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The Naphthalene–β-Naphthol System

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Abstract—The phase relations in the naphthalene–β-naphthol system have been determined by calorimetry, X-ray diffraction and optical microscopy. Three stable solid phases occur; α which is a solid solution of β-naphthol in naphthalene, βI which is a solid solution of naphthalene in the metastable form of β-naphthol and βII which is a solid solution of naphthalene in the stable form of β-naphthol. The main features of the phase diagram are a peritectic at 367.3 K with a miscibility gap from 62% to 77% β-naphthol, and a eutectoid at about 355 K. The differences between this diagram and those published previously are discussed.

1. Introduction

The form of the equilibrium phase diagram between naphthalene and β-naphthol is still in doubt despite the fact that it has been determined on numerous occasions since the late 19th century.(1–7) All the early workers(1–4) agreed that the system showed complete solid solubility and a monotonic variation of melting point with composition; that is, it was of Roozeboom's Type I.(8) However, the solidus determined by Rudolfi(3) showed points of inflexion which might be interpreted as an indication of a peritectic and an associated miscibility gap in the solid.

In 1939 Neuhaus(9) expressed the view that the system should not exhibit complete solid solubility since naphthalene and β-naphthol are not isostructural, i.e. having the same space group and number of molecules in the unit cell; naphthalene being monoclinic, space group $P2_1/a$, $Z = 2$,(11) while β-naphthol, also monoclinic has space group Ia,† $Z = 8$.(12) This opinion was reiterated more recently by Kitaigorodskii.(10) The inconsistency between the experimental and theoretical viewpoints was overcome in 1942 when Kofler(5)

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† In Ref. 7 β-naphthol was incorrectly placed in space group $P2_1/a$.

pointed out that β-naphthol existed in two crystalline modifications; the stable room temperature form II, and the form I which is metastable with respect to II and apparently isostructural with naphthalene. Kofler(5) found that form I was stabilized by, and formed a complete series of solid solutions with naphthalene. Coppens and Heairfield(13) partially determined the structure of β-naphthol I and found that it was isostructural with, and had very similar lattice parameters to naphthalene.

Despite the attention which this system has received, the two most recent phase diagrams,(6,7) which were published almost simultaneously, differ from one another and from the previous work in several essential details. The present work was undertaken in an attempt to understand the origin of these differences by re-examining some of the critical compositions. This has led to a modified version of the naphthalene–β-naphthol diagram which is in substantial accord with the experimental results of both Baumgarth, Chanh, Gay, Lascombe and Le Calve(6) and Robinson, Rossell, Scott and Legge.(7) This diagram indicates that the phase relations in this system are more complex than had previously been suspected.

2. Review of Recent Work

The phase diagrams determined by Baumgarth *et al.*(6) and Robinson *et al.*(7) are shown in Figs. 1 and 2 respectively. There is reasonable agreement between the actual experimental results for the solidus and liquidus in most regions of the diagram, although there are major differences in the interpretation of the phase relations in the solid. There are three main points of disagreement between the two diagrams. The first concerns the stable form of β-naphthol. Baumgarth *et al.* state that the II → I transition takes place between 118 and 120 °C on heating, so that the form I has a narrow region of stability just below the melting point, while Robinson *et al.* imply that the form II is stable up to the melting point.

The second point of disagreement concerns the solubility of naphthalene in β-naphthol at room temperature and the phase changes in β-naphthol rich alloys. The diagram of Baumgarth *et al.* indicates that naphthalene is virtually insoluble in β-naphthol while that of Robinson *et al.* shows appreciable solid solubility (~16%)

