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Chemistry of Organic Eutectics: *p*-Phenylenediamine–*m*-Nitrobenzoic Acid System Involving the 1:2 Addition Compound

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The phase diagram of *p*-phenylenediamine–*m*-nitrobenzoic acid system, determined by the thaw-melt method, show the formation of two eutectics and a 1:2 addition compound. The linear velocity of crystallization of pure components, eutectics and addition compound, measured by determining the rate of movement of growth front in a capillary, suggests that crystallization data obey the Hillig–Turnbull equation. Using experimental values of heats of fusion, determined by the DTA method, entropy of fusion, heat of mixing and excess thermodynamic functions were calculated and the results are explained on the basis of cluster formation in the melts. Microscopic studies reveal that the eutectics have different characteristics microstructures as compared to those of parent components. X-Ray diffraction data suggest that there is preferential ordering of atomic planes in the formation of the eutectics.

The chemistry[1–5] of eutectics and addition compounds has become a field of active investigation due to their unusual physical properties, not normally shown by the parent components. The metallic eutectics and intermetallic compounds constitute an interesting area of investigation[6,7] in metallurgy and materials science. However, the various studies carried out on these systems are inadequate and incomplete as high transformation temperature, opacity and difficulties involved in purification present serious problems. Apart from these, wide difference in densities of the two components forming the metal eutectics causes density driven convection effects, which in turn, affect their solidification. These difficulties can be avoided by taking organic systems[8–18] which are being used as model systems for detailed investigation of the parameters which control solidification. Further, the experimental techniques, required for their investigation, are simpler and more convenient as compared to those adopted in metallic systems.

A critical scanning of the existing literature[19,20] reveals that most of the organic systems studied in the past are simple eutectic type. There is only a limited number of cases in which two components form a molecular compound with congruent melting point. The formation of such molecular compounds has been established on the basis of phase diagrams which exhibit a characteristic maximum surrounded by two eutectics corresponding to the stoichiometry of the molecular compound formed. Hogan et al.[21] established a unique crystallographic orientation relationship between the constituent phases and their mating planes. Gruzleski and Winegard[22] observed perfect lamellar grains in Sn–Cd eutectics but in a number of other systems the eutectic grains do not exhibit a fixed crystal orientation with respect to external lines of force. Bassi and Sharma[23] have studied the IR spectra of the naphthalene–benzoic acid eutectic system and infer that a specific orientation exists between the constituents.

With a view to elucidate the chemistry of organic eutectics and 1:2 addition compounds, *p*-phenylenediamine (PPD)–*m*-nitrobezoic aicd (NBA) system was undertaken and its phase diagram, linear velocity of crystallization, heat of fusion, microstructrure, and X-ray diffraction have been studied.

Experimental

Materials and Purification: *p*-Phenylenediamine (High Purity Chemicals, India) was purified by repeated distillation under reduced pressure and was stored in colored bottles to avoid exposure to light. *m*-Nitrobenzoic acid (Aldrich, West-Germany) was purified by recrystallization from 1 per cent hydrochloric acid. The purity of each compound was checked by determining its melting point which was in good agreement with literature value.

Phase Diagram Study: Phase diagram of *p*-phenylenediamine–*m*-nitrobenzoic acid system was determined[24,25] by the thaw-melt method. Mixtures of various proportion covering the entire range of composition were taken in long necked glass test tubes and were sealed. The mixtures were subjected to number of alternate melting in liquid paraffin followed by chilling in ice to make it homogeneous. The mixtures were taken out by breaking the test tubes and were further homogenized by grinding in a mortar with due care to avoid moisture or any contamination. The melting and thaw temperatures were determined by Toshniwal Melting Point Apparatus.

