Thermochimica Acta, 191 (1991) 271–284
Elsevier Science Publishers B.V., Amsterdam

Some physicochemical studies on organic eutectics and 1 : 2 addition compound; benzidine–β-naphthol system

U.S. Rai and Santhi George

Department of Chemistry, Banaras Hindu University, Varanasi-221005, U.P. (India)

(Received 25 March 1991)

Abstract

With a view to elucidating the chemistry of the benzidine–β-naphthol system, its phase diagram was determined by the thaw–melt method. The solidification behaviour of the pure components, the eutectics and the addition compound was studied at different degrees of supercooling by the capillary method. From the data obtained by X-ray diffraction, thermal and microscopic studies, it can be inferred that the eutectics are not simple mechanical mixtures of the components involved. Infrared and NMR spectral investigations were carried out to clarify the nature of bonding between the two components forming the addition compound.

INTRODUCTION

The chemistry [1,2] of eutectics and intermetallic compounds is an interesting topic in the area of materials science and metallurgy. The growth morphology of eutectics depends on the characteristics of the individual phases which solidify with either faceted or nonfaceted interfaces. This behaviour is related to the nature of the solid–liquid interface and can be predicted, for the pure materials, from their entropy of fusion data. Because of their low transformation temperature, ease of purification, transparency, wide choice of materials and minimized convection effects, organic systems [3–9] are being used increasingly as model systems for unravelling the mysteries of solidification. Eutectics in which the parent components have low entropy of fusion simulate the metallic solidification, and have been studied [10,11] in detail. Faceted–nonfaceted organic eutectics are chosen as the analogues of the Al–Si type system, and much has been added [12–14] to the knowledge about them. Faceted–faceted eutectics, which are of great importance for carrying out unusual reactions [15], have been the least studied. Several organic reactions which occur at very high temperature, and are not possible under ordinary conditions, have been successfully carried out in eutectic media. Sometimes very unusual reaction products are formed in eutectic melts. Because of their –OH and $-NH_2$ groups and low melting points, benzidine (BZ)–β-naphthol (BN) eutectics may be very useful for these reactions. In the present article the results on the phase diagram, linear velocity of crystallization, heat of fusion, X-ray diffraction, microstructure and spectral behaviour of the benzidine–β-naphthol system are reported.

EXPERIMENTAL

Materials and purification

AR grade benzidine (from CDH, India) and β-naphthol (obtained from Fluka, Switzerland) were used in the present investigation. The purity of each compound was checked by determining its melting point and comparing this value with the values reported in the literature.

Phase diagram

The phase diagram of the benzidine–β-naphthol system was determined by the thaw–melt method [16,17]. In this method, mixtures of two components covering the entire range of composition were prepared in different long-necked test tubes. These mixtures were homogenized by melting followed by chilling in ice, and their thawing and melting temperatures were determined using a Toshniwal melting point apparatus equipped with a precision thermometer.

Linear velocity of crystallization

The linear velocity of crystallization for each of the pure components, the eutectics and the addition compound was determined by the capillary method [18,19].

Heat of fusion

Heats of fusion of the pure components, the eutectics and the addition compound of the BZ–BN system were determined by the DSC method [20] using a Mettler TA 3000 system.

X-ray diffraction

X-ray diffraction patterns of the pure components, the eutectics and the addition compound were recorded [21,22] on a computerized X-ray diffraction unit, PW 1710 model, using Cu Kα radiation.

Spectral studies

The IR spectra of the pure components, the eutectics and the addition compound were recorded in the region 4000–625 cm^{-1} in a nujol mull

