

Physical Chemistry of Binary Organic Analogues of Nonmetal-Nonmetal Eutectics

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Phase diagram of phenanthrene with each of benzidine, *o*-phenylenediamine and β -naphthylamine, determined by the thaw-melt method, shows the formation of a eutectic in all the systems. The values of linear velocity of crystallization (v) determined at different undercoolings (ΔT) by measuring the rate of movement of solid/liquid interface in a capillary show their linear dependence in the logarithmic plots of $\log v$ vs. $\log \Delta T$. From the values of enthalpy of fusion of pure components and eutectics the values of enthalpy of mixing were calculated.

INTRODUCTION

The ever growing demand of materials has been compelling the chemists, physicists and metallurgists to develop new materials with specific properties at low cost. The fundamental understanding of solidification process¹⁻³ and properties of polyphase alloys have become a subject of current interest. Metal eutectics^{4,5} and intermetallic compounds⁶ constitute an interesting area in metallurgy and materials science. However, the transparent binary alloy models⁷⁻¹¹ are of special importance to metallurgists and materials scientists as they permit visual observation of phase transformations and the process during solidification. Low transformation temperature, ease of purification, transparency, minimised convection effects and wider choice of materials are the special features which have prompted a number of research groups to undertake some physico-chemical studies on organic eutectics. Further, the organic systems are more suitable for a detailed study of the parameters which control solidification because the experimental techniques required for their investigations are simpler and more convenient as compared to those adopted in metallic systems. In view of the above, in the present article, phase diagram, growth kinetics and thermochemistry of three binary organic systems, namely, phenanthrene (Ph), benzidine (Bz), phenanthrene-*o*-phenylenediamine (OPD) and phenanthrene- β -naphthylamine (NPA) have been reported.

EXPERIMENTAL

While phenanthrene (Thomas Baker & Co., Mumbai) was purified by fractional crystallization with ethanol, β -naphthylamine (Sojul Chem., Moscow) was recrystallized from boiling ethanol. *o*-Phenylenediamine obtained from Fluka AG, Switzerland was purified by repeated distillation under reduced pressure. Analytical grade benzidine (CDH, India) was used in the present investigation. The purity of each compound was checked by determining its melting point and comparing it with the literature values.

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Phase-diagram: Phase-diagram of each of Ph-Bz, Ph-OPD and Ph-NPA systems was determined by the thaw-melt method¹¹ where mixtures of two components are prepared in different test tubes in the entire compositional range. These mixtures are then homogenized by the process of repeating melting in silicone oil followed by chilling in ice-cold water 3 to 4 times. Melting and thawing temperatures of these mixtures are then determined using a Toshniwal melting point apparatus attached with a precision thermometer.

Growth kinetics: Values of linear velocity of crystallization of the pure components and the eutectics were determined¹³ at different undercoolings by measuring the rate of movement of solid-liquid interface in a U-tube using a stop watch and a sliding microscope.

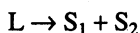
Enthalpy of fusion: The enthalpy of fusion of the pure components and the eutectics was determined by their DTA patterns obtained from Stanton Redcroft STA-780 series unit. All the runs were carried out with heating rate 2°C/min, chart speed 10 mm/min and chart sensitivity 100 μV/10 mV. The sample weight range was 5–10 mg of each estimation. Using benzoic acid as a standard substance, the heat of fusion of unknown compound was determined¹⁴ using the following equation:

$$\Delta H_x = \frac{\Delta H_s \cdot W_s \cdot A_x}{W_x \cdot A_s} \quad (1)$$

where ΔH_x is the heat of fusion of the unknown sample and ΔH_s is the heat of fusion of the standard substance. W and A are weight and peak area, respectively, and suffixes x and s indicate the corresponding quantities for the unknown and standard substances.

RESULTS AND DISCUSSION

Phase-diagram: Phase-diagrams of Ph-Bz, Ph-OPD and Ph-NPA systems are given in Figs. 1 to 3. In each case the melting point of phenanthrene is 100°C and it decreases by the addition of increasing amount of the other component till it reaches the minimum point reported as E in the figures. This is the eutectic point in each system. On further addition of the second component the melting point rises till it reaches the pure component of the system. At the eutectic point E , the three phases, namely, solid A, solid B and solution of A and B (where A and B are two components) are in equilibrium. When the temperature of the solution of eutectic composition is brought below the eutectic horizontal it decomposes to give two solids as shown in the following equation:



The composition and melting point of eutectics are given in Table-1.