Linear Velocity of Crystallization: The linear velocity of crystallization of pure components, eutectics and addition compound was determined[26,27] by measuring the rate of movement of growth front in a capillary. A Pyrex glass tube (length 15 cm and inner diameter 0.5 cm) in the u form was washed and dried before filling the test sample to determine the linear velocity of crystallization. The tube containing the molten sample free from air bubbles was mounted of a wooden board fitted with a scale. The entire assembly was then kept in an oil thermostat maintained at a temperature slightly above the melting point of the material taken in the tube. The temperature of the bath was allowed to fall and set at a temperature a few degrees below the melting point. At each temperature, when the tube attained the temperature of the bath, a seed crystal of the same substance was added to

one end of the tube for nucleation to set in. As soon as the seed crystal was added, nucleation followed by crystallization took place linearly in the tube and the time required for the crystal front to travel a known distance, was noted with the help of a travelling microscope and a stop watch.

Heat of Fusion: The heat of fusion of pure components, eutectics, and addition compound were determined[27-29] by their DTA patterns obtained from Stanton Redcroft STA-780 series unit.

Microstructure: To record[30] microstructures of pure components, eutectics, and addition compound, a small amount of the sample was taken on a well washed and dried glass slide and placed in an oven maintained at a temperature slightly higher than the melting point of the sample. On complete melting, a coverslip was glided over the melt and allowed to cool. After a few minutes, the supercooled melt was nucleated by the solid of the same composition and care was taken to have unidirectional freezing. After the complete freezing, the slide was placed on the platform of a Leitz Laborlux D, optical microscope and the different regions of the slide were observed. The microphotographs of suitable magnification were taken with the help of a camera attached with the microscope.

X-Ray Diffraction Studies: X-Ray diffraction patterns of pure components, eutectics, and addition compound were recorded[27,31] on a computerized X-ray diffraction unit, PW 1710 model, using Cu $K\alpha$ radiation.

Results and Discussion

a) Phase-Diagram: The phase diagram of *p*-phenylenediamine–*m*-nitrobenzoic acid system, given in Fig. 1, shows the formation of a 1:2 addition compound with congruent melting point surrounded by the two eutectics E_1 and E_2 having 0.18 and 0.88 mole fraction of *m*-nitrobenzoic acid, respectively. The melting temperature of the molecular compound and eutectics E_1 and E_2 are 163.0, 124.0, and 130.0 °C, respectively. For each eutectic, the addition compound serves as one of the components. The flat maximum, observed in this system, suggests that the addition compound is dissociated[32] in the molten state. From the first eutectic point E_1 onwards, on addition of the second component, the melting point again rises, attains a maximum at C. Where the composition of liquid and solid phases are identical. The existence of an eutectic point on either side of the maximum provides an information about the large stability of the molecular complex formed.

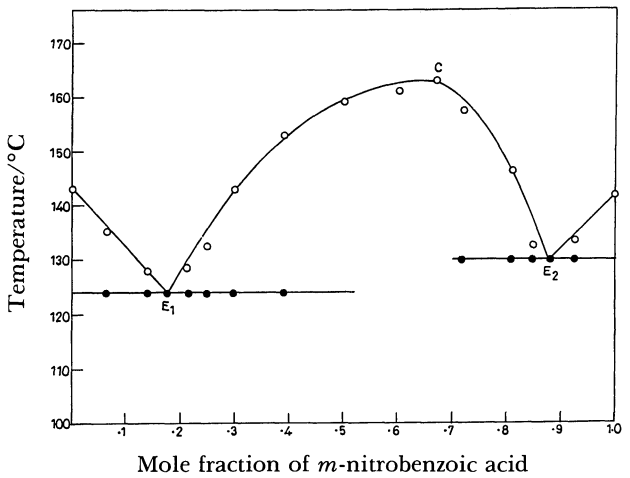

Fig. 1. Phase diagram for *p*-phenylenediamine–*m*-nitrobenzoic acid system. ○ Melting temperature. ● Thaw temperature.

b) Growth Kinetics: The linear velocity of crystallization (v) of pure components, eutectics, and 1:2 addition compound, determined at different undercooling (ΔT) is given in Fig. 2 in the form of $\log v$ versus $\log \Delta T$ plot. The linear dependence of growth velocity and undercooling suggests that the crystallization data obey the Hillig–Turnbull[33] relation:

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

where u and n are constants depending on the nature of solidification of the sample under investigation. The experimental values of these constants are given in Table 1. It is evident from this table that most of the