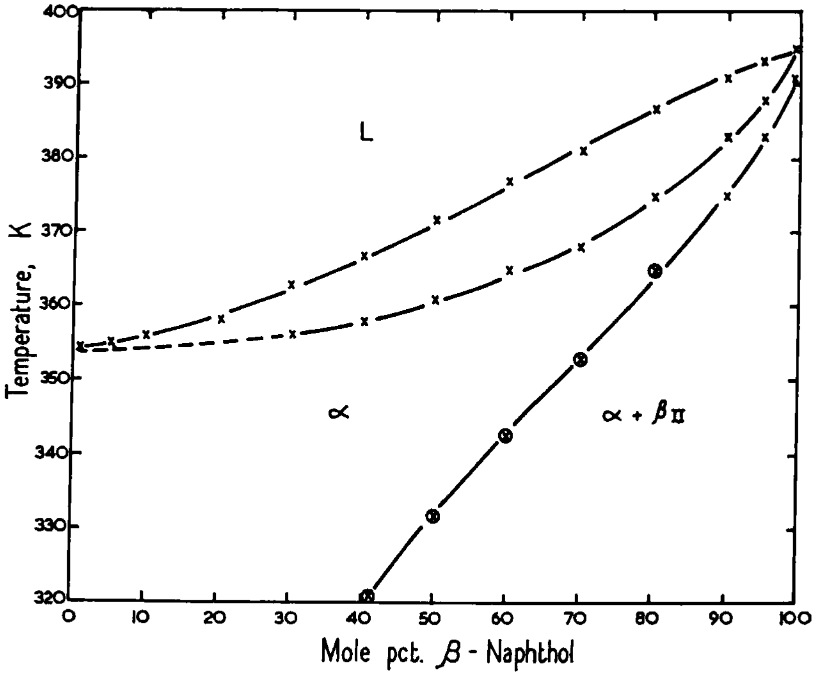

Figure 1. Phase diagram for naphthalene–β-naphthol (after Baumgarth *et al.*(6)).

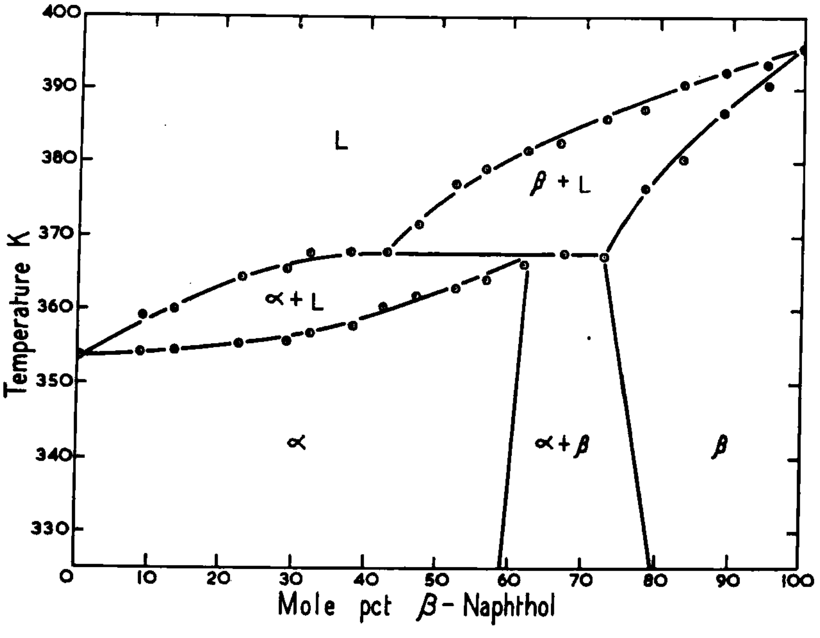

Figure 2. Phase diagram for naphthalene–β-naphthol (Robinson *et al.*(7)).

with the β II structure stable up to the melting point. In addition, Baumgarth *et al.* indicate that a phase change from two phase ($\alpha+\beta$ II) to single phase β I occurs just below the solidus in these β-naphthol rich alloys.

The third major point of disagreement between the two diagrams is the extent of solid solubility of the two components at temperatures just below the solidus. Baumgarth *et al.* indicate complete miscibility between naphthalene and β-naphthol I at the solidus temperature, with the naphthalene (or β-naphthol I) structure persisting at all compositions, while Robinson *et al.* found that a peritectic reaction occurred with a resulting miscibility gap in the solid.

Since both phase diagrams were determined using differential thermal analysis and X-ray diffraction, it seems likely that details of specimen preparation were critical in determining whether metastable or stable equilibria were studied. It may be noted that where solid state diffusion is necessary to establish equilibrium in organic systems, such equilibrium may be established slowly, if at all.