TABLE-1
COMPOSITION AND MELTING POINT OF EUTECTICS IN DIFFERENT SYSTEMS

S. No.	System	Composition (mole fraction of second component)	Melting point (°C)
1.	Phenanthrene (I)-benzidine (II)	0.245	88.0
2.	Phenanthrene (I)- <i>o</i> -phenylenediamine (II)	0.480	83.0
3.	Phenanthrene (I)- β -naphthylamine (II)	0.350	77.5

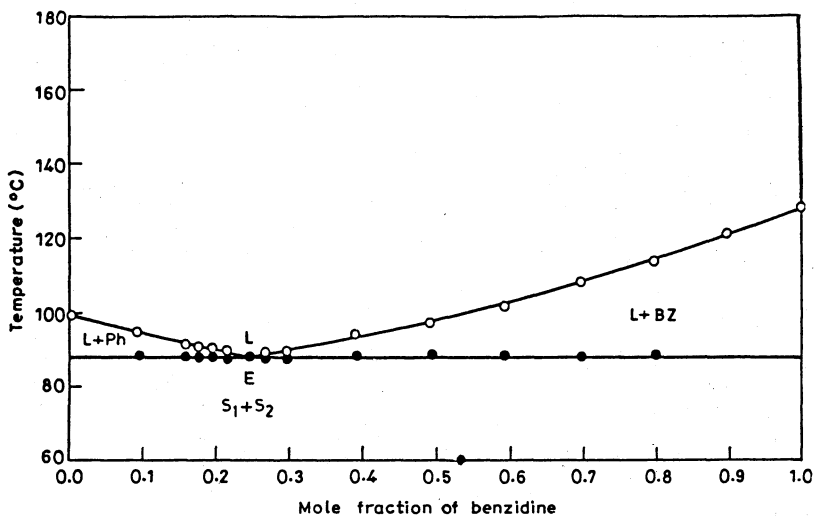


Fig. 1 Phase-diagram of phenanthrene-benzidine system
 ○ Melting point ● Thawing point

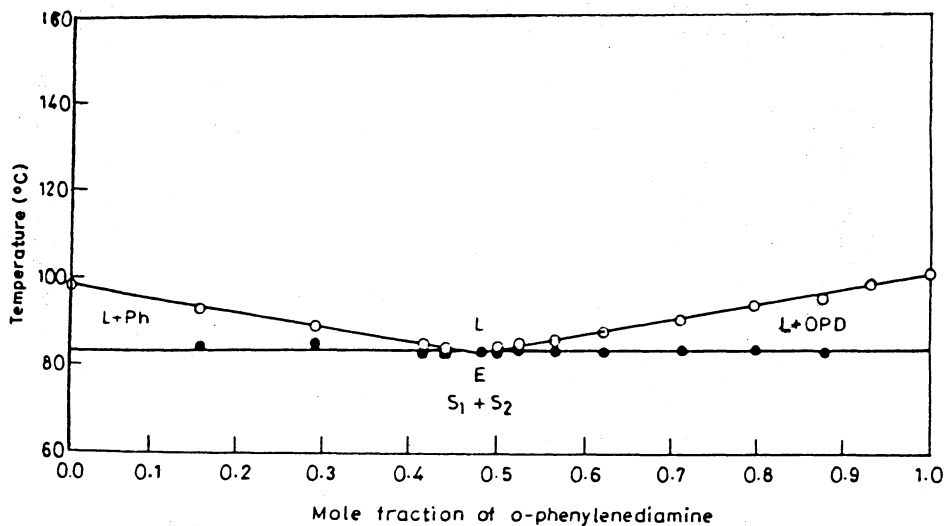


Fig. 2 Phase-diagram of phenanthrene-*o*-phenylenediamine system
 ○ Melting point ● Thawing point