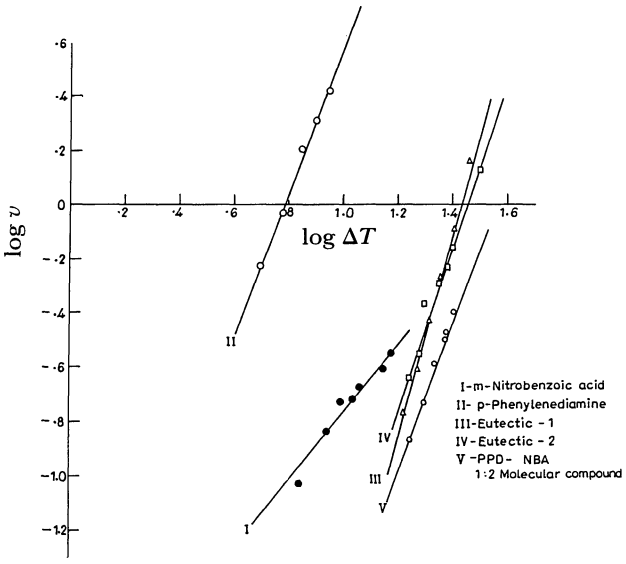

Fig. 2. Linear velocity of crystallization at various degrees of undercooling for *p*-phenylenediamine–*m*-nitrobenzoic acid systems.

Table 1. Values of u and n for Pure Components, Eutectics, and Addition Compounds

Compound	u / mm s^{-1} $deg.^{-1}$	n
p-Phenylenediamine	1.0×10^{-2}	2.6
m-Nitrobenzoic acid	6.0×10^{-3}	1.5
Eutectic-1	4.5×10^{-6}	3.8
Eutectic-2	2.0×10^{-5}	3.3
1:2 Addition compound	3.3×10^{-5}	2.7

values of n are close to three, suggesting thereby a cubic relationship[1-4] between growth velocity and undercooling. However, in some cases, deviation from three are also observed. While values of n smaller than 3 suggest less rapid variation in the growth velocity with undercooling, those of higher than 3 suggest most rapid variation in the growth velocity with undercooling, in comparison to that observed when n=3.

From the values of u, given in Table 1, it can be inferred that addition compound of p-phenylenediamine–m-nitrobenzoic acid (PPD–NBA) system crystallizes at a rate slower than those of parent components. Studies[25,27] on crystal morphology of addition compounds indicate that they crystallize as a definite chemical entity. However, during crystallization, the two components from the melt have to enter the crystal lattice simultaneously in such a way that the composition of melt conforms to the respective molar ratios of the two components. Due to this, the linear velocity of crystallization of the addition compounds may by expected to be of the order of the growth velocity of the species crystallizing with slower rate.

The solidification rates of both eutectics E_1 and E_2 are lower than those of parent components and the addition compound. The first eutectic (E_1), having a low molar concentration of NBA, solidifies more slowly than the second eutectic (E_2) with a high molar concentration of NBA. These results may by explained on the basis of the mechanism proposed by Winegard et al.[34] 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 eutectic is lower than that of either component. Thus, the solidification of both the eutectics E_1 and E_2 takes place by alternate nucleation of the two components. For both the euectics the addition compound with melting point higher than PPD and NBA acts as one of the components and nucleates first.

c) Thermochemistry: The experimentally determined values of heats of fusion of parent components, eutectics, and addition compound are given in Table 2. If the eutectics were simple mechanical mixture of the two components involving no heat of mixing or any type of association in the melt, the heats of fusion $(\Delta_f h)_e$ would simply be given by the mixture law[35]

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

where x_1 and x_2 are the mole fractions and $\Delta_f h_1^\circ$ and $\Delta_f h_2^\circ$ are the experimental values of heats of fusion of parent components 1 and 2, respectively. The heats of fusion, calculated from the mixture law, are also given in the same table. It is evident from the table that the values of heat of fusion, calculated from Eq. 2, are higher than the experimental values. This difference can be attributed to the formation of clusters in the eutectic melt. It can be imagined that during cluster formation, heat liberated may lower the actual values of heat of fusion. The experimental value of heat of fusion of addition compound and its theoretical values, calculated by the mixture law, are also given in Table 2. It is evident that the calculated value is higher than the experimental value. A similar type of cluster formation and explanation can be suggested to justify this observation also.