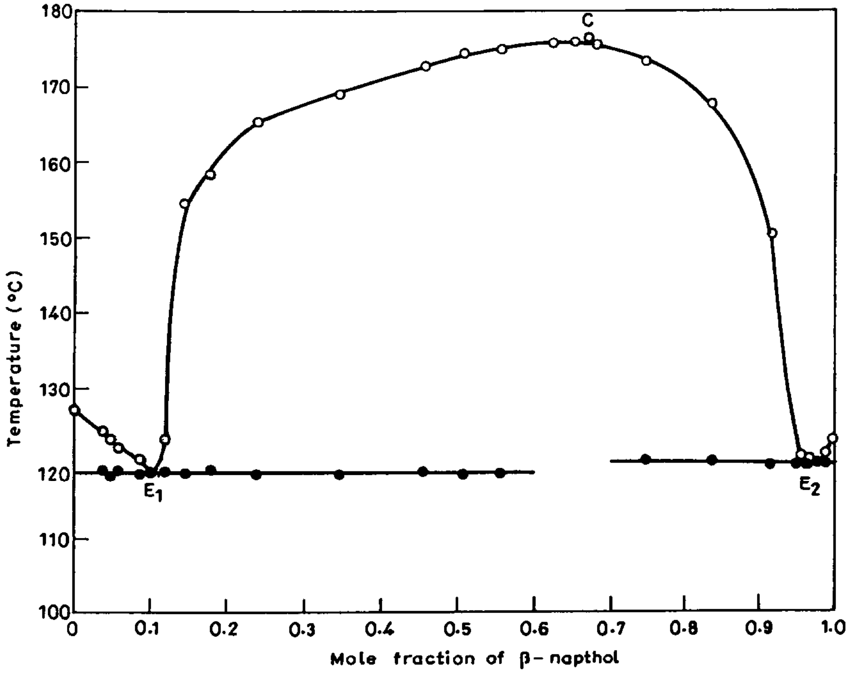

Fig. 1. Phase diagram of benzidine–β-naphthol system: (○) melting temperature; (●) thaw temperature.

using a Perkin–Elmer 783 infrared spectrometer. $CDCl_3$ was used as a solvent for recording the proton NMR spectra of the pure components and the addition compound on a JEOL FX 90 Q fourier transform NMR spectrometer.

Microstructure

Microstructures of the eutectics and the addition compound were recorded [23,24] by placing the slide containing the unidirectionally solidified sample on the platform of a Leitz Labourlux D optical microscope fitted with a camera.

RESULTS AND DISCUSSION

Phase diagram

The phase diagram of the benzidine–β-naphthol system, expressed in the form of the temperature-composition curve in Fig. 1, shows the formation of one 1:2 addition compound with congruent melting point surrounded by two eutectics, E_1 and E_2, containing 0.990 and 0.025 mole fraction of benzidine, respectively. The melting point of pure benzidine is

127.0 ° C; it decreases continuously with the addition of β-naphthol and attains a minimum at E_1 (118.0 ° C) when the BZ mole fraction is 0.990. With continued addition of β-naphthol the melting point rises to attain its maximum temperature of 176.0 ° C at C, and it decreases from there to attain a minimum temperature, 120.0 ° C, at E_2. The phase diagram may be supposed to consist of two simple eutectic type phase diagrams placed side by side. A flatness in the maximum at C suggests that the addition compound is dissociated [25] in the molten state. A maximum point on the liquidus line, a good length of the middle branch and the existence of a eutectic point on either side of the maximum all indicate the considerable stability of the molecular complex formed. From the phase diagram the phases involved in the different regions can easily be worked out.

Linear velocity of crystallization

For each of the pure components, the eutectics and the addition compound, the linear growth rate (V) data determined by measuring the rate of movement of the moving front at different supercoolings (ΔT) are given in Fig. 2 in the form of log V versus log ΔT plots. The linear dependence between the growth velocity and the supercooling suggests that the crystallization data obey the equation [26]

$$V = u(\Delta T)^n \qquad (1)$$

where u and n are constants depending on the behaviour of solidification of the materials involved. The experimental values of these constants are reported in Table 1. The values of n, being close to 2, suggest a square relationship between the growth velocity and the supercooling. The deviation of the n value from 2, observed for the pure components, may be due to the difference between the bath temperature and the temperature of the growing interface. In the present investigation, both components have high enthalpy of fusion and would release an appreciable amount of heat in every crystallization event, causing the interface to attain a temperature higher than that of the bulk.

