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Physicochemical studies on organic eutectics and the 1:1 addition compound: benzidine–α-naphthol system

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The phase-diagram of the benzidine–α-naphthol system, determined by the thaw-melt method, shows the formation of a 1 : 1 addition compound surrounded by two eutectics. From the linear velocity of crystallization data on pure components, eutectics and the addition compound, determined by the capillary method at different undercoolings, it can be inferred that they obey the Hillig–Turnbull equation. The X-ray diffraction studies suggest that the eutectics are not simply mechanical mixtures of two components. Heats of fusion data on the pure components, eutectics and addition compound, determined by differential scanning calorimetry, show that there is an associative interaction between the two components forming the eutectic melt. While the microstructural studies reveal that the microstructures of eutectics and the addition compound differ widely from those of the parent components, the spectral investigations suggest intermolecular hydrogen bonding between the two components.

1. Introduction

The modern age of science demands materials with specific properties. The search for fundamental understanding of the solidification process and the properties of polyphase alloys [1, 2] has witnessed immense activity in the last two decades. The metallic [3] eutectics and intermetallic compounds constitute an interesting area of investigation in metallurgy and materials science, from the point of view of producing new materials of commercial and technical importance. Owing to the low transformation temperature, ease of purification, transparency, minimized convection effects and wider choice of materials, the organic systems [4–6] are more suitable for a detailed investigation of the parameters which control solidification, which in turn, govern the properties of materials. The added advantages mentioned above have prompted a number of research groups [7–13] to undertake some physicochemical investigations on organic eutectics and addition compounds.

A critical scanning of the existing literature [1–4] reveals that studies on the chemistry and characterization of organic eutectics and addition compounds have received much attention during recent years. However, much less attention has been focused on an understanding of the solidification process, microstructure, crystal structure and the nature of bonding between the components forming the eutectics and the addition compounds in such systems. As the organic eutectics and the molecular complex are respective analogues of metal eutectics and intermetallic compounds, a systematic physicochemical study of model systems [14] involving organic compounds may be of potential importance in unravelling the mysteries of solidification, bonding and microstructure. In view of this, a binary organic system involving benzidine (BZ) and α-naphthol (AN) has been chosen to study its phase diagram, linear velocity of crystallization, microstructure, X-ray diffraction, thermochemistry and spectral behaviour.

2. Experimental procedure

2.1. Materials and purification

AR grade benzidine and α-naphthol 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.

2.2. Phase diagram

The phase diagram of the benzidine–α-naphthol system was determined by the thaw–melt method [15, 16]. 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 Toshniwal melting point apparatus attached with a precision thermometer.

2.3. Linear velocity of crystallization

The linear velocity of crystallization for each of the pure components, eutectics and the addition compound, was determined by the capillary method [17, 18].

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2.4. Heat of fusion

Heats of fusion of pure components, eutectics and the addition compound of the BZ–AN system were determined [19] by the differential scanning calorimetry (DSC) method using a Mettler TA 3000 system.

2.5. X-ray diffraction

X-ray diffraction (XRD) patterns of the pure components, eutectics and addition compound were recorded [20] on a computerized X-ray diffraction unit, PW 1710 model, using CuK_α radiation.

2.6. Microstructure

The microstructures of the eutectics and addition compound were recorded [21] by placing the slide containing the unidirectionally solidified sample on the platform of a Leitz Laborlux D, optical microscope attached with a camera.

2.7. Spectral studies

Infrared spectra of the pure components, eutectics and addition compound were recorded in the region 4000–625 cm^{-1}, in nujol mull using a Perkin–Elmer 783 infrared spectrometer. $CDCl_3$ was used as a solvent for recording the proton nuclear magnetic resonance (NMR) spectra of pure components and the addition compound on a Jeol, FX 90 Q Fourier Transform NMR spectrometer.