3. Experimental Techniques

In view of the possible influence of experimental technique on the results obtained, the procedures used are described in some detail. The sample preparation follows closely that described by Robinson *et al.*: ingots weighing about 200 mg were prepared from zone-refined naphthalene, and from zone-refined and vacuum sublimed β-naphthol, each containing less than 30 p.p.m. total impurities, by melting under dry nitrogen in sealed pyrex ampoules of 3 mm bore. The ampoules were shaken for about 30 minutes to ensure thorough mixing of the melts and were then quenched into iced brine. Finally each sample was annealed for a week at 329 K to facilitate solid state equilibration, followed by a further period of not less than four weeks at room temperature.

For calorimetric work, samples weighing about 10 mg were prepared by sealing coarse pieces of the alloys into gas-tight aluminium pans. These samples were heated at 4 K min^{-1} in a Perkin–Elmer DSC-1B scanning calorimeter which was calibrated with high purity gallium, naphthalene and indium. At least three runs using fresh samples were carried out for each alloy composition; the interpretation of the calorimetric curves has been discussed previously in some detail.(7,14)

For X-ray examination, samples were finely powdered and mixed with thoria as an internal standard. Room temperature studies were made using a Guinier–Hagg focusing camera with samples sealed between two thicknesses of aluminium foil to prevent evaporation; the transparent adhesive tape commonly used was not satisfactory for critical work owing to its tendency to dissolve some naphthalene from the sample. Studies above room temperature were made using a 19 cm powder camera with samples sealed in pyrex tubes. A polyester putty was used for sealing as cements containing volatile solvents could affect the specimen; shellac which is normally dissolved in alcohol was notably bad in this respect.

4. Results and Discussion

Since earlier work had established the broad outline of the phase diagram only a few compositions whose behaviour was critical to resolving the disagreements were studied. The experimental points determined by calorimetry, X-ray diffraction and optical microscopy are plotted in Fig. 3, together with those determined in the previous investigations by Baumgarth *et al.* and Robinson *et al.* Although the resultant phase diagram is more complex than those originally reported, it reconciles most of the available data. The phase relations are best discussed by considering the alloy compositions for which there are critical differences between the various diagrams.

PURE β-NAPHTHOL

It is well established that β-naphthol grown from the melt is initially form I, and that on cooling it transforms to form II(5,6,13) but it is not clear whether there is a temperature range in which form I is stable. Since the polymorph stable at the melting point must have the higher melting point, a sufficiently accurate determination of the relative melting points of the two forms would resolve the question of stability. Calorimetric measurements were carried out on pure β-naphthol aged at room temperature (form II), and also on samples solidified from the melt immediately prior to measurement (form I). The results were inconclusive, but in contrast to the results of Baumgarth *et al.*, the melting curves for form II showed no sign of a shoulder which might be associated with the II → I transition.

Optical microscopy using a hot stage was more informative than the calorimetric measurements. Following Kofler,(5) β-naphthol was melted between a glass slide and cover slip and then allowed to solidify to form I. The specimen was held for a short time at 370 K until some, but not all, of the sample had transformed to form II. The temperature was then raised to 390 K, which halted the transformation and resulted in a metastable two-phase structure. It was found that on slowly heating such a sample the crystals of form I (i.e. those present immediately after solidification) invariably melted first, leaving briefly crystals of form II (resulting from the transformation) in molten form I. This sequency of events is illustrated in Fig. 4. The actual difference in melting points was too small to measure accurately, being less than 0.2 K, but it was sufficient to establish that form II is the stable modification of β-naphthol at the melting point.

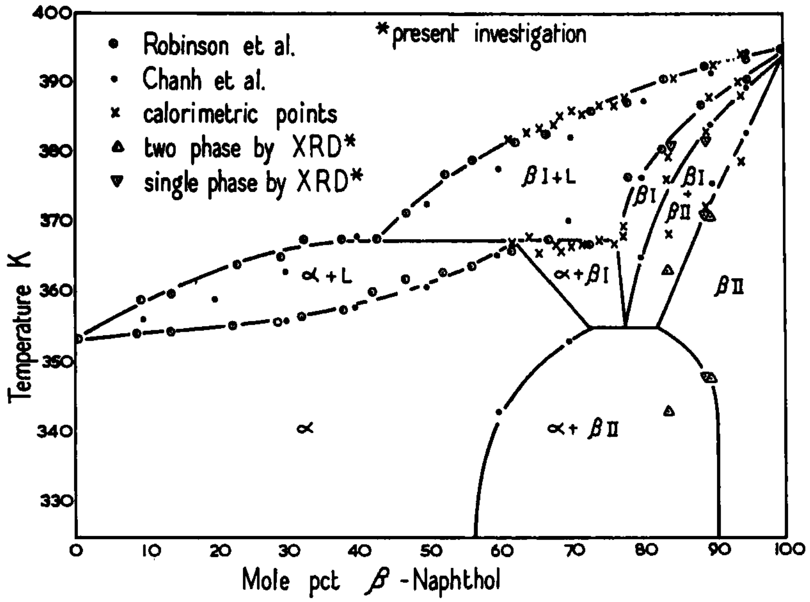

Figure 3. Revised phase diagram for naphthalene–β-naphthol (this work).

