Thermochimica Acta, 175 (1991) 215–227
Elsevier Science Publishers B.V., Amsterdam

SOME PHYSICOCHEMICAL STUDIES ON BINARY ORGANIC EUTECTICS

U.S. RAI and H. SHEKHAR

Chemistry Department, Banaras Hindu University, Varanasi 221005, Uttar Pradesh (India)

(Received 27 July 1990)

ABSTRACT

Solid–liquid equilibrium data on binary systems of phenanthrene with *p*-chloronitrobenzene, *p*-dibromobenzene and diphenyl show the formation of simple eutectics in each case. The linear growth velocity (v) of pure components and eutectics at different undercoolings (ΔT) obey the Hillig–Turnbull equation $v = u(\Delta T)^n$ where u and n are constants. The observed solidification behaviour of the eutectics is explained by the mechanism proposed by W.C. Winegard, S. Mojka, B.M. Thall and B. Chalmers, Can. J. Chem., 29 (1951) 320. The experimental values for the heat of fusion of eutectics, compared with the theoretical values calculated from the law of mixtures, suggest a cluster formation in the eutectic melt. Using heats of fusion data, excess thermodynamic function, surface energy and critical radius were calculated in order to throw light on the mechanism of solidification and the nature of the interaction between the components forming the eutectic. The microstructural examinations of pure components and eutectics suggest thinly branched eutectic structures resulting from coupled growth of the component phases.

INTRODUCTION

With a view to developing new materials of technological and commercial importance, the eutectic alloys are being widely studied by chemists, metallurgists and materials scientists. The fundamental interest lies in the study of the crystallization mechanisms, microstructure, thermochemistry and thermodynamics of eutectics. Owing to low transformation, ease of purification, transparency, minimised convection effects and a wider choice of materials, the organic systems [1–3] are more suitable than the metallic systems and therefore are being used as model systems for the detailed investigation of the parameters which control solidification. Also, the simple and easy experimental techniques used on these systems have prompted a number of active research groups [1–10] to work on some physicochemical aspects of organic eutectics.

In binary systems of phenanthrene (Ph) with *p*-chloronitrobenzene (PCN), *p*-dibromobenzene (PDB) and diphenyl (DP), each component has a high enthalpy of fusion; these systems are an organic analog of nonmetal–nonmetal systems. A systematic study on such a system can throw light on different aspects of faceted–faceted [11] eutectics. In the present article, binary organic systems of phenanthrene with PCN, PDB and DP have been selected and their phase diagram, linear velocity of crystallization, thermochemistry and microstructure have been studied.

EXPERIMENTAL

Materials and their purification

Phenanthrene (Thomas Backer & Co., Bombay), *p*-chloronitrobenzene (SD'S Lab-Chem. Industry, Bombay) and diphenyl (SOJUZ Chem., Moscow) were purified by fractional crystallisation with ethanol. *p*-Dibromobenzene (obtained from Fluka AG, Switzerland) was recrystallized using boiling ethyl alcohol. The purity of the compounds was confirmed by determining their melting points which were in good agreement with those quoted in reference literature.

Phase diagram study

The phase diagrams of Ph–PCN, Ph–PDB and Ph–DP systems were determined by the thaw–melt method [12,13]. Mixtures of different compositions were made in glass test tubes by repeated heating followed by chilling in ice. Finally, the mixtures were ground to a fine powder using a glass mortar. The melting and thawing temperatures were determined in a Toshniwal melting point apparatus using a precision thermometer.

Linear velocity of crystallization

The linear velocity of crystallization of pure components and eutectics was determined by capillary method [14,15]. The rate of advance of the crystal boundaries at different undercoolings was recorded using a travelling microscope.

Heat of fusion

Heats of fusion of pure components and their eutectics were measured [16,17] by the DTA method using a Stanton Redcroft STA-780 series unit.

Microstructure

For morphological examination [18,19] of pure components and eutectics, a small amount of sample was put on a glass slide and carefully melted and covered with a coverslip so that no air bubbles remained between the glass slide and the coverslip. It was undercooled from one side of the slide to facilitate unidirectional solidification. Pictures of different regions of the slide were taken with a camera attached to an optical microscope (Leitz Laborlux D).