Heat of mixing[24] (ΔH_m) which is the difference between the experimental and calculated values of heat of fusion is given by

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

where $(\Delta_f h)_{exp.}$ is the heat of fusion of the eutectic, determined experimentally, x_i and $\Delta_f h_i^\circ$ are the mole fraction and heat of fusion of the end components, respectively. It is evident from Table 2 that the heats of mixing for eutectic (E_1), eutectic (E_2), and addition compound are −6.1, −6.5, and −3.6 kJ mol^{-1}, respectively. Thermochemical studies[36] 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 $\Delta H_m > 0$,

Table 2. Experimental and Calculated Values of Heat of Fusion of Eutectics and Addition Compound

Compound	Calculated by mixture law	Experimental value
	kJ mol^{-1}	kJ mol^{-1}
p-Phenylenediamine	—	24.9
m-Nitrobenzoic acid	—	21.4
Eutectic-1	24.3	18.2
Eutectic-2	21.8	15.3
1:2 Addition compound	22.5	18.9

clustering of molecules for $\Delta H_m<0$ and molecular solutions for $\Delta H_m=0$. The large negative values of ΔH_m of eutectics sugget clustering of molecules in the eutectic melt. These results are quite different from those of simple eutectic sytems where merely ordering of the parent phases has been suggested in the melts. It seems there is considerable enhancement in the interactions due to the presence of 1:2 molecular complex in the eutectic melts.

In order to know the nature of interaction between the components forming the eutectics, some thermodynamic functions such as excess freen energy (g^E), excess enthalpy of mixing (h^E), and excess entropy of mixing (s^E) were calculated using the following equations:

$$-\ln x_i\gamma_i^1 = \frac{\Delta_f h_i^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_i^\circ}\right) \quad (4)$$

$$g^E = RT(x_1\ln\gamma_1^1 + x_2\ln\gamma_2^1) \quad (5)$$

$$h^E = -RT^2\left(x_1\frac{\delta\ln\gamma_1^1}{\delta T} + x_2\frac{\delta\ln\gamma_2^1}{\delta T}\right) \quad (6)$$

$$s^E = -R\left(x_1\ln\gamma_1^1 + x_2\ln\gamma_2^1 + x_1T\frac{\delta\ln\gamma_1^1}{\delta T} + x_2T\frac{\delta\ln\gamma_2^1}{\delta T}\right) \quad (7)$$

where γ_i and T_i° are activity coefficient and melting temperature of the component indicated by the suffix and T and R are the eutectic temperature and gas constant, respectively. The values of $\delta\ln\gamma_i^1/\delta T$ were calculated by differentiating Eq. 4 and taking slope of the liquids line near the eutectic point. The details of calculation of excess thermodynamic functions were reported earlier.[35] The values of excess functions are reported in Table 3. The positive values of excess free energy give measure of the departure of the system from ideal behavior and suggest weak interactions between the components forming the eutectic melts.

Table 3. Excess Thermodynamic Functions of Eutectics

Compound	g^E	h^E	s^E
	J mol^{-1}	J mol^{-1}	J K^{-1} mol^{-1}
Eutectic-1	435.5	1851.0	3.6
Eutectic-2	585.7	5011.0	11.0

Table 4. Entropy of Fusion and Jackson's Roughness Parameter (α)

Compound	ΔS	$\Delta S/R$
	kJ K^{-1} mol^{-1}	
p-Phenylenediamine	0.0598	7.22
m-Nitrobenzoic acid	0.0516	6.21
Eutectic-1	0.0458	5.51
Eutectic-2	0.0381	4.58
1:2 Addition compound	0.0434	5.24

The positive values of h^E and s^E correspond to the excess free energy and are measure of the excess free energy and measure of excess enthalpy of mixing and excess entropy of mixing, respectively.