NAPHTHALENE–89% β-NAPHTHOL

Calorimetric curves obtained by heating well annealed samples of this composition showed a small premelting peak, from 371 to 383 K which is a few degrees below the solidus temperature. There was no corresponding peak on cooling, nor was there a peak when samples were melted, solidified and immediately reheated. Samples which were melted, cooled and allowed to stand for some hours before reheating did show the premelting peak. We had observed this peak previously, but as it did not appear to be reproducible, we erroneously dismissed it as spurious. Similar premelting peaks were also observed with alloys containing 84 and 94% β-naphthol.

Baumgarth *et al.* observed a peak below the solidus temperature both on cooling and on heating for compositions from 80 to 100% β-naphthol. The peak observed on heating they interpret as defining the boundary of a two-phase, $\alpha + \beta$ II, field.

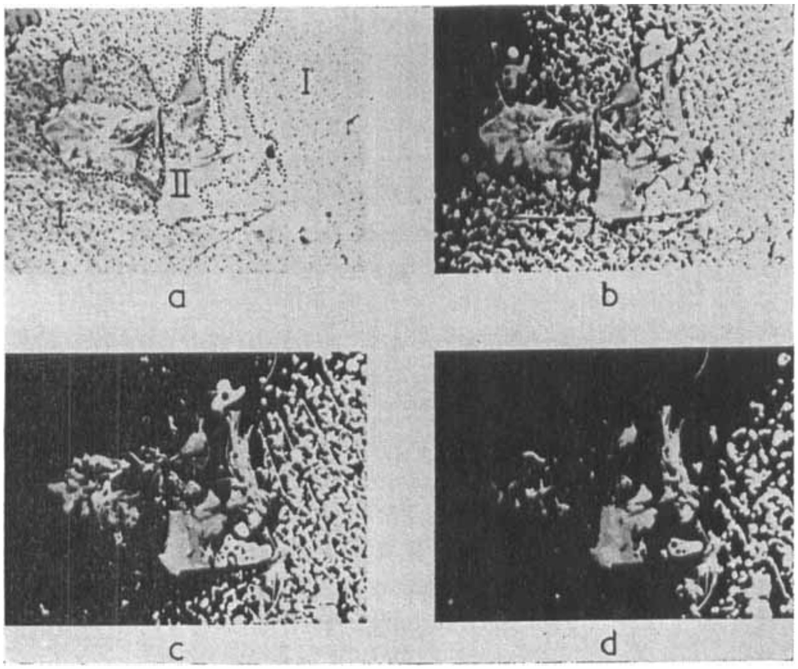

Figure 4. Melting of pure β-naphthol: (a) two-phase field showing grains of form II in a matrix of form I; (b), (c) and (d) successive stages in the melting of this field. Polarized light, × 44.

Optical microscopy of the 89% alloy showed clearly the nature of the transformations indicated by the calorimetry. Immediately after freezing specimens were single phase, consisting of a few large grains which we assume to have the β I structure. On standing at room temperature, a phase change occurred yielding many small grains: the onset of this transformation was very sluggish, particularly in thin specimens where the β I structure sometimes persisted for a week or more, but once initiated, the transformation was substantially complete even in the thinnest specimens within twelve hours. In the relatively thick samples used for calorimetry, it is to be expected that the transformation will be much more rapid. When the transformed specimen was heated, there was no observable change, e.g. grain growth, below 378 K; between 378 and 383 K (about the same temperature range as the premelting peak observed calorimetrically) there was a rapid transition back to the β I structure and the original crystal grains were regenerated. This sequence is illustrated in Fig. 5.

