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THERMOCHEMICAL STUDIES ON ORGANIC EUTECTICS AND MOLECULAR COMPLEXES

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The phase diagrams of the binary systems of picric acid with naphthalene, anthracene and phenanthrene, and of α-naphthol with *p*-toluidine, determined by the thaw-melt method, show the formation of a molecular complex and two eutectics in each system. The heats of the pure components, eutectics and molecular complexes were determined by differential scanning calorimetry. Comparison of the experimental heats of fusion with the theoretical values calculated via the mixture law suggests cluster formation in the melts. The entropy of fusion, enthalpy of mixing and excess thermodynamic functions were also calculated from the heat of fusion data.

During recent years, the chemistry of eutectics [1–4] has been a field of active investigation, due to their having unusual physical properties not normally shown by the parent components. The metallic eutectics [5–7] and intermetallic compounds constitute an interesting area of the current investigations 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. Additionally, a wide difference in density of the two components forming the metal eutectics causes density-driven convection effects, which in turn, affect their solidification. Due to the low transformation temperature, ease in purification, transparency, minimized convection effects and wider choice of materials, organic systems [8–14] are more suitable and are widely used as model systems for detailed investigations of the parameters which control solidification. Further, the experimental techniques required for their investigation are simpler and more convenient than those adopted in metallic systems.

Most of the organic systems studied in the past are of simple eutectic type [15, 16]. However, there are other cases in which the two components form a molecular complex [17–20] with a congruent melting point. The formation of such molecular compounds has been established on the basis of phase diagrams which exhibit a

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characteristic maximum, surrounded by two eutectics, corresponding to the stoichiometry of the molecular compound formed. While simple eutectics may be regarded as mechanical mixtures, the systems with molecular compounds may definitely not be so, owing to the molecular interactions, which impart directional characteristics to them in the solid state.

Recently, Shukla and Singh [17] reported the results of relative undercooling, linear velocity of crystallization and phase diagram studies for the naphthalene—picric acid and anthracene—picric acid systems. Because of the lack of heat of fusion data, they could not test the validity of the mixture law. In the present paper, the phase diagrams of the binary systems of picric acid with naphthalene, anthracene and phenanthrene and of α-naphthol with *p*-toluidine have been studied. The heats of fusion of the pure components, eutectics and addition compounds were determined by means of differential scanning calorimetry. From the phase diagrams and the heat of fusion data, the entropy of fusion, enthalpy of mixing and excess thermodynamic functions were calculated in an attempt to shed light on the nature of the interactions between the components of the melts.

Experimental

Materials and purification

Naphthalene (BDH, Analar), anthracene (BDH, Analar), and picric acid (BDH, LR) were further purified by fractional crystallization and sublimation. Phenanthrene (BDH, LR) was purified by repeated distillation under vacuum and recrystallization from petroleum ether. α-Naphthol was purified by repeated distillation under low pressure and finally by zone-melting. *p*-Toluidine was purified by fractional crystallization from a water-ethanol mixture. The purities of all compounds were confirmed by determining their melting points, which were in good agreement with literature values.

Phase diagram study

The phase diagrams of the picric acid—naphthalene, picric acid—anthracene, picric acid—phenanthrene and α-naphthol—*p*-toluidine systems were determined [21, 22] by the thaw-melt method. Mixtures of various compositions, covering the entire range of composition, were taken in glass test-tubes and were sealed. The contents of each sealed test tube were subjected to repeated melting in liquid paraffin, followed by chilling in ice. The samples were taken out by breaking the tubes, and were ground separately to fine powders in a mortar, care being taken to avoid any contamination. The melting and thaw temperatures were determined with a Toshnival Melting Point Apparatus.

Heats of fusion

The heats of fusion of the pure components, the eutectics and the addition compounds were determined [23] with a Perkin-Elmer DSC-2 with computer-aided data acquisition and analysis by differential scanning calorimetry. All runs were carried out at a rate of 2 mcal s^{-1}, a chart speed of 5 mm min^{-1} and a chart range of 10 mV. The heating rate was 1.25 deg min^{-1} and the sample weight was 5–10 mg for each estimation. Whenever a transition such as melting, boiling, dehydration or crystallization occurs in the sample material, an endothermic or exothermic reaction takes place. The change in power required to maintain the sample holder at the same temperature as that of the reference holder during the transition is recorded from the peak obtained in the pattern. The chart abscissa indicates the transition temperature, and the peak area indicates the total energy transfer to or from the sample.

