

Articles

Solidification Behaviour of Binary Organic Eutectics and 1 : 2 Addition Compounds

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Due to possibility of visual observation of phase transformations and processes during solidification, the transparent binary alloy models are important in materials and metallurgical sciences. As such, phase diagram, linear velocity of crystallization, microstructure and spectral behaviour of binary organic systems of benzidine with resorcinol and catechol involving formation of addition compound with congruent melting point have been studied. While their phase diagrams show the formation of two eutectics and a 1 : 2 (B : RC, B : CT) addition compound in each case, the crystallization data obey the Hillig-Turnbull equation. The microstructural investigations give the characteristic morphology of the eutectics and the addition compounds, the spectral studies suggest intermolecular hydrogen bonding between two components forming the molecular complex.

Introduction

The modern age of science demands materials with specific properties. Metallic eutectics and intermetallic compounds offer an interesting area of investigation¹⁻³ in metallurgy and materials science from the point of view of producing new materials of commercial and technological importance. While high transformation temperature and opacity cause considerable inconvenience in experimentation of these systems, that of the density driven convection effects give rise to erroneous results on solidification. A critical scanning of the existing literature⁴⁻⁸ reveals that due to low transformation temperature, ease of purification, transparency, minimised convection effects and wider choice of materials, study on the chemistry and characterization of organic eutectics and addition compounds has received potential importance and organic systems are being used as model⁹⁻¹⁰ systems for detailed physicochemical investigations. Most of the organic systems studied^{11,12} in the past are of simple eutectic type. There is only a limited number of cases in which two components form a molecular compound with congruent melting point. With a view to elucidate the chemistry of organic eutectics and addition compounds, binary systems of benzidine (B) with resorcinol (RC) and catechol (CT) were chosen and their phase diagram, linear velocity of crystallization, microstructure and spectral behaviour were studied.

Experimental

Materials and Purification. AR grade benzidine (CDH, India) which is used as a reagent for detection of blood was directly used in the present investigation. Resorcinol (E Merck, India) and pyrocatechol (BDH) were purified by repeated distillation under reduced pressure and were stored in coloured bottles to avoid exposure to light. The melting point of each compound was compared with its literature value to assess its purity.

Phase-Diagram. The phase-diagrams of benzidine-resorcinol and benzidine catechol systems were determined by the thaw-melt method^{13,14}. In this method, mixtures of two components of different compositions covering the entire range of composition in mole fraction were prepared in long-necked test tubes. These mixture were homogenized by melting in silicon oil followed by chilling in ice. The samples were taken out by breaking the test tubes and their melting points were determined using a melting point apparatus attached with a precision thermometer.

Linear Velocity of Crystallization. The linear velocity of crystallization for pure components, eutectics and addition compounds was determined^{15,16} by measuring the rate of movement of solid-liquid interface in a capillary.

Microstructure. Microstructures of pure components, eutectics and addition compounds were determined^{17,18} by placing the slide containing the sample under a microscope (Leitz Laborlux D, Optical Microscope) attached with a camera.

Spectral Studies. IR spectra of the pure components, eutectics and the addition compounds were recorded in the region, 4000-625 cm⁻¹, in nujol mull using a Perkin-Elmer 783 infrared spectrophotometer. CDCl₃ was used as a solvent to record proton NMR spectra of pure components and the addition compound on a Jeol, FX 90 Q. Fourier transform spectrometer.

Results and Discussion

Phase-Diagram. The solid-liquid equilibrium data on B : RC and B : CT systems are given in Figures 1, 2 in the form of temperature versus composition plots. Each curve shows the formation of 1 : 2 addition compound with congruent melting point surrounded by two eutectics, *E*₁ and *E*₂. The compositions and the melting points of the eutectics and the addition compounds are reported in Table 1. It is evident from the figures that the melting point of benzidine

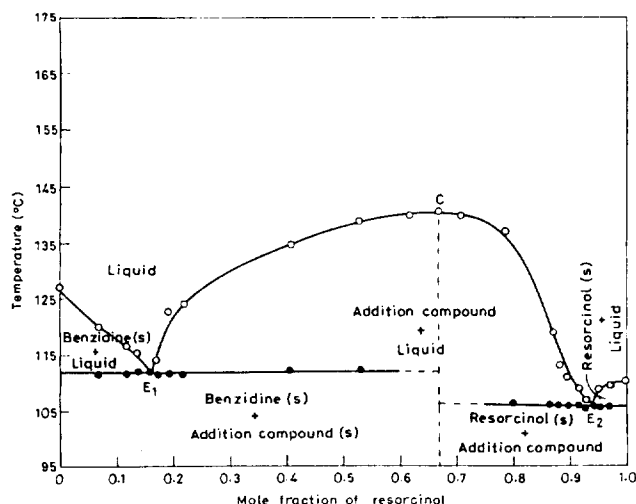


Figure 1. Phase diagram of benzidine-resorcinol system. ▲: Melting temperature, ■: Thaw temperature.