Growth Kinetics: According to Hillig and Turnbull¹⁵ the growth velocity (v) of a material is related to the undercooling (ΔT) by the relation

$$v = u(\Delta T)^n \quad (2)$$

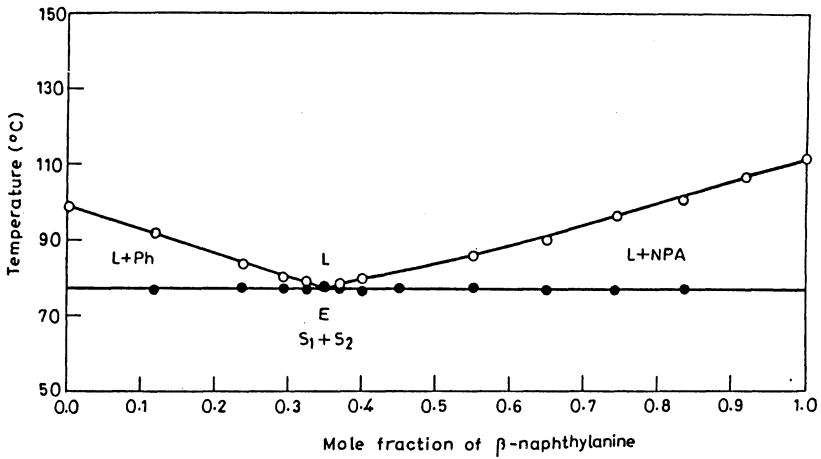


Fig. 3 Phase-diagram of phenanthrene- β -naphthylamine system
 ○ Melting point ● Thawing point

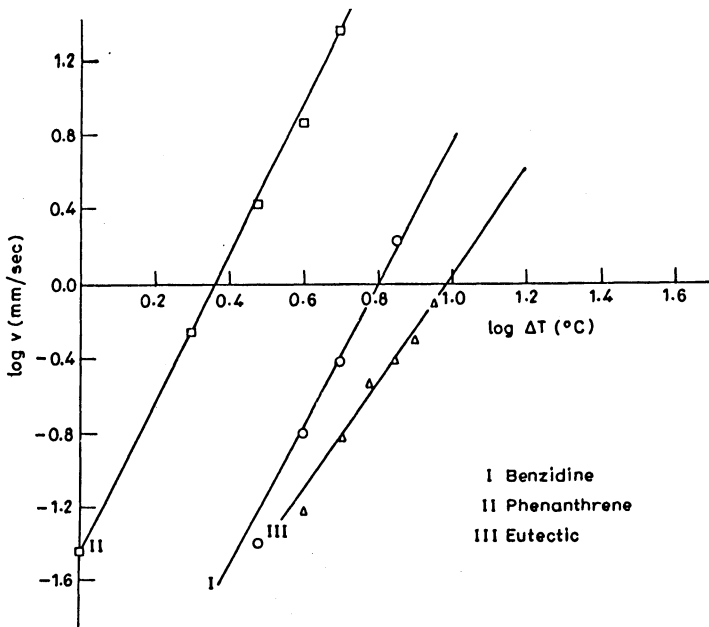


Fig. 4 Linear velocity of crystallization of phenanthrene-benzidine system which can be written in the logarithmic form as given below:

$$\log v = \log u + n \log (\Delta T) \tag{3}$$

Evidently a plot of $\log v$ on Y-axis and $\log \Delta T$ on X-axis should give a straight line where the values of u and v can be calculated from the intercept of the line

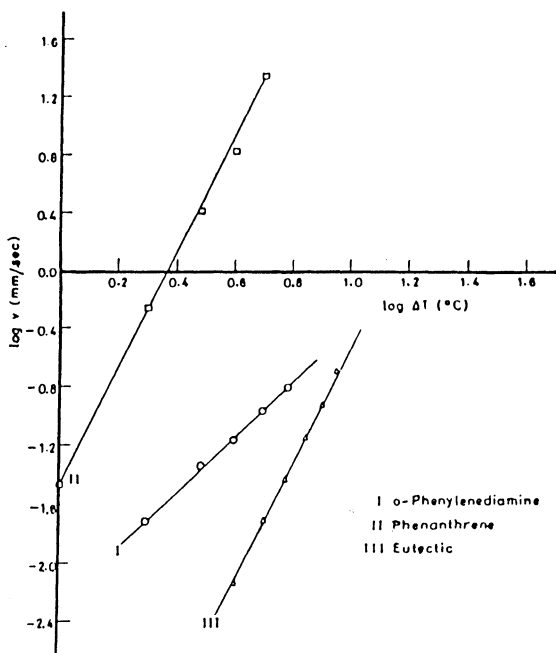


Fig. 5 Linear velocity of crystallization of phenanthrene-*o*-phenylenediamine system

