

STOICHIOMETRY, THERMODYNAMIC FUNCTIONS AND STABILITY OF SOME CHARGE TRANSFER COMPLEXES

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ABSTRACT

The stoichiometry of charge transfer complexes formed between Schiff base donors and aromatic hydrocarbon acceptors was established by solid–liquid phase equilibrium diagram studies. The thermodynamic functions of some stable charge transfer complexes were determined by differential scanning calorimetry and the area under the curve of the congruent compound is fixed as the criterion to predict the relative strength of charge transfer complexes on the basis of thermodynamic parameters.

INTRODUCTION

Solid charge transfer (CT) complexes are also called organic metals because of their high electrical conductivity comparable to those of metals. Quinolinium TCNQ was the best organic conductor at the time of our research [1]. A large number of complexes formed between various donors and acceptors have immense application in basic and applied sciences [2–4]. Therefore, to synthesize a new type of CT complexes one must know their stoichiometry and stability. Bearing this in mind, we have initiated our research in this direction by fusibility diagram studies, since diagrams of systems with more than one component provide valuable information about the equilibrium state between the various components and their phases, and for the synthesis of material with special properties [5]. In this article we have reported the stoichiometry, thermodynamic functions and relative stability of some solid CT complexes formed between Schiff bases as donors and aromatic hydrocarbons as acceptors.

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EXPERIMENTAL

All the electron donors (Schiff bases) were synthesized and purified by a method reported in the literature [6]. The acceptors (aromatic hydrocarbons) used were obtained commercially and purified by recrystallization.

Various compositions of donors and acceptors over a whole range of mole fraction were prepared by grinding together the requisite amounts of donors and acceptors in the presence of ether as solvent. The ether was removed by evaporation under low pressure and precautions were taken to avoid moisture from the beginning.

A small amount of sample was sealed in a capillary and the melting point of the same was recorded. The uncertainty in the measurement of temperature was $\pm 0.5^\circ\text{C}$. The average melting and solidification points were used in the present investigation. The melting points over a whole range of mole fraction of different systems were recorded and the temperature-composition plots for various systems were drawn. Some representative curves are shown in Figs. 1-4.

Heat of fusion (ΔH_f) was calculated for some of the representative complexes on a Du Pont differential scanning calorimeter using Al_2O_3 as reference. The observed values of ΔH_f along with the entropy of fusion (ΔS_f) and free energy of fusion (ΔG_f) are tabulated in Table 1.

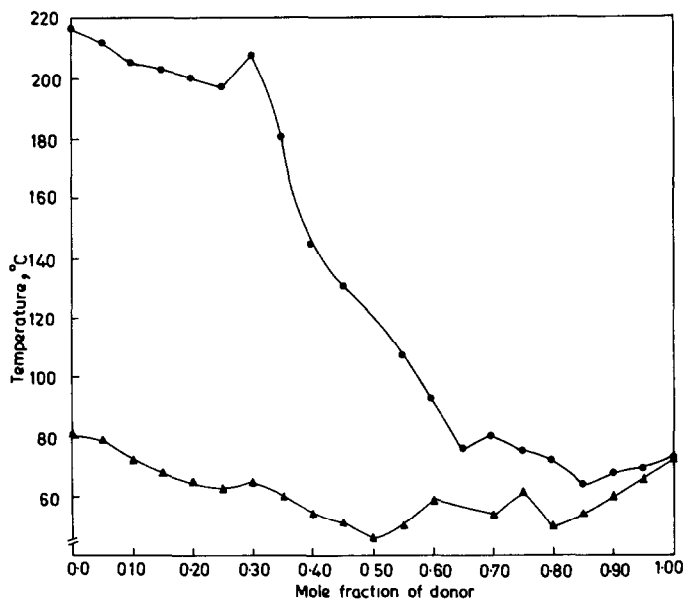


Fig. 1. Fusibility diagrams of: (●—●) anthracene + $\phi\text{-CH=N-}\phi\text{-OCH}_3$; (▲—▲) naphthalene + $\phi\text{-CH=N-}\phi\text{-OCH}_3$ systems.

