SOME THERMOCHEMICAL STUDIES ON BINARY FACETED ORGANIC EUTECTICS AND 1:1 MOLECULAR COMPLEXES

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Abstract

The phase diagrams of binary organic systems of benzidine with pyrogallol and *p*-nitrophenol give a double simple eutectic type phase diagram showing formation of a 1:1 molecular complex with congruent melting point and two eutectics. The growth data on the pure components, the eutectics and the molecular complexes, determined by measuring the rate of movement of growth front in a capillary, justify the square relationship between growth velocity and undercooling. While enthalpy of mixing values suggest intermolecular hydrogen bonding, the excess thermodynamic functions reveal strong interactions among the components forming eutectics and addition compounds.

Keywords: complexes, eutectics, phase diagram

Introduction

The past decade has witnessed [1–6] an immense activity both in the fundamental understanding of the solidification and properties of polyphase alloys and in the technological developments of 'in situ' composites for particular applications. The basic purpose of these investigations is to produce a low cost material with high strength, ductility and low density at high temperature. Because of their unusual anisotropic properties which results from their aligned microstructure, the composite materials offer diverse possibilities for the development and production of the materials of commercial and technical importance. As such, the directionally solidified eutectic composites with high strength/density ratio may be of potential importance for the construction of supersonic aircraft, high pressure tanks, thermoelectric devices and in the production of permanent magnets. Due to low transformation temperature ease in purification, transparency and wider choice of materials a number of research groups [7–12] have undertaken some physicochemical investigations on organic eutectics and addition compounds.

A critical scanning of the current literature [7–12] on organic eutectics and addition compounds reveals that studies on the chemistry and characterization of organic composites and molecular complexes have received much importance during recent years. However, much less attention has been focussed on understanding of solidification process, microstructure and the nature of bonding between the components forming the eutectics and addition compounds. As the organic eutectics and the molecular complexes are analogues of metal eutectics and intermetallic compounds, respectively, a systematic physicochemical study of model systems involving organic compounds may be of potential importance in unravelling the mysteries of solidification and microstructure. In view of this, two binary organic systems, namely, benzidine (BZ)-p-nitrophenol (PNP) and benzidine-pyrogallol (PG), have been chosen to study their phase diagram, linear velocity of crystallization and thermal behaviour.

Experimental

Materials and purification

AR grade benzidine (CDH, India) was directly used in the present investigation. p-nitrophenol (SISCO-CHEM Industries, India) and pyrogallol (S.D. Fine-Chem. Pvt. Ltd., India) were purified by repeated distillation under reduced pressure and were stored in coloured bottles to avoid exposure to light. The melting point of each compound was compared with its literature value to asses its purity.

Phase diagram

The phase diagrams of benzidine-p-nitrophenol and benzidine-pyrogallol systems were determined by the thaw-melt method [13–14]. In this method, mixtures of two components in different proportions covering the entire range of composition in mole fraction were prepared in long necked test tubes. These mixtures were homogenized by melting in silicone oil followed by chilling in ice. The tubes containing the mixtures were then broken separately and the mixtures were ground to a fine powder. The melting point of each mixture was determined by a melting point apparatus attached with a precision thermometer.

Linear velocity of crystallization

The linear velocity of crystallization data for the pure components, the eutectics and the addition compounds were determined [15–16] by measuring the rate of movement of the solid–liquid interface in a capillary.