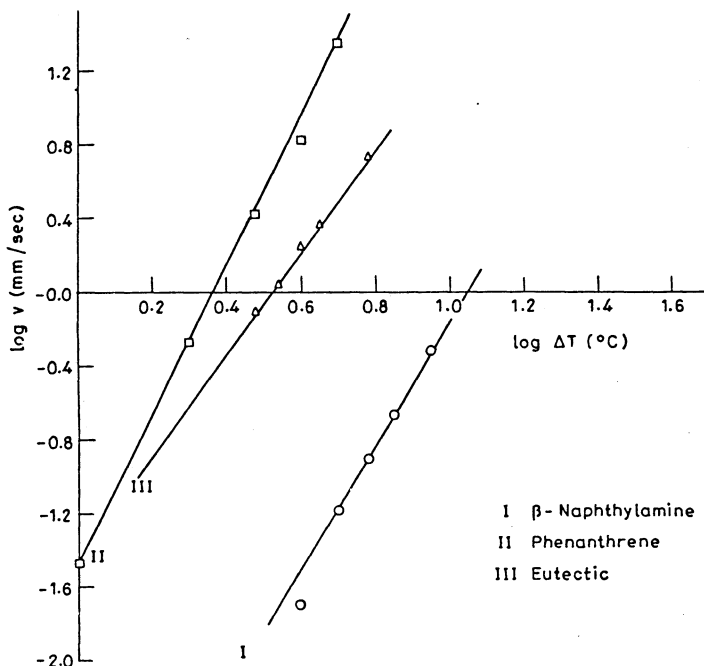


Fig. 6 Linear velocity of crystallization of phenanthrene- β -naphthylamine system

from Y-axis and slope of the line, respectively. Linear plots for three systems under investigation are given in Figs. 4 to 6 and the values of constants u and n are given in Table-2. The basic criterion¹⁶ for the determination of growth mechanism is the comparison of the temperature dependence of linear velocity of crystallization with the theoretically predicted relations. Normal growth generally occurs on the rough interface and for this there is direct proportionality between crystallization velocity and the undercooling. Lateral growth is facilitated by the presence of steps, jogs, bends etc., and under such condition the relationship for the spiral mechanism follows the parabolic law given by the equation (2).

TABLE-2
VALUES OF u AND n FOR PURE COMPONENTS AND EUTECTICS

S. No.	System	u ($m \text{ sec}^{-1} \text{ deg}^{-1}$)	n
1.	Phenanthrene-benzidine		
	(i) Phenanthrene	3.39×10^{-2}	4.0
	(ii) Benzidine	8.91×10^{-4}	4.0
	(iii) Eutectic	1.44×10^{-3}	2.9
2.	Phenanthrene- <i>o</i> -phenylenediamine		
	(i) <i>o</i> -Phenylenediamine	5.37×10^{-3}	1.9
	(ii) Eutectic	9.08×10^{-5}	3.9
3.	Phenanthrene- β -naphthylamine		
	(i) β -Naphthylamine	3.01×10^{-4}	3.3
	(ii) Eutectic	3.63×10^{-2}	2.7

The values of u given in Table-2 give an idea about the mechanism of solidification. According to Winegard *et al.*¹⁷, 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 starts nucleating. Now, there are two possibilities. First, the two initial crystals may grow side-by-side. This explains the cases in which the rate of solidification of eutectics is 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 eutectic is lower than that of either component. Since the value of u is a measure of growth rate of the material, the solidification of the eutectic of Ph-OPD system may be accounted for by the alternate nucleation mechanism, and in the case of Ph-NPA and Ph-Bz the solidification takes place by the side-by-side growth of two phases.

