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The Naphthalene–Azulene Phase Diagram

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Abstract—The phase relationships between naphthalene and azulene have been determined by differential scanning calorimetry and X-ray diffraction. The naphthalene–azulene system is a simple eutectic, with a misability gap from 10 to 31% azulene at the eutectic temperature of 345.6 K. The eutectic point occurs at 18% azulene.

1. Introduction

Current interest in the naphthalene-azulene phase diagram is centred around the spectroscopy of "mixed crystals" of naphthalene containing small amounts of azulene.(1–6) This has included studies of the polarization ratios and vibrational structure in the electronic spectrum(1,3,4,5) and dipole moments in the excited state.(5) An assumption made in all these investigations is that azulene goes into substitutional solid solution in naphthalene. This has been justified by general dimensional arguments, rather than an actual knowledge of the phase relationships between the compounds. However, it is essential for the interpretation of the spectroscopic results that the crystals should be single phase. A knowledge of the phase diagram, and especially the extent of terminal solid solution of azulene in naphthalene, is thus desirable.

Most of the work described here was carried out at A.N.U. in conjunction with spectroscopic investigations of azulene. The work in the Division of Tribophysics was restricted to calorimetric studies

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of a few selected compositions, containing not more than 30% azulene, which tended to exhibit anomalous behaviour; and to the X-ray diffraction measurements.

2. Experimental

The naphthalene–azulene alloys were prepared by melting zone-refined samples of the component compounds in pyrex capsules sealed under nitrogen, agitating the melt for 10–15 min and then air-cooling to room temperature: the alloys (20 to 100% azulene) were then kept at ambient temperature until required. However, severe segregation during cooling was encountered with alloys containing less than 20% azulene; in order to obtain homogeneous samples of these alloys it was necessary to quench the melts into iced brine and then give an additional homogenization treatment of 20 hours at 341 °K.

The binary phase diagram between naphthalene and azulene was determined by differential scanning calorimetry and X-ray diffraction, as described in detail elsewhere.(7,8,9) The solidus and liquidus of 35 alloys were determined calorimetrically and the phases present in alloys representative of the single and two phase regions so defined were confirmed by X-ray diffraction.

3. Results

Naphthalene and azulene form a simple eutectic system (Fig. 1). The experimental results on which the diagram is based are discussed most conveniently in terms of the solid phases present in the alloys.

0 TO 10% AZULENE (NAPHTHALENE (α) SOLID SOLUTION)

Calorimetric studies on the first batch of specimens to be prepared showed a eutectic peak at compositions as low as 5% azulene. However, this proved to be due to segregation of the two components during the relatively slow cooling from the melt, resulting in the formation of some eutectic alloy which would not be present at equilibrium. The eutectic peak in such samples could be eliminated by extended annealing just below the eutectic temperature, although if eutectic segregation had occurred the time necessary for homogenization was of the order of a month. The specimen preparation

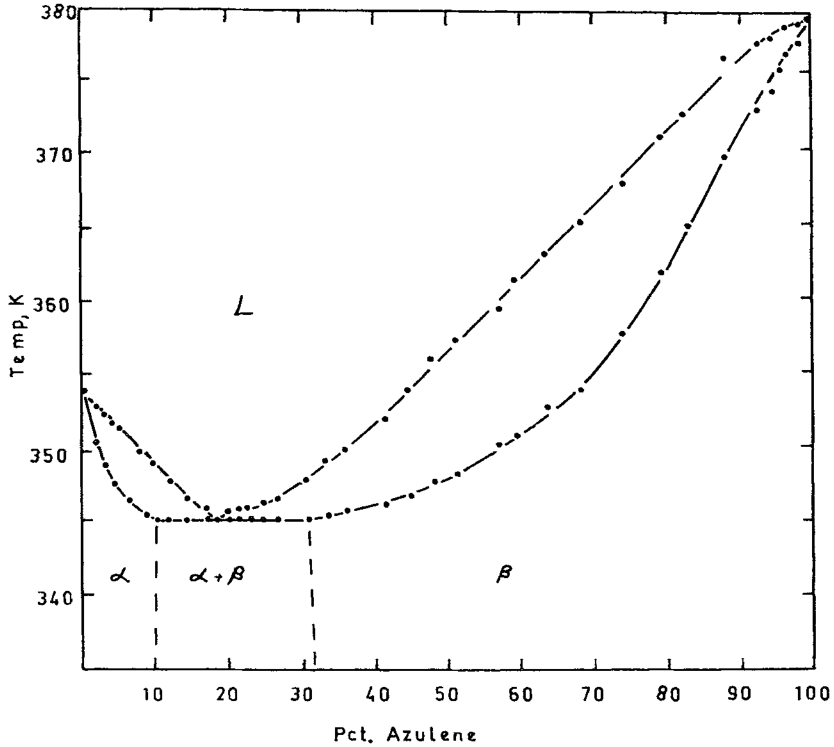

Figure 1. The naphthalene–azulene phase diagram.

technique was modified, therefore, as described above. Calorimetric runs in which the heating and cooling rate through the solidus and liquidus was varied, together with the holding time below the eutectic temperature, indicated that the second preparation technique produced equilibrated homogeneous samples.

Samples containing more than 10% azulene invariably showed a eutectic peak, indicating that this was the solubility limit of azulene in naphthalene. This was confirmed by X-ray diffraction; powder photographs of 3.5% azulene alloy were single phase (α) while the 10% azulene alloy, though predominantly α-phase, also showed a trace of β phase.

