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Note

STOICHIOMETRY AND STABILITY OF SOME SOLID STATE CHARGE TRANSFER COMPLEXES FORMED IN IMIDAZOLE–HYDROCARBON SYSTEMS

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ABSTRACT

The compositions of charge transfer complexes of imidazole with some aromatic hydrocarbons (naphthalene, anthracene, phenanthrene and biphenyl) were established through phase diagram studies. The enthalpies and entropies of fusion of these complexes were estimated by differential scanning calorimetry. The relative stabilities of the solid state charge transfer complexes in the donor–acceptor systems studied could not be predicted from the areas under the curves of the congruent compounds in the phase diagrams.

As part of our investigation into the stoichiometry and thermodynamics of solid state charge transfer complexes [1–3], the complexes formed between imidazole (donor) and aromatic hydrocarbons (acceptor) (i.e. naphthalene, anthracene, biphenyl and phenanthrene) were studied. Phase diagrams of the donor–acceptor binary systems were used to determine the stoichiometry of the charge transfer complexes formed between the component molecules. The results are reported in this note.

EXPERIMENTAL

Analytical reagent grade aromatic hydrocarbons supplied by BDH were purified by crystallization from a suitable solvent [4]. The sample of imidazole was obtained from Aldrich and was used as received without any further treatment. The details of the experimental technique involved in the

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phase studies have been described elsewhere [1]. Heats of fusion ΔH_f were determined from the DSC curves obtained with a Du Pont differential scanning calorimeter Model 900, using indium as reference.

RESULTS AND DISCUSSION

The stoichiometric compositions and the eutectic temperatures of the congruent melting compounds in the binary systems, as obtained from the phase diagram studies, are recorded in Table 1. The last two columns of Table 1 give the congruent points and the ratios of the areas under the curves for the various congruent compounds in the phase diagrams. The heats of fusion of the charge transfer complexes of the imidazole–anthracene system (as obtained by differential scanning calorimetry) together with their entropies of fusion ΔS_f and free energies of fusion ΔG_f are recorded in Table 2.

The unusual stoichiometries in these systems (Table 1) may perhaps be explained on the basis that various energetically favourable geometries of orientation are possible because of the different proportions of donors and

TABLE 1

The characteristic parameters of the phase diagrams of some complexes

Systems	Stoichiometric ratio (DA)	Eutectic point (°C)	Congruent point (°C)	Δ
Imidazole–anthracene	1:4	190, 188	214.0	10:9:5:6
	1:2	188, 175	200.0	
	3:2	175, 168	183.0	
	3:1	168, 88	186.0	
Imidazole–naphthalene	1:3	73, 57	78.0	6:4:5
	3:2	57, 65	71.0	
	3:1	65, 78	83.0	
Imidazole–phenanthrene	1:9	99, 97	101.0	6:12:5:5:7:5:7
	3:7	97, 91	101.0	
	2:3	91, 92	94.0	
	1:1	92, 86	95.0	
	3:2	86, 81	89.0	
	3:1	81, 80	90.0	
	9:1	80, 84	87.0	
Imidazole–biphenyl	1:3	62, 61	69.0	3:4:2
	1:1	61, 55	90.0	
	4:1	55, 72	87.0	

Δ = ratio of areas.

TABLE 2

Thermodynamic functions of molecular complexes in anthracene–imidazole system

Stoichiometric ratio (DA)	Congruent point (°C)	ΔH_f (kJ mol^{-1})	ΔS_f (J mol^{-1} K^{-1})
1:4	218.4	84.35	171.60
1:2	203.0	29.78	62.57
3:2	185.0	96.27	210.21
3:1	188.0	9.82	21.30

$\Delta G_f = 0$.

acceptors [1–3]. The absence of 1 : 1 stoichiometry in some systems may be due to their instability around the melting temperatures.

The relative stabilities of the complexes in the imidazole–anthracene system determined on the basis of the thermodynamic functions for fusion (Table 2) do not follow the trend obtained from the areas under the curves of the congruent compounds with the corresponding stoichiometries. In view of this observation, these areas do not implicitly reflect the dependence on the thermodynamic functions and hence the stability of the complexes in these systems. This is in line with our earlier observations on the charge transfer complexes of urea and thiourea donors with the same set of aromatic hydrocarbon acceptors [3].

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