3. Results and discussion

3.1. Phase diagram

The phase diagram of the benzidine–α-naphthol system, expressed in the form of a temperature – composition curve in Fig. 1, shows the formation of a 1:1 addition compound with congruent melting point surrounded by two eutectics, E_1 and E_2. The eutectics E_1 and E_2 have 0.62 and 0.13 mole fractions of benzidine, respectively. The melting point of pure benzidine is 127.0 °C and it decreases with addition of α-naphthol and attains a minimum at E_1 at 97.0 °C. With continued addition of α-naphthol, the melting point rises to attain the maximum temperature of 100.5 °C at C, and it then decreases to attain a minimum temperature 85.0 °C at E_2. The phase diagram may be supposed to consist of two simple eutectic-type phase diagrams, placed side-by-side. The maximum in the phase diagram being flat suggests that the addition compound is dissociated [22, 23] 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, point to the large stability of the molecular complex formed.

3.2. Linear velocity of crystallization

The linear velocity of crystallization, v, data on pure components, eutectics and the addition compound, determined by measuring the growth rates of the moving front at different undercoolings, ΔT, are given in Fig. 2 in the form of log v versus log ΔT plots. The linear dependence of growth velocity and undercooling suggests that the crystallization data obey the Hillig–Turnbull [24] equation

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

where u and n are constants depending on the behaviour of solidification of the materials under investigation. The experimental values of these constants are reported in Table I. The values of n, being close to 2, suggest a square relationship between the growth velocity and undercooling. The deviation in n from 2, observed in pure components, may be due to the difference in bath temperature and the temperature of the growing interface. In the present investigation,

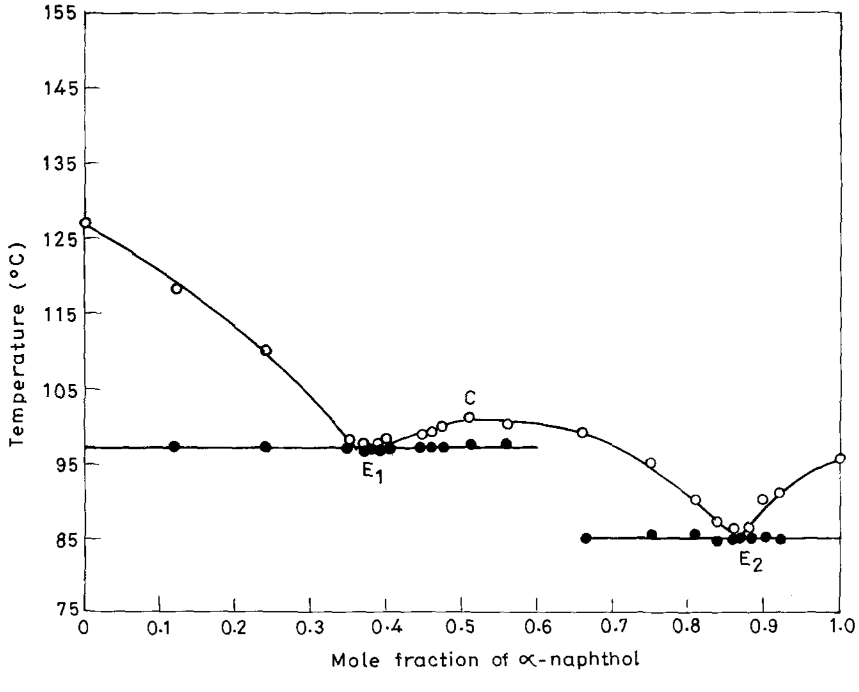

Figure 1 Pase diagram of the benzidine–α-naphthol system. (○) Melting temperature, (●) thawing temperature.

