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PHYSICOCHEMICAL STUDIES ON ORGANIC EUTECTIC AND MONOTECTIC ALLOYS
1,4-dibromobenzene–resorcinol system

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Abstract

Phase diagram, growth kinetics, thermal behaviour and microstructure of a monotectic system involving a non-metal–non-metal binary organic analogue are discussed here. The eutectic, monotectic and consolute temperatures are: 87.1, 107.2 and 149.0°C respectively, at 0.968, 0.154 and 0.521 mole fractions of 1,4-dibromobenzene. The upper consolute temperature lies 41.8°C above the monotectic horizontal. Growth kinetics data of the pure and binary materials show the obeyence of Hillig–Turnbull equation. Enthalpy of fusion data obtained from Mettler DSC-4000 was used to calculate the heat of mixing, entropy of fusion, Jackson's roughness parameter, excess thermodynamic functions, interfacial energy and radius of critical nucleus. The optical microphotographs of the eutectic and monotectic show their characteristic features.

Keywords: growth kinetics, microstructure, monotectic alloy, organic eutectic alloy, phase diagram

Introduction

Materials have been dominant forces in the cultures of advancing civilizations. Creating advanced materials with respect to structure, reliability and cost is a perpetual goal of scientists. Majority, if not most of the materials in today's technologies is polyphase in nature. The interaction among the constituent phases results in a newer material with unusual properties which can be modified according to desired specifications by changing the shape and distribution of phases. The fundamental understanding of solidification that has a pronounced effect on the processing of materials is a fascinating endeavor for scientists.

Among the binary polyphase materials, the metallic eutectics [1, 2], monotectics [3–5] and intermetallic compounds [6] constitute an established field of investigation in metallurgy and materials science. But many aspects of solidification and phase transformation phenomena can be inferred only indirectly and incompletely due to high transformation temperatures, optical opacity, large density driven convection effects and a limited choice of materials. Also, the experimentation and handling techniques are not sim-

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ple. The transparent organic analogues [7], due to their advantageous features, present the opportunity of direct observation and investigation of solidification and phase-transformation phenomena. These materials have low transformation temperatures, minimized density driven convection effects, easier handling and experimentation methods, optical transparency and a wider choice of materials. This has prompted a number of research groups to use organic analogues of metallic and non-metallic systems [8, 9] as models for detailed physicochemical investigations.

The literature [10, 11] studied so far reveals that the binary eutectics and addition compound forming systems have received proper attention because of their potential for generating technically important materials. Monotectic systems [12, 13] with liquid phase immiscibility are still a mystery due to the complexities associated with the miscibility gap. Literature in the past few decades shows that there are good prospects for monotectic systems also. Shuttle experiments on these systems can unfold various mysteries such as wetting behaviour, quality of dispersed in situ composites, nucleation behaviour in immiscible region, morphological changes, among others. Materials processing can benefit from such studies leading to the improvement of industrial products and services. With these pieces of information, we have chosen an organic analogue of non-metal–non-metal system, namely, 1,4-dibromobenzene (PDBB)–resorcinol (RES) system to study some physicochemical aspects. Both the components, namely, PDBB and RES possess high enthalpy of fusion and simulate non-metallic solidification [14, 15].

Experimental

Purification of compounds

PDBB (Fluka, Switzerland) was purified by recrystallising from diethyl ether while RES (E. Merck, India) was purified by repeated distillation under reduced pressure. The purity of both the components was checked by determining the melting point and comparing its value with that reported in the literature [16].

Phase diagram

A phase diagram helps in knowing the accurate composition and melting point of binary alloy materials. Thaw-melt method [17] was used to determine the phase diagrams. A number of long necked test tubes are taken and labeled with different compositions varying from 0 to 100%. Masses of the two components are taken accordingly which is followed by sealing of the tubes. After sealing the test tubes, each composition is homogenized for the first time by melting in silicone oil bath followed by chilling in ice cold water. It was observed that, some of the initial and final compositions show the presence of a single liquid phase in the molten state while rest of the mixtures show two immiscible liquid layers which change to a single liquid phase at certain higher temperature. The miscible compositions are repeatedly homogenized followed by chilling for 4–5 times to ensure a thorough mixing of the components. The mixtures are then solidified, powdered and their thaw and melting points are noted with the help of a Toshniwal melting point apparatus. The immiscible compositions are used to determine the complete miscibility temperature. The thaw, melting and complete miscibility temperatures are plotted *vs*. respective compositions to get the phase diagram of PDBB–RES system.