Enthalpy of fusion

The values of enthalpy of fusion of pure components, eutectics and molecular complexes were determined by the DSC method using DuPont-9900 Thermal Analysis apparatus.
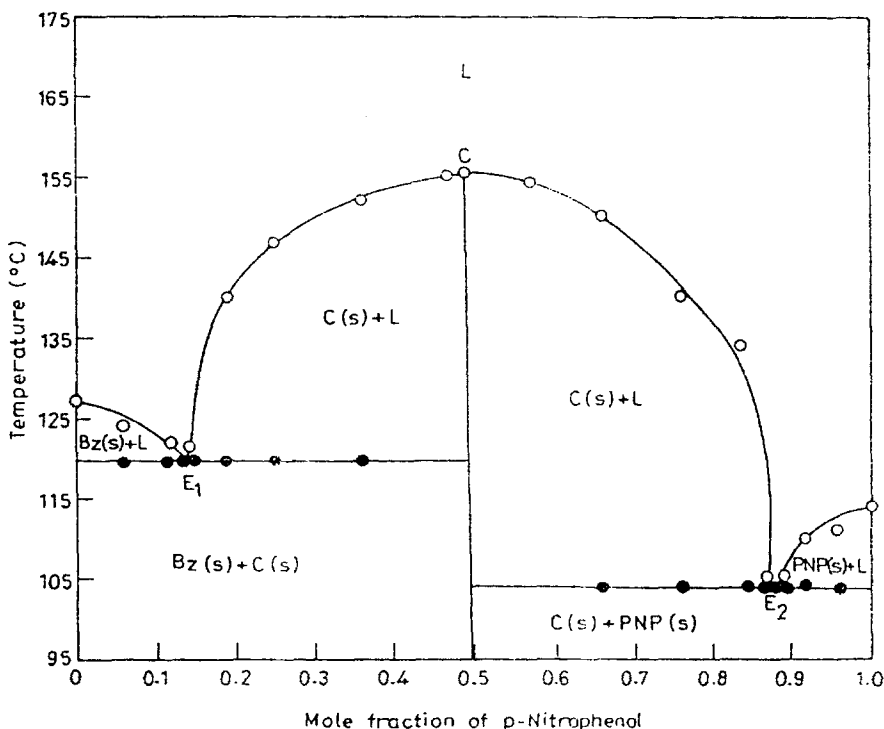

Fig. 1 Phase diagram of benzidine–*p*-nitrophenol system; o-melting temperature; •-Thaw temperature

Results and discussion

Phase diagram

The solid–liquid equilibrium data on BZ-PNP and BZ-PG systems are given in Figs 1–2 in the form of temperature–composition curves. Each plot shows the formation of a 1:1 addition compound (C) with congruent melting point surrounded by two eutectics, E_1 and E_2. The compositions and the melting points of the eutectics and the addition compounds are reported in Table 1. It is evident from the figures that the melting point of benzidine decreases with the addition of the second component and it attains a minimum value at the eutectic point E_1. From the first eutectic point E_1 onwards, on addition of the second
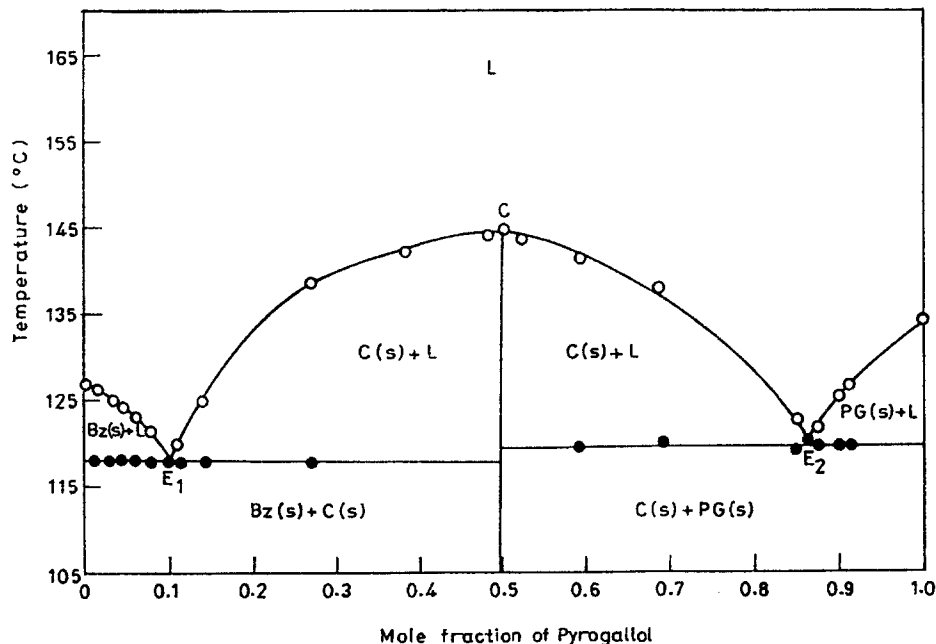
**Fig. 2** Phase diagram of benzidine–p-pyrogallol system; o-melting temperature; •-Thaw temperature

component, the melting point again rises and attains a maximum at C where the composition of the liquid and the solid phases are identical. This maximum temperature is the congruent melting point of the addition compound.

