Journal of Thermal Analysis, Vol. 32 (1987) 1381–1385

ON THE COMPOSITIONS AND STRENGTHS OF CHARGE-TRANSFER COMPLEXES

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(Received March 14, 1986; in revised form December 9, 1986)

The compositions of charge-transfer complexes of urea and thiourea with some aromatic hydrocarbons (naphthalene, anthracene, phenanthrene and biphenyl) have been established through phase diagram studies. The enthalpies and entropies of fusion of these complexes have been estimated by differential scanning calorimetry. It is observed that the relative stabilities of the solid-state charge-transfer complexes in the donor-acceptor systems studied cannot be predicted from the areas under the curves of the congruent compounds in the phase diagrams.

The solid-state charge-transfer complexes, also called organic metals, have often been found to exhibit marked stability and to possess unusual properties [1, 2]. Prior to the synthesis of new solid-state charge-transfer complexes, it is desirable to have an outline knowledge of their compositions and stabilities. Phase diagram studies on donor-acceptor binary mixtures can be made the basis for determination of the stoichiometry of solid-state charge-transfer complexes formed from them [3]. Further, the areas under the curves for different congruent compounds in the phase diagrams are proportional to the relative strengths of these complexes [3–5]. In our earlier studies [6] on the donor-acceptor compounds of some Schiff base donors and aromatic hydrocarbons, the thermodynamic properties of some representative complexes were determined with a differential scanning calorimeter, and it was observed that the relative stabilities of these molecular complexes could be qualitatively predicted from the areas under the temperature *vs.* composition plots of the component molecules. As an extension to that work, we have now carried out similar studies on the solid-state charge-transfer complexes of urea and thiourea donors with aromatic hydrocarbon acceptors (naphthalene, anthracene, biphenyl and phenanthrene). The results of these studies are reported here.

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Experimental

All chemicals (AR grade) were procured commercially and were purified by crystallization from a suitable solvent [7]. The details of the experimental technique involved in the phase diagram studies were described earlier [6]. Heats of fusion, ΔH_f, were determined from the DSC curves obtained with a DuPont differential scanning calorimeter (Model 990), using alumina as reference material.

Results and discussion

The temperature *vs.* composition plots for the donor-acceptor binary systems under investigation are shown in Fig. 1. The stoichiometric compositions and the eutectic temperatures of the congruent melting compounds in the various binary systems as obtained from Fig. 1 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 different congruent compounds in the phase diagrams. The heats of fusion for some representative charge-transfer complexes as obtained by differential scanning calorimetry are listed in Table 2, along with the entropies of fusion for these complexes.

It is observed from the phase diagrams (Fig. 1) that most of the donor-acceptor systems exhibit congruent melting behaviour, indicating the presence of stable

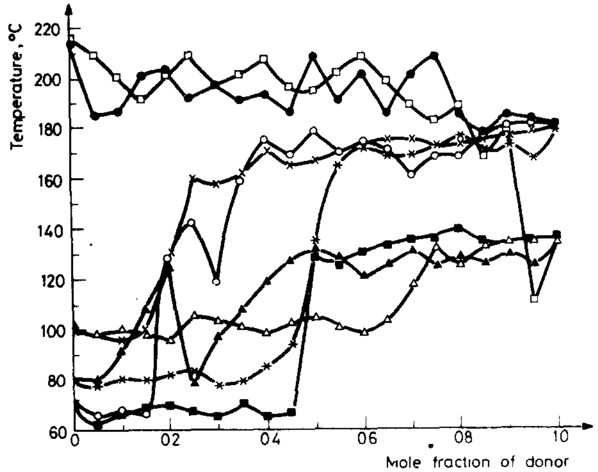

Fig. 1 Phase diagrams for various donor—acceptor binary systems; *–* thiourea-naphthalene; × – × thiourea-phenanthrene: ▲–▲ urea-naphthalene; △–△ urea-phenanthrene; □–□ urea-anthracene; ■–■ urea-biphenyl; ○–○ thiourea-biphenyl; ●–● thiourea-anthracene