Results and discussion

Phase diagram

The phase diagrams of the binary systems of picric acid with naphthalene, anthracene and phenanthrene and of α-naphthol with *p*-toluidine are given in Figs 1 to 4. Each phase diagram shows the formation of two eutectics and a molecular complex with congruent melting point. Each molecular complex is surrounded by the two eutectics E_1 and E_2. The compositions and the melting points of the

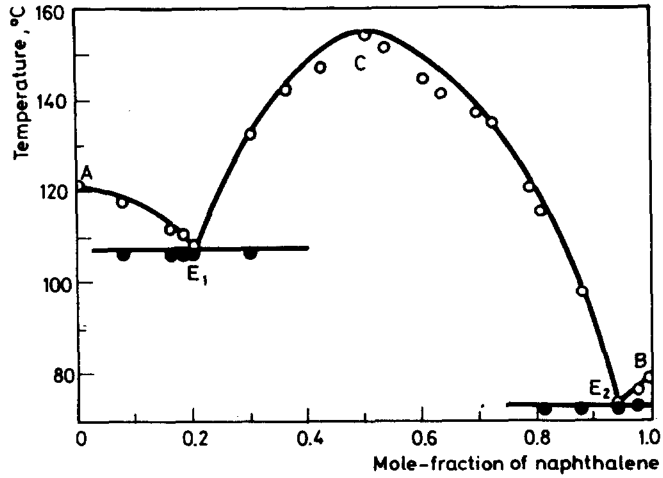

Fig. 1 Phase diagram of naphthalene—picric acid system. ○ Melting points; ● Thaw points

Table 1 Compositions and melting points of eutectics and molecular complexes of binary organic systems

System	Composition (mole fraction of first component)	Melting point, °C
1 Naphthalene—picric acid		
i) Eutectic 1	0.215	107.5
ii) Eutectic 2	0.940	73.5
iii) Molecular complex	0.500	155.0
2 Anthracene—picric acid		
i) Eutectic 1	0.102	109.5
ii) Eutectic 2	0.625	130.0
iii) Molecular complex	0.500	140.0
3 Phenanthrene—picric acid		
i) Eutectic 1	0.210	103.0
ii) Eutectic 2	0.835	85.0
iii) Molecular complex	0.500	145.0
4 α-Naphthol—*p*-toluidine		
i) Eutectic 1	0.175	31.0
ii) Eutectic 2	0.595	51.5
iii) Molecular complex	0.500	58.5

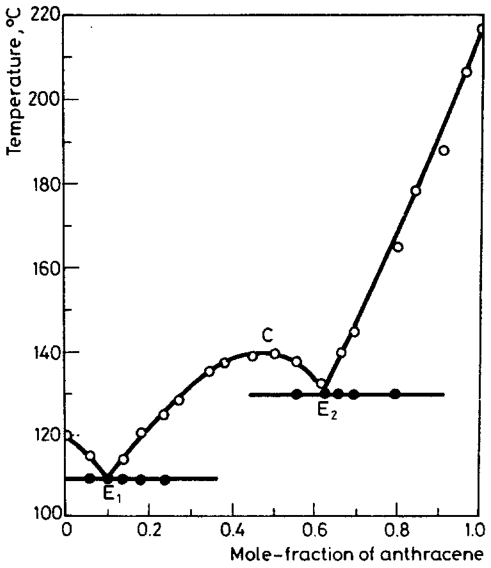

Fig. 2 Phase diagram of anthracene—picric acid system. ○ Melting points; ● Thaw points

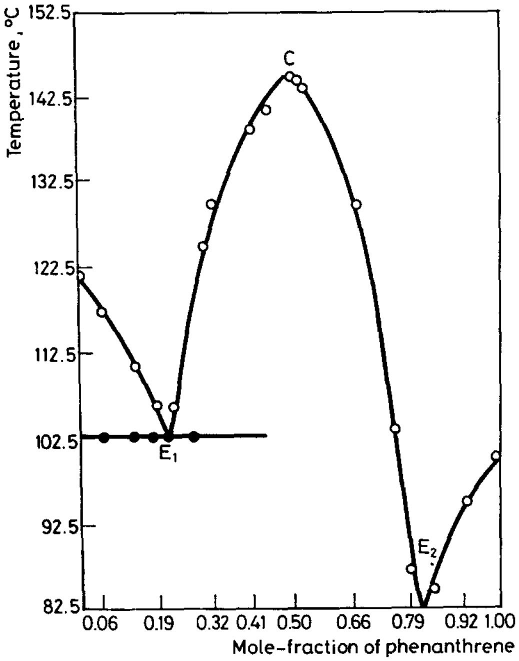

Fig. 3 Phase diagram of phenanthrene—picric acid system. ○ Melting points; ● Thaw points

