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ELECTRICAL CONDUCTIVITY AND PHASE TRANSITION STUDIES OF SOME SELECTED CONGO RED-METAL COMPLEXES

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Abstract

The electrical properties of Congo Red dye (*L*) and its metal (*M*) complexes of *M*:*L* molar ratios of 1:1 and 2:1, where *M*=Cr(III), Fe(III), Cu(II), Zn(II), Zr(IV), Th(IV) and UO_2(II), indicated semiconducting behaviour. The activation energies and electrical conductivities depend on the ionic charge of the metal chelates. The activation energies of 1:1 metal complexes are greater than those of 2:1 metal complexes. The conductivity data obtained are interpreted on the basis of the molecular structure of the Congo Red complexes. One phase transition was obtained during DTA study of Congo Red dye at 212°C. This phase transition may be due to the rotation of the two naphthalene rings and the N=N groups around the diphenyl group centre.

Keywords: complexes, Congo Red-metal complexes, electrical conductivity, phase transition

Introduction

Organic dyes have been the subject of many investigations since they have a variety of applications. The resistance of some dyes such as Methyl Red, Alizarin Yellow, Brilliant Green and Congo Red are of the order 10^7–10^{11} ohm m [1]. Congo Red is a well known azo-compound which is used as a direct dye, *pH* indicator [2–6], corrosion inhibitor in acid media [7], and it is also used for the identification of some cations of rare earth metals [8]. However, there are few studies regarding relation between the structure of Congo Red and its electrical conductivity. This study deals with the establishment of the electrical properties of the complexes of Congo Red with Cr(III), Fe(III), Cu(II), Zn(II),

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Zr(IV), Th(IV) and UO_2(II) using electrical conductivity measurements of the solid complexes and spectroscopic techniques.

Experimental

The chemicals used in this study were pure reagents purchased from B.D.H. and Merck.

The solid complexes were prepared by mixing a solution of metal chloride, (0.01 mol/l) or (0.02 mol/l), dissolved in double distilled water, added to a solution of Congo Red (0.01 mol/l) in 20 ml of pure ethanol. The mixture was stirred for half an hour. The solid complexes which precipitated were then filtered off, washed several times with double distilled water to remove any traces of metal ions, finally washed with ether, and then dried in vacuum.

A Perkin-Elmer Spectrophotometer Lambda 3B was used to obtain the UV and visible spectra of th ligand and its metal complexes.

A Shimadzu Differential Thermal Analyzer Model 50 was used to obtain the DTA curves of Congo Red and its metal complexes. The puritz of the samples was checked by thin layer chromatography and also by the method described by Gutmann and Lyons [9]. The samples under investigation have constant R_f values of 0.67, 0.68, 0.71, 0.72, 0.76, 0.78 and 0.82 for the Cr(III), Fe(III), Cu(II), Zn(II), Zr(IV), Th(IV) and UO_2(II) complexes, respectively, within a given small temperature interval (ΔT). This indicates that the purification of these samples is good enough to carry out the conductivity measurements.

The complexes under investigation were heated at 220°C to remove the water of crystallization before conductivity measurements.

The d.c. conductivity of the anhydrous samples was measured in an evacuated glass cell using th potential drop method [10, 11]. The temperature of the samples was measured using a Ni–NiAl thermocouple calibrated in the range 350–750 K, with a digital mutimeter (DEL-JAP, HC-5010 EC). The finely ground solid was compressed in a hydraulic press up to 5 tons cm^{-2} to pellet form of a diameter of 8 mm and thickness of 2 mm. The two surfaces were polished, coated with silver paint and checked for good contact. The electrical resistivity was measured with a Keithley 130 digital multimeter.

Results and discussion

The electrical conductivities of Congo Red and its metal complexes were studied in the temperature range 350–750 K. In all cases an increase in conductivity with increasing temperature was observed which indicates that these complexes lie in the range of typical semiconductors [12]. The plots of $\ln \sigma$ *vs.*

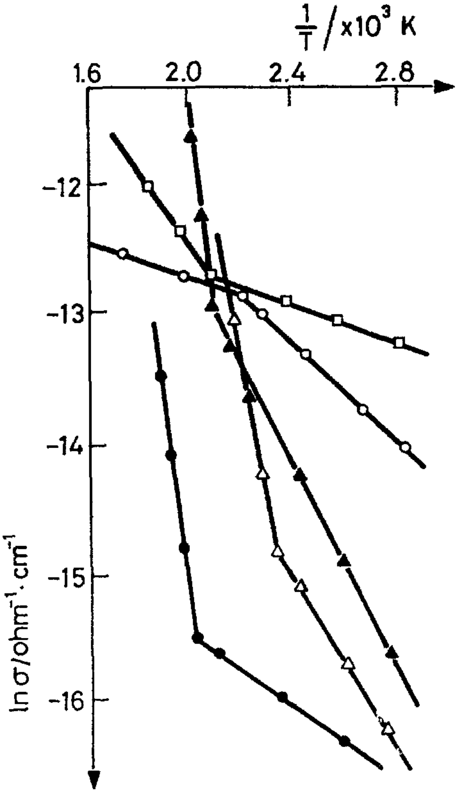


Fig. 1 The ln of the conductivity *vs.* 1000/*T* of transition metal complexes with Congo Red dye

1/*T* (σ=conductivity and *T* is the absolute temperature) of the compounds under investigation (Figs 1 and 2) obeyed the equation:

$$\sigma=\sigma^{\circ}\exp(-E/kT)$$

where σ° is a constant, *E* is the thermal activation energy and *k* is the Boltzmann constant.