A further increase in the mole fraction of the second component causes a decrease in the melting point of the mixture with a minimum at the second eutectic point E_2. A maximum on the liquidus, a good length of the middle branch of the

Table 1 Composition and melting point of eutectics and addition compounds of each system

Systems	Composition (mole fraction of benzidine)	Melting point/ °C
1. Benzidine–p-nitrophenol		
(I) Eutectic-1	0.8731	120.0
(II) Eutectic-2	0.1177	104.0
(III) 1:1 addition compound	0.5140	155.5
2. Benzidine–pyrogallol		
(I) Eutectic-1	0.9018	118.0
(II) Eutectic-2	0.1385	120.0
(III) 1:1 addition compound	0.4963	145.0

curve and the existence of a eutectic point on either side of the maximum point to high stability [17] of the molecular complex formed by the reaction between the two components in the following manner:

$$A + B \leftrightarrows AB \rightarrow AB(\text{solid})$$
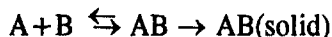
If there is no dissociation in the molten addition compound, the phase diagram would show a sharp maximum. However, when dissociation occurs in the molten state, the products of dissociation lower the effective mole fraction of the solute, and the curve would be flattened. For each eutectic the addition compound serves as one of the components. The observed maxima in both the systems under investigation are flat, indicating [16] thereby that the addition compounds are dissociated in the molten state. From the phase diagrams it can also be inferred that the addition compounds in these systems are capable of existing in solid form in equilibrium with a liquid of the same composition.

Table 2 Values of u and n of each system

Systems	$u/$ $\text{mm sec}^{-1}\,^{\circ}\text{C}^{-1}$	n
1. Benzidine–p-nitrophenol		
(I) Benzidine	0.000105	4.00
(II) p-nitrophenol	0.026300	1.50
(III) Eutectic-1	0.001202	1.75
(IV) Eutectic-2	0.000263	2.67
(V) 1:1 addition compound	0.000603	2.00
2. Benzidine–pyrogallol		
(I) Pyrogallol	0.007244	2.50
(II) Eutectic-1	0.000724	1.86
(III) Eutectic-2	0.006918	1.50
(IV) 1:1 addition compound	0.000005	3.33

Linear velocity of crystallization

The linear velocity of crystallization (v) of each of the pure components, the eutectics and the addition compounds was determined at different undercoolings (ΔT) by the capillary method. According to Hillig and Turnbull [18], the growth velocity is related to the undercooling by the following equation:

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

where u and n are constants depending on the solidification behaviour of the material. The constants u and n were calculated from the linear plots (Figs 3–4) of $\log v$ vs. $\log\Delta T$ and the values are reported in Table 2. It is evident from the Table that most of the values of n are close to 2 suggesting thereby a square relationship between v and ΔT. However, the deviations [19] in the values of n from 2, observed in some cases, may be due to the difference in the bath temperature and the temperature of growing interface. In the present investigation,
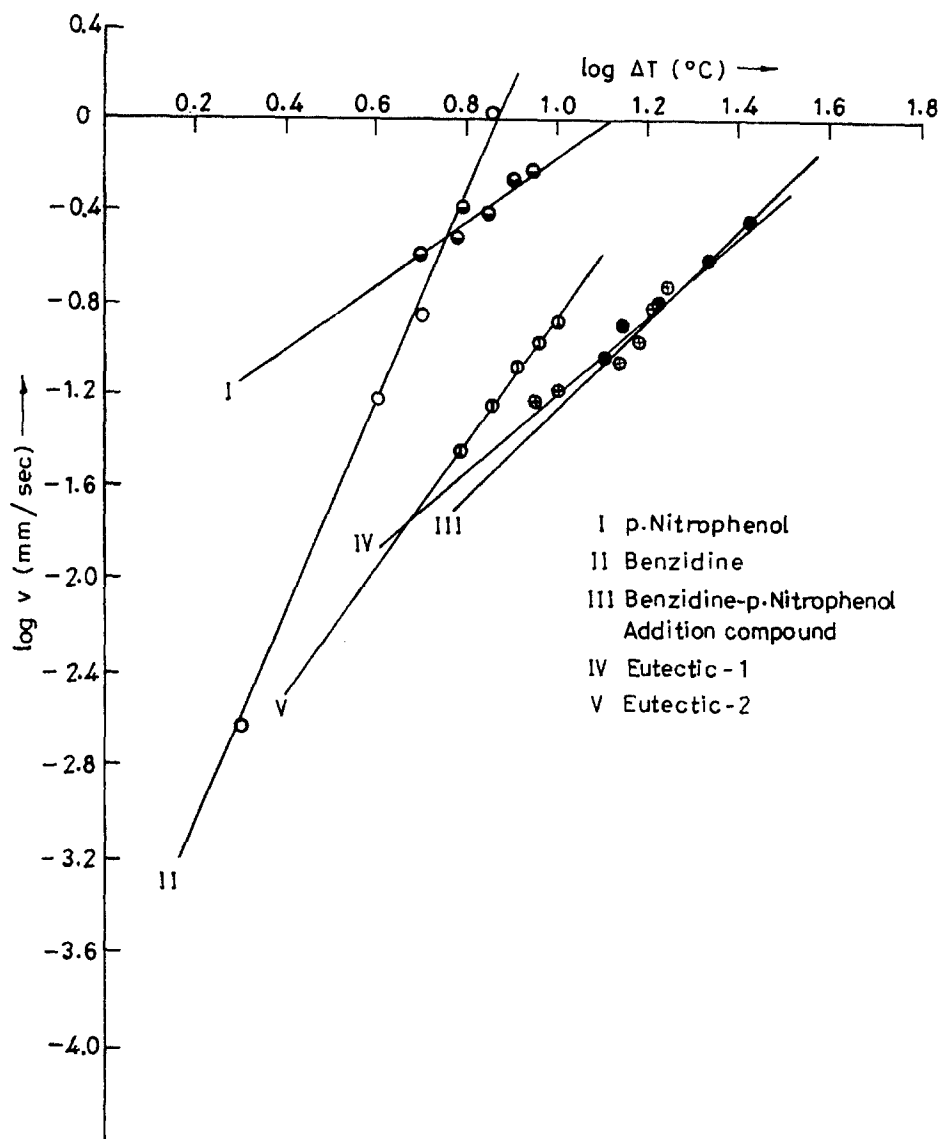

Fig. 3 Linear velocity of crystallization of benzidine–p-nitrophenol system
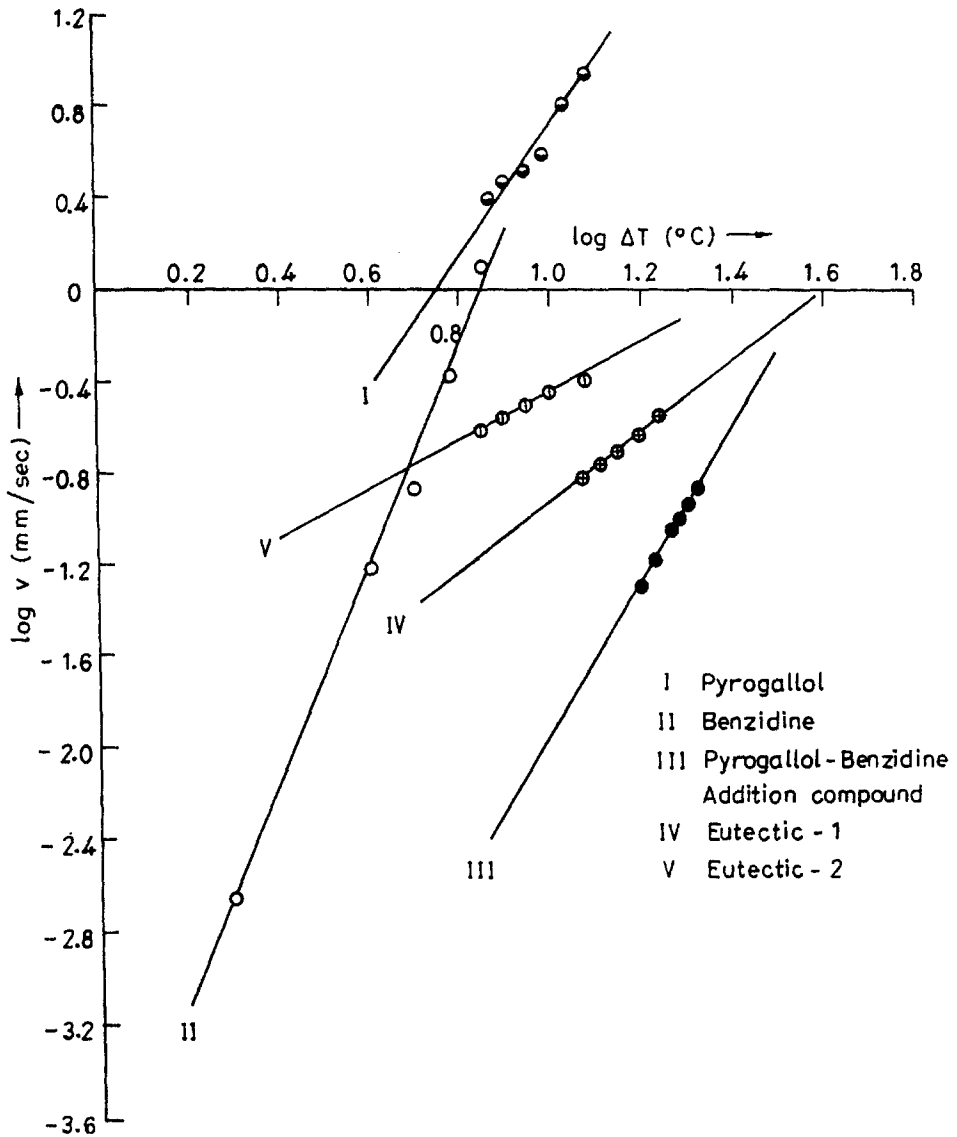
Fig. 4 Linear velocity of crystallization of benzidine–pyrogallol system