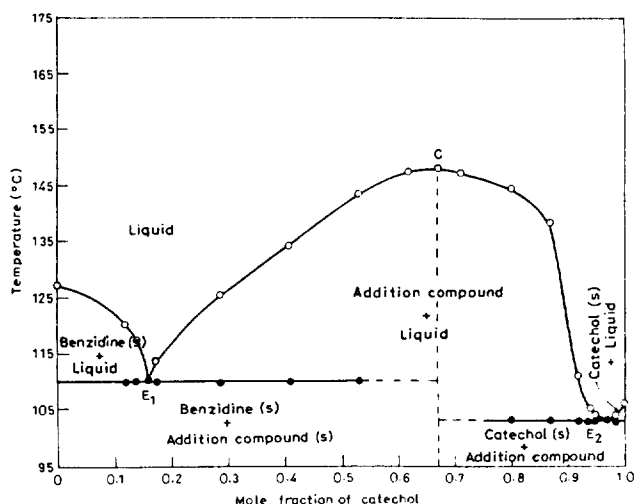
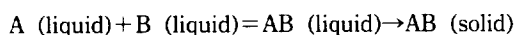


Figure 2. Phase diagram of benzidine-catechol system. ▲: Melting temperature, ■: Thaw temperature.

decreases with the addition of the second component and it attains a minimum value at the eutectic point E_1 . From the first eutectic point E_1 onwards, on addition of the second component, the melting point again rises and attains a maximum at C where the composition of the liquid and solid phases are identical at different temperature^{19,20}. This maximum temperature is the congruent melting point of the addition compound. A further increase in the mole fraction of the second component (Resorcinol or Catechol) causes a decrease in the melting point of the mixture with a minimum at the second eutectic point E_2 . A maximum on the liquidus, a good length of the middle branch of the curve and the existence of a eutectic point on either side of the maximum point to high stability^{21,22} of the molecular complex formed by the reaction between the two components in the following manner:



If there is no dissociation in the molten addition com-

Table 1. Composition and Melting Point of Eutectics and Addition Compounds of Each System

System	Composition (mole fraction of benzidine)	Melting point (°C)
1. Benzidine-resorcinol		
(a) Eutectic-1	0.85	112.0
(b) Eutectic-2	0.06	106.0
(c) 1 : 2 (B : RC) Addition compound	0.33	140.5
2. Benzidine-catechol		
(a) Eutectic-1	0.85	110.0
(b) Eutectic-2	0.03	103.0
(c) 1 : 2 (B : CT) Addition compound	0.33	147.5

pound, the phase diagram would show a sharp maximum²⁰. Actually some decomposition of the compound into its constituents nearly always occurs, the presence of products of dissociation in the liquid phase depresses the hypothetical melting point the compound would have if there had been no decomposition, and so the curve is flattened. For each eutectic the addition compound serves as one of the components. The observed maxima in both the systems under investigation are flat, indicating thereby that the addition compounds are dissociated in molten state. From the phase diagram it can also be inferred that the addition compound in these systems are capable of existing in solid form in equilibrium with a liquid of the same composition.

Linear velocity of crystallization. The linear velocity of crystallization (v) of pure components, eutectics and the addition compounds was determined by the capillary method at different undercoolings (ΔT). According to Hillig-Turnbull²³, the linear velocity of crystallization is related with undercooling by the following equation:

$$v = u (\Delta T)^n \quad (1)$$

where u and n are constants depending on the solidification behaviour of the material. A plot of $\log v$ versus $\log \Delta T$ results a straight line with n and $\log u$ as the slope and the intercept with y -axis, respectively. The linear plots are given in Figures 3, 4 and the values of the constants u and n are reported in Table 2. It is evident from the table that most of the values of n are close to two suggesting thereby a square relationship between v and ΔT . However, the deviations¹³ in the values of n from 2, observed in some cases, may be due to the difference in the bath temperature and the temperature of growing interface. Large deviations in the values of n from 2 in benzidine, catechol and 1 : 2 (B : RC) addition compound may be attributed to the nature of these compounds. In the present investigation, both components belong to high enthalpy of fusion (benzidine -19.1 kJ/mole, resorcinol -21.7 kJ/mole, catechol -22.7 kJ/mole, 1 : 2 (B : RC) addition compound -23.1 kJ/mole, 1 : 2 (B : CT) addition compound -27.0 kJ/mole), and as a consequence to that each crystallization step results a release of more amount of heat causing the interface to attain higher temperature than that of the bath temperature.

