pct naphthalene alloy; dendrites of pro-eutectic α phase plus solidified eutectic × 85.

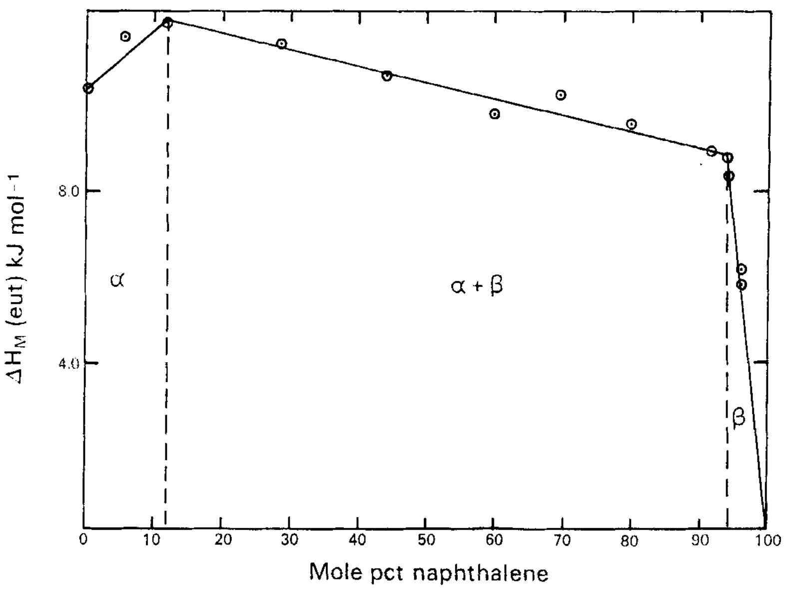

Figure 7. The heat effect associated with the onset of rotation of camphor molecules in alloys containing 0 to 100 pct camphor.

3. Discussion

Both naphthalene-camphor and naphthalene-anthracene form eutectic mixtures with limited terminal solid solubility. The point of interest is whether this is primarily the result of symmetry considerations or of differences in molecular volumes. Consider first the naphthalene-camphor system.

The naphthalene molecule consists of two conjugated six-membered rings and the crystal symmetry is monoclinic ($P2_1/a$). The volume occupied by each molecule, calculated from the size of the unit cell (a = 8.235 Å, b = 6.003 Å, c = 8.658 Å, β = 122° 55′)[13] is 180 Å^3. On the other hand, camphor has an almost spherical molecule, a cubic crystal symmetry ($F\bar{4}3m$) and the volume occupied by each molecule, calculated from the size of the unit cell (a = 10.0 Å), is 250 Å^3. Thus neither symmetry nor volume relations between the components are favourable for extensive solid solution, although up to 12 mole pct naphthalene will dissolve in camphor (Fig. 4).

In the second system under consideration, naphthalene and anthracene form a eutectic mixture even though the molecular and crystal symmetries of the two components are identical. There is, however, a considerable difference in molecular volumes; that occupied by the anthracene molecule, calculated from the size of the unit cell (a = 8.561 Å, b = 6.036 Å, c = 11.163 Å, β = 124° 42′)[14] being 236 Å^3 compared with 180 Å^3 for naphthalene. Since symmetry considerations do not limit solubility in this case, it appears that the extremely limited solubility (Fig. 2) is due to the difference in molecular volumes, it being nearly as difficult to fit a small solute molecule into a large host as to do the converse.

The third system which we have investigated was anthracene-carbazole, the results for which have been published previously.[5] In this case, the molecular and crystal symmetries of the compounds are different but the molecular volumes are similar, the volume occupied by the carbazole molecule, calculated from the size of the unit cell (a = 7.779 Å, b = 5.722 Å, c = 19.15 Å)[15] being 212 Å^3 compared with 236 Å^3 for anthracene. In contrast to the other two systems investigated, the terminal solid solution is fairly extensive, the limit of solubility of anthracene in carbazole being 22 mole pct. At the anthracene-rich end of the diagram the situation is complicated somewhat by the occurrence of a superlattice, but at room temperature approximately 24 mole pct carbazole dissolves in anthracene before a phase change occurs.