RESULTS AND DISCUSSION

Phase diagram

The phase diagrams of the Ph–PCN, Ph–PDB and Ph–DP systems, determined by the thaw–melt method, are reported in the form of temperature–composition curves in Figs. 1–3. Each system shows the formation of a simple eutectic, and as shown below, at the eutectic temperature a binary solution (L) is in equilibrium with two solid phases S_1 and S_2.

$$L \rightleftharpoons S_1 + S_2$$

The melting point of Ph is 99.0 °C and in each phase diagram it decreases with the addition of the second component; PCN, PDB or DP. In Ph–PCN, Ph–PDB and Ph–DP systems, the minimum temperatures at 43.5, 55.0 and 60.5 °C, respectively, are the eutectic points and correspond to 0.44, 0.43 and 0.23 mole fraction of phenanthrene. At the eutectic temperature three phases, namely a liquid phase L and two solid phases S_1 and S_2, are in equilibrium and the system is invarient. In the region indicated by L a homogeneous binary liquid solution exists while the two solid phases S_1 and S_2 exist below the horizontal line. In each case, in the L + Ph region located on the left side of the diagram a binary liquid and solid Ph exist while in a

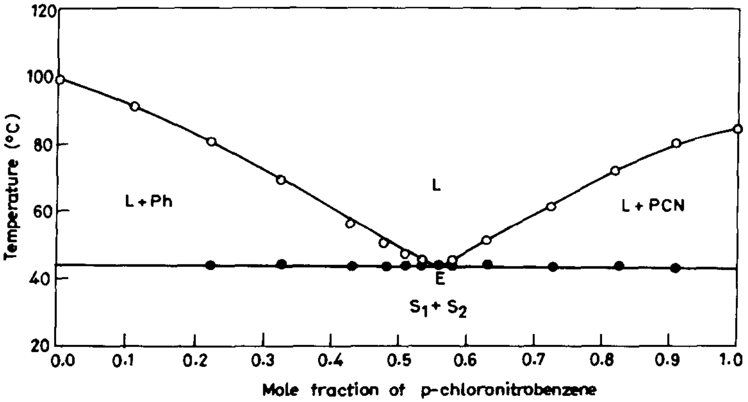

Fig. 1. Phase diagram of the phenanthrene–*p*-chloronitrobenzene system: ○, melting temperature; ●, thawing temperature.

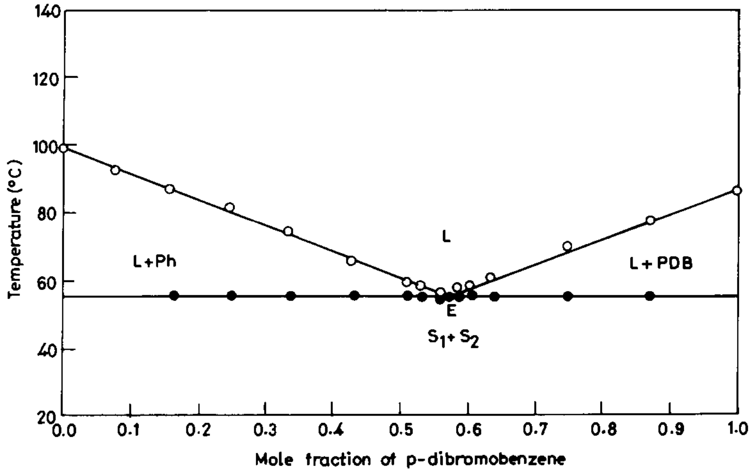

Fig. 2. Phase diagram of the phenanthrene–*p*-dibromobenzene system: ○, melting temperature; ●, thawing temperature.

similar region located on the right side of the diagram a binary liquid and the second component of the system coexist.