There is a break in each plot suggesting a transition temperature and two different thermal activation energies as indicated in Table 1. This break may be caused by a change from intrinsic to extrinsic conductivity or a change in the type of packing, which can be seen from the relatively high activation energy of conduction obtained above the transition temperature.

The TG and DTA curves of Congo Red and its metal complexes, shown in Fig. 3, allow the following statements:

i- Lattice water molecules associated with complex formation are completely removed at 110°C.

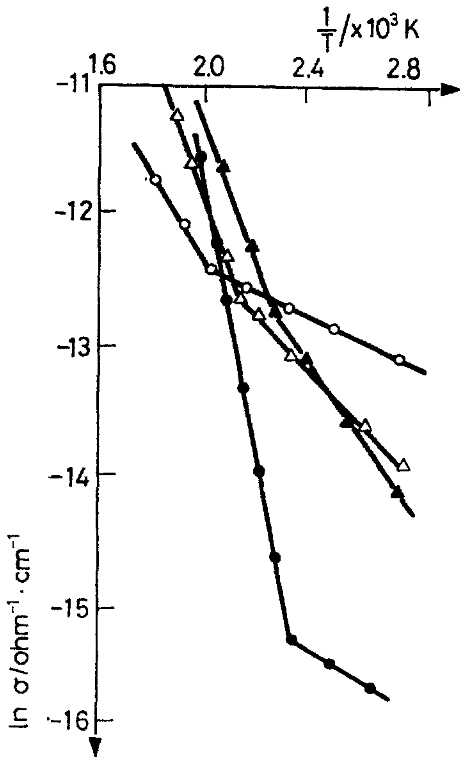


Fig. 2 The ln of the conductivity *vs.* 1000/*T* of rare earth metal complexes with Congo Red dye

ii- The breaks in the TG curves of the complexes are obtained in the temperature range 200–230°C corresponding to loss of one or two coordinated water molecules. Thus, the hydrated complexes are converted to the corresponding anhydrous complexes. This break is not observed in the TG curve of the Congo Red dye.

iii- In the DTA curves of Congo Red, the sharp DTA endotherm at 212°C (Fig. 3), may represent a phase change. This phase transition may represent the rotation of the two naphthalene ringsand the N=N groups relative to the diphenyl group centre. Also a broad endotherm in the DTA curves of Congo Red metal complexes are observed in the temperature range 230–285°C. The broad DTA endotherms of the metal complexes indicate a slow change in the phase transition.

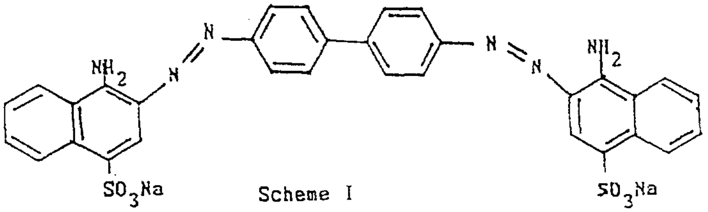
In an attempt to interpret the phase transition phenomenon, one may presume that Congo Red has two molecular configurations, the *cis* as given in Scheme I, and the trans as in Scheme II.

Table 1 Conductivities, activation energies and break temperatures of Congo Red and its complexes

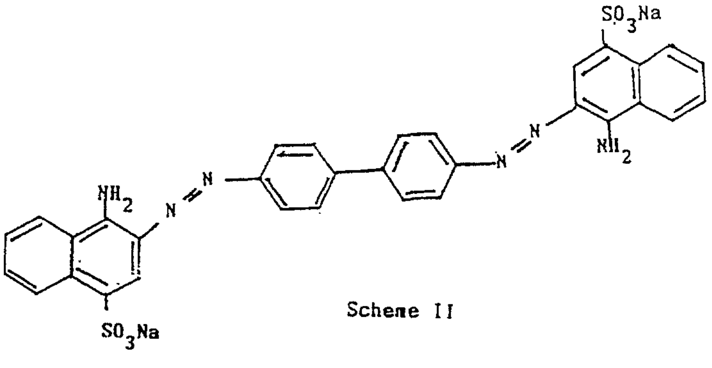
Sample	σ_1/ohm^{-1}cm^{-1} 10^{-7} (at 300 K)	σ_2/ohm^{-1}cm^{-1} 10^{-5} (at 400 K)	E_1/ev	E_2/ev	Break temp./ K
Congo Red	1.56	0.80	0.29	0.92	360
[ZrL]Cl_4	9.75	2.35	0.10	0.23	476
[CrL]Cl_3	7.92	2.22	0.12	0.24	444
[FeL]Cl_3	6.82	2.02	0.13	0.34	487
[ThL]Cl_4	5.60	1.62	0.15	0.53	410
[UO_2L]$(CH_3COO)_2$	1.57	1.85	0.24	0.29	398
[CuL]Cl_2	1.13	1.21	0.25	0.72	465
[ZnL]Cl_2	1.05	0.75	0.33	0.95	421
[Th_2L]Cl_8	12.50	2.40	0.08	0.25	432
[$(UO_2)_2$L]$(CH_3COO)_4$	7.45	2.80	0.12	0.34	422