X-ray powder photographs of the 89% alloy at room temperature showed only the lines characteristic of the β-naphthol II structure, indicating that the alloy is a solid solution of naphthalene in β-naphthol II, though the lattice parameters of this solution did not differ significantly from those of pure β-naphthol.(7) On heating to 371 K some weak β I lines appeared, but the alloy was still predominantly β II. Above 371 K, transformation was rapid and at 381 K the structure was almost entirely β I.

We interpret these results as indicating that 89% β-naphthol exists at room temperature as a homogeneous solid solution with the β-naphthol II structure. This transform to the β I structure on heating over a temperature range of a few degrees, within which β I and β II can coexist. The transformations are therefore essentially diffusionless, which is consistent with the kinetics observed. The alternative hypothesis implied by Baumgarth *et al.*'s diagram (Fig. 1), that the transformations involve segregation of β II and α (cooling) and solution of β II in α (heating), requires extensive solid state diffusion and an extended temperature range for the transition. This does not seem to accord well with our observations, in particular that there is no microscopically observable change on heating prior to rapid and complete transformation at about 380 K.

NAPHTHALENE–(60–80)% β-NAPHTHOL

The major point of disagreement between Baumgarth *et al.* and Robinson *et al.* is the mutual solubility of naphthalene and β-naphthol at temperatures just below the solidus. To re-examine this question, ten samples with compositions within the limits of the peritectic horizontal reported previously by Robinson *et al.* were prepared as described above. When these samples were heated from room temperature at 4 K min^{-1}, the first deviation from the base line of the DSC output curve occurred in the temperature range 366.0 to 367.5 K and at the same temperature, within experimental error, for each composition. If, however, samples were melted, cooled and immediately remelted a second, somewhat higher, melting point was obtained. This higher melting point did depend on composition

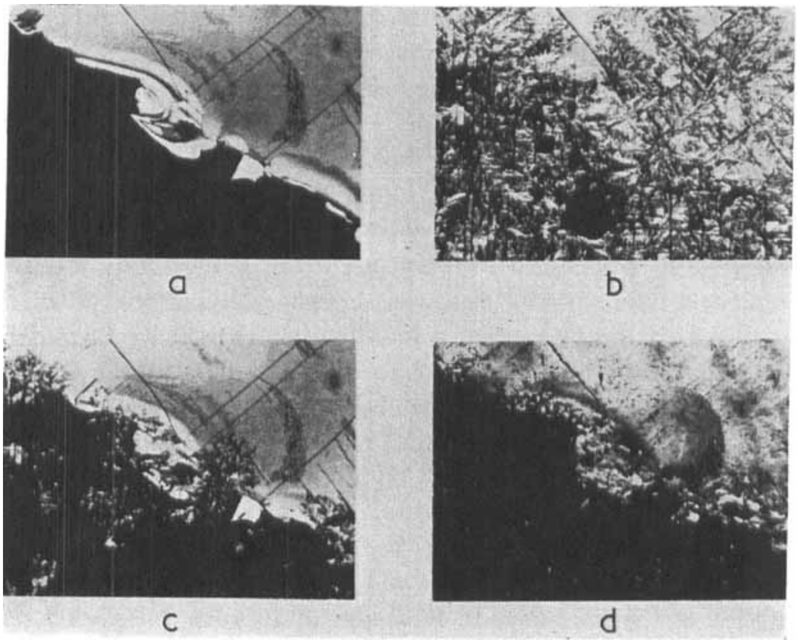

Figure 5. Phase transitions in naphthalene–89% β-naphthol: (a) as frozen showing two grains of β I; (b) after 4 hrs at 300 K: β II regions developing; (c) after 12 hrs at 300 K: complete transformation to β II; (d) heated to 385 K: transformation back to β I (note the reappearance of the original grain structure). Polarized light, ×26.

and agreed with the solidus determined by Baumgarth *et al.* (Figs. 2 and 3).

It is apparent that difficulties in attaining true equilibrium are a source of some of the discrepancies in this region of the diagram. X-ray diffraction suggests that at least above 360 K equilibrium is attained rapidly. However, for the X-ray work time is measured in hours rather than the minutes required for calorimetric measurements, so that it is not certain that either of the solidus temperatures determined above represents the equilibrium value. In an attempt to resolve this question, samples were held isothermally at 360 K (i.e. about 7 K below the presumed peritectic temperature) before determining the melting range: the results, which were by no means conclusive, lay between the two melting points determined previously.