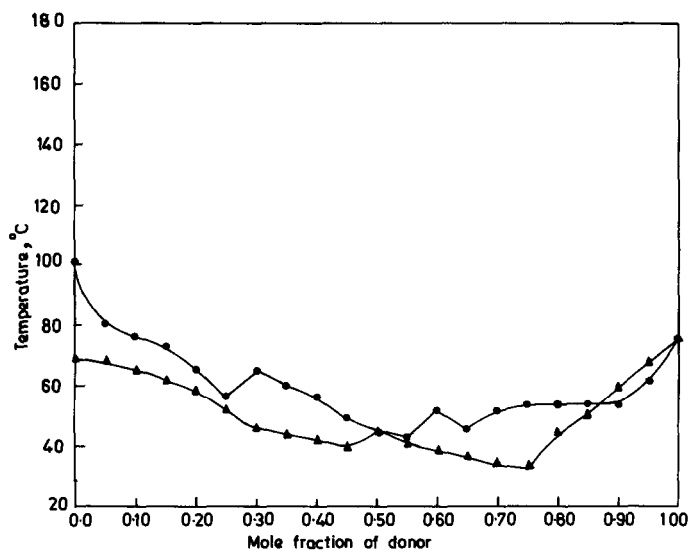


Fig. 2. Fusibility diagrams of: (●—●) phenanthrene + ϕ -CH=N- ϕ -OCH₃; (▲—▲) diphenyl + ϕ -CH=N- ϕ -OCH₃ systems.

TABLE 1

Thermodynamic functions of some representative solid molecular complexes

Systems	Stoichiometry (D:A)	C.pt. ^a (°C)	ΔH_f (kcal mol ⁻¹)	ΔS_f (e.u.)
Cl- ϕ -CH=N- ϕ -naphthalene	3:7	174	51.83	115.95
	3:2	64	26.71	79.27
ϕ -CH=N- ϕ -anthracene	1:1	192	8.88	19.05
ϕ -CH=N- ϕ -OC ₂ H ₅ -anthracene	3:7	187	63.97	139.06
ϕ -CH=N- ϕ -OC ₂ H ₅ -diphenyl	1:1	44	11.07	34.91
ϕ -CH=N- ϕ -OCH ₃ -naphthalene	3:7	70	56.88	165.83
	3:2	65	34.08	100.73
	3:1	67	23.21	68.26
ϕ -CH=N= ϕ -OCH ₃ -anthracene	3:7	203	55.24	116.05
ϕ -CH=N- ϕ -OCH ₃ -phenanthrene	3:7	70	46.41	133.75
	3:2	57	26.33	79.77
ϕ -CH=N- ϕ -OCH ₃ -diphenyl	1:1	55	9.59	26.26
ϕ -CH=N- ϕ -NO ₂ -diphenyl	1:1	125	11.48	28.84
HO- ϕ -CH=N- ϕ -naphthalene	1:4	84	26.32	73.72
	3:2	190	28.50	61.55
HO- ϕ -CH=N- ϕ -phenanthrene	1:4	131	21.45	53.10

^a C.pt. = Congruent point, $\Delta G_f = 0$.

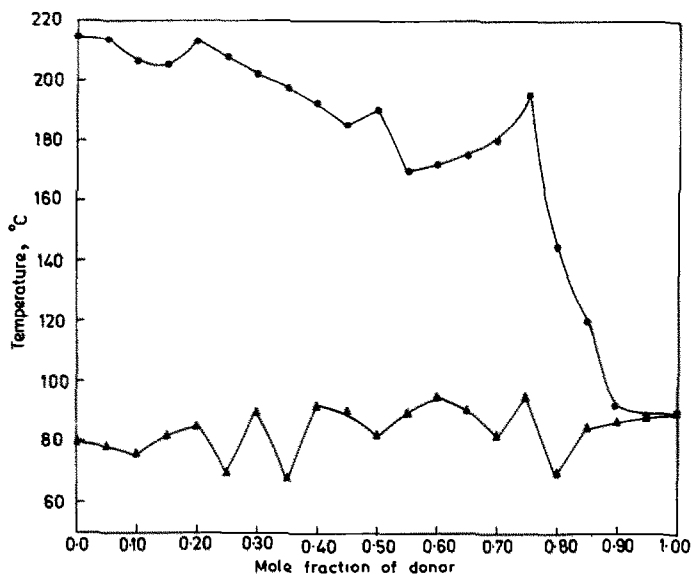


Fig. 3. Fusibility diagrams of: (●—●) anthracene + $\phi\text{-CH=N-}\phi\text{-I}$; (▲—▲) naphthalene + $\phi\text{-CH=N-}\phi\text{-I}$ systems.