Thermochemistry: The values of enthalpy of fusion determined by the DTA method given in Table-3. In order to know the nature of interaction between two components in the melt the value of enthalpy of fusion, calculated by the mixture law¹⁸ is also given in the same table. If the eutectics are simple mechanical mixtures of two components without any association of the molecules in the melt, the experimental values of enthalpy of fusion and the calculated values would be the same. The difference of the experimental and the calculated values of enthalpy

of fusion is reported in the last column of the table. It is evident from the values reported in the table that the enthalpy of mixing is positive in Ph-Bz and Ph-OPD systems and it is negative in Ph-NPA system. Thermochemical studies¹⁹ suggest that the structure of eutectic melt depends on the sign and the magnitude of the enthalpy of mixing. Three types of structures are suggested: quasi-eutectic for enthalpy of mixing ($\Delta_m H$) > 0, clustering of molecules of $\Delta_m H < 0$ and molecules solution for $\Delta_m H = 0$. Thus, in the Ph-NPA system clustering of molecules takes place while in Ph-Bz and Ph-OPD systems a quasi-eutectic structure is formed.

TABLE-3
ENTHALPY OF FUSION OF PURE COMPONENTS AND EUTECTICS AND
ENTHALPY OF MIXING OF EUTECTICS

S. No.	Material	Calculated value (kJ mol ⁻¹)	Experimental value (kJ mol ⁻¹)	Enthalpy of mixing of eutectics (kJ mol ⁻¹)
1.	Phenanthrene (Ph)	—	18.1	—
2.	Benzidine (Bz)	—	19.1	—
3.	<i>o</i> -Phenylenediamine (OPD)	—	17.1	—
4.	β -Naphthylamine (NPA)	—	25.8	—
5.	Ph-Bz-eutectic	18.4	19.2	0.8
6.	Ph-OPD-eutectic	17.6	22.3	4.7
7.	Ph-NPA-eutectic	20.8	20.0	-0.8

It is well known that the excess thermodynamic function gives a quantitative idea about the deviation of the system from ideal behaviour. 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. With a view to know the nature of interactions 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 equations²⁰:

$$g^E = RT(x_1 \ln \gamma_1^1 + x_2 \ln \gamma_2^1) \quad (4)$$

$$h^E = -RT \left(x_1 \frac{\partial \ln \gamma_1^1}{\partial T} + x_2 \frac{\partial \ln \gamma_2^1}{\partial T} \right) \quad (5)$$

$$s^E = -R \left(x_1 \ln \gamma_1^1 + x_2 \ln \gamma_2^1 + x_1 T \frac{\partial \ln \gamma_1^1}{\partial T} + x_2 \frac{\partial \ln \gamma_2^1}{\partial T} \right) \quad (6)$$

It is evident from equations (4) to (6) that activity coefficient and its variation with temperature are required to calculate the excess thermodynamic function. The activity coefficient (γ_i^1) is calculated using the relation

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

where x_i^1 , $\Delta_f h_i^\circ$ and T_i° are mole fraction, heat of fusion and melting temperature of component i , respectively; R is the gas constant and T is the melting

temperature of the eutectic. The values of excess thermodynamic functions are given in Table-4. The positive values of g^E predict²¹ that the interaction between like molecules is stronger than between unlike molecules. Thus, in the present investigation interactions between Ph-Ph, OPD-OPD, Bz-Bz and NPA-NPA molecules will be stronger than those between dissimilar molecules. The values of h^E and s^E correspond to the excess free energy and are a measure of excess enthalpy of mixing and excess entropy of mixing, respectively.

TABLE-4
EXCESS THERMODYNAMIC FUNCTIONS OF EUTECTICS

S. No.	System	g^E (J mol ⁻¹)	h^E (kJ mol ⁻¹)	s^E J mol ⁻¹ K ⁻¹)
1.	Phenanthrene-benzidine	799.8	16.7	44.1
2.	Phenanthrene- <i>o</i> -phenylenediamine	1228.0	15.7	40.8
3.	Phenanthrene- β -naphthylamine	396.9	15.6	43.4

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