Growth kinetics

The log of the linear velocity of crystallization (v) for the pure components and eutectics of the Ph–PCN, Ph–PDB and Ph–DP systems, determined by measuring the growth rate of moving fronts in a capillary at different undercoolings, is plotted vs. $\log(\Delta T)$, Figs. 4–6. The linear depen-

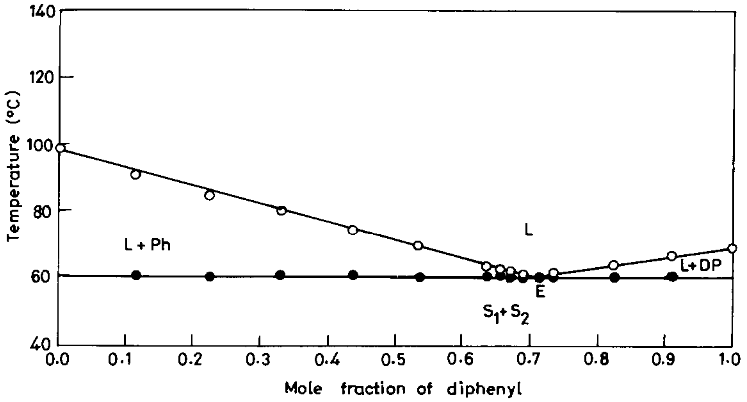

Fig. 3. Phase diagram of the phenanthrene–diphenyl system: ○, melting temperature; ●, thawing temperature.

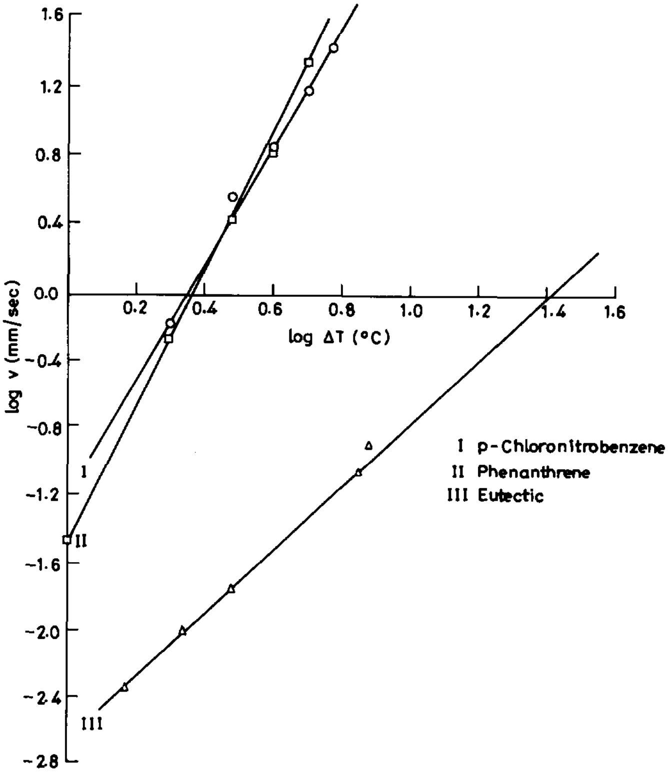

Fig. 4. Linear velocity of crystallization of phenanthrene, *p*-chloronitrobenzene and their eutectic.

dence of growth velocity and undercooling suggests that the crystallization data obey the Hillig–Turnbull [20] equation:

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

where u and n are constants determined by the solidification behaviour of the materials under investigation. The values of these constants are given in Table 1. Because the value of n for eutectics is close to two, a squared relationship between the growth velocity and the undercoolings is suggested. The deviation [12] of n from two, observed in pure components, may be attributed to the difference between the bath and growing interface temperatures. From the values of u (given in Table 1) it can be inferred that in all three systems the eutectics crystallize at a slower rate than the pure components. Studies [21] on the crystal morphology of eutectics indicate that the eutectic solidification begins with the nucleation of one of the phases. This continues until the surrounding liquid becomes rich in the other component (of lower melting point) and a stage is reached when the second component also starts to form a nucleus. In each system the lower rate of solidification