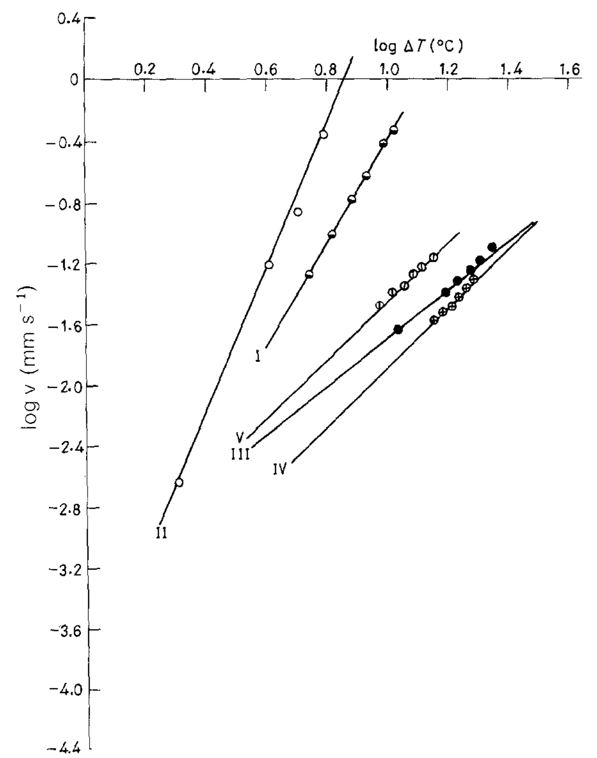

Figure 2 Linear velocity of crystallization of benzidine–α-naphthol. I, α-naphthol; II, benzidine; III, benzidine–α-naphthol addition compound; IV, eutectic 1; V, eutectic 2.

both components having high enthalpy of fusion would release a great amount of heat in every crystallization event and would cause the interface to attain a temperature higher than that of the bulk.

The values of constant u are given in Table I. It is well known that u gives a measure of the rate of crystallization. It is evident from the table that the value of u of the addition compound is higher than those of the pure components. Studies on crystal morphology suggest that the addition compounds crystallize as a definite chemical entity. During crystallization, the two compounds from the melt conform to their respective molar ratios. Owing 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 at a slower rate.

From the values of u given in Table I, it is also inferred that the crystallization velocity of E_1 lies between those of the parent components, whereas that of E_2 is higher than those of benzidine and α-naphthol. These results may be explained on the basis of the mechanism proposed by Winegard *et al.* [25]. 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. 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. The second possibility is that there may be alternate nucleation of the two components. This explains the solidification phenomena in cases where the crystallization velocity of the eutectics is lower than that of either component. The addition compound behaves as one of the components in both the eutectics. In the case of E_1, the crystallization starts with the nucleation of benzidine first, followed by the nucleation of the addition compound. Now the two phases grow side-by-side. Similarly, in the case of E_2, the solidification starts with the nucleation of the addition compound first, followed by the nucleation of α-naphthol and the two phases grow side-by-side.

TABLE I Values of u and n of the BZ–AN system

Materials	u (mm s^{-1} °C^{-1})	n
(I) Benzidine	0.000 1047	4.0
(II) α-naphthol	0.000 1995	3.0
(III) Eutectic-1	0.000 1585	2.0
(IV) Eutectic-2	0.000 4571	2.0
(V) 1:1 Addition compound	0.000 5495	1.6

3.3. Thermochemical studies

It is well known that the idea about mode of crystallization, structure of eutectic melt and the nature of interaction between two components forming the eutectic and addition compound can be obtained from a knowledge of heats of fusion data on pure components, eutectics and the molecular complex. The experimental values of heats of fusion of the pure components, the eutectics and the addition compound are reported in Table II. For the purpose of comparison, the values of heat of fusion, calculated using the mixture law given by the following equation, are also reported in Table II

$$(\Delta_f h)_e = x_1 \Delta_f h_1^\circ + x_2 \Delta_f h_2^\circ \qquad (2)$$

where x and $\Delta_f h^\circ$ are the mole fraction and heat of fusion, respectively, of the component indicated by the subscript. It is evident from the table that the calculated values of heat of fusion are higher than those of the experimental values. If a eutectic is a simple mechanical mixture of the two components involving no heat of mixing or any type of association in the melt, the heat of fusion can simply be given by the mixture law [26]. However, when a solid eutectic melts there is considerable possibility of association and mixing, both causing violation of the mixture law. The difference between experimental and calculated values can be attributed to the formation of clusters [27] in the eutectic melt. It can be imagined that during cluster formation heat liberated may lower the actual value of heat of fusion. In the present eutectic system where one component contains the hydroxyl group and the other member has the amino group, due to a tendency for hydrogen bond formation, the cluster formation will be favoured. This is one of the reasons why the experimental values of heats of fusion of eutectics are lower than those calculated from Equation 2.