It is possible to consider the compositions of the terminal solid solutions in terms of the immediate environment of the solute (i.e. minor component) molecules. The strict concept of nearest neighbours is not particularly appropriate to systems of low symmetry, but it is possible in camphor, naphthalene and anthracene to identify a shell of twelve molecules closely adjacent to, but at different distances from a central molecule which may be treated as " nearest neighbours ". Assuming that the solute is randomly distributed in the solvent lattice, the probability that a solute molecule will have at least one other solute molecule as a nearest neighbour is thus $[1-(1-C)^{12}]$ where C is the molar concentration of the solute.

For naphthalene dissolved in camphor the limit of solubility is 12 mole pct which corresponds to 78 pct of the naphthalene molecules having at least one naphthalene neighbour. Only 6 moles pct of camphor are soluble in naphthalene and at this concentration 52 pct of camphor molecules have a camphor neighbour. Anthracene is almost insoluble in naphthalene but at the other end of the diagram 3 mole pct of naphthalene dissolve in anthracene, and even at this low concentration, 31 pct of the naphthalene molecules will have at least one other naphthalene adjacent to them in the crystal lattice. These figures suggest that, in the absence of any tendency to form a superlattice, solute-solute pairs are quite frequent even in dilute solutions.

None of the three systems under consideration fulfil Kitaigorodskii's criteria for complete solid solubility to be possible and, in each case, only limited solubility was observed. However, the variation in the degree of solid solubility from system to system is of interest. The maximum solubility is observed in the anthracene-carbazole system in which the molecular volumes are similar but symmetry considerations are unfavourable for extensive solid solubility. In contrast, the minimum solubility is observed in the anthracene-naphthalene system where the symmetry requirements are fulfilled but the molecular volumes are dissimilar. In the naphthalene-camphor system the symmetry requirements are not fulfilled and the molecular volumes are dissimilar, although the longest dimension of the naphthalene molecule is almost the same as that of the camphor molecule. In this case the terminal solid solubility is intermediate between the two other systems.

Kitaigorodskii's thesis is that in molecular crystals the crystal structure is determined primarily by the geometrical packing of "hard" molecules which gives the densest structure, the chemical nature of the molecules being relatively unimportant. He suggests, therefore, that volume relationships are decisive in solid state solubilities between such compounds, providing symmetry requirements are met. The present results support his general conclusions, and show that when molecular volumes are comparable, extensive, though not complete, solid solubility can occur even if symmetry requirements are not fulfilled. Conversely, even if the molecular and crystal symmetries of the two components are the same, volume considerations place a severe restriction even on the number of small solute molecules that can be substituted for larger molecules.

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REFERENCES

1. Kitaigorodskii, A. I., " Organic Chemical Crystallography ", English translation by Consultants Bureau Inc., New York (1961).
2. Kitaigorodskii, A. I., *Dokl. Akad. Nauk SSSR* **113**, 604 (1957).
3. Robinson P. M. and Scott, H. G., *Acta Met.* **15**, 1581 (1967).
4. Robinson, P. M. and Scott, H. G., *J. Crystal Growth* **1**, 187 (1967).
5. Robinson, P. M. and Scott, H. G., *Mol. Cryst.* **5**, 387 (1969).
6. Hultgren, R., Orr, R. L., Anderson, P. D. and Kelley, K. K., " Selected Values of Thermodynamic Properties of Metals and Alloys ", John Wiley and Sons Inc., New York (1963).
7. " The Handbook of Physics and Chemistry ", 43rd ed., The Chemical Rubber Publishing Co., Ohio (1961).
8. Powles, J. G., *J. Chem. Phys.* **5**, 1648 (1963).
9. Rudolfi, E., *Z.S. Physik. Chem.* **66**, 705 (1909).
10. Naboikin, Yu. V., Soifer, L. M., Dobrokhobova, V. K. and Uglanova, V. V., after *Chem. Abst.* 10636 f, 57 (1962).
11. Grechnyi, Ya. V., *Dokl. Akad. Nauk SSSR* **74**, 259 (1950).
12. Schafer, K., Wagnerand, V. and Engelbach, H., *Chemische Berichte* **89**: 327 (1956).
13. Abrahams, S. C., Robertson, J. Monteath and White, J. G., *Acta Cryst.* **2**, 238 (1949).
14. Sinclair, V. C., Robertson, J. M. and Mathieson, A. McL., *Acta Cryst.* **3**, 251 (1950).
15. Robinson, P. M. and Scott, H. G., *Mol. Cryst.* **5**, 405 (1969).