both components have high enthalpy of fusion, and as a consequence to that each crystallization step results a release of more amount of heat causing the interface to attain higher temperature than that of the bath temperature.

From the values of u (Table 2) for pure components and the addition compounds, it can be inferred that the crystallization rate of the addition compound of the BZ-PNP system lies between the end members, and the growth velocity

of the addition compound of BZ-PG system is less than the parent components. Studies [20] on crystal morphology of the 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 the melt conform to the respective molar ratios of the components. Due 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 with a slower rate.

It is evident that for E_1 of BZ-PNP system, which is formed between the addition compound and benzidine, the value of u is higher than those of the components while in the case of E_2 formed between the addition compound and PNP, it is lower than those of the end members. In the case of benzidine–pyrogallol system, the value of u for E_1 (formed between benzidine and the addition compound) is higher than both the components while for E_2 (formed between the addition compound and pyrogallol) it lies between the corresponding components. These results may be explained on the basis of the mechanism proposed by Winegard et al. [21]. 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 components, and a stage is reached when the second component starts nucleating. Now, there are two possibilities: (i) the two initial crystals may grow side-by-side, (ii) there may be alternate nucleation of the components. While the former explains the cases in which the rates of solidification of eutectics are not lower than those of the parent components, the latter justifies the cases in which the growth rate of eutectic is lower than its components. Thus, the solidification of both the eutectics of BZ-PG system and E_1 of BZ-PNP system takes place by the side-by-side growth of the two components. The second eutectic (E_2) of BZ-PNP system solidifies by the alternate nucleation mechanism. In all the eutectics under investigation the addition compound behaves [22] as one of the components, and its melting point being higher than those of the components it nucleates first. The second component nucleates following the nucleation of the addition compound.

Thermochemical studies

The idea about the mode of crystallization, structure of eutectic melt and the nature of interaction between two components forming the eutectic and the addition compound can be obtained from the knowledge of heats of fusion data on the pure components, the eutectics and the molecular complexes. While the experimental values of heat of fusion of eutectics were determined using DuPont-9900 DSC apparatus, the calculated values of heat of fusion were obtained from the mixture law [23]. For the purpose of comparison, the experimental and the calculated values of heat of fusion for the eutectics are re-

ported in Table 3. It is evident from the table that the calculated values of heat of fusion are higher than those of the experimental values. If eutectic is a simple mechanical mixture of 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. However, when a solid eutectic melts, there is considerable possibility of association and mixing, both causing violation of the mixture law. The difference between the experimental and the calculated values may be attributed to the formation of clusters in the eutectic melt. According to Rastogi et al. [20], cluster formation would be favoured if molecules can associate by intermolecular hydrogen bonding. Such possibilities are very likely in the system under investigation because of the presence of $-NH_2$ group on benzidine and $-NO_2$ and $-OH$ groups on p-nitrophenol and pyrogallol.