The values of the constant u, which give a measure of the rate of crystallization, are reported in Table 1. It is evident from the table that the value of u for the addition compound is higher than those for the pure components. Studies on crystal morphology suggest that the addition compound crystallizes as a definite chemical entity. From the values of u given in Table 1, it can also be inferred that the crystallization velocity of E_1 is higher than those of its components, namely, benzidine and the addition compound. On the other hand, the value of u for the eutectic E_2 is less than those of the components (β-naphthol and the addition compound). These results may be explained on the basis of the mechanism proposed by Winegard et al. [27]. According to these workers, the eutectic solidification

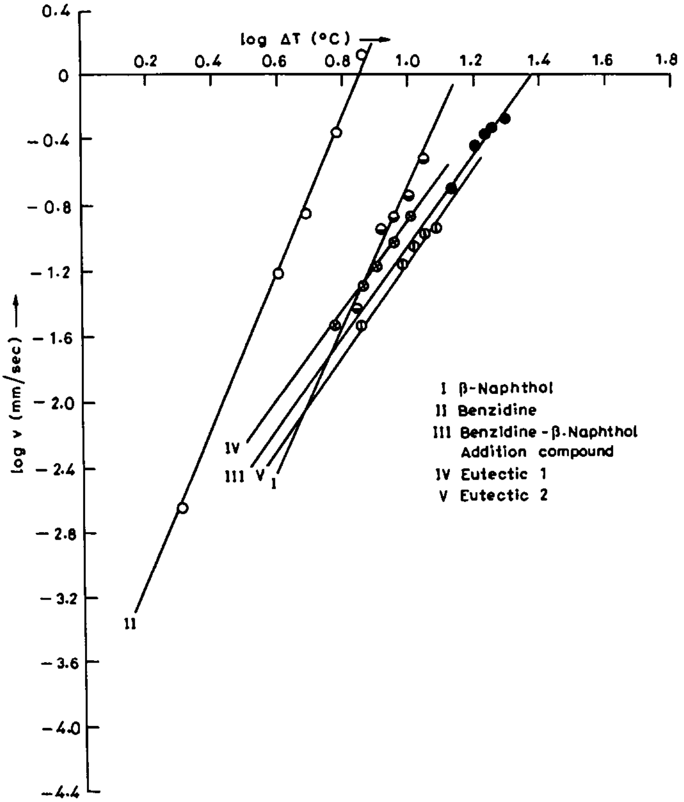

Fig. 2. Linear velocity of crystallization of benzidine–β-naphthol system.

begins with the formation of the nucleus of one of the phases. This grows until the surrounding liquid becomes rich in the other component, 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 no lower than those of the parent components. The second possibility is that there may be alternate nucleation of the two components. This

TABLE 1

Values of u and n for benzidine–β-naphthol

System	u (mm s^{-1})	n
Benzidine	0.0001047	4.0
β-Naphthol	0.00001047	4.0
Eutectic 1	0.0002512	2.7
Eutectic 2	0.0001148	2.7
1:2 Addition compound	0.0001585	2.7

TABLE 2

Heat of fusion and heat of mixing of BZ–BN system

Materials	Heat of fusion (kJ mol^{-1})	Entropy of fusion (kJ mol^{-1}K^{-1})	Roughness parameter ($\Delta s_f/R$)	Heat of mixing (kJ mol^{-1})
Benzidine	19.10	0.0478	5.77	-
β-Naphthol	22.18	0.0560	6.77	-
Eutectic 1				
(exptl.)	18.76			
(calc.) [a]	19.44	0.0480	5.80	−0.68
Eutectic 2				
(exptl.)	20.11			
(calc.) [a]	22.10	0.0512	6.19	−1.99
1:2 Addition compound				
(exptl.)	30.65			
(calc.)	49.66	0.0683	8.25	−19.01

[a] $(\Delta_f h)_e = x_1\Delta_f h_1^0 + x_2\Delta_f h_2^0$, where x and $\Delta_f h$ are the mole fraction and the heat of fusion, respectively, of the component indicated by the subscript.

explains the solidification phenomena in cases where the crystallization velocity of the eutectic is lower than that of either component. For both the eutectics, the addition compound behaves as one of the components. In the case of E_1, the crystallization starts with the nucleation of the addition compound followed by the nucleation of benzidine. Now the two phases grow side by side. However, in the case of E_2, the solidification starts with the nucleation of the addition compound followed by the nucleation of β-naphthol, and the two phases grow by the alternate nucleation mechanism.