Growth kinetics

The growth kinetics of the pure components as well as the binary compositions was studied by the Capillary method [18]. In this method, the linear velocity of crystallization was determined at different desired undercoolings in a capillary. The well washed tube is mounted on a wooden board fitted with a scale and the molten material is transferred to it. The entire assembly is then kept in a silicone oil thermostat at a temperature slightly above the melting point of the experimental material, with care to see that the open ends of the tube are slightly above the oil surface. Temperature of the bath is then allowed to fall and set at a desired undercooling. When the material attains the temperature of the bath, a seed crystal of the same material is added to one end of the tube to start nucleation. As soon as nucleation starts and the crystallization front starts moving forward, the movement of the solid–liquid front is recorded with the help of a travelling microscope and a stop watch. At each undercooling, 4 to 5 readings are taken for each material.

Heat of fusion

The values of enthalpy of fusion for the pure components, eutectic and monotectic are determined [19] by the DSC method using a Mettler DSC-4000 system. The equipment is calibrated by using indium as a standard material. The amount of sample and heating rate are about 5 mg and 10°C min^{-1}, respectively, for each material.

Microstructure

With a view to record [20] the microstructure of the pure components, the eutectic and the monotectic, slides were prepared and placed on the platform of a Leitz laborlux D optical microscope and interesting regions were photographed with a camera attached to it.

Results and discussion

Phase diagram

The PDBB–RES system shows a typical monotectic phase diagram in the form of temperature-composition curves (Fig. 1). At the extreme left and right sides of the diagram, the compositions represent pure RES (*mp*. 110.5°C) and pure PDBB (*mp*. 87.4°C), respectively. The melting point of RES goes on decreasing with increasing addition of PDBB up to point *M* (the monotectic point), after which, even a slight ad-

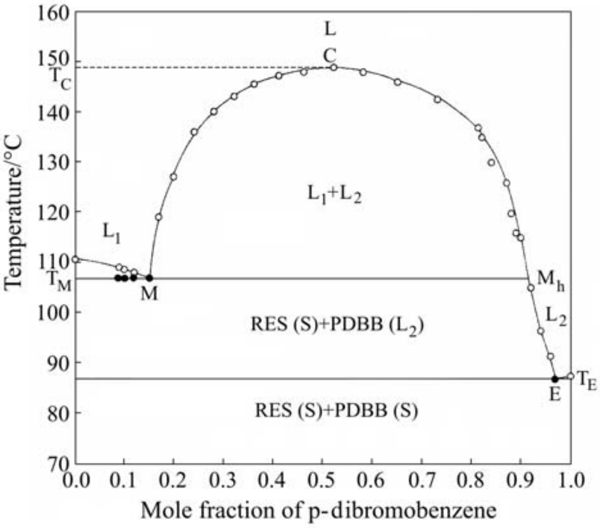

Fig. 1 Phase diagram of *p*-dibromobenzene–resorcinol system: o – melting temperature; • – thaw temperature

dition of PDBB, causes the appearance of two immiscible layers. In Fig. 1, the immiscibility region is shown by area L_1+L_2 bounded by the curve MCM_h. The points shown by white circles on the curve MCM_h represent the complete miscibility temperatures above which the two liquids appear as a single homogeneous liquid L. The point C at the top of the curve represent the critical solution point or consolute point and the corresponding temperature (149.0°C) is known as the critical solution temperature (T_c). The miscibility temperature starts increasing after point M, attains its maximum at point C, then decreases till it attains the monotectic horizontal (M_h). The miscibility curve is still continued in the region ($S+L_2$) that lies between the eutectic and monotectic horizontal lines and ends at point E, the eutectic point. The area L_1+L_2 may be regarded to be made up of an infinite number of tie lines which connect the two liquid phases L_1 and L_2 at the extreme sides of the diagram. These tie lines become progressively shorter until the ultimate tie line at the top of the area reduces to a point C that corresponds to the critical solution temperature. There are three types of phase separation processes occurring in such systems:

$$(i)\ L\leftrightarrow L_1+L_2 \quad (ii)\ L_1\leftrightarrow S_1+L_2 \quad \text{and} \quad (iii)\ L_2\leftrightarrow S_1+S_2$$