eutectics and addition compounds, determined from the phase diagrams, are reported in Table 1. Each phase diagram may be presumed to consist of two simple eutectic-type phase diagrams, placed side by side, in which the molecular complex serves as one of the components. The maxima for all the systems are flat, indicating that the addition compounds are dissociated [17] in the molten state. From the phase diagrams, it can also be inferred that all the systems involve molecular compounds capable of existing as a solid compound in eqilibrium with a liquid of the same composition. From the first eutectic point E_1 onwards, on addition of the second component, the melting point again rises, and attains a maximum at C, where the compositions of the liquid and solid phases are identical. This maximum temperature corresponds to the congruent melting point of the addition compound. A maximum point on the liquidus line, a good length of the middle branch and the existence of a eutectic point on either side of the maximum provide information about the appreciable stability of the molecular complex formed.

Thermochemistry

The experimental results on the heats of fusion of the parent components, eutectics and addition compounds are given in Table 2. If the eutectics were a simple

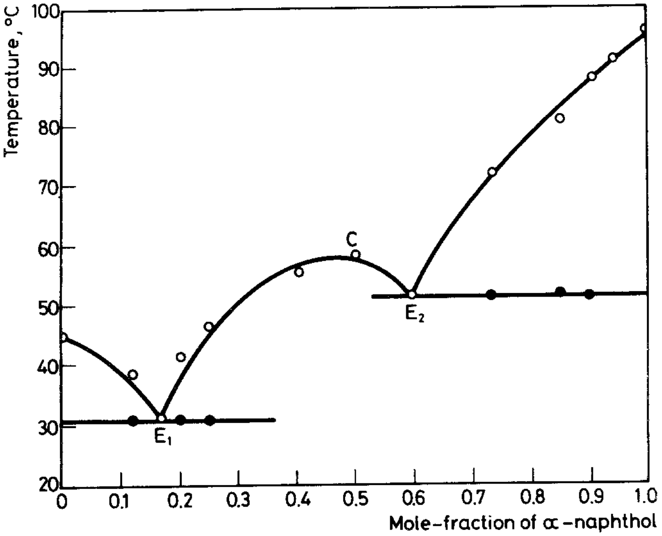

Fig. 4 Phase diagram of α-naphthol—*p*-toluidine system. ○ Melting points; ● Thaw points

mixture of the two components, involving no heat of mixing or any type of association in the melt, the heat of fusion would simply be given by the mixture law [20]:

$$(\Delta_f h)_e = x_1 \Delta_f h_1^0 + x_2 \Delta_f h_2^0 \qquad (1)$$

where x_1 and x_2 are the mole fractions and $\Delta_f h_1^0$ and $\Delta_f h_2^0$ are the heats of fusion of parent components 1 and 2, respectively. The heats of fusion calculated from the mixture law are given in the same Table. It is evident from the Table that the heats of fusion calculated from Eq. (1) 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, the heat liberated may lower the actual value of the heat of fusion. Cluster formation will be favoured if the molecules can associate via certain weak intermolecular forces. In eutectic systems where one or both components contain hydroxy groups, there will be a tendency to form hydrogen-bonds, and as a result cluster formation will be favoured. This is one of the reasons why the experimental heat of fusion values are lower than those calculated from Eq. (1). The experimental heats of fusion of the molecular complexes, and their theoretical values calculated via the mixture law, are also given in Table 2. In all cases, the calculated values are higher than the experimental ones. To justify this observation, a similar type of cluster formation and explanation can be suggested.