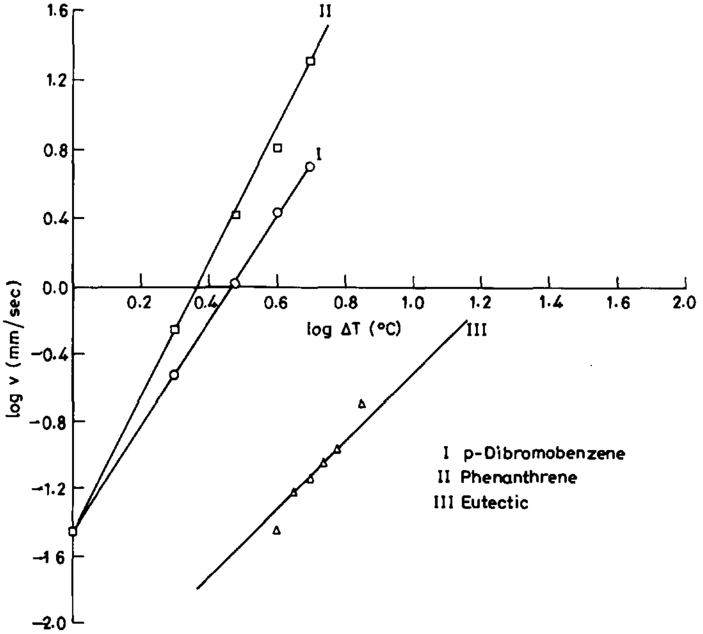

Fig. 5. Linear velocity of crystallization of phenanthrene, *p*-dibromobenzene and their eutectic.

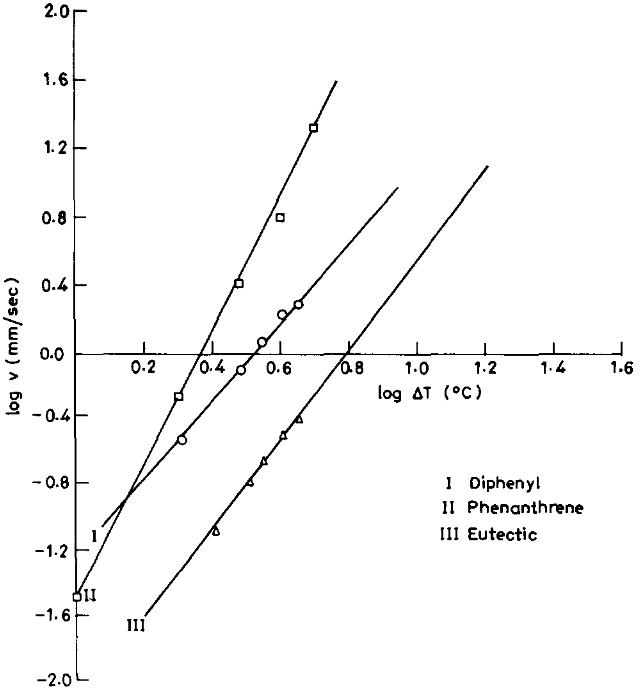

Fig. 6. Linear velocity of crystallization of phenanthrene, diphenyl and their eutectic.

TABLE 1

Values of u and n

Material	n	u (mm s^{-1} K^{-1})
Phenanthrene	4.0	3.39×10^{-2}
p-Chloronitrobenzene	3.4	6.46×10^{-2}
p-Dibromobenzene	3.0	3.47×10^{-2}
Diphenyl	2.3	6.17×10^{-2}
Ph–PCN eutectic	1.9	2.29×10^{-3}
Ph–PDB eutectic	2.0	2.88×10^{-3}
Ph–DP eutectic	2.5	6.92×10^{-3}

of the eutectic than those of the parent components points to the alternate nucleation [22] of the two phases involved.

Thermochemistry

Heat of fusion

The heats of fusion of pure components and eutectics are given in Table 2. For the purposes of comparison, values of the heats of fusion of the eutectics, calculated by the mixture law [23], are also given in Table 2. If the eutectic is assumed to be a mechanical mixture of two components involving

TABLE 2

Heat of fusion, entropy of fusion and interfacial energy

Material	Heat of fusion (kJ mol^{-1})	Entropy of fusion (J mol^{-1} K^{-1})	Roughness parameter ($\Delta S_f/R$)	Interfacial energy (erg cm^{-2})
Phenanthrene	18.1	48.7	5.9	22.1
p-Chloronitrobenzene	18.5	51.7	6.2	29.4
p-Dibromobenzene	20.3	56.3	6.8	31.2
Diphenyl	16.8	49.0	5.9	20.8
Ph–PCN eutectic (experimental)	16.4	51.7	6.2	26.2
Ph–PCN eutectic (law of mixtures)	18.3	57.8	7.0	
Ph–PDB eutectic (experimental)	17.3	52.7	6.3	27.3
Ph–PDB eutectic (law of mixtures)	19.3	58.8	7.1	
Ph–DP eutectic (experimental)	15.6	46.8	5.6	21.2
Ph–DP eutectic (law of mixtures)	17.2	51.6	6.2	

no heat of mixing or any type of association, the heat of fusion would be given by

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

where x and $\Delta_f h^0$ are the mole fraction and the heat of fusion of the component indicated by the subscript, respectively. It can be inferred from the values for the heats of fusion given in Table 2 that the eutectics are not simple mechanical mixtures of the two components.