The entropies of fusion, ΔS, of pure components, eutectics, and addition compound were calculated using the following relation:

$$\Delta S = \frac{\Delta_f h}{T} \quad (8)$$

where $\Delta_f h$ is the heat of fusion and T is the fusion temperature, and are given in Table 4. For all samples the ΔS values are positive indicating an increase of randomness during melting.

According to Hunt and Jackson[36] the type of growth from a eutectic melt depends upon a factor α, defined by equation

$$\alpha = \xi\frac{\Delta S}{R} \quad (9)$$

where ξ is a crystallographic factor depending upon the geometry of the molecules and has the values less or equal to one. $\Delta S/R$, also known as Jackson's

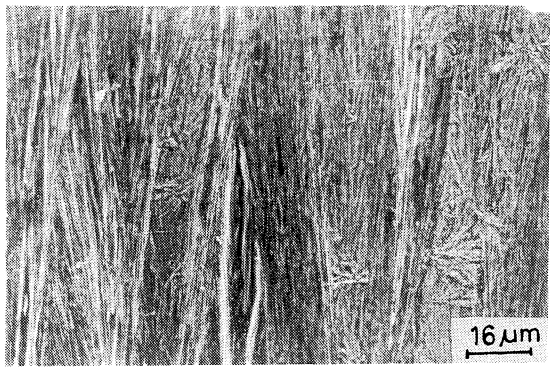

Fig. 3. Microstructure of directionally solidified *p*-phenylenediamine–*m*-nitrobenzoic acid eutectic-1 containing 0.82 mole fraction of *p*-phenylenediamine (×480).

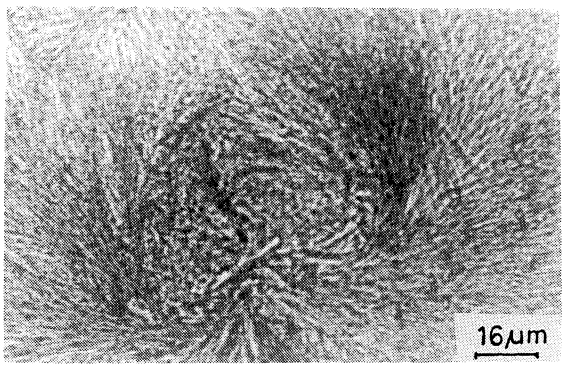

Fig. 4. Microstructure of directionally solidified *p*-phenylenediamine–*m*-nitrobenzoic acid eutectic-2 containing 0.12 mole fraction of *p*-phenylenediamine (×480).

roughness parameter, is the entropy of fusion in dimensionless unit where R is the gas constant. When $\alpha<2$, non-faceted growth occurs whereas a faceted growth appears if $\alpha>2$. For both the eutectics $\Delta S/R$ values are greater than 2, which indicate that they exhibit faceted growth. The microstructures of both the eutectics, given in Figs. 3 and 4, confirm this conclusion.

d) Microstructure: A prediction of microstructure of eutectics can be made from the Spengler's equation[37]

$$\theta = \frac{T_1 - T_E}{T_2 - T_E} \quad (10)$$

where T_1 and T_2 are the melting temperatures of low melting and high melting components, respectively, and T_E in the eutectic temperature. The normal eutectics are formed when θ lies between 0.1 and 1.0 but when it lies between 0.01 to 0.1, anomalous structures are obtained and when it acquires values less than 0.01, divorced structures are formed. The calculated θ values for both eutectics E_1 and E_2 are 0.4872 and 0.3636, respectively. The microstructure of first eutectic E_1 (Fig. 3) with 0.82 mole fraction of PPD shows cellular structure whereas the second eutectic E_2 (Fig. 4) containing 0.12 mole fraction of PPD has radial growth structure. These observations fit very well in the Spengler's equation.