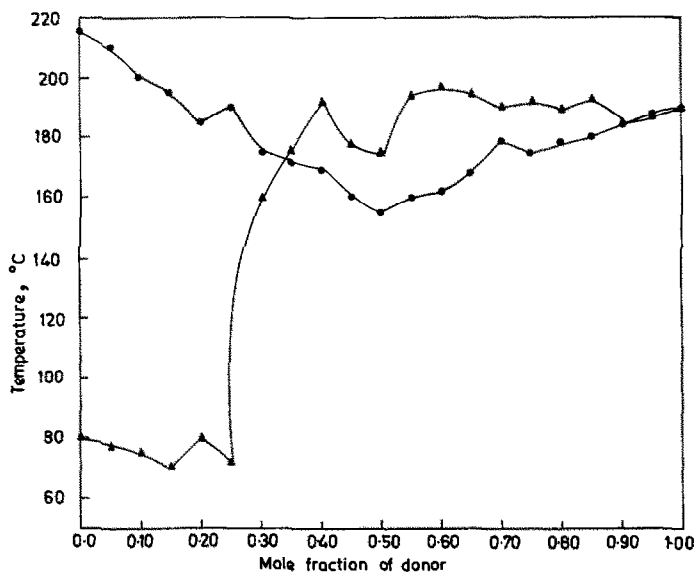


Fig. 4. Fusibility diagrams of: (●—●) anthracene + $\text{HO-}\phi\text{-CH=N-}\phi$; (▲—▲) naphthalene + $\text{HO-}\phi\text{-CH=N-}\phi$ systems.

RESULTS AND DISCUSSION

The melting point of a pure donor decreases on the addition of a small quantity of the acceptor and the presence of a congruent composition with a

TABLE 2
The characteristic parameters of fusibility diagrams and enthalpies of some complexes

Schiff base	Naphthalene				Anthracene			
	Stoichiometry (D:A) (ΔH_f)	E.p.t.s. ^a (°C)	C.pt. ^b (°C)	Δ^c	Stoichiometry D:A (ΔH_f)	E.p.t.s. (°C)	C.pt. (°C)	Δ
$\phi\text{-CH=N-}\phi$	3:7	52,52	58	6:1	1:3	215,205	107	11:10:1
	7:3	34,30	58		1:1(8.88)	185,180	192	
$\phi\text{-CH=N-}\phi\text{-OH}$	2:3	230,220	235	2:1:3	1:3	189,178	195	3:1
	1:1	220,213	238		3:1	172,182	188	
	7:3	250,247	263					
$\phi\text{-CH=N-}\phi\text{-OCH}_3$	3:7(56.88)	63,60	65	5:4:2	3:7(55.24)	197,180	207	7:2
	3:2(34.05)	50,56	59		7:3	76,75	80	
	3:1(23.21)	54,50	62					
$\phi\text{-CH=N-}\phi\text{-OC}_2\text{H}_5$	3:2	41,40	46	—	3:7(63.97)	180,182	185	
$\phi\text{-CH=N-}\phi\text{-Cl}$	3:1	45,50	52		\times^e			
$\phi\text{-CH=N-}\phi\text{-Br}$	\neq^d							
$\phi\text{-CH=N-}\phi\text{-I}$	1:4	87,70	85	2:1:2:3:1	1:4	205,208	213	3:1:3
	3:7	70,68	90		1:1	185,170	190	
	2:3	68,90	92		3:1	180,145	195	
	3:2	90,91	95					
$\phi\text{-CH=N-}\phi\text{-NO}_2$	3:17	73,110	121	1:1:1:1:3	1:3	189,185	192	1:2
	9:11	115,125	144		7:3	118,123	130	
	11:9	125,130	142					
	13:7	130,132	140					
	9:1	147,138	150					