TABLE II Heat of fusion, entropy of fusion, roughness parameter and heat of mixing of the BZ–AN system

Materials	Heat of fusion ($\mathrm{kJ\,mol^{-1}}$)	Entropy of fusion ($\mathrm{kJ\,mol^{-1}\,K^{-1}}$)	Roughness parameter, $\Delta s_f/R$	Heat of mixing ($\mathrm{kJ\,mol^{-1}}$)
(I) Benzidine	19.10	0.0478	5.77	–
(II) α-naphthol	22.71	0.0616	7.44	–
(III) Eutectic 1:				
Experimental	18.74	0.0506	6.11	– 1.73
Calculated	20.47	–	–	–
(IV) Eutectic 2:				
Experimental	19.68	0.0550	6.64	– 2.56
Calculated	22.24	–	–	–
(V) 1:1 Addition compound:				
Experimental	19.38	0.0519	6.27	– 1.49
Calculated	20.87	–	–	–

The heat of mixing, ΔH_m, which is the difference between the experimental and the calculated values of heat of fusion can be calculated from the equation

$$\Delta H_m = (\Delta_f h)_{\mathrm{exp}} - \Sigma x_i \Delta_f h_i^{\circ} \qquad (3)$$

where $(\Delta_f h)_{\mathrm{exp}}$ is the heat of fusion of the eutectic determined experimentally, and x_i and $\Delta_f h_i^{\circ}$ are the mole fraction and the heat of fusion of the end components, respectively. It is clear from the values of heat of mixing (Table II) of E_1 and E_2 that they are highly negative. Thermochemical studies [28] 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–AN system suggest clustering of molecules in the eutectic melt.

The experimental value of heat of fusion of the addition compound determined by the DSC method, is reported in Table II. Assuming this compound in an undissociated state in the molten form, the theoretical value of its heat of fusion was calculated by the mixture law, and this value is also given in Table II for the purpose of comparison. It is evident from the table that the heat of mixing, which is defined as the difference between experimental and the calculated values of heat of fusion, is highly negative. This highly negative value suggests [27] that the presence of the addition compound enhances the attraction between the components. It is well known that the addition compound is formed by the reaction between two components in the following manner

$$\mathrm{A + B \rightleftharpoons AB\ (liquid) \rightarrow AB\ (solid)} \qquad (3)$$

When the 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.

TABLE III Excess thermodynamic functions for the BZ–AN system

Excess thermodynamic functions	Eutectic 1	Eutectic 2
g^2 ($\mathrm{J\,mol^{-1}}$)	1 180.99	324.18
h^E ($\mathrm{J\,mol^{-1}}$)	29 614.24	– 1027.81
s^E ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	76.85	– 3.78

The deviation from the ideal behaviour can best be expressed in terms of excess thermodynamic functions which give a more quantitative idea about the nature of molecular interactions. It 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 the interaction between the 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

$$g^E = RT(x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l) \qquad (4)$$

$$h^E = -RT^2\left(x_1 \frac{\delta \ln \gamma_1^l}{\delta T} + x_2 \frac{\delta \ln \gamma_2^l}{\delta T}\right) \qquad (5)$$

$$s^E = -R\left(x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l + x_1 T \frac{\delta \ln \gamma_1^l}{\delta T} + x_2 T \frac{\delta \ln \gamma_2^l}{\delta T}\right) \qquad (6)$$

It is evident from Equations 4–6 that the activity and its variation with temperature are required in order to calculate excess functions. The activity coefficient, γ_i^l, of component i in the eutectic melt was calculated using the equation

$$-\ln x_i^l \gamma_i^l = \frac{\Delta_f h_i^{\circ}}{R}\left(\frac{1}{T} - \frac{1}{T_i^{\circ}}\right) \qquad (7)$$

where x_i, $\Delta_f h_i^{\circ}$ and T_i° 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 the calculation were reported earlier [26]. The positive values (Table III) of g^E suggest that the interaction between like molecules is stronger than that between the unlike molecules. The values of h^E and s^E correspond to the excess of free energy and are a measure of excess enthalpy of mixing and excess entropy of mixing, respectively.