Even after the spurious eutectic peak had been removed by suitable sample preparation, some low azulene alloys continued to give a melting curve with two distinct maxima. It was thought initially that this indicated a transition in the terminal solid solution prior to melting. However, it was later demonstrated by computer simulation that such double peaks can arise fortuitously when a binary solid solution melts, particularly if the liquidus and solidus are well separated as is the case here.⁽¹⁰⁾

10 TO 31% AZULENE (TWO PHASE REGION)

The calorimetric curves for alloys containing from 10 to 31% azulene showed a sharp peak at 345.6 K associated with the melting of the eutectic mixture, together with a (more or less) broad peak over the temperature range in which the pro-eutectic solid and liquid co-exist. The variation in the relative peak heights with composition indicated that the eutectic point was at 18% azulene and the end of the eutectic horizontal at 31% azulene.

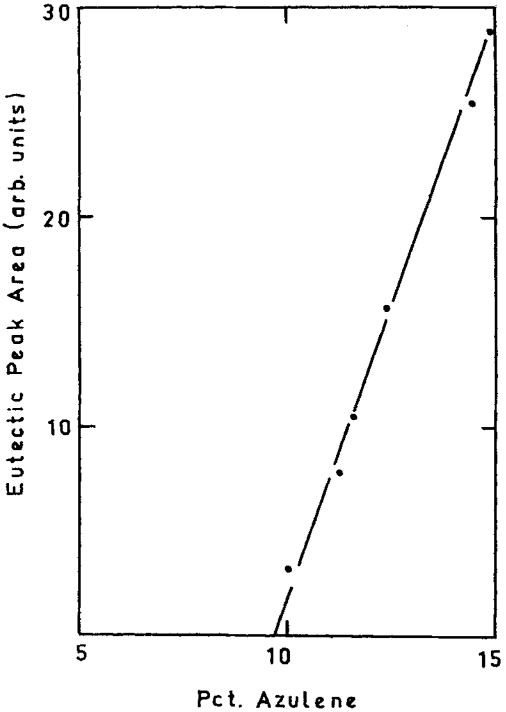

Figure 2. The variation in area of the eutectic peak with composition for naphthalene-rich naphthalene–azulene alloys.

The solubility limit of azulene in naphthalene deduced from the appearance of the eutectic peak was confirmed by the plot of the eutectic peak area versus composition, linear extrapolation of which to zero area gives 10% azulene as the limit of solid solubility (Fig. 2).

X-ray diffraction powder patterns showed that the 15, 20 and 25% azulene alloys were indeed two phase mixtures of α (naphthalene structure) and β (azulene structure).

31 TO 100% AZULENE (AZULENE (β) SOLID SOLUTION)

In calorimetric measurements a single broad peak, indicating the melting of a solid solution, was observed for alloys containing more than 31% azulene.

X-ray powder diffraction patterns confirmed that alloys containing 33, 40, 60 and 80% azulene were single phase solid solutions with the azulene structure. The variation in lattice parameter with composition for these alloys is shown in Fig. 3; the standard deviation for the values was approximately 0.01 Å in *a*, *b* and *c* and 0.15° in β.

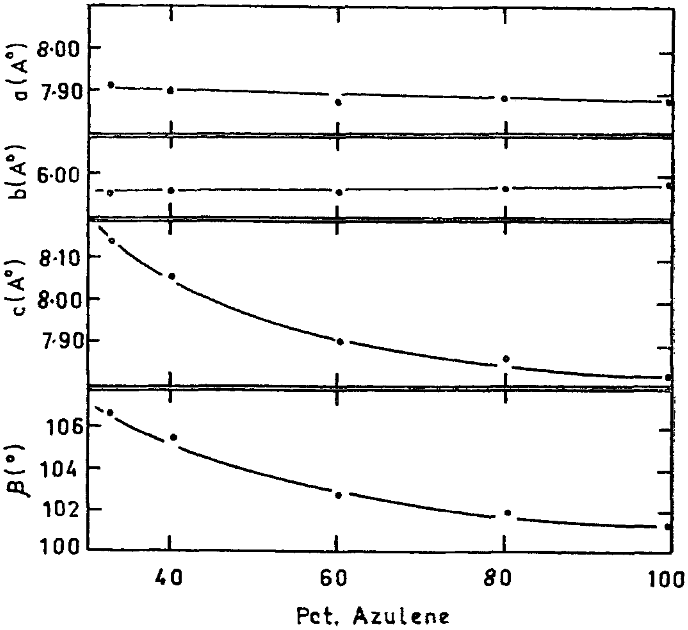

Figure 3. The variation in lattice parameters of the azulene-rich β terminal solid solution with composition.

The *a* and *b* parameters did not vary appreciably with composition but the changes in *c* and β were large, and well in excess of experimental error. The variations of *c* and β with composition indicate that the azulene-rich terminal solid solution extends to at least 33% azulene.

4. Conclusions

The naphthalene–azulene system is a simple eutectic, with a miscibility gap from 10 to 31% azulene at the eutectic temperature of 345.6 K. The eutectic point occurs at 18% azulene. The apparent extension of the miscibility gap below 10% azulene, as evidence by a eutectic peak in some calorimetric curves, is a consequence of segregation which is severe in this system, especially in naphthalene-rich alloys.

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