TABLE 2 (continued)

Schiff base	Naphthalene				Anthracene			
	Stoichiometry (D:A) (ΔH_f)	E.pts. ^a (°C)	C.pt. ^b (°C)	Δ°	Stoichiometry D:A (ΔH_f)	E.pts. (°C)	C.pt. (°C)	Δ
HO- ϕ -CH=N- ϕ	1:4(26.32)	70,72	80	1:7:6:3:3	1:3	185,175	190	5:4
	2:3	175,178	192		7:3	168,175	179	
	3:2(28.50)	194,195	197					
	3:1	190,189	192					
	7:3	189,185	193					
H ₃ CO- ϕ -CH=N- ϕ	1:3	48,50	58	3:2	2:3	172,137	178	1:5
	3:2	50,41	52		1:1	137,193	201	
Cl- ϕ -CH=N- ϕ	1:3(26.71)	58,53	60	4:3:2	3:7(51.83)	155,165	171	-
	3:2	38,56	58					
	3:1	40,41	47					
<i>Phenanthrene</i>								
ϕ -CH=N- ϕ	<i>Diphenyl</i>							
	7:3	137,125	155	7:1	1:1	42,40	47	-
ϕ -CH=N- ϕ -OH	4:1	125,145	150		3:7	120,115	132	4:2:4:3
					2:3	115,112	120	
ϕ -CH=N- ϕ -OCH ₃	3:7(46.41)	56,60	65	4:1	1:1(9.59)	40,41	45	-
	3:2(26.33)	43,46	52		4:1	157,160	165	
ϕ -CH=N- ϕ -OC ₂ H ₅	3:1	49,48	58	-	1:1(11.07)	32,32	38	-
	3:17	90,93	95	1:1:1:1	1:1(11.48)	117,118	122	2:1
ϕ -CH=N- ϕ -NO ₂	1:3	93,98	100		13:7	125,126	130	
	7:3	132,130	137					
4:1	130,132	135						

ϕ -CH=N- ϕ -Cl	1:4	81,73	85	10:1:1:1	×	85	1:2:1:5
	3:2	42,42	45				
	3:1	41,5,43	45				
	9:1	45,45	47				
ϕ -CH=N- ϕ -Br	3:17	73,70	80	2:2:2:1	≠	80	1:2:1:5
	3:7	53,54	68				
	1:1	46,50	54				
	4:1	45,43	50				
ϕ -CH=N- ϕ -I	1:4	90,81	98	3:2:2:1	≠	98	1:2:1:5
	2:3	75,72	82				
	3:2	63,68	72				
	3:1	65,72	80				
HO- ϕ -CH=N- ϕ	1:4(21,45)	98,105	130	1:3:3:1	3:17	70,79	1:2:1:5
	1:1	145,152	159				
	7:3	178,182	189				
	4:1	182,178	186				
H_3CO - ϕ -CH=N- ϕ	≠			1:1	1:1	38,39	-
Cl- ϕ -CH=N- ϕ	1:4	89,85	91	3:2:1	1:3	51,40	5:2:2
	2:3	75,70	80				
	3:1	38,42	92				

^a E.pts. = Eutectic points.

^b C.pt. = Congruent point.

^c Δ = Ratio of area.

^d ≠ - Melt formation.

^e × - No complexation.