More definite evidence for the existence of a peritectic was obtained by cooling 70% β-naphthol from 390 K at 4 K min^{-1}. A sharp peak from 371 to 367 K corresponded to primary solidification of the alloy, and this was followed by a tail extending to 353 K (Fig. 6(a)). Holding isothermally at 367 K for 5 min reduces the area of this tail (Fig. 6(b)), and holding at 367 K for 20 min eliminates it completely (Fig. 6(c)). Figure 6(d) merely repeats Fig. 6(a) to ensure that the sample properties have not changed. We associate this tail with a reaction occurring immediately after the primary solidification: this reaction is inconsistent with the hypothesis of complete solid solubility as proposed by Baumgarth *et al.* and others(1–4) and is most readily explained by the presence of a peritectic in the system: the enthalpy of the reaction calculated from the area of the tail is 9.30 kJ mole^{-1}. In addition, the microstructure of alloys close to 70% β-naphthol is indicative of a peritectic reaction.(3)

Additional evidence for a miscibility gap is provided by the variation of enthalpy of fusion with composition. The enthalpies of fusion of the ten alloys in the range 60 to 80% β-naphthol were determined from calorimetric measurements and, together with the values previously determined for other compositions, are plotted in Fig. 7. It is clear that this plot is quite different to the monotonic variation of enthalpy of fusion with composition, charactristic of systems with complete solid solubility. The form of the plot indicates

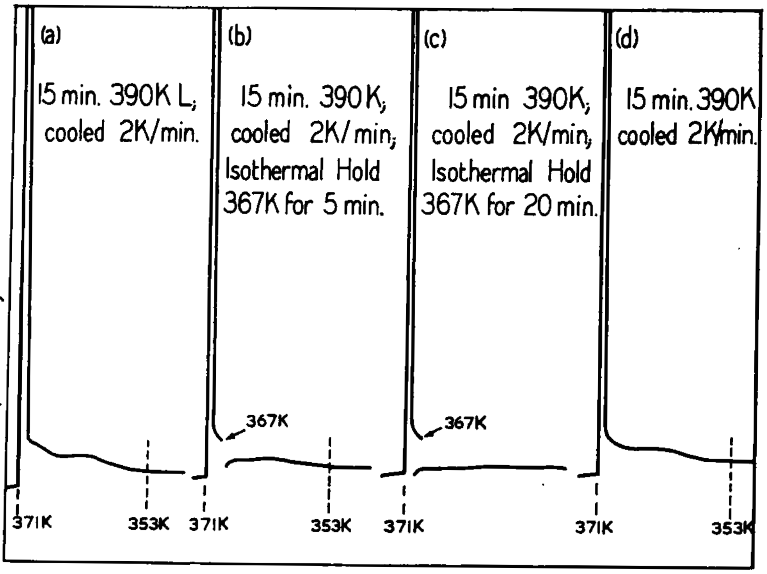

Figure 6. DSC traces for cooling of naphthalene–70% β-naphthol: (a) continuously cooled at 4K min^{-1}; (b) with 5 min isothermal hold at 367K; (c) with 20 min at 367K; (d) repeat of (a) at end of series.

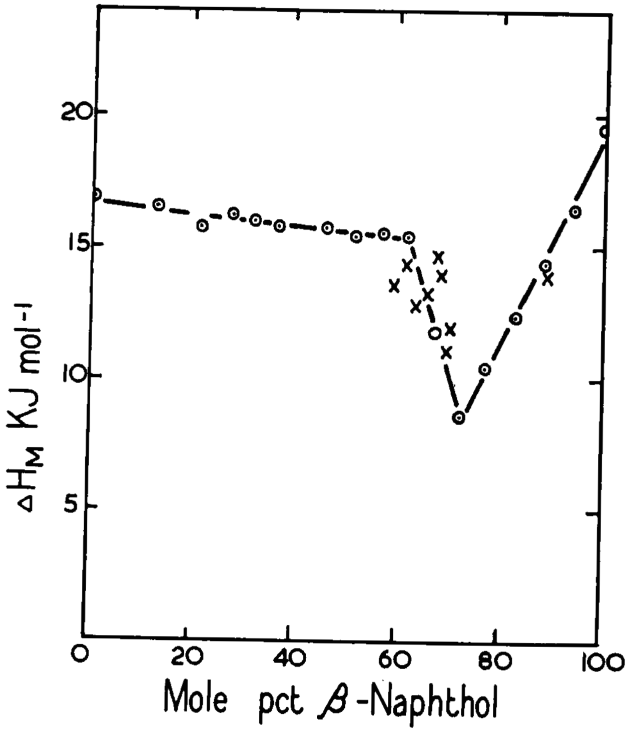

Figure 7. Variation of enthalpy of fusion with composition for naphthalene–β-naphthol alloys.