TABLE IV *d* values and relative intensity (RI) of benzidine, eutectic 1 and the addition compound of BZ–AN system

Benzidine		Eutectic 1		1:1 Addition compound	
d (nm)	RI	*d* (nm)	RI	*d* (nm)	RI
1.435	3	–	–	–	–
–	–	1.105	7	–	–
–	–	–	–	1.099	5
1.020	4	–	–	–	–
0.949	4	–	–	–	–
0.903	3	–	–	–	–
–	–	–	–	0.880	6
–	–	0.867	7	–	–
0.701	4	0.700	21	0.696	13
–	–	0.632	57	0.634	84
0.628	12	–	–	–	–
–	–	–	–	0.607	8
0.574	20	–	–	–	–
–	–	0.563	35	0.563	15
0.542	29	–	–	–	–
0.540	30	–	–	–	–
0.507	20	–	–	–	–
0.494	22	0.497	36	0.497	13
0.482	60	–	–	–	–
0.479	34	–	–	–	–
–	–	0.468	84	0.467	100
–	–	0.452	100	0.452	54
0.445	39	–	–	–	–
0.440	100	–	–	0.441	24
–	–	0.436	64	–	–
0.423	70	0.420	64	0.421	39
0.412	73	0.410	48	0.411	14
0.404	28	–	–	–	–
0.386	19	0.390	77	0.391	39
0.383	40	–	–	0.383	13
0.372	21	0.369	40	0.368	24
0.358	15	–	–	0.358	8
0.347	13	0.349	26	0.349	9
0.342	19	–	–	–	–
0.335	40	0.335	34	0.334	15
–	–	0.333	50	–	–
0.325	8	–	–	0.329	32
0.318	11	–	–	0.317	7
0.312	20	–	–	–	–
0.304	10	0.309	56	0.309	28
0.298	9	–	–	–	–
0.291	14	0.291	23	0.292	8
0.283	7	0.282	16	0.282	5
0.275	5	0.278	15	0.278	6
–	–	0.270	14	0.272	5
0.264	5	0.264	12	0.263	5
–	–	0.255	14	0.254	7
–	–	0.253	14	–	–
–	–	0.245	13	0.247	7
–	–	–	13	0.241	3
–	–	0.235	16	0.235	6
0.230	4	0.228	12	0.227	3
–	–	0.222	12	–	–
0.218	5	0.216	9	0.214	3
–	–	0.209	14	0.209	5
–	–	–	–	0.201	4
–	–	0.198	9	0.198	3
0.190	5	0.190	13	0.192	4
–	–	–	–	0.189	5
–	–	–	–	0.183	6
–	–	0.179	8	–	–
0.174	4	–	–	–	–
0.172	3	0.170	8	0.170	3
–	–	–	–	0.152	2
–	–	–	–	0.151	2
–	–	–	–	0.139	11

TABLE V *d* values and relative intensity (RI) of α-naphthol, eutectic 2 and addition compound of the BZ–AN system

α-naphthol		Eutectic 2		1:1 Addition compound	
d (nm)	RI	*d* (nm)	RI	*d* (nm)	RI
–	–	1.197	13	–	–
1.18	40	–	–	–	–
–	–	–	–	1.099	5
–	–	0.983	3	–	–
–	–	–	–	0.880	6
–	–	–	–	0.696	13
0.660	30	0.665	16	–	–
–	–	–	–	0.633	84
–	–	–	–	0.607	8
–	–	0.593	100	–	–
0.585	90	–	–	–	–
–	–	0.568	19	–	–
0.560	35	–	–	0.563	15
–	–	0.518	9	–	–
–	–	–	–	0.497	13
–	–	0.490	7	–	–
0.482	8	–	–	–	–
–	–	–	–	0.467	100
–	–	0.462	26	–	–
–	–	0.449	6	0.452	54
0.438	45	–	–	0.441	24
–	–	0.432	3	–	–
–	–	0.425	3	0.421	39
–	–	–	–	0.411	14
0.404	18	0.400	10	–	–
0.386	16	0.389	8	0.391	39
–	–	0.380	8	0.383	13
–	–	0.372	23	–	–
0.363	100	0.367	27	0.368	24
–	–	0.360	19	0.357	8
–	–	0.350	10	0.348	9
0.343	6	0.346	7	–	–
–	–	0.331	8	0.334	15
–	–	–	–	0.329	32
0.320	60	0.323	13	–	–
–	–	0.317	10	0.317	7
–	–	0.306	2	0.309	28
0.294	40	0.296	12	0.292	8
–	–	0.279	3	0.282	5
–	–	–	–	0.278	6
0.270	40	0.273	8	0.272	5
–	–	0.266	3	0.263	45
–	–	0.262	2	–	–
–	–	0.257	2	0.254	7
–	–	0.251	2	–	–
–	–	0.244	2	0.248	7
0.240	4	–	–	0.241	3
0.233	4	0.236	3	0.235	6
–	–	0.230	2	0.227	3
0.225	6	0.225	2	–	–
–	– 6	0.220	4	–	–
0.218	10	0.213	2	0.214	3
0.209	6	0.205	3	0.210	5
0.202	16	–	–	0.202	4
–	–	0.197	3	0.198	3
0.192	25	0.195	3	0.192	4
–	–	–	–	0.189	5
0.181	16	0.182	2	0.182	6
0.175	20	0.176	3	–	–
0.173	4	–	–	0.170	3
0.165	4	–	–	–	–
0.161	4	–	–	–	–
0.159	4	–	–	–	–
0.155	2	0.156	2	0.152	2
–	–	–	–	0.151	2
–	–	–	–	0.138	11
0.126	8	–	–	–	–
0.121	4	–	–	–	–
0.117	2	–	–	–	–
0.114	2	–	–	–	–
0.108	2	–	–	–	–
0.102	2	–	–	–	–

3.4. X-ray diffraction

Hogan *et al.* [29] have observed a definite orientation relationship between two phases of metal eutectics. A similar observation was made by Bassi and Sharma [30] in the case of binary organic eutectics. Contrary to these observations, Savchenko [31] believes that the formation of eutectics leads to merging of electron energy levels. In order to clarify these conflicting ideas, some preliminary investigations on the organic eutectics, pure components and addition compounds were carried out and the results are reported in Tables IV and V. It is evident from the reported data that for each eutectic the number of reflections of the pure components and the addition compound are comparable to the number of reflections of their corresponding eutectic. This suggests that the pure components, the eutectics and the addition compound belong to the same crystal system and have similar lattices. The reported data in Table IV reveal that, in general, the reflections of benzidine show either an increase in intensity or their absence in the eutectic E_1. Similarly, the addition compound, the second component of eutectic E_1, shows either an increase in intensity of reflection or indicates its disappearance in the eutectic. Strong reflections of benzidine at *d* values 0.574, 0.542, 0.540, 0.507, 0.482, 0.479, 0.445, 0.440, 0.423, 0.404, 0.383, 0.335 nm and those of the addition compound at 0.441 and 0.329 nm are absent in their eutectic. In contrary to what has been observed in E_1, in the case of E_2 (Table V), strong reflections of its components, namely, α-naphthol and the addition compound, show a decrease in intensity. In addition, strong reflections of α-naphthol at *d* values 1.180, 0.585, 0.560, 0.438 nm and those of the addition compound at 0.633, 0.467, 0.441 and 0.329 nm are absent in eutectic E_2.

If a eutectic is a simple mechanical mixture of two components, the X-ray patterns of the two components should be exactly superimposed on the eutectic composite. From the XRD data of 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 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 [20, 32] that the eutectics are not simply a mechanical mixture of two components. In them, there is orientation of some atomic planes during their formation.

3.5. Microstructure

The properties of alloys are largely determined by their microstructure. This is, in turn, controlled by the types, relative amounts and morphology of phases present. In particular, the solidification process plays an important role in imparting the various microstructural features observed in alloys. According to Jackson and Hunt [12], the type of growth from a eutectic melt depends on a factor α defined as

$$\alpha = \varepsilon \frac{\Delta s_f}{R} \tag{8}$$

where ε is a crystallographic factor depending upon the geometry of the molecule and has the value less than or equal to 1. $\Delta s_f / R$, also known as the Jackson's roughness parameter, is the entropy of fusion in dimensionless unit. When $\alpha < 2$, the interface is atomically diffuse and migrates by continuous growth resulting in non-faceted growth. On the other hand, if $\alpha > 2$, the interface is atomically close-packed and it migrates by a lateral growth process involving ledges.

In the present investigation, for both components, the value of α is greater than 2, the result being that they would exhibit lateral growth. The microstructure of eutectics and the addition compound are given in Figs 3–5. Microstructure of eutectic E_1 (Fig. 3) reveals that one of the phases nucleates first and the second phase solidifies radiating outward. The microstructure of eutectic E_2 given in Fig. 4 shows its lamellar growth. The microstructure of the addition compound given in Fig. 5 suggests that its solidification takes place like a pure component, showing facets.

3.6. Spectral studies

The infrared spectrum of benzidine shows three bands at 3180, 3320 and 3400 cm^{-1} characteristic of symmetric and asymmetric stretching vibrations of the

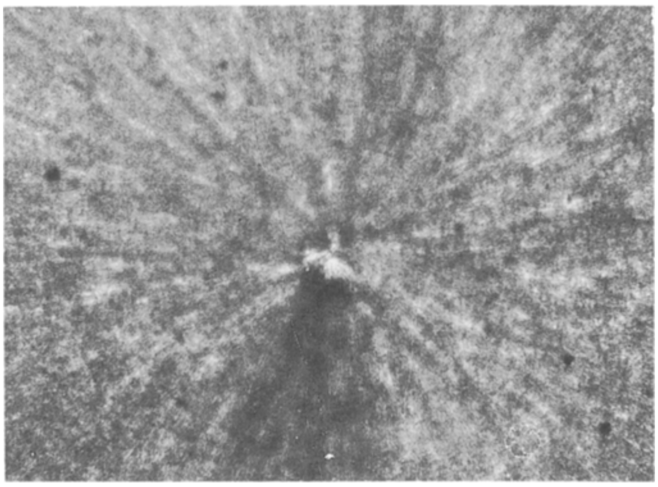

Figure 3 Microstructure of benzidine–α-naphthol eutectic, E_1, ×100.

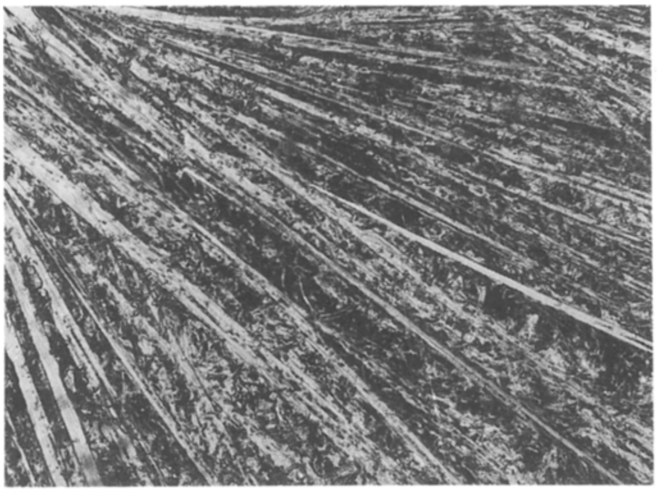

Figure 4 Microstructure of benzidine–α-naphthol eutectic, E_2, × 100.

Figure 5 Microstructure of benzidine–α-naphthol addition compound, × 100.

$-NH_2$ group, whereas α-naphthol exhibits a broad band in the region 3100–3350 cm^{-1} due to –OH stretching vibrations. The spectrum of the molecular complex shows bands at 3280, 3370 and 3430 cm^{-1}. The positive shifts [33] in the stretching frequencies of the $-NH_2$ group indicate that the hydrogens of the $-NH_2$ group are not involved in hydrogen bonding. Thus, it appears that there may be hydrogen bonding between hydrogens of the –OH group and nitrogens of the $-NH_2$ group in the addition compound.

The proton NMR spectrum of benzidine shows an $-NH_2$ peak at $\delta = 3.52$ and ring protons are obtained as multiplets in the range, $\delta = 6.48$–7.37. α-Naphthol exhibits an OH signal at $\delta = 5.59$ and phenyl ring multiplets are obtained in the range $\delta = 6.63$–8.00, while the NMR spectrum of the addition compound exhibits the $-NH_2$ signal at $\delta = 3.90$ and phenyl ring signals in the range $\delta = 6.63$–8.4. The –OH signal is absent from its original position as in α-naphthol, is shifted down-field and is merged with the phenyl ring signals. The down-field shift of the –OH signal in the addition compound may be due to involvement of hydrogen atom of the –OH group in the intermolecular hydrogen bonding with nitrogen of the $-NH_2$ group. Consequently, deshielding in NH_2 proton is also found in the spectrum of the addition compound.

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References

1. C. C. COCH, *Int. Mater. Rev.* **33** (1988) 201.
2. N. B. SINGH and K. D. DWIVEDI, *J. Sci. Ind. Res.* **41** (1982) 98.
3. R. ELLIOTT, *Int. Metals Rev.* **22** (1977) 161.
4. R. P. RASTOGI, D. P. SINGH, NAMWAR SINGH and NARSINGH B. SINGH, *Mol. Cryst. Liq. Cryst.* **73** (1981) 7.
5. R. P. RASTOGI, N. B. SINGH and K. D. DWIVEDI, *Ber. Bunzenges Phys. Chem.* **85** (1981) 85.
6. K. PIGON and A. KRAJEWSKA, *Thermochim. Acta* **58** (1982) 299.
7. H. SONG and A. HELLAWELL, *Metall. Trans.* **20A** (1989) 171.
8. M. E. GLICKSMAN, N. B. SINGH and M. CHOPRA, *Manufact. Space* **11** (1983) 207.
9. P. S. BASSI, N. K. SHARMA and M. K. SHARMA, *Cryst. Res. Technol.* **18** (1983) 1191.
10. ATSUSHI TOGASHI and YOSHIO MATSUNGA, *Bull. Chem. Soc. Jpn* **60(b)** (1987) 1171.
11. V. E. KAMPAR, *Russ. Chem. Rev.* **51(2)** (1982) 107.
12. K. A. JACKSON and J. D. HUNT, *Trans. Met. Soc. AIME* **236** (1966) 1129.

13. W. F. KAUKLER and D. O. FRAZIER, *J. Crystal Growth* **71** (1985) 340.
14. N. B. SINGH, N. N. SINGH and R. K. LAIDLAW, *J. Solid State Chem.* **71** (1987) 530.
15. N. B. SINGH, U. S. RAI and O. P. SINGH, *J. Crystal Growth* **71** (1985) 353.
16. U. S. RAI and K. D. MANDAL, *Mol. Cryst. Liq. Cryst.*, in **182A** (1990) 387.
17. N. B. SINGH and NARSINGH B. SINGH, *Krist. Technik* **13** (1978) 1175.
18. U. S. RAI and K. D. MANDAL, *Bull. Chem. Soc. Jpn*, **63** (1990) 1496.
19. U. S. RAI, O. P. SINGH and N. B. SINGH, *J. Chim. Phys.* **84** (1987) 483.
20. U. S. RAI and K. D. MANDAL, *Cryst. Res. Technol.* **23** (1988) 871.
21. R. P. RASTOGI and V. K. RASTOGI, *J. Crystal Growth* **5** (1969) 345.
22. U. S. RAI and K. D. MANDAL, *Thermochim. Acta* **138** (1989) 219.
23. B. M. SHUKLA, N. P. SINGH and NARSINGH B. SINGH, *Mol. Cryst. Liq. Cryst.* **104** (1984) 265.
24. W. B. HILLIG and D. TURNBULL, *J. Chem. Phys.* **24** (1954) 914.
25. W. C. WINEGARD, S. MOJKA, B. M. THALL and B. CHALMERS, *Can J. Chem.* **29** (1957) 320.
26. U. S. RAI, O. P. SINGH, N. P. SINGH and NARSINGH B. SINGH, *Thermochim. Acta* **71** (1983) 373.
27. N. P. SINGH, B. M. SHUKLA, NAMWAR SINGH and NARSINGH BAHADUR SINGH, *J. Chem. Engng Data* **30** (1985) 49.
28. N. SINGH, NARSINGH B. SINGH, U. S. RAI and O. P. SINGH, *Thermochim. Acta* **95** (1985) 291.
29. L. M. HOGAN, R. W. KRAFT and F. D. LEMKEY, in "Advances in Materials Research", Vol. 2, edited by H. Herman (Wiley, New York, 1971) p. 83.
30. P. S. BASSI and N. K. SHARMA, *Ind. J. Chem.* **14(A)** (1976) 693.
31. P. S. SAVCHENKO, *Russ. J. Inorg. Chem.* **4** (1959) 187.
32. N. P. SINGH and B. M. SHUKLA, *Cryst. Res. Technol.* **20** (1985) 345.
33. C. A. McAULIFFE, *Inorg. Chim. Acta* **60** (1982) 90.

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