TABLE 3
Relative stability of molecular complexes formed between D and A

Schiff base	Naphthalene	Anthracene	Phenanthrene	Diphenyl
ϕ -CH=N- ϕ	3:7 > 7:3	1:3 > 1:1 > 4:1	≠	1:1
ϕ -CH=N- ϕ -OH	7:3 > 2:3 > 1:1	1:3 > 3:1	7:3 > 4:1	3:7 = 11:9 > 4:1 > 2:3
ϕ -CH=N- ϕ -OCH ₃	3:7 > 3:2 > 3:1	3:7 > 7:3	3:7 > 3:2	1:1
ϕ -CH=N- ϕ -OC ₂ H ₅	3:2	3:7	3:1	1:1
ϕ -CH=N- ϕ -NO ₂	9:1 > 9:11 > 3:17 = 11:9 = 13:7	1:3	7:3 > 1:3 = 3:17 > 4:1	1:1 > 13:7
ϕ -CH=N- ϕ -Cl	×	×	1:4 > 3:2 > 9:1	×
ϕ -CH=N- ϕ -Br	≠	1:3	3:17 = 3:7 = 1:1 > 4:1	≠
ϕ -CH=N- ϕ -I	3:2 > 1:4 = 2:3 > 3:7 = 3:1	1:4 = 3:1 > 1:1	1:4 > 2:3 = 3:2 = 3:1	≠
HO- ϕ -CH=N- ϕ	2:3 > 3:2 > 3:1 = 17:3 > 1:4	1:3 > 7:3	1:1 = 7:3 > 1:4 = 1:1	4:1 > 2:3 > 1:1 = 3:17
H ₃ CO- ϕ -CH=N- ϕ	1:3 > 3:2	1:1 > 2:3	≠	1:1
Cl- ϕ -CH=N- ϕ	1:3 > 3:2 > 3:1	3:7	1:4 > 2:3 > 3:1	1:3 > 1:1 = 3:1

congruent melting point indicates the existence of a stable molecular complex [5]. Perusal of the individual phase diagrams of the Schiff base–aromatic hydrocarbon systems (Figs. 1–4, Table 2) reveals that hydrocarbon acceptors form congruent compounds of unusual stoichiometries. The absence of the 1 : 1 stoichiometry in some cases may be due to the instability of the 1 : 1 complex at high temperatures [6,7]. The formation of complexes of unusual stoichiometries in these donor–acceptor systems could perhaps best be explained on the basis that when a donor is added to an acceptor, the molecules arrange themselves in an order which is energetically favourable for charge transfer interactions. Different proportions of donors and acceptors offer different energetically favourable geometries of orientation. Consequently, molecular complexes of different composition result [7].

The area under the curves of congruent compounds with compositions 3 : 7, 3 : 2, 3 : 1 in ϕ -CH=N- ϕ -OCH₃-naphthalene, 3 : 7, 3 : 2 in ϕ -CH=N- ϕ -OCH₃-phenanthrene and 1 : 4, 3 : 2 in HO- ϕ -CH=N- ϕ -naphthalene systems in the temperature–composition plot in Figs. 1, 2 and 4, respectively, follow the expected trend of thermodynamic functions of these complexes (Table 1) as ϕ -CH=N- ϕ -OCH₃-naphthalene (3 : 7 > 3 : 2 > 3 : 1), ϕ -CH=N- ϕ -OCH₃-phenanthrene (3 : 7 > 3 : 2) and HO- ϕ -CH=N- ϕ -naphthalene (3 : 2 > 1 : 4) where the quantities within the parentheses correspond to the stoichiometries of the complexes. These areas, therefore, implicitly reflect the dependence on the enthalpies of these complexes. Hence if this trend in area under the temperature–composition plot of the congruent compound is taken as the basis for the strength of molecular complexes, one can qualitatively predict the relative stability of the molecular complexes. The relative stability predicted on the basis of the area under the curve of the congruent compound is reported in Table 3. However, no fixed relationship exists between the stoichiometry of eutectic components and their melting points.

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REFERENCES

- 1 M.R. Bryce and L.C. Murphy, *Nature (London)*, 309 (1984) 119.
- 2 R. Foster, *Organic Charge Transfer Complexes*, Academic Press, New York, 1969; *Molecular Association*, Academic Press, New York, 1975; *Molecular Complexes*, Vol. 2, Elek Sciences, London, 1974.

- 3 S.N. Bhat, V.P. Shedbalkar and H. Kuroda, *Indian J. Chem.*, 21A (1982) 1015.
- 4 L.N. Ferguson, *The Modern Structural Theories of Organic Chemistry*, Howard University, 1963.
- 5 G. Briegleb, *Electronen-Donator-Acceptor Komplexe*, Springer Verlag, Berlin, 1961.
- 6 R.A. Singh, A. Varshney and S.N. Bhat, *J. Indian Chem. Soc.*, 58 (1981) 643.
- 7 H.S. Randhawa and L.S. Sandhu, *Z. Phys. Chem. (Leipzig)*, 267 (1986) 168.