that the miscibility gap extends from about 62 to 72% β-naphthol, though this apparent width could be influenced by non-equilibrium effects. As was reported previously, the enthalpy of the peritectic reaction was calculated to be 9.70 ± 0.42 kJ mole^{-1}, in good agreement with the value determined from the cooling curve for the 70% β naphthol alloy.

In contrast to the results of calorimetry and microscopy, X-ray diffraction studies on the 70% β-naphthol alloy appeared to support the hypothesis of complete solid solubility at the solidus temperature. This alloy was clearly two phase ($\alpha + \beta$ II) at room temperature and at 345 K, although the proportion of β II was reduced at the higher temperature: at 360 K the alloy was apparently single phase α. These results are consistent with the diagram of Baumgarth *et al.* rather than that of Robinson *et al.* which would require 70% β-naphthol to be two phase ($\alpha + \beta$ II) at all temperatures below the solidus.

The X-ray evidence can be reconciled with that from calorimetry and optical microscopy if it is assumed that the products of the peritectic reaction are the α and β I phases, which are difficult to distinguish by X-ray diffraction. On further cooling, the β I phase transforms to β II to give the equilibrium ($\alpha + \beta$ II) structure at room temperature.

5. Conclusions

In the light of the new experimental data presented above and considering also the diagrams of Baumgarth *et al.*(6) and Robinson *et al.*(7), we now believe that the phase equilibria in the naphthalene–β-naphthol system are essentially as illustrated in Fig. 3. Three stable solid phases occur; α which is a solid solution of β-naphthol in naphthalene, β I which is a solid solution of naphthalene in the metastable form of β-naphthol, and β II which is a solid solution of naphthalene in the stable form of β-naphthol.

The principal features of the diagram are a peritectic at 367.3 K with a miscibility gap from 62 to 77% β-naphthol, and a eutectoid at about 355 K. This diagram differs from that published previously by Robinson *et al.* by the introduction of a stable β I field at high temperatures and high β-naphthol concentrations, and the introduction of a eutectoid and the associated two-phase fields necessary to satisfy the thermodynamic restrictions for an equilibrium phase diagram.

The new diagram presented here also differs from that of Baumgarth *et al.* who consider that there is no peritectic and hence a continuous transition between the isostructural phases α and β I, and also that naphthalene is almost insoluble in stable β-naphthol so that the β II field is negligible in area. They also consider that pure β-naphthol is stable in the β I configuration for a few degrees below its melting point.

Since the peritectic which we propose involves a narrow miscibility gap between the isostructural phases α and β I (which differ only slightly in lattice parameters) the two phase region is not in practice distinguishable by X-rays. Thus the X-ray observations of Baumgarth *et al.* as to the crystal structures present just below the solidus, with which we in general agree, are consistent either with complete solid solubility or an α–β I miscibility gap. The calorimetric results, however, require a miscibility gap to account for both the variation of the enthalpy of fusion with composition and more particularly the transformation occurring after solidification in the naphthalene–70% β-naphthol alloy.

Turning finally to the stability of the β I structure in pure β-naphthol, there appears to be definite disagreement about the experimental results. In the absence of other evidence, this seems to indicate a difference in sample purity. Baumgarth *et al.* do not estimate the purity of their material apart from describing it as " analytical grade subsequently sublimed ". Without additional analysis, this description is scarcely definitive, but may refer to material less pure than that prepared by recrystallization from ethanol, zone refining and vacuum sublimation.

We conclude, therefore, that Fig. 3 correctly represents the phase equilibria in naphthalene–β-naphthol, with the qualification that boundaries between solid phases should be regarded as indicative rather than absolute. We further believe that differences between this and other published diagrams for the system can be explained largely by difficulties in establishing true equilibrium, and possibly also by differences in purity of the components.

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