The heat of mixing [24] (ΔH_m) which is the difference between the experimental and the calculated values of heat of fusion can be calculated by the equation,

$$\Delta H_m = (\Delta_f h)_{exp} - \Sigma\ x_i \Delta_f h_i^{\circ} \tag{2}$$

where $(\Delta_f h)_{exp}$ 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 of E_1 and E_2 reported in Table 3 that they are highly negative. Thermochemical studies [16] suggest that the structure of 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 BZ-PNP and BZ-PG systems suggest clustering of molecules in the eutectic melt.

The experimental values of heat of fusion of the addition compound determined by the DSC method, is reported in Table 3. Its theoretical value is also given in the same table for the purpose of comparison. The theoretical value of heat of fusion of the addition compound was calculated using the following equation:

$$\frac{\Delta_f h}{R}\left[\frac{1}{T} - \frac{1}{T_c}\right] = -\ln(X_A)^m(X_B)^n + \ln(X_A)_c^m(X_B)_c^n \tag{3}$$

where T_c denotes the congruent melting temperature and the quantities with the subscript c denote the mole fraction corresponding to that which would exist in the molten addition compound. It is evident from Table 3 that the value of heat of mixing of the addition compound, which is defined as the difference between the experimental and the calculated values of heat of fusion is highly negative.

Table 3 Heat of fusion and heat of mixing for benzidine–p-nitrophenol and benzidine–pyrogallol systems

Systems	Material	Heat of fusion/ kJ mol^{-1}	Heat of mixing/ kJ mol^{-1}
1. Benzidine–p-nitrophenol	Benzidine	19.10	–
	p-nitrophenol	18.25	–
	Eutectic-E$_1$		
	(Expt.)	16.78	–5.06
	(Calc.)	21.84	
	Eutectic-E$_2$		
	(Expt.)	17.11	–3.78
	(Calc.)	20.89	
	Addition compound		
	(Expt.)	20.35	–16.43
	(Calc.)	36.78	
2. Benzidine–pyrogallol	Pyrogallol	18.55	–
	Eutectic-E$_1$		
	(Expt.)	16.67	–4.72
	(Calc.)	21.39	
	Eutectic-E$_2$		
	(Expt.)	21.68	–0.17
	(Calc.)	21.85	
	Addition compound		
	(Expt.)	21.20	–16.42
	(Calc.)	37.62	

This suggests [25] that the presence of the addition compound enhances the attraction among the components. It is well known that the addition compound is formed by the reaction between two components in the following manner.

$$A + B \leftrightarrows AB \text{ (solid)} \rightarrow AB \text{(solid)} \qquad (4)$$
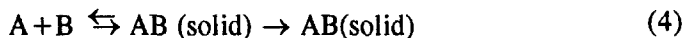
When solid addition compound melts, the components still remain in the association form. This association is favoured by the presence of hydroxyl and amino groups in the components.

The deviation from ideal behaviour can best be expressed in terms of excess thermodynamic functions which give 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

Table 4 Excess thermodynamic functions of eutectics of benzidine-p-nitrophenol and benzidine–pyrogallol systems

Systems/material	$g^E/$ kJ mol^{-1}	$h^E/$ kJ mol^{-1}	$s^E/$ J K^{-1}mol^{-1}
1. Benzidine–p-nitrophenol system			
Eutectic-E_1	981.6	4020.3	7.7
Eutectic-E_2	585.2	5176.7	12.2
2. Benzidine–pyrogallol system			
Eutectic-E_1	580.0	1201.3	1.6
Eutectic-E_2	712.3	4383.4	9.3

ideal system at the same temperature and pressure. In order to know the nature of interaction between two components forming the eutectics, some thermodynamic function such as excess free energy (g^E), excess enthalpy (h^E) and excess entropy (s^E) were calculated using the following equations:

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

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

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

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

$$-\ln x_i^l\gamma_i^l = \frac{\Delta_f h_i^o}{R}\left[\frac{1}{T} - \frac{1}{T_i^o}\right] \tag{8}$$

where x_i, $\Delta_f h_i^o$ and T_i^o 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 by the slope of the liquidus line near the eutectic point. The details of calculation are reported earlier [23]. The calculated values of excess functions are given in Table 4. The positive values of g^E suggest [26] 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 free energy and are

a measure of excess enthalpy of mixing and excess entropy of mixing, respectively.

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