Heat of mixing

The heat of mixing (ΔH_m) which is the difference between the experimental and calculated values of the heat of fusion is given by

$$\Delta H_m = (\Delta_f h)_{exp} - \sum (x_i \Delta_f h_i^0) \tag{3}$$

where $(\Delta_f h)_{exp}$ is the heat of fusion of the eutectic, determined experimentally, and x and $\Delta_f h_i^0$ are the mole fraction and heat of fusion of the end components, respectively. It is evident from Table 2 that the heats of mixing of all eutectics are negative. Thermochemical studies [24] suggest that the structure of eutectic melt depends on the sign and magnitude of the enthalpy of mixing. Three types of structures are suggested: quasieutectic for $\Delta H_m > 0$, clustering of molecules for $\Delta H_m < 0$ and the molecular solution for $\Delta H_m = 0$. The large negative values of ΔH_m of eutectics suggest clustering of molecules in the eutectic melt.

Entropy of fusion

The entropy of fusion (ΔS) of pure components and the eutectics can be calculated using the following equation:

$$\Delta S = \frac{\Delta_f h}{T} \tag{4}$$

where $\Delta_f h$ is the heat of fusion and T is the fusion temperature. The values for the entropy of fusion (given in Table 2) are positive in all cases; this points to an increase in the randomness of the system during melting. It is evident from Table 2 that the calculated values for the entropy of fusion of eutectics are higher than experimental values. This suggests an ordering in the eutectic melt as a result of associative interaction between two components forming the melt.

Excess thermodynamic functions

The possibility of heats of mixing and association being generated during eutectic melting leads to violation of the mixture law. In order to discover the nature of the interactions between the components forming the eutectics, the thermodynamic functions — excess heat of mixing (h^E), excess entropy of mixing (s^E) and excess free energy of mixing (g^E) were calculated using the following equations [23]:

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

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

$$h^E = -RT^2\left(x_1 \frac{\delta \ln \gamma_1^l}{\delta T} + x_2 \frac{\delta \ln \gamma_2^l}{\delta T}\right) \tag{7}$$

The activity coefficient, γ_i, of a component i present in the system is given by equation

$$-\ln(x_i^l \gamma_i^l) = \frac{\Delta_f h_i^0}{R}(T^{-1} - T_i^{-1}) \tag{8}$$

where x_i^l, γ_i^l, $\Delta_f h_i^0$ and T_i^0 are the mole fraction, activity coefficient, heat of fusion and melting temperature of component i, respectively. R is the gas constant and T is the eutective temperature of the system. The values of $\delta \ln \gamma_i^l/\delta T$ can be determined by the slope of the liquidus curve near the eutectic point in the phase diagram. The values of the excess thermodynamic functions are given in Table 3. In general the value of the excess free energy is a measure of the departure of the system from ideal behaviour. The reported excess thermodynamic data substantiate the earlier conclusion of an appreciable interaction between the parent components during the formation of eutectics. The negative value of excess free energy in the case of the Ph–PCN and Ph–PDB systems indicates the possibility of a stronger association [25] between unlike molecules while the positive value in the Ph–DP system suggests an association of weaker nature between unlike molecules and of stronger nature between like molecules. Its sign provides information regarding a change in density of the eutectic during the phase transformation. The excess entropy is a measure of the change in configurational energy due to a change in potential energy and indicates an increase in randomness.