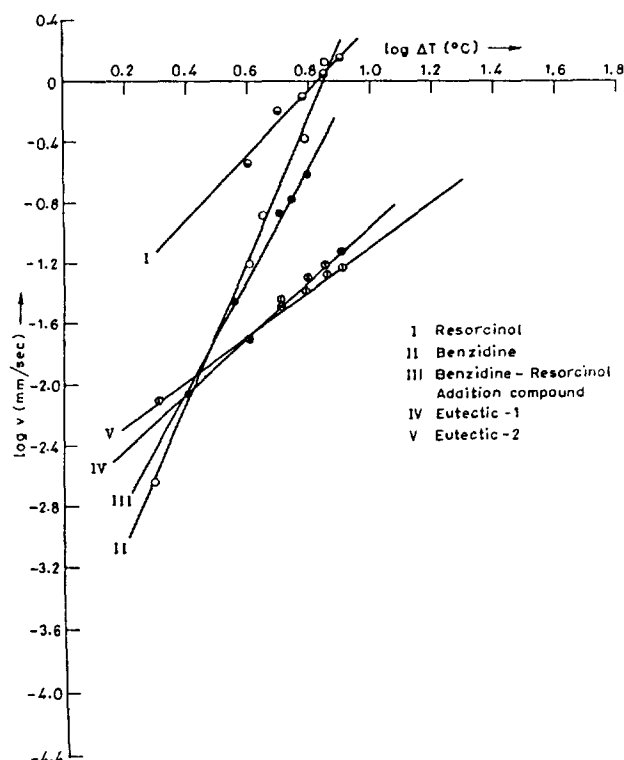


Figure 3. Linear velocity of crystallization of benzidine-resorcinol system.

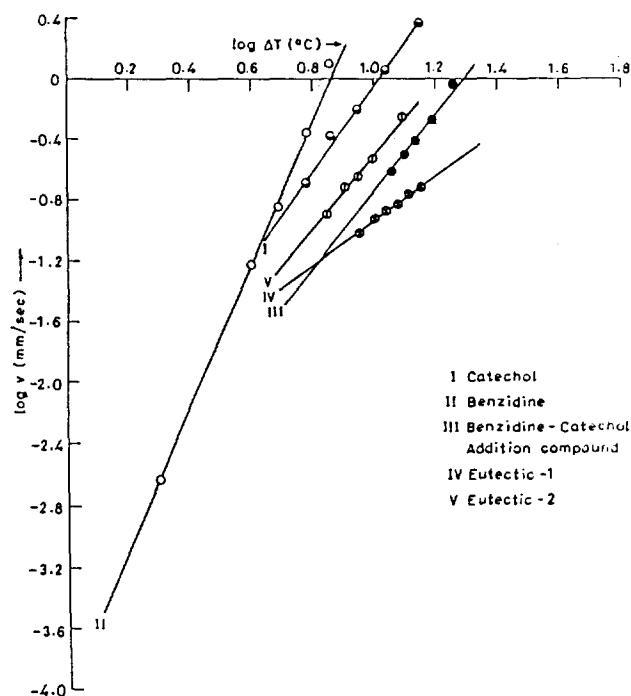


Figure 4. Linear velocity of crystallization of benzidine-catechol system.

From the values of u (Table 2) for pure components and the addition compounds, it can be inferred that the crystallization rate of the adduct of each system lies between two components. Studies^{24,25} on crystal morphology of addition

Table 2. Values of u and n

System	u (mm/sec/deg)	n
1. Benzidine-resorcinol		
(a) Benzidine	0.000105	4.0
(b) Resorcinol	0.0182	2.0
(c) Eutectic-1	0.00166	2.0
(d) Eutectic-2	0.00263	1.6
(e) 1 : 2 (B : RC) Addition compound	0.000316	3.3
2. Benzidine-catechol		
(a) Catechol	0.00132	2.8
(b) Eutectic-1	0.003981	1.5
(c) Eutectic-2	0.001202	2.4
(d) 1 : 2 (B : CT) Addition compound	0.000575	2.5

compound 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 melt conform to the respective molar ratios of the two components. Due to this, the linear velocity of crystallization of the addition compound may be expected to be of the order of the growth velocity of the species crystallizing with a slower rate.

