ARTICLES

SOME PHYSICOCHEMICAL STUDIES ON ORGANIC EUTECTICS AND 1:2 ADDITION COMPOUNDS: *p*-PHENYLENEDIAMINE–α-NAPHTHOL AND *p*-PHENYLENEDIAMINE–β-NAPHTHOL SYSTEMS

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ABSTRACT

Phase diagrams of *p*-phenylenediamine–α-naphthol and *p*-phenylenediamine–β-naphthol systems determined by thaw melt method show the formation of 1:2 addition compounds. The solidification behaviour of pure components, eutectics and addition compounds, studied by measuring the rate of movement of growth front in a capillary, suggests that crystallization data obey Hillig–Turnbull equation. Infrared spectral studies of pure components and addition compounds indicate weak interactions among the components forming the molecular complex.

INTRODUCTION

THE solid state chemistry of eutectics is an interesting[1-3] topic in materials science and metallurgy. The chemistry of eutectics has been a field of active investigation[4,5] during the recent past because eutectics have unusual physical properties not normally shown by the parent components. Metallic eutectics constitute an interesting area of research in metallurgy and materials science. However, owing to their low transformation temperature, ease in purification and transparency, and because of the wider choice of materials, organic eutectics are more suitable for investigation and have attracted the attention of many research groups[6-11]. Further, experimental techniques for organic systems are simpler and more convenient compared to those adopted for metallic systems. Besides, the small density difference of the two components forming an organic eutectic minimize density-driven convection effects on solidification. Most of the studies[12,13] in the past were on simple eutectic types. There are only a limited number of cases in which two components form 1:1 addition compounds[14-16] with congruent melting points. The molecular compounds are of potential technical interest since they are quite common in metallurgical systems. To the best of our knowledge there are no reports on studies of 1:2 addition compounds of organic origin that are organic analogues of intermetallic compounds. With a view to throw some light on solidification mechanisms and nature of interactions among the components forming eutectics and addition compounds, the phase diagram, linear velocity of crystallization and infrared spectral behaviour of *p*-phenylenediamine–α-naphthol (PPD–AN) and PPD–β-naphthol (PPD–BN) systems were studied.

METHODS

Phase diagrams of PPD–AN and PPD–BN were determined by the thaw melt method[17]. The linear velocity of crystallization was studied by the technique described earlier[18,19] using a glass U-tube (internal diameter 0.5 cm) with a 15-cm-long flat portion. The infrared spectra of pure components, eutectics and addition compounds were recorded[20] in nujol in the 4000–600 cm^{-1} region on a Perkin–Elmer 783 infrared spectrophotometer.

RESULTS AND DISCUSSION

Solid–liquid equilibrium data for PPD–AN and PPD–BN are plotted in figures 1 and 2 respectively. In both cases, there is a maximum, surrounded by two eutectics, and a molecular complex of 1:2 stoichiometry with congruent melting is formed. In the case of PPD–AN the two eutectics E_1 and E_2 have 0.38 and 0.93 mole fractions of AN, whereas in