Thermochemical studies

Some idea of the mode of crystallization, the structure of the eutectic melt and the nature of interaction between the two components forming the eutectic and the addition compound can be obtained from the knowledge of heats of fusion data for the pure components, the eutectics and the molecular complexes. For the purpose of comparison, the experimental and the calculated [28] values of heat of fusion for the eutectics are reported in Table 2. It is evident from the table that the calculated values of heat of fusion are higher than the experimental values. If a eutectic is a simple mechanical mixture of two components involving no heat of mixing or any type of association in the melt, the heat of fusion can be obtained simply by the mixture law. However, when a solid eutectic melts there is a considerable possibility of association and mixing, both causing violation of the mixture law. The difference between the experimental and the calculated values can be attributed to the formation of clusters [29] in the eutectic melt. In the present eutectic system both the components have a tendency for hydrogen bond formation, resulting in favourable conditions for cluster formation in the melt.

The heat of mixing [30] (ΔH_m), which is the difference between the experimental and the calculated values of the heat of fusion, can be calculated by the equation

$$\Delta H_m = (\Delta_f h)_{exp} - \sum x_i \Delta_f h_i^0 \qquad (2)$$

where $(\Delta_f h)_{exp}$ is the heat of fusion of the eutectic determined experimentally, and x_i and $\Delta_f h_i^0$ are the mole fraction and the heat of fusion of the final components, respectively. The values of heat of mixing of E_1 and E_2 reported in Table 2 are clearly highly negative. Thermochemical studies [29] suggest that the structure of the eutectic melt depends on the sign and magnitude of the enthalpy of mixing. Three types of structure are suggested: quasieutectic for $\Delta H_m > 0$, clustering of molecules for $\Delta H_m < 0$ and molecular solution for $\Delta H_m = 0$. The negative values of ΔH_m for the eutectics of the BZ–BN system suggest clustering of molecules in the eutectic melt.

The experimental value of the heat of fusion of the addition compound, determined by the DSC method, is reported in Table 2. The theoretical value is also given in the table for the purpose of comparison. The theoretical value of heat of fusion of the addition compound was calculated using the equation

$$\frac{\Delta_f h}{R}\left(\frac{1}{T} - \frac{1}{T_e}\right) = -\ln(x_A)^m (x_B)^n + \ln(x_A)_c^m (x_B)_c^n \qquad (3)$$

where T_e denotes the congruent melting temperature and the quantities with the subscript c denote the mole fraction corresponding to that which would exist in the molten addition compound. It is evident that the heat of mixing, which is defined as the difference between the experimental and the calculated values of heat of fusion, is highly negative. This highly negative value suggest [31] that the presence of the addition compound enhances the attraction among the components. It is well known that the addition compound is formed by the reaction between two components in the following manner:

$$A + B \rightleftharpoons AB(\text{liquid}) \rightarrow AB(\text{solid}) \qquad (4)$$

When a solid addition compound melts, the components still remain in the associated form, This association is favoured by the presence of hydroxyl and amino groups in the components.

The deviation from ideal behaviour can best be expressed in terms of excess thermodynamic functions, which give a more quantitative idea about the nature of molecular interactions. The excess thermodynamic function is defined as the difference between the thermodynamic function of mixing for a real system and the corresponding value for an ideal system at the same temperature and pressure. In order to know the nature of interaction between two components forming the eutectics, some thermodynamic functions such as excess free energy (g^E), excess enthalpy (h^E), and excess entropy (s^E) were calculated using the following equations:

$$g^E = RT(x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l) \tag{5}$$

$$h^E = -RT^2 \left(x_1 \frac{\partial \ln \gamma_1^l}{\partial T} + x_2 \frac{\partial \ln \gamma_2^l}{\partial T} \right) \tag{6}$$

$$s^E = -R \left(x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l + x_1 T \frac{\partial \ln \gamma_1^l}{\partial T} + x_2 T \frac{\partial \ln \gamma_2^l}{\partial T} \right) \tag{7}$$