On comparison of the values of u of pure components and the eutectics, it is evident that for E_1 of B : RC system, which is formed between the addition compound and benzidine, the value of u is higher than those of both components namely benzidine and addition compound while it lies between two components of E_2 , namely resorcinol and the addition compound. In the case of benzidine-catechol system, the value of u for E_1 (formed between benzidine and the addition compound) is higher than those of benzidine and the addition compound while for E_2 (formed between catechol and the addition compound), it lies between the two components, namely catechol and the addition compound. In both the systems, for E_1 and E_2 , the addition compound behaves as one of the parent components. These results may be explained on the basis of the mechanism proposed by Winegard *et al.*²⁶ According to them, the 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 component, and a stage is reached when the second component starts nucleating. There are two possibilities, in the solidification of both eutectics. 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. The second possibility is that there may be alternate nucleation of the two components and this explains the cases in which the eutectic solidification rates are lower than those of the parent components. Since the rates of solidification of eutectics are higher than those of parent components, the solidification of both eutectics in B : RC and B : CT systems takes place by the side-by-side growth of the two components.

Microstructure. According to Hunt and Jackson²⁷ the type of growth from a eutectic melt depends upon a factor α , defined by equation



Figure 5. Microstructure of benzidine-resorcinol addition compound $\times 600$.



Figure 8. Microstructure of benzidine-resorcinol eutectic (E_2) $\times 100$.



Figure 6. Microstructure of benzidine-resorcinol addition compound $\times 600$.



Figure 9. Microstructure of benzidine-catechol eutectic (E_1) $\times 100$.



Figure 7. Microstructure of benzidine-resorcinol eutectic (E_1) $\times 600$.

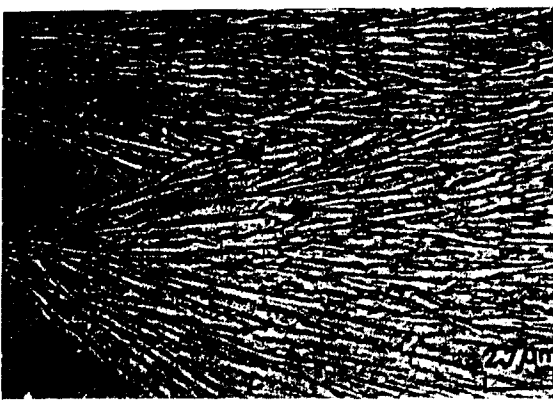


Figure 10. Microstructure of benzidine-catechol eutectic (E_2) $\times 100$.

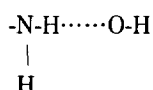
$$\alpha = \xi \frac{\Delta S_f}{R} \quad (2)$$

where ξ is a crystallographic factor depending upon the geometry of molecules and has the value less than or equal to one. $\Delta S_f/R$, also known as Jackson's roughness parameter is the entropy of fusion in dimensionless unit and R is the gas constant. When $\alpha < 2$, non-faceted growth occurs and a faceted growth appears if $\alpha > 2$. In the present investigation

both components have high enthalpy of fusion, the results being that they would exhibit faceted growth. The microstructures of eutectics and the addition compounds are given in Figures 5-10. As expected, the addition compounds of B : RC and B : CT systems given in Figures 5 and 6, respectively, show the faceted growth in each case. The first eutectic of B : RC system given in Figure 7 shows a lamellar growth of the two components, namely, the addition compound

and benzidine. The second eutectic formed between the addition compound and resorcinol shows (Figure 8) that different grains grow in different orientations and they meet at the grain boundaries. The first eutectic of B : CT system, shown in Figure 9, suggests that one of the phases (addition compound) nucleates first and the second phase radiate outward from this nucleus. In the second eutectic of B : CT system (Figure 10) there is growth of different eutectic colonies in different directions.

Spectral Studies. Infrared spectrum of benzidine in nujol gives three peaks: i) 3190, ii) 3320 and iii) 3400 cm^{-1} due to NH stretching vibration and those of resorcinol and catechol both give a broad band in the region, 3450-3100 cm^{-1} . The IR spectrum of the addition compound of B : RC system shows three peaks: i) 3280, ii) 3360 and iii) 3510 cm^{-1} and that of the addition compound of B : CT system gives three peaks at i) 3280, ii) 3370 and iii) 3500 cm^{-1} . A shift of the peaks of NH stretching vibration of benzidine in the addition compound to higher frequency region because of the shortening of -NH bonds which are not involved in the hydrogen bonding²⁸ may be due to formation¹⁷ of inter-molecular hydrogen bonds between -NH₂ hydrogen and -OH through the lone pair of oxygen as shown below:



This observation is also supported by the comparison of NMR spectra of pure components and addition compounds where the molecular complexes show a shift of δ_{NH} peak to lowfield side with a broadening in it. However, the signals of ring proton of the components retain the same position in the addition compound.

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