First of these, concerns the phase separation of liquid L in the two-phase region (L_1+L_2) as the liquid of the composition corresponding to point C is cooled below the critical solution temperature T_c. The second reaction is the monotectic phase separation reaction and is similar to the eutectic reaction except that both the phases produced are not solids. This reaction occurs when a liquid of monotectic composition is cooled through the monotectic temperature, T_M. As a result of cooling below T_M, the liquid L_1 which is rich in one component (RES) decomposes into a solid phase S_1 rich in the first component (RES) and another liquid phase L_2, rich in the second component (PDBB). The third reaction is the eutectic reaction. When a liquid of eutectic composition is cooled below the eutectic temperature, the phase separation reaction results in two solids S_1 and S_2. The eutectic, monotectic and upper consolute temperatures are 87.1, 107.2 and 149.0°C at 0.968, 0.154 and 0.521 mole fractions of PDBB, respectively.

Growth kinetics

The growth kinetics data for the PDBB–RES system in the form of plots of logΔT *vs.* log$v$ are shown in Fig. 2. Linearity of these plots is in accordance with the Hillig–Turnbull equation [21, 22],

$$v=u(\Delta T)^{n} \tag{1}$$

where u and n are constants depending on the solidification behaviour of the materials under investigation. The experimental values of these constants are given in Table 1. The basic criterion for the determination of growth mechanism is the comparison of the temperature dependence of linear velocity of crystallization with the theoretically predicted equations. In pure components as well as in various organic eutectics, normal and lateral growth mechanisms have been discussed. While normal growth generally occurs on rough interface in which case there is direct proportionality between crystallization velocity and undercooling, lateral growth is facilitated by the presence of steps, jogs, bends etc. and under such conditions, the relationship for the spiral mechanism follows the parabolic law Eq. (1). In majority of cases, n assumes a value that is greater than unity suggesting that the growth mechanism obeys the parabolic law. In the present case, the value of n is quite close to 2 suggesting thereby, a square relationship between growth velocity, v and undercooling ΔT. Two

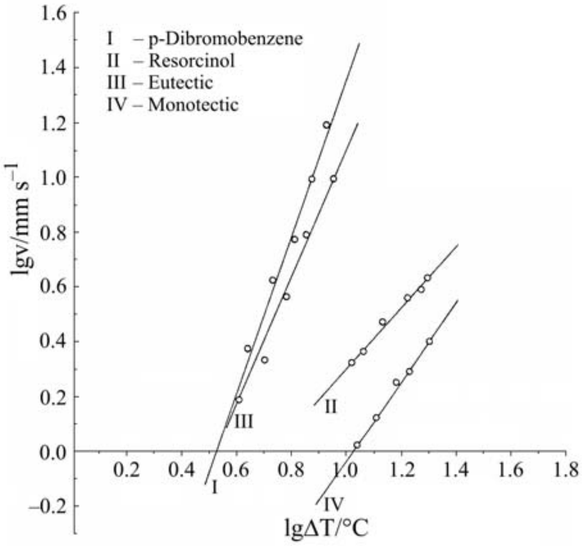

Fig. 2 Linear velocity of crystallization of *p*-dibromobenzene, resorcinol, their eutectic and monotectic

theories [23] have been developed to explain the square relationship between v and ΔT. The deviations in the values of n from 2, observed in some cases, is due to the difference between the bath temperature and the temperature of the growing interface. While a value of n less than 2 suggests less rapid variation in the growth velocity with undercooling, a value greater than 2 suggests more rapid variation in v in comparison to the cases where n is equal to 2.

Table 1 Values of u and n for pure components, eutectic and monotectic in PDBB–RES system

Materials	u/mm sec^{-1} °C^{-1}	n
p-dibromobenzene	$3.3\cdot 10^{-5}$	2.8
Resorcinol	$1.4\cdot 10^{-1}$	1.2
Eutectic	$5.5\cdot 10^{-2}$	2.3
Monotectic	$3.2\cdot 10^{-2}$	1.5

The values of u, reported in Table 1 are obtained from the linear velocity of crystallization plots. The u value is a measure of the linear velocity of crystallization of the concerned material. It is evident from the values of u that the linear velocity of crystallization of the eutectic and monotectic lie in between those of the pure components, representing a similar trend in the growth velocity. These variations are explained by the mechanism proposed by Winegard *et al*. [24]. According to them, the eutectic solidification begins with the formation of 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 also starts nucleating. Now, there are two possibilities: first, the two initial crystals may grow side by side and secondly, there may be alternate nucleation of the two components. The side by side nucleation mechanism explains the intermediate growth velocity of the binary materials in comparison to the pure components. It is now observed in the PDBB–RES system that the u value for the monotectic is smaller than the eutectic, indicating thereby, a similar trend in the growth velocity. The difference between the growth velocity of eutectic and monotectic may be ascribed to the different mode of heat flow and diffusion during the solidification of the binary materials [25].