It is evident that the activity and its variation with temperature are required to calculate the excess functions. The activity coefficient (γ_i^l) of component i in the eutectic melt was calculated using the equation

$$-\ln x_i^l \gamma_i^l = \frac{\Delta_f h_i^0}{R} \left[\frac{1}{T} - \frac{1}{T_i^0} \right] \tag{8}$$

where x_i, $\Delta_f h_i^0$ and T_i^0 are the mole fraction, heat of fusion and melting temperature of the component i, respectively, R is the gas constant and T is the melting temperature of the eutectic. The variation of activity coefficient with temperature was calculated from the slope of the liquidus line near the eutectic point. The details of calculation are reported earlier [28]. The positive values of g^E (Table 3) suggest that the interaction between like molecules is stronger than that between unlike molecules. The values of h^E and s^E correspond to the excess free energy, and are measures of the excess enthalpy of mixing and the excess entropy of mixing, respectively.

X-ray diffraction

Critical scanning of the current literature [32] reveals that there are two conflicting ideas about the nature of and bonding in eutectics. One group of workers believes that a binary eutectic is a mixture of two kinds of

TABLE 3 .

Excess thermodynamic functions for benzidine–β-naphthol system

Material	g^E (J mol^{-1})	h^E (J mol^{-1})	s^E (J K^{-1} mol^{-1})
Eutectic 1	708.09	18562.01	45.66
Eutectic 2	206.87	9881.12	24.62

crystals, favourably oriented with respect to each other; the other group is of the opinion that the eutectic grains do not exhibit a fixed orientational relationship. In order to clarify the position, the X-ray diffraction patterns of the pure components, the eutectics and the addition compounds were recorded, and the results are reported in Tables 4 and 5. It is evident from the reported data that the number of reflections of pure components and the addition compound is comparable with the number of reflections of their corresponding eutectic. It can be inferred from this observation that they belong to the same crystal system and have similar lattices. Table 4 reveals that, in general, the strong reflections of benzidine either show a decrease in intensity or are absent in the eutectic. Strong reflections of the addition compound show a similar trend in the eutectic, whereas weak reflections generally show an increase in intensity. From the results reported in Table 5 it can be pointed out that, in general, reflections of benzidine do not show any significant change in the eutectic. In contrast, all the reflections of the addition compound show a remarkable change in intensity in the eutectic.

The X-ray patterns of the two components should be exactly superimposed on the eutectic composite if a eutectic is a simple mechanical mixture of two components. From the diffraction data on the pure components, the eutectics and the addition compound, it can be inferred that there is a marked difference in the interplanar distance and the relative intensity. The variation in relative intensity of the reflections of pure components in the eutectics, and the absence of reflections of pure components in eutectics and those of eutectics in pure components, suggest that the eutectics are not simply a mechanical mixture of two components. There is orientation of some atomic planes within the eutectics during their formation.

Spectral studies

The IR spectrum of benzidine shows three absorption peaks: (i) 3195, (ii) 3315 and (iii) 3400 cm^{-1}, due to –NH stretching vibrations. β-Naphthol shows a broad band in the region 3220–3280 cm^{-1} due to the –OH stretching vibration. The addition compound of benzidine and β-naphthol gives two peaks: (i) 3280 and (ii) 3370 cm^{-1}. A shift of –NH peaks from 3315 and 3400 to 3280 and 3370, respectively, suggests intermolecular hydrogen bonding between the two components forming the addition compound. The proton NMR spectra of β-naphthol and benzidine in $CDCl_3$, show one –OH proton signal at $\delta = 5.54$ and a –NH proton signal at $\delta = 3.52$. The proton NMR spectrum of the addition compound of the BZ–BN system shows two peaks: (i) at $\delta = 1.70$ and (ii) at $\delta = 2.27$, demonstrating an upfield shift of the –NH and –OH signals. This upfield shift of the –NH and –OH signals also suggests intermolecular hydrogen

TABLE 4

Values of *d* and relative intensity (RI) of benzidine, eutectic 1 and addition compound of BZ–BN system