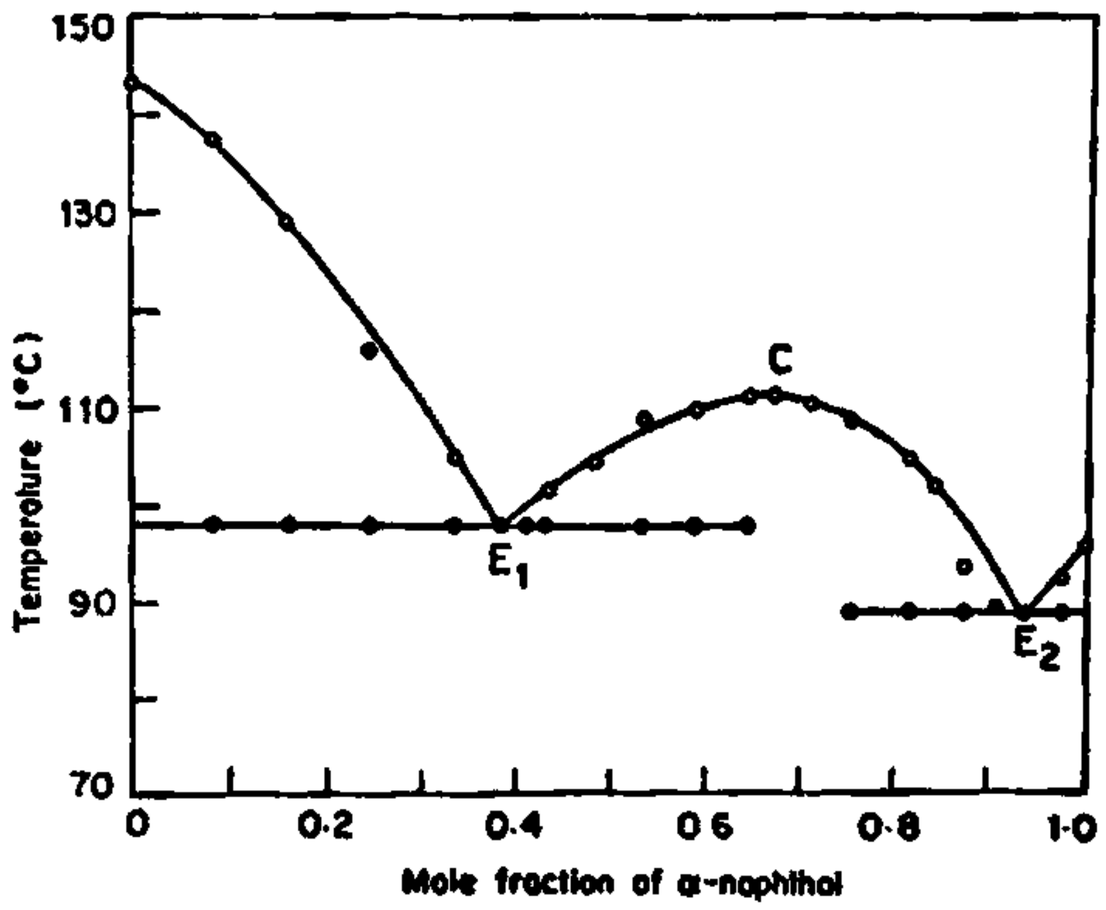

Figure 1. Phase diagram for PPD–AN. ○, Melting temperatures; ●, thaw temperatures.

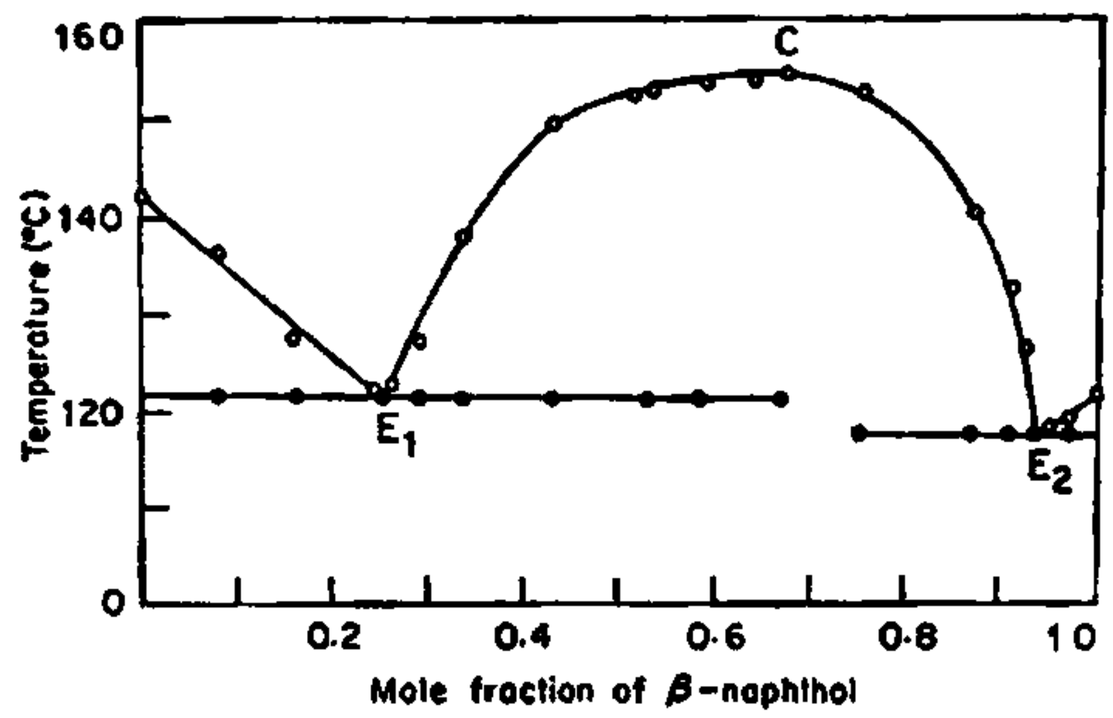

Figure 2. Phase diagram for PPD–BN. ○, Melting temperatures; ●, thaw temperatures.