e) X-Ray Diffraction Studies: Some preliminary investigations on X-ray diffraction of pure components, eutectics, and addition compound were carried out, and the experimental results are given in Tables 5 and 6. It is evident from these tables that for each eutectic number of reflections are comparable with number of reflections of pure components and addition compound. In general, strong reflections of PPD and the addition compound either show a drastic decrease in intensities or are missing in eutectic (E_1). A similar trend is observed in the case of eutectic (E_2) formed between *m*-nitrobenzoic acid and 1:2 addition compound. In addition, some strong reflections are observed in eutectic (E_2) which are absent in either

Table 5. "*d*" Values and Relative Intensity (RI) of PPD, E_1, and Addition Compound of PPD–NBA System

p-Phenylenediamine		Eutectic-1		1:2 Addition compound	
d/Å	RI	*d*/Å	RI	*d*/Å	RI
—	—	14.96	51	—	—
11.60	10	—	—	—	—
—	—	7.46	40	7.50	26
—	—	—	—	6.57	27
—	—	—	—	6.42	50
—	—	—	—	5.86	13
5.74	100	5.73	96	—	—
—	—	5.28	100	—	—
—	—	4.86	25	—	—
4.75	70	—	—	4.67	58
—	—	4.50	30	4.53	30
4.42	900	4.44	50	4.37	21
4.18	30	4.18	26	—	—
4.02	80	4.01	50	3.95	89
3.87	60	3.87	30	—	—
—	—	3.80	24	—	—
3.78	50	3.75	24	3.75	100
3.65	10	3.63	30	3.56	23
—	—	—	—	3.55	24
3.48	70	3.48	40	3.45	60
3.37	20	3.40	50	—	—
3.31	20	3.33	30	—	—
3.27	60	—	—	3.27	23
—	—	—	—	3.22	81
—	—	—	—	3.18	19
3.08	60	3.12	37	3.05	11
3.01	20	3.01	17	2.92	9
2.88	20	2.88	22	—	—
—	—	2.86	18	2.86	16
2.81	10	2.82	19	—	—
2.68	20	2.68	14	—	—
2.54	20	—	—	—	—
2.43	20	2.49	15	2.40	11
2.21	10	—	—	2.17	8

Table 6. "*d*" Values and Relative Intensity (RI) of NBA, E_2, and Addition Compound of PPD–NBA System

m-Nitrobenzoic acid		Eutectic-2		1:2 Addition compound	
d/Å	RI	*d*/Å	RI	*d*/Å	RI
—	—	7.75	21	—	—
—	—	—	—	7.50	26
—	—	7.26	25	—	—
—	—	6.71	100	—	—
6.55	37	—	—	6.57	27
—	—	—	—	6.42	50
—	—	—	—	6.86	13
—	—	5.31	83	—	—
—	—	5.15	81	—	—
4.93	7	—	—	—	—
4.79	6	4.77	63	—	—
—	—	4.66	21	4.67	58
4.49	17	—	—	4.53	30
—	—	4.35	54	4.37	21
4.16	7	—	—	—	—
4.04	6	4.00	33	—	—
—	—	3.93	25	3.95	89
3.86	100	—	—	—	—
—	—	—	—	3.75	100
—	—	3.68	92	—	—
3.60	5	—	—	3.56	23
—	—	3.55	21	3.55	24
—	—	3.47	82	3.45	60
3.39	13	3.37	21	—	—
3.25	39	3.25	21	3.27	23
—	—	—	—	3.22	81
—	—	—	—	3.18	19
—	—	3.01	29	3.05	11
2.97	18	2.96	21	2.92	9
2.87	12	—	—	2.86	16
2.67	11	2.78	17	—	—
2.49	5	2.55	25	—	—
2.40	5	—	—	2.40	11
—	—	2.24	17	—	—
2.08	5	2.11	15	2.17	8

component.

If a eutectic is a simple mechanical mixture of two components, the X-ray patterns of the two components should be exactly superimposed[38] on the eutectic composite. From the X-ray data on pure components, eutectics, and the addition compound, it is clear that there is a marked difference in the interplanar distances and the relative intensities of the composite material and the individual components. These experimental results infer that the eutectics are not simply the mechanical mixture of the two components. In them, there is orientation of some atomic planes during their formation. These findings are further supported by the thermal studies carried out on this system.

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