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Note

STRUCTURE OF EUTECTIC MELTS; BINARY ORGANIC SYSTEMS

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Since the early sixties, eutectic crystallization has been a very active field for metallurgists [1–3] and chemists [4,5]. Inspite of the great influence of the prefreezing phenomena on microstructure, very little has been added to the structure of eutectic melts. Complete miscibility has been observed in the melts of simple eutectics [6,7] but several studies [8–10] indicate the presence of considerable microheterogeneity. Thermochemical studies suggested that the structure of eutectic melts depends on the sign and magnitude of the enthalpy of mixing. Three types of structures were suggested; quasieutectic for $\Delta H_m > 0$, clustering of molecules for $\Delta H_m < 0$, and molecular solutions for $\Delta H_m = 0$. In the present article we report the results of the thermochemical measurements of simple organic eutectics. Attempts have been made to correlate the enthalpy of mixing and eutectic composition. The results are compared with the phenanthrene–succinonitrile system where a very high enthalpy of mixing was measured and a large miscibility gap was observed.

EXPERIMENTAL

Phase-diagrams were determined by the thaw–melt method as described in ref. 6. The details of the purification method are also described therein. The enthalpy of fusion was measured with a Perkin-Elmer DSC-2 equipped with a computer-aided data acquisition and analysis system. The calibration was done with indium as the temperature standard. The measurements were made in hermetically sealed Al pans and all runs were carried out at a heating rate of 2 mcal s^{-1} and a chart speed of 2 mm min^{-1}.

RESULTS AND DISCUSSION

The values of enthalpies of mixing are given in Table 1. The eutectic compositions of the systems chosen for the present study are also reported in

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TABLE 1
Enthalpy of mixing and eutectic composition

System	Composition of eutectic (mole fraction of component I)	ΔH_m (kJ mol^{-1})
Naphthalene (I)–catechol (II)	0.82	2.62
Naphthalene (I)–*m*-nitroaniline (II)	0.79	2.57
Naphthalene (I)–1-naphthol (II)	0.61	2.46
Naphthalene (I)–*p*-chloronitrobenzene (II)	0.56	1.61
Naphthalene (I)–phenanthrene (II)	0.57	1.68
1-Naphthol (I)–2-naphthol (II)	0.67	0.92
Phenanthrene (I)–*m*-dinitrobenzene (II)	0.66	1.30
Phenanthrene (I)–succinonitrile (II)	0.025	4.67

this table. Except for the phenanthrene–succinonitrile system, all systems were simple eutectics. In the systems, eutectic compositions are far from equimolar composition, the enthalpies of mixing are reasonably high. The eutectic point shifts towards the component of lower melting temperature (the phenanthrene–*m*-dinitrobenzene system was an exception). This indicates that the eutectic composition is connected to the enthalpy of mixing in a definite manner. This type of behaviour was observed by Zalkin [8,9] in metallic systems, and he explained the structure of melts on the basis of colloidal theories. Unlike the case of Zalkin, we observed that in all systems, except phenanthrene–succinonitrile, the components were completely miscible in the liquid state. To check the miscibility and the layering, we centrifuged the melts of the 1-naphthol–2-naphthol and naphthalene–1-naphthol eutectics at different speeds. The melt of naphthalene–1-naphthol started separating just above 300 r.p.m., while a speed higher than 500 r.p.m. was needed for the melt of the 1-naphthol–2-naphthol eutectic. The melts were suddenly quenched and it was observed that 1-naphthol settles at the bottom in both cases. This supports the idea that immiscibility can be brought about by centrifuging the melts. Where ΔH_m is reasonably high, a low acceleration is sufficient to cause the microscopic layering. However, for a system like 1-naphthol–2-naphthol, a very high acceleration is needed. Similar results were reported by Kumar [10,11] for the Al–Zn eutectic. He observed the groupings of Al atoms (25–50 Å) in the composition range 0–20 at% of Al, and Zn atoms (15–25 Å) in the range 60–100 at% of Zn. All these results suggest that eutectics are formed at a definite composition at which all the dispersion medium is solvated by a cloud of particles of the disperse phase. The composition depends on the nature of the interaction between the components and the process of dispersion. At the eutectic composition the minor component is highly dispersed and interacts strongly with the dispersion medium. The enthalpy of mixing is responsible, to some extent, for these interactions. There are some unresolved problems, such as shape and degree of micelle formation, which can be understood only after careful X-ray studies of eutectic melts.

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