Benzidine		Eutectic 1		1:2 Addition compound	
d (Å)	RI	*d* (Å)	RI	*d* (Å)	RI
14.35	3	–	–	–	–
–	–	–	–	12.75	10
–	–	11.70	18	–	–
10.20	4	–	–	–	–
9.49	4	–	–	–	–
9.03	3	–	–	–	–
–	–	8.73	10	–	–
–	–	–	–	8.61	100
7.01	4	–	–	–	–
–	–	6.55	5	6.50	48
6.28	12	–	–	–	–
–	–	6.19	7	–	–
–	–	5.93	7	–	–
5.74	20	5.70	14	–	–
5.42	29	–	–	–	–
5.40	30	5.37	22	–	–
5.07	20	5.02	14	–	–
4.94	22	–	–	–	–
4.82	60	–	–	–	–
4.79	34	–	–	–	–
–	–	4.72	13	–	–
–	–	4.73	23	–	–
–	–	4.53	32	4.56	12
4.45	39	4.44	70	4.45	53
4.40	100	4.36	100	4.35	17
4.23	70	4.23	49	–	–
4.12	73	–	–	–	–
4.04	28	4.08	97	4.09	12
–	–	3.98	42	3.99	3
3.86	19	–	–	3.86	6
4.83	40	3.83	21	–	–
3.72	21	–	–	3.75	2
–	–	3.68	20	–	–
3.58	15	3.56	21	3.58	14
–	–	3.53	18	–	–
3.47	13	3.45	13	3.46	3
3.42	19	3.39	23	–	–
3.35	40	3.33	17	3.34	14
3.25	8	–	–	3.27	7
3.18	11	3.20	24	–	–
3.12	20	3.10	22	–	–
3.04	10	3.02	18	3.03	14
2.98	9	2.98	18	–	–
2.91	14	2.89	14	2.91	3
2.83	7	2.80	11	–	–
2.75	5	2.72	11	2.71	2

TABLE 4 (continued)

Benzidine		Eutectic 1		1:2 Addition compound	
d (Å)	RI	*d* (Å)	RI	*d* (Å)	RI
–	–	–	–	2.69	3
2.64	5	–	–	2.64	2
–	–	2.59	8	2.60	2
–	–	2.48	7	2.50	5
–	–	2.38	15	2.42	1
–	–	2.34	6	2.35	1
2.30	4	–	–	2.32	2
–	–	2.24	5	2.27	7
2.18	5	2.21	6	2.19	2
–	–	2.13	6	2.15	2
–	–	2.09	5	2.10	2
–	–	2.01	7	2.02	5
–	–	1.99	5	–	–
–	–	1.97	7	–	–
–	–	1.94	5	1.95	2
1.90	5	1.91	6	–	–
–	–	1.86	7	–	–
–	–	1.84	6	–	–
–	–	1.83	6	1.83	3
1.74	4	–	–	1.79	2
1.72	3	–	–	–	–
–	–	–	–	1.67	2
–	–	–	–	1.55	1

bonding, as concluded from the IR spectral studies. It may be pointed out that, as a result of intermolecular hydrogen bonding, the electron density in the vicinity of the NH and OH protons increases owing to the lone pair of electrons present on N and O atoms becoming attached to the hydrogen atom. This causes an increase in the electron density in the vicinity of the NH and OH protons, resulting in upfield shifting of the proton signals.

Microstructure

In general, the properties of alloys are determined by their microstructure which, in turn, is controlled by the type, relative amount and morphology of the phases involved. In various microstructural features observed in alloys, the solidification process plays a very significant role. Thermal conductivity, entropy of fusion of the phases involved, the structure of the solid–liquid interface and the degree of supercooling are the other parameters [33] which control the microstructure of alloys. The microstructures of the eutectics and the addition compound are given in Figs. 3–5. The microstructure of eutectic E_1 (Fig. 3) shows the growth of the different

TABLE 5

Values of *d* and relative intensity (RI) of β-naphthol, eutectic 2 and addition compound of BZ–BN system