TABLE 3

Excess thermodynamic functions for eutectics

Material	g^E (J mol^{-1})	h^E (kJ mol^{-1})	s^E (J mol^{-1} K^{-1})
Ph–PCN eutectic	−556.8	8.9	29.9
Ph–PDB eutectic	−87.4	0.4	1.5
Ph–DP eutectic	760.6	26.3	76.4

Interfacial energy and critical nucleus size

Interfacial energy is an important thermo-physical property required to show the relationship between the size of the critical nucleus and the undercooling. Measurement of the solid–liquid interface energy [26] is extremely difficult and unfortunately its magnitude varies from 50 to 100% from one worker to other. However, Glicksman et al. [27] have proposed an empirical method for the calculation of interfacial energy from the heat of fusion and the values obtained agree well with experimental values. The same method was used to calculate the interfacial energy in the present investigation. According to Chadwick [28] the critical size of the nucleus (r^*) is related to the undercooling (ΔT) by the following relationship:

$$r^* = \frac{2\gamma T_m}{L\Delta T} \tag{9}$$

where γ is the interfacial energy (Table 2) and T_m and L are the melting temperature and the enthalpy of fusion of the compound per unit volume, respectively. The critical size of the nucleus for the components and eutectics was calculated at different undercoolings and the values are presented in Table 4. It can be concluded from Table 4 that the size of the critical nucleus decreases with increasing undercooling values.

Microstructure

The microstructure of a material has been found to be significant in deciding its mechanical, electrical, magnetic and optical properties. The

TABLE 4

Critical size of nucleus at different undercoolings

Undercooling ΔT (°C)	Critical radius $\times 10^6$ (cm)						
	Ph	PCN	PDB	DP	Ph–PCN eutectic	Ph–PDB eutectic	Ph–DP eutectic
1.0	16.47		11.49				
1.5					9.72		
2.0	8.24	6.91	7.01	7.56			
2.2					6.63		
2.5							6.48
3.0	5.49	4.61	4.73	5.04	4.86		5.40
3.5				4.32			4.63
4.0	4.12	3.45	3.55	3.78		3.71	4.05
4.5				3.36			3.60
5.0	3.29	2.76	2.84			2.97	
5.5						2.70	
6.0		2.30				2.48	
7.0					2.08	2.12	
7.5					1.94		

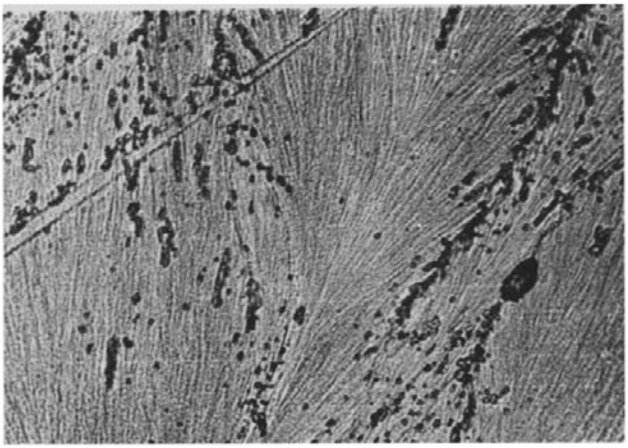

Fig. 7. Microstructure of Ph–PCN eutectic, (magnification, 600×).

growth morphology developed by a eutectic system during solidification depends on the growth characteristics of individual constituent phases, on the basis of which, phases solidify with either faceted or non-faceted interfaces. This behaviour is related to the nature of the solid–liquid interface and can be predicted from the value of the entropy of fusion. According to Hunt and Jackson [11] the type of growth from a eutectic melt depends upon a factor α, defined as:

$$\alpha = \xi \frac{\Delta_f h}{RT} = \xi \frac{\Delta S_f}{R} \tag{10}$$

where ξ is a crystallographic factor depending upon the geometry of the molecules and has a value less than or equal to one. $\Delta S_f/R$ (also known as

Fig. 8. Microstructure of Ph–PDB eutectic, (magnification, 600×).

Fig. 9. Microstructure of Ph–DP eutectic, (magnification, 600×).

Jackson's roughness parameter) is the entropy of fusion (dimensionless) and R is the gas constant. When α is greater than two the solid–liquid interface is atomically smooth and exhibits faceted growth. When α is less than two the solid–liquid interface is atomically rough and exhibits non-faceted growth. The values of Jackson's roughness parameter ($\Delta S_f/R$) are given in Table 2. In all the systems under investigation the $\Delta S_f/R$ values are greater than two, which indicates that they exhibit faceted growth. According to Podolinsky et al. [9] the eutectic structure is controlled by the influence of the eutectic components on the branching behaviour of opposite eutectic phases. All eutectics can be classified into two groups. Thinly branched eutectic structures can be formed in systems where the interface roughness of one of the phases increases under the influence of the second component. Conglomerate eutectics can be formed in systems where the surface roughness of both eutectic phases decreases under the influence of components of opposite eutectic phases. The values of the roughness parameter for pure components and eutectics are shown in Table 2. It is evident from these values that the roughness parameter of one of the components increases in the case of the Ph–PCN and Ph–PDB systems and it decreases for both components in Ph–DP systems. The observed thinly branched, complex regular and anomalous microstructures in Ph–PCN, Ph–PDB and Ph–DP systems, respectively, (Figs. 7–9) are in accordance with the observations made by Podolinksky et al. [9].