L = ligand

At low temperature, the molecules of Congo Red exist in the cis form. The molecules in the ground energy state have a reduced activation energy, thus scheme I is favoured. By thermal rotation, the trans configuration is favoured above the transition temperature. It supports this conclusion that the uv-visible spectral reflectance of Congo Red in the solid phase at room temperature exhibits two bands at 322 and 440 nm. These two bands are shifted to lower wave-



Scheme I



Scheme II

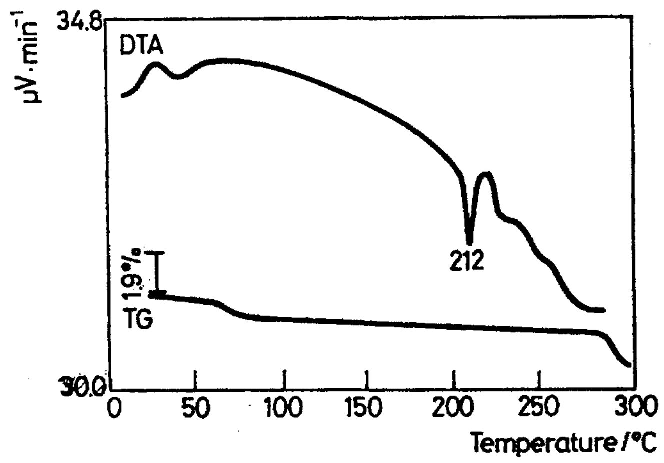


Fig. 3a Thermal analysis data of Congo Red dye

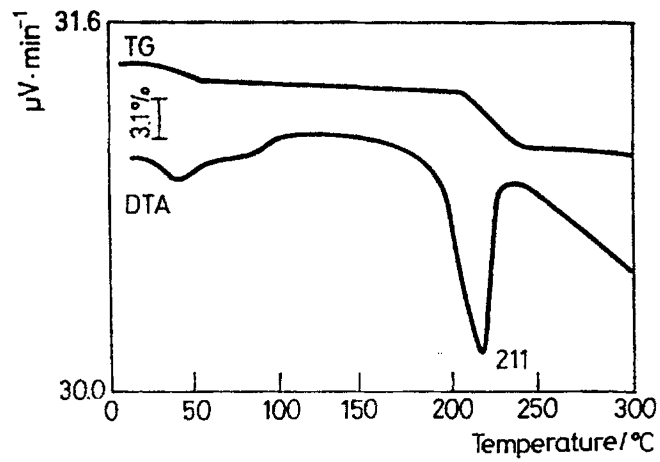


Fig. 3b TG and DTG curves of Cr(III) complex with Congo Red dye

lengths 288 and 408 nm, when the sample is heated at 220°C (above the transition temp.). Generally, the cis configuration of a compound absorbs with lower intensity due to shorter distance between the ends of the chromophore [13]. If this is true, one could attribute the phase conducting at low temperature with low activation energy to the *cis*-form (scheme I), whereas the phase conducting at higher temperatures would be the *trans*-form (scheme II).

The first activation energies (E_1) of the complexes at low temperatures follow the order:

Zr(IV)<Th(IV)<Cr(III)<UO_2(II),(2:1)<Fe(III)<UO_2(II),(1:1)<Cu(II)<Zn(II).

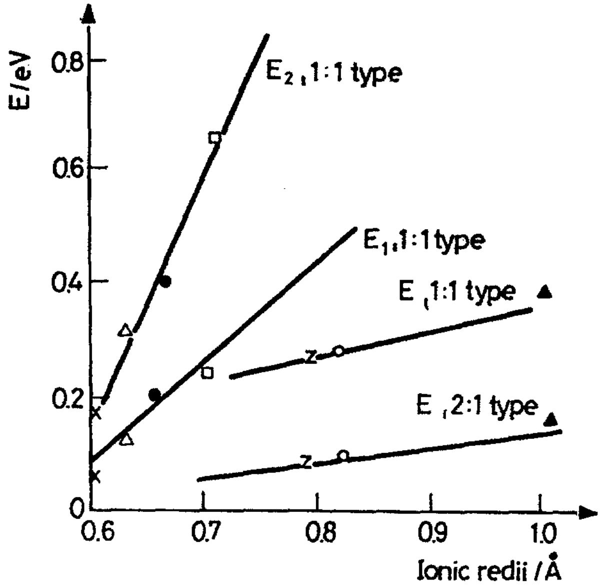