The enthalpy of mixing [25], (ΔH_m), which is the difference between the

Table 2 Heats of fusion, enthalpies of mixing, entropies of fusion and Jackson's roughness parameters

System	Material	Heat of fusion, kJ mol^{-1}	Enthalpy of mixing, kJ mol^{-1}	Entropy of fusion, kJ K^{-1} mol^{-1}	Roughness parameter (α), $\left(\frac{\Delta S}{R}\right)$
Naphthalene—picric acid	Naphthalene	19.654		0.0556	6.72
	picric acid	20.027		0.0506	6.11
	E_1 (expt.)	19.390	−0.56	0.0509	6.15
	(calc.)	19.95			
	E_2 (expt.)	18.88	−1.13	0.0545	6.58
	(calc.)	19.676			
	Mol. complex				
	(expt.)	15.650	−4.19	0.0366	4.42
	(calc.)	19.840			
Anthracene—picric acid	Anthracene	27.986		0.0572	6.91
	E_1 (expt.)	16.840	−3.98	0.0440	5.32
	(calc.)	20.820			
	E_2 (expt.)	23.190	−1.81	0.0575	6.95
	(calc.)	25.000			
	Mol. complex				
	(expt.)	9.870	−14.14	0.0239	2.89
	(calc.)	24.010			
Phenanthrene—picric acid	Phenanthrene	17.894		0.0480	5.80
	E_1 (expt.)	19.040	−0.54	0.0506	6.11
	(calc.)	19.580			
	E_2 (expt.)	15.660	−2.63	0.0437	5.28
	(calc.)	18.290			
	Mol. complex				
	(expt.)	11.330	−7.63	0.0271	3.27
	(calc.)	18.960			
α-Naphthol—*p*-toluidine	α-Naphthol	22.802		0.0618	7.74
	p-Toluidine	18.124		0.0570	6.89
	E_1 (expt.)	17.850	−1.09	0.0587	7.09
	(calc.)	18.940			
	E_2 (expt.)	19.220	−1.69	0.0592	7.15
	(calc.)	20.910			
	Mol. complex				
	(expt.)	17.570	−2.89	0.0530	6.40
	(calc.)	20.460			

experimental and calculated values of the heats of fusion, is given by

$$\Delta H_m = (\Delta_f h)_{\text{exp.}} - \sum (x_i \Delta_f h_i^0) \tag{2}$$

where $(\Delta_f h)_{\text{exp.}}$ is the experimentally determined heat of fusion of the eutectic and x_i and $\Delta_f h_i^0$ are the mole fractions and heats of fusion of the end-components. It is evident from Table 2 that in all cases the heats of mixing are negative. Complete miscibility was observed in the melts of simple eutectics, but several studies indicate the presence of considerable microheterogeneity. Thermochemical studies [26] suggest that the structure of the eutectic melt depends on the sign and magnitude of the enthalpy of mixing. Three types of structures are suggested; quasi-eutectic for $\Delta H_m > 0$, clustering of molecules for $\Delta H_m < 0$, and molecular solutions for $\Delta H_m = 0$. The negative values of ΔH_m for the eutectics and molecular complexes in all the systems under investigation suggest the clustering of molecules in the melt, and substantiate the earlier conclusion drawn on the basis of the mixture law. It is evident from Table 2 that the values of enthalpy of mixing of the eutectics are smaller than those of the molecular complexes. This is due to weak interactions for the eutectic compositions. It is also very interesting that some of the eutectics have a very low enthalpy of mixing, and one might argue in favour of the possibility of simple molecular solutions instead of weak interactions. These results are quite different from those for simple eutectic systems, where merely ordering of the parent phases has been suggested in the melts. It seems that there is a considerable enhancement of the interactions, due to the presence of the 1 : 1 molecular complex in the eutectic melts.

In order to learn the nature of the interaction between the components of the eutectics in the present systems, some thermodynamic functions, such as excess free energy (g^E), excess enthalpy (h^E) and excess entropy (s^E), were calculated by using the following equations:

$$-\ln x_i^1 \gamma_i^1 = \frac{\Delta_f h_i^0}{R}\left(\frac{1}{T} - \frac{1}{T_i^0}\right) \tag{3}$$

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

$$h^E = -RT^2\left(x_1 \frac{\partial \ln \gamma_1^1}{\partial T} + x_2 \frac{\partial \ln \gamma_2^1}{\partial T}\right) \tag{5}$$