β-Naphthol		Eutectic 2		1:2 Addition compound	
d (Å)	RI	*d* (Å)	RI	*d* (Å)	RI
–	–	15.93	3	–	–
15.60	6	–	–	–	–
–	–	–	–	12.75	10
–	–	–	–	8.61	100
7.90	30	7.93	38	–	–
–	–	–	–	6.50	48
5.90	4	5.85	2	–	–
5.30	4	5.28	4	–	–
5.00	10	–	–	–	–
4.54	100	4.56	100	4.56	12
–	–	–	–	4.48	53
4.34	4	4.34	5	4.35	17
4.07	25	4.10	27	4.09	12
–	–	–	–	3.99	3
3.90	4	3.94	4	–	–
–	–	–	–	3.86	6
3.71	10	3.72	7	3.75	2
3.53	20	3.55	21	3.58	14
–	–	3.50	5	3.46	3
3.33	20	3.34	18	3.34	14
–	–	–	–	3.27	7
3.15	10	3.16	11	–	–
–	–	–	–	3.03	14
2.91	10	2.91	9	2.91	3
2.78	8	2.78	4	–	–
–	–	–	–	2.71	2
2.68	8	2.68	5	2.69	2
–	–	–	–	2.64	3
–	–	–	–	2.60	2
2.53	2	2.53	2	2.50	2
2.47	2	–	–	–	–
2.42	10	2.42	5	2.42	5
–	–	–	–	2.34	1
–	–	–	–	2.32	1
2.24	4	2.25	2	2.27	2
–	–	–	–	2.19	7
2.14	2	–	–	2.15	2
2.07	4	–	–	2.10	2
–	–	–	–	2.02	5
1.94	4	1.95	3	1.95	2
–	–	–	–	1.83	3
1.79	4	–	–	1.79	2
1.72	4	–	–	–	–
1.62	4	–	–	1.67	2
1.57	2	–	–	1.56	1

Fig. 3. Microstructure of benzidine–β-naphthol eutectic (E_1). Original magnification × 100.

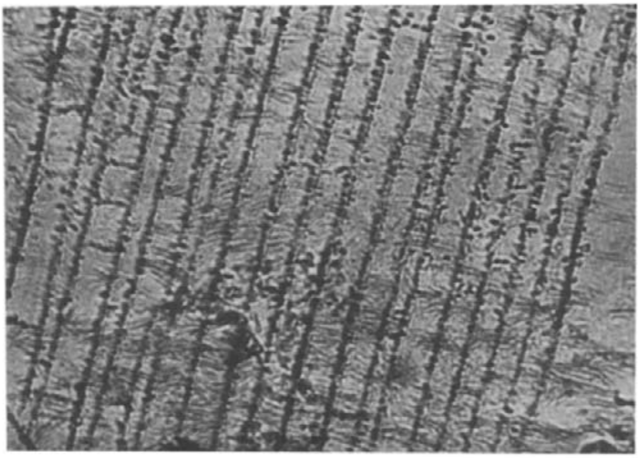

Fig. 4. Microstructure of benzidine–β-naphthol eutectic (E_2). Original magnification × 600.

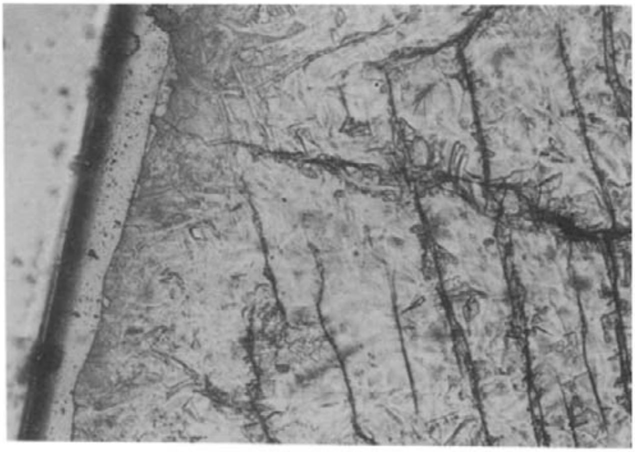

Fig. 5. Microstructure of benzidine–β-naphthol addition compound. Original magnification × 100.

eutectic colonies in which the two phases grow in lamellar fashion. Figure 4 gives the microstructure of the eutectic E_2 in the broken lamellar form. This type of microstructure is very common in systems involving phases with high enthalpy of fusion, as applies to the system under investigation. The faceted growth of the addition compound observed in Fig. 5 suggests that the molecular complex solidifies like the pure components.

ACKNOWLEDGEMENTS

Thanks are due to Professor K.N. Mehrotra, Head, Department of Chemistry, Banaras Hindu University for providing research facilities. Thanks are also due to Dr. K. Krishnan, V.S.S.C., Trivandrum for providing DSC data.

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