Table 1 The characteristic parameters of the phase diagrams of some complexes

System	Stoichiometric ratio	E. pts. °C	C. pt. °C	Δ
Urea-naphthalene	1:4	108, 78	124	2:3:2:1:1
	1:1	126, 127	130	
	7:3	125, 124	130	
	4:1	124, 125	127	
	9:1	125, 124	128	
Urea-anthracene	1:3	200, 197	208	3:4:5:2:4
	2:3	200, 195	207	
	3:2	201, 197	207	
	4:1	181, 166	187	
	9:1	166, 110	178	
Urea-phenanthrene	1:9	98, 98	100	3:4:4:5
	1:3	96, 103	105	
	1:1	102, 100	104	
	3:1	117, 125	132	
Urea-biphenyl	1:4	68, 67	70	2:1:2:8
	1:2	65, 65	70	
	1:1	66, 126	128	
	4:1	135, 133	138	
Thiourea-naphthalene	1:9	78, 80	81	1:2:8:6:4
	1:3	83, 78	84	
	3:2	168, 172	175	
	4:1	175, 173	179	
	9:1	173, 169	176	
Thiourea-anthracene	1:4	201, 192	203	2:1:1:1:1:2
	3:7	192, 191	198	
	2:3	191, 186	193	
	1:1	186, 191	208	
	3:2	191, 185	201	
	3:1	201, 185	208	
Thiourea-phenanthrene	1:3	133, 160	163	1:2:3
	2:3	165, 168	174	
	2:1	175, 175	178	
Thiourea-biphenyl	1:9	65, 66	67	1:5.7:6:8
	1:3	128, 119	142	
	2:3	159, 169	175	
	1:1	169, 170	178	
	3:2	170, 170	174	

E. pts.—Eutectic points (there are two eutectic points for each congruent compound—one towards the donor and the other towards the acceptor end, on the composition axis of the phase diagram).

C. pt.—Congruent point.

Δ—Ratio of areas.

Table 2 Thermodynamic functions of some representative solid molecular complexes

System	Stoichiometric ratio	C. pt. °C	ΔH_f, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}
Urea-naphthalene	1:4	122	63.11	159.8
	7:3	130	79.33	196.8
	1:1	132	17.26	42.6
Urea-anthracene	3:2	209	70.18	145.6
	1:3	207	74.06	154.3
	2:3	204	91.96	192.7
Thiourea-anthracene	1:1	209	32.52	67.6
	3:7	194	193.11	413.4
	3:2	201	73.31	154.7
Thiourea-biphenyl	2:3	174	87.86	196.6
	1:3	143	64.62	155.3
	3:2	173	74.90	167.9

C. pt.—Congruent point; $\Delta G = 0$

molecular complexes [8]. The unusual stoichiometries of the complexes in these systems (see Table 1) could perhaps best be explained on the basis that different energetically favourable geometries of orientation are possible because of the different proportions of donors and acceptors [5, 6]. The absence of 1:1 stoichiometry in some systems may be due to the instability of these 1:1 complexes around the melting temperatures.

On the basis of the thermodynamic functions for the fusion processes (Table 2), the relative stabilities of the complexes follow the sequences 7:3>1:4>1:1 for urea-naphthalene; 2:3>1:3>3:2 for urea-anthracene; 3:7>3:2>1:1 for thiourea-anthracene; and 2:3>3:2>1:3 for the thiourea-biphenyl system. However, it is observed from the phase diagrams that the areas under the curves corresponding to the above stoichiometries (Table 1) do not follow the trends of the thermodynamic functions, as has been observed earlier for molecular complexation between Schiff base donors and aromatic hydrocarbon acceptors [6]. Therefore, these areas can not implicitly reflect the dependence on the thermodynamic functions of the complexes in these systems. In view of this, it appears that no general relationship can be deduced between the areas under the curves for the congruent compounds in the phase diagrams and the strengths of the complexes. Further studies on a wide range of charge-transfer complexes are required to generalize the conclusions on the systems studied.

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One of the authors (R.S.) is grateful to I.C.A.R. (India) for financial assistance.

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Zusammenfassung — Die Zusammensetzung von Donator-Akzeptor-Komplexen von Harnstoff und Thioharnstoff mit einigen aromatischen Kohlenwasserstoffen, nämlich Naphthalin, Anthracen, Phenanthren und Biphenyl, wurde durch Phasendiagrammuntersuchungen ermittelt. Schmelzenthalpie und -entropie dieser Komplexe wurden mittels DSC bestimmt. Es wurde festgestellt, daß die relative Stabilität der festen Donator-Akzeptor-Komplexe nicht aus der Fläche unter der Kurve im Phasendiagramm der kongruenten Verbindungen vorausgesagt werden kann.

Резюме — На основе фазовых диаграмм установлен состав комплексов с переносом заряда (КПЗ) мочевины и тиомочевины с такими ароматическими углеводородами, как нафталин, антрацен, фенантрен и бифенил. С помощью ДСК установлена энтальпия и энтропия плавления этих комплексов. Показано, что относительная устойчивость твердотельных КПЗ в изученных донороно-акцепторных системах не может быть установлена, исходя из площади под кривой на фазовой диаграмме конгруэнтных соединений.