ACKNOWLEDGEMENT

Thanks are due to Professor P. Chandra, the Head of the Chemistry Department, Banaras Hindu University, Varanasi 2221005 Uttar Pradesh (India), for providing research facilities.

REFERENCES

1 R. Elliot, Int. Metals Rev., 22 (1977) 161.
2 N.B. Singh and K.D. Dwivedi, J. Sci. Ind. Res., 41 (1982) 98.
3 K.A. Jackson and J.D. Hunt, Trans. Metall. Soc. AIME, 236 (1966) 1129.
4 R.P. Rastogi, D.P. Singh, N. Singh and N.B. Singh, Mol. Cryst. Liq. Cryst., 73 (1981) 7.
5 R.N. Grugel, T.A. Lograsso and A. Hellawell, Metall. Trans., 15A (1984) 1003.
6 M.E. Glicksman, N.B. Singh and M. Chopra, Manuf. Space, 11 (1983) 207.
7 J.E. Smith, D.O. Frazier and W.F. Kaukler, Scr. Metall., 18 (1984) 677.
8 K. Pigon and A. Krajewska, Thermochim. Acta, 58 (1982) 299.
9 V.V. Podolinsky, Y.N. Taran and V.G. Drykin, J. Cryst. Growth, 96 (1989) 445.
10 C.C. Coch, Int. Mater. Rev., 33 (1988) 20.
11 J.D. Hunt and K.A. Jackson, Trans. Metall. Soc. AIME, 236 (1966) 843.
12 N.B. Singh, U.S. Rai and O.P. Singh, J. Cryst. Growth, 71 (1985) 353.
13 R.P. Rastogi and K.T.R. Varma, J. Chem. Soc., (1956) 2097.
14 U.S. Rai and K.D. Mandal, Bull. Chem. Soc. Jpn., 63 (1990) 1496.
15 N.B. Singh and N.B. Singh, Krist. Tech., 13 (1978) 1175.
16 U.S. Rai and K.D. Mandal, Can. J. Chem., 67 (1989) 239.
17 J.W. Dodd and K.H. Tonge, Thermal Method, in B.R. Curell (Ed.), Analytical Chemistry by Open Learning, Wiley, Chichester, 1987, p. 120.
18 R.P. Rastogi, N.B. Singh and N.B. Singh, J. Cryst. Growth, 37 (1977) 329.
19 U.S. Rai and K.D. Mandal, Mol. Cryst. Liq. Cryst., 182B (1990) 387.
20 W.B. Hillig and D. Turnbull, J. Chem. Phys., 24 (1956) 914.
21 W.C. Winegard, S. Mojka, B.M. Thall and B. Chalmers. Can. J. Chem., 29 (1951) 320.
22 U.S. Rai, O.P. Singh and N.B. Singh, J. Chem. Phys., 84 (1987) 483.
23 U.S. Rai, O.P. Singh, N.B. Singh and N.B. Singh, Thermochim. Acta, 71 (1983) 373.
24 N. Singh, N.B. Singh, U.S. Rai and O.P. Singh, Thermochim. Acta, 95 (1985) 291.
25 J. Wisniak and A. Tamir, Mixing and Excess Thermodynamic Properties (a literature source book), Phys. Sci. Data 1, Elsevier, New York (1978).
26 U.S. Rai, O.P. Singh and N.B. Singh, Can. J. Chem., 65 (1987) 2639.
27 M.E. Glicksman, R. Schaefer and J.D. Ayers, Philos. Mag., 32 (1975) 725.
28 G.A. Chadwick, Metallography of Phase Transformations, Butterworths, London, 1972, p. 61.