PPD–BN the corresponding mole fractions of BN are 0.25 and 0.93. The eutectic temperatures for E_1 and E_2 in PPD–AN are 98.5 and 89.0°C respectively, and the corresponding eutectic temperatures in PPD–BN are 121.5 and 118.0°C. The melting points of the resulting addition compounds in PPD–AN and PPD–BN are 115.5 and 154.5°C respectively. From the phase diagrams it can be inferred that each system forms two eutectics and one 1:2 addition compound with congruent melting point indicated at C in the figures. For each eutectic, the addition compound serves as one of the components. The maximum in these systems is flat, indicating that the addition compounds are dissociated in the molten state. From the phase diagram it can also be inferred that these systems have addition compounds capable of existing as a solid in equilibrium with a liquid of the same composition.

Using the capillary method, the linear velocity of crystallization of the pure components, eutectics and 1:2 addition compounds was determined at different undercoolings. The experimental data plotted in the form of log v vs log ΔT are given in figures 3 and 4. The linearity of the logarithmic plots indicates the validity of the Hillig–Turnbull[21] relation

$$v = u(\Delta T)^n,$$

where u and n are constants and ΔT is undercooling. The experimental values of these constants are given in table 1. Various theories[17] have been developed for the growth mechanism of eutectics and predict a square relation between crystallization velocity and undercooling. The values of n in the present investigation are very close to two. The deviations[10] in values of n from 2, observed in some cases, may be due to the difference between bath temperature

Figure 3. Linear velocity of crystallization at various degrees of undercooling for PPD AN. [I, α-Naphthol; II, *p*-phenylenediamine; III, AN PPD addition compound; IV, Futectic 1; V, Futectic 2.]

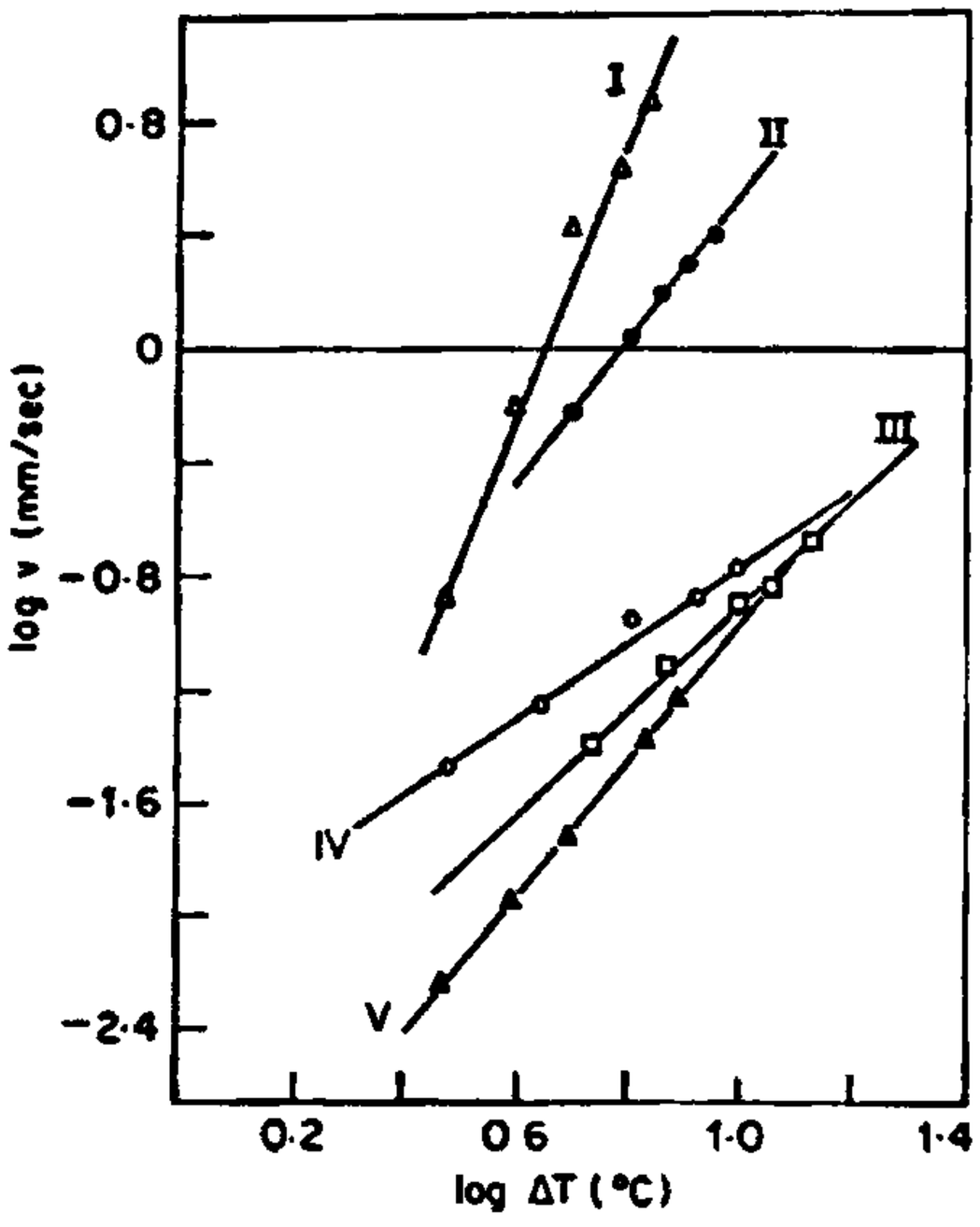

Figure 4. Linear velocity of crystallization at various degrees of undercooling for PPD–BN. [I, β-Naphthol; II, *p*-phenylenediamine; III, BN–PPD addition compound; IV, Eutectic 1; V, Eutectic 2.]