Thermochemistry

The values of enthalpy of fusion are very important in understanding the mechanism of solidification. The process of solidification comprises of two stages: (*i*) nucleation and (*ii*) growth. While nucleation depends on solid-liquid interfacial energy, the growth step depends on the manner in which particles from the liquid phase are added on to the solid-liquid interface. In addition, interfacial energy, enthalpy of mixing and excess thermodynamic functions which can be calculated from the enthalpy of fusion, throw light on the mechanism of solidification and the nature of interaction between the components forming the eutectic melt.

Table 2 Heat of fusion, entropy of fusion, Jacksons roughness parameter and heat of mixing for PDBB–RES system

Materials	Heat of fusion/ kJ mol^{-1}	Entropy of fusion/ J mol^{-1} K^{-1}	Roughness parameter/α	Heat of mixing/ kJ mol^{-1}
p-dibromobenzene	20.6	57.3	6.9	–
Resorcinol	21.0	54.8	6.6	–
PDBB–RES Eutectic (experimental)	21.1	58.7	7.1	–
PDBB–RES Eutectic (calculated)	20.6	–	–	0.5
PDBB–RES Monotectic (experimental)	23.0	60.4	7.3	–

The values of enthalpy of fusion for pure components and binary materials are given in Table 2. If the eutectic mixture does not involve either heat of mixing or any type of association in the melt, for such a mechanical mixture the enthalpy of fusion is given by the mixture law [26],

$$(\Delta_f h)=x_1\Delta_f h_1^0+x_2\Delta_f h_2^0 \tag{2}$$

For the purpose of comparison, the value of heat of fusion of the eutectic calculated by the mixture law, given by Eq. (2) is also given in Table 2. In Eq. (2), x and $\Delta_f h^0$ are the mole fraction and heat of fusion, respectively of the component indicated by the subscript. In general, when solid eutectic melts, there is considerable possibility of association and heat of mixing, both causing violation of the mixture law. The value of enthalpy of mixing, $\Delta_{mix}H$ of a simple eutectic is given by the difference between the experimental and calculated values of enthalpy of fusion of eutectic, and is given by

$$\Delta_{mix}H=(\Delta_f h)_{exp}-(\Delta_f h)_{cal} \tag{3}$$

where $(\Delta_f h)_{exp}$ is the heat of fusion determined experimentally and $(\Delta_f h)_{cal}$ is its value calculated by Eq. (2). The value of enthalpy of mixing is 0.5 kJ mol^{-1}. Thermochemical studies [27] suggest that the structure of a binary eutectic melt depends on the sign and magnitude of heat of mixing. As such, three types of structure are suggested (*i*) quasi-eutectic for which $\Delta_{mix}H>0$, (*ii*) ordering of molecules for which $\Delta_{mix}H<0$ and (*iii*) molecular solution for which $\Delta_{mix}H=0$. The value of $\Delta_{mix}H$ being positive suggests that there is quasieutectic structure in the binary organic eutectic melt. It appears that the components form clusters and these clusters have repulsive type of interaction among themselves.

The difference between the thermodynamic functions of mixing for a real system and the corresponding value for an ideal system at the same temperature and pressure is called the excess thermodynamic function [28]. This gives a quantitative measure of deviation from ideal behaviour and molecular interactions. It is denoted by superscript E and represents the excess of a given thermodynamic property of a solution over that in the ideal solutions. With a view to know the nature of interaction between the components forming the eutectic melt, 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 [29]:

$$g^{\mathrm{E}} = RT(x_1 \ln\gamma_1^{\mathrm{l}} + x_2 \ln\gamma_2^{\mathrm{l}}) \tag{4}$$