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

where the different terms involved in Eqs (3)–(6) have their usual meanings. Equation (3) is obtained by considering the general condition of phase equilibrium for the two phases, and assuming that the heat of fusion is independent of temperature and that the two components are miscible in the liquid phase only. This equation was used to calculate the activity coefficients of the end-members at the eutectic point. The values of $\partial \ln \gamma_1^1/\partial T$ were calculated by differentiating Eq. (3) and taking the slope of the liquidus line near the eutectic point. The details of the calculation of the excess thermodynamic functions and the significance of the terms involved in Eqs (3)–(6) were reported earlier [24]. The values of the excess functions are given in Table 3. The values of g^E are positive in all cases except the two eutectics in the anthracene—picric acid system and eutectic E_1 in the α-naphthol—*p*-toluidine system. The values of h^E and s^E corresponding to g^E are reported in the same Table. It is well known that 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, is called the excess thermodynamic function. This quantity represents the excess (positive or negative) of a given thermodynamic property of the solution over that in the ideal (reference) solution. The value of the excess free energy is a measure of the departure [27] of the system from ideal behaviour. The excess enthalpy and excess entropy values correspond to the excess free energy, and they are measures of the excess enthalpy and excess entropy of mixing, respectively. These suggest an appreciable interaction between the two components of the eutectics.

The entropies of fusion, ΔS, of the pure components, eutectics and addition compounds were calculated by using the following equation:

$$\Delta S = \frac{\Delta_f h}{T} \tag{7}$$

Table 3 Excess thermodynamic functions for eutectic 1 and eutectic 2 in the binary organic systems

System	g^E, J mol^{-1}	h^E, J mol^{-1}	s^E, J K^{-1} mol^{-1}
1 Naphthalene—picric acid			
E_1	1378.6	4012.4	6.9
E_2	153.4	234.5	0.2
2 Anthracene—picric acid			
E_1	−150.1	349.9	1.3
E_2	−731.6	−6.5	1.8
3 Phenanthrene—picric acid			
E_1	868.7	5727.6	12.9
E_2	409.4	5503.0	14.2
4 α-Naphthol—*p*-toluidine			
E_1	−196.6	−8192.4	−26.3
E_2	305.7	−8523.4	−27.2

where $\Delta_f h$ is the heat of fusion and T is the fusion temperature. The data are given in Table 2. In all cases, the ΔS values are positive, indicating an increase of randomness during melting. Hunt and Jackson [8] state that the type of growth from a eutectic melt depends upon a factor, α, defined by the equation

$$\alpha = \xi \frac{\Delta S}{R} \tag{8}$$

where ξ is a crystallographic factor depending upon the geometry of the molecules and has values of less than or equal to one. $\Delta S/R$, also known as Jackson's roughness parameter, is the entropy of fusion in dimensionless units and R is the gas constant. When $\alpha < 2$, non-faceted growth occurs, whereas faceted growth appears if $\alpha > 2$. In all cases, $\Delta S/R$ values are greater than 2, which indicates that they exhibit faceted growth. The observations made under the microscope confirm this conclusion.

* * *

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Zusammenfassung — Die Phasendiagramme der binären Systeme von Pikrinsäure mit Naphthalin, Anthrazen und Phenanthren sowie von α-Naphthol mit *p*-Aminotoluol wurden bestimmt. In jedem System zeigt sich die Bildung eines Molekülkomplexes sowie je zwei Eutektika. Mittels DSC wurden die Schmelzwärmen der reinen Komponenten, der eutektischen Mischungen und der Molekülkomplexe ermittels. Der Vergleich der experimentell ermittelten Schmelzwärmen mit den mittels der Mischungsregel errechneten Werten läßt auf eine Clusterbildung in der Schmelze schließen. Weiterhin wurden aus den Schmelzwärmen auch Werte für Schmelzentropie und Mischungsenthalpie errechnet.

Резюме — Найденные методом расстаивание — расплав фазовые диаграммы двойных систем пикриновой кислоты с нафталином, антраценом и фенантреном, а также α-нафтола с п-толуидином показали образование в каждой системе молекулярного комплекса и двуз эвтектик. Методом ДСК определены теплоты плавления чистых компонент, эвтектик и молекулярных комплексов. Сопоставление экспериментально полученных теплот плавления с теоретически вычисленными на основе закона смеси, предполагает образование кластеров в расплавах. Исходя из данных теплот плавления были также вычислены энтропия плавления, энтальпия смешения и избыточные термодинамические функции.