Table 1 *Values of u and n for PPD, AN, BN, and their eutectics and addition compounds*

System	*u* (mm/sec. deg)	*n*
PPD–AN		
PPD	0.01023	2.60
AN	0.00239	2.50
1:2 Addition compound	0.07243	1.14
Eutectic 1	0.00141	2 60
Eutectic 2	0.00763	1.80
PPD–BN		
BN	0.00092	4.66
1:2 Addition compound	0.00174	1.84
Eutectic 1	0.00945	1.33
Eutectic 2	0.00078	2.40

and temperature of growing interface. It is evident from figure 3 that the addition compound in PPD–AN crystallizes at a rate slower than that of PPD but faster than that of AN. From figure 4 it can be inferred that the crystallization rate of the PPD–BN addition compound is lower than the rates of both components. Studies on the crystal morphology of addition compounds indicate that they crystallize as a definite chemical entity. However, during crystallization the two components from the melt have to enter the crystal lattice simultaneously in such a way that the composition of the melt conforms to a 1:2 molar ratio of the two components. Because of this, the linear velocity of crystallization of the addition compounds may be expected to be of the order of the velocity of the species crystallizing at the slower rate.

It is evident from figure 3 that in PPD–AN the crystallization velocities of E_1 and E_2 are lower than those of the parent components and the 1:2 addition compound. E_1, with a low molar concentration of AN, solidifies faster than E_2, which has a high molar concentration of AN. The crystallization data for PPD–BN, given in figure 4, show that the crystallization rate of E_1 is lower than those of its parent components but higher than those of the addition compound and E_2. These results may be explained on the basis of the mechanism proposed by Winegard *et al*[22]. According to them eutectic solidification begins with the formation of the nucleus of one of the phases. This would grow until the surrounding liquid becomes rich in the other components and a stage is reached when the second component starts nucleating. Now there are two possibilities. First, the two initial crystals may grow side by side. This explains the cases in which the rates of solidification of eutectics are not lower than those of the parent components and addition compounds. The second possibility is that there may be alternate nucleation of the two components. This explains the solidification in the cases where the crystallization velocity of the eutectics is lower than those of the parent components and addition compounds. The solidification of the first eutectic E_1 of PPD–BN may take place by side-by-side growth of the two phases, whereas solidification of both eutectics of PPD–AN and the second eutectic E_2 of PPD–BN takes place by alternate nucleation of the two components. In these systems, the 1:2 addition compound behaves as one of the parent components for both the eutectics. The infrared spectrum of pure PPD has two weak characteristic bands, one at 3380 cm^{-1} and the other at 3300 cm^{-1}. The IR spectrum of AN gives a broad characteristic band[23] in the 3150–3350 cm^{-1} region. But the 1:2 addition compound of PPD–AN gives two strong bands, one at 3380 cm^{-1} and the other at 3300 cm^{-1}. The IR spectrum of pure BN also shows a broad characteristic band in the 3150–3350 cm^{-1} region. But the IR spectrum of the 1:2 addition compound of PPD–

BN gives two strong bands, one at 3380 cm^{-1} and the other at 3300 cm^{-1}. The increase in intensity[23] of 3380 cm^{-1} and 3300 cm^{-1} bands observed in the 1:2 addition compounds of AN and BN with PPD is due to intermolecular hydrogen bonding between the two components in each system.

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NEWS

S&T CO-OPERATION BETWEEN INDIA AND JAPAN

A joint meeting of the India–Japan Study Committee was held in New Delhi on March 2 and 3, 1989. The Indian delegation was headed by Sri Abid Hussain, Member, Planning Commission, and the Japanese team by Dr T. Mukaibo, Chairman, Atomic Energy Commission, Japan.

Some important recommendations of the India–Japan Study Committee include: (i) the establishment of a specific mechanism for taking up joint research projects in the fields of science and technology; (ii) increasing personnel exchanges between India and Japan, particularly involving scholars and scientists; (iii) the setting up of Indo–Japanese Information Centre to facilitate information exchange and development of contacts; and (iv) conducting joint studies in social sciences.