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

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

The values of activity coefficient and its variation with temperature are calculated by the equation,

$$-\ln x_{\mathrm{i}}^{\mathrm{l}} \gamma_{\mathrm{i}}^{\mathrm{l}} = \frac{\Delta_{\mathrm{f}} h_{\mathrm{i}}^0}{R} \left(\frac{1}{T} - \frac{1}{T_{\mathrm{i}}^0} \right) \tag{7}$$

where $x_{\mathrm{i}}^{\mathrm{l}}$, $\gamma_{\mathrm{i}}^{\mathrm{l}}$, $\Delta_{\mathrm{f}} h_{\mathrm{i}}^0$ and T_{i}^0 are the mole fraction, activity coefficient, 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 (superscript *l* denotes liquid). The details of calculation of variation of activity coefficient with temperature is reported earlier [29]. The values of the excess functions calculated by the above procedure is given in Table 3. The value of g^E being positive suggests [30] that there is strong attractive interaction among the like molecules. Thus, PDBB–PDBB and RES–RES attractions will be stronger than PDBB–RES association. The positive values of h^E and s^E very much related to g^E are measure of excess enthalpy of mixing and excess entropy of mixing, respectively.

Table 3 Excess thermodynamic functions for PDBB–RES eutectic

Material	g^E/J mol^{-1}	h^E/kJ mol^{-1}	s^E/J mol^{-1} K^{-1}
PDBB–RES Eutectic	400.0	62.2	171.8

The solid liquid interfacial tension affects the enthalpy of fusion value. In addition, the solid–liquid interface plays an important role in determining the kinetics of phase transformation. When a liquid is cooled below its equilibrium temperature, the liquid phase does not solidify spontaneously. This is because under the equilibrium condition, it contains clusters of molecules. As long as the clusters are well below the critical size [31] they cannot grow to form a crystal and no solid is formed. During growth, the radius of critical nucleus is influenced by undercooling as well as the interfacial energy of the surface involved. The interfacial energy (σ) is given by

$$\sigma = \frac{C \Delta_{\mathrm{f}} h}{(N)^{1/3} (V_{\mathrm{m}})^{2/3}} \tag{8}$$

where N is Avogadro number, V_m is the molar volume and C is a constant which lies between 0.30 to 0.35.

The values of interfacial energy using equation are given in Table 4. The literature [32–33] during the past two decades is replete with various attempts to understand and explain the process of solidification involving various interesting phenomena of monotectic alloys. The role of wetting, in a phase separation process is of immense importance. In view of this, the applicability of Cahn's wetting condition has been tested in the present case. It is evident from the values of interfacial energy that non-wetting condition, given by,

$$\sigma_{SL_2} > \sigma_{SL_1} + \sigma_{L_1L_2} \tag{9}$$

is satisfied in the present case. Where σ is the interfacial energy between the faces denoted by the subscripts. The value of $\sigma_{L_1L_2}$ has been calculated using the equation [34]

$$\sigma_{L_1L_2} = \sigma_{SL_1} + \sigma_{SL_2} - \sqrt{\sigma_{SL_1}\sigma_{SL_2}} \tag{10}$$

The size of the critical nucleus (r^*) can be calculated by the equation,

$$r^* = \frac{2\sigma T_m}{\Delta_f h \Delta T} \tag{11}$$

where T_m, $\Delta_f h$ and ΔT are melting temperature, heat of fusion and degree of undercooling, respectively.

The values of the size of critical nucleus at different undercoolings calculated using Eqs (8) and (11) are given in Table 5. It is evident that the size of critical nucleus decreases with increase in undercooling. Thus high undercooling favours formation of critical nucleus of smaller size. This may be ascribed to the increased amplitude of molecular vibration at higher temperatures.

Table 4 Interfacial energy values of PDBB, RES and their monotectic

Materials	Values/erg cm^{-2} mol^{-1}	$\sigma_{SL_1}+\sigma_{L_1L_2}$/erg cm^{-2} mol^{-1}
σ_{SL_1}(PDBB)	44.1	44.3
σ_{SL_2}(RES)	50.9	–
$\sigma_{L_1L_2}$(PDBB–RES)	0.2	–

Theoretical studies on entropy of fusion of a eutectic predicts structure, stability and ordering in the melt. The values of entropy of fusion ($\Delta_f S$) of the pure components, eutectic and the monotectic were calculated using the following equation [35]:

$$\Delta_f S = \frac{\Delta_f h}{T} \tag{12}$$

where $\Delta_f h$ is the heat of fusion and T is the fusion temperature.

Table 5 Radius of critical nucleus for pure and binary materials at different degrees of undercooling for PDBB–RES system

Undercooling/ ΔT/°C	Critical radius· 10^{-8}/ cm			
	p-Dibromobenzene	Resorcinol	Eutectic	Monotectic
4.0			3.8	
4.4	3.5			
5.0			3.0	
5.4	2.9			
6.0			2.5	
6.4	2.4			
7.0			2.2	
7.4	2.1			
8.4	1.8			
9.0			1.7	
10.5		1.8		
11.0				1.5
11.5		1.6		
13.0				1.3
13.5		1.4		
15.0				1.1
16.5		1.1		
17.0				1.0
18.5		1.0		
19.5		0.9		
20.0				0.8

The values of entropy of fusion being positive suggests that there is an increase in randomness during melting. Higher value of entropy of fusion in binary materials suggests that entropy factor is more effective in melting eutectic and monotectic in comparison to that of the pure components.

Microstructure

It is well known that microstructure gives shape, size and distribution of phases in polyphase materials. The significance of microstructure lies in deciding the mechanical, electrical, magnetic and optical properties of a material. Desired type of microstructure [36] generating required properties can be had by controlling the solidification process, adding small amounts of impurities and selecting appropriate combination of materials, besides other variables, e. g. entropy of fusion, structure of solid–liquid interface and undercooling which have a pronounced effect on the microstructure of alloys.

The growth morphology developed by a eutectic system during solidification, depends on the growth characteristic of individual component phases on the basis of which they solidify either with faceted or a non-faceted interface. This behaviour is related to the nature of solid–liquid interface and can be predicted from the value of their entropy of fusion. Hunt and Jackson [37] suggested that the type of growth from a eutectic melt depends upon a factor α, defined as,

$$\alpha = \frac{\xi \Delta_f h}{RT} = \frac{\xi \Delta_f S}{R} \tag{13}$$

where ξ is a crystallographic factor depending upon the geometry of molecules and has the value less than or equal to one, $\Delta_f S/R$, also known as Jacksons roughness parameter, is entropy of fusion in dimensionless unit and R is the gas constant.

If $\alpha<2$, the solid–liquid interface is rough and exhibits non-faceted growth. On the other hand if $\alpha>2$, the solid–liquid interface is smooth and shows faceted growth. In the present system, the value of α being greater than 2 in all the cases suggests that phases grow showing facets.

The microstructures of PDBB–RES system are given in Figs 3–5. The microstructure of eutectic (Fig. 3) shows eutectic colonies lying parallel to each other. Within the colonies, the micromorphologies show lamellar structure where constituent phases are present in the form of alternate lamellae. The monotectic microstructures (Figs 4 and 5) show a regular lamellar structure. With further growth, one of the constituent

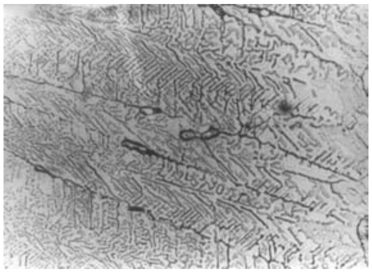

Fig. 3 Microstructure of *p*-dibromobenzene–resorcinol eutectic ×500

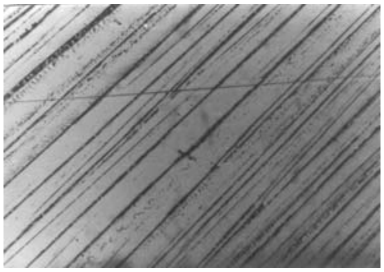

Fig. 4 Microstructure of *p*-dibromobenzene–resorcinol monotectic ×500

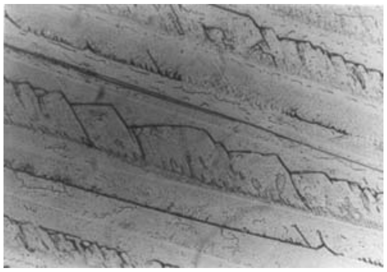

Fig. 5 Microstructure of *p*-dibromobenzene–resorcinol monotectic ×500 (after further growth)

phases show faceting behaviour (Fig. 5). As one of the component phases is present in small amount (0.154 mole fraction of PDBB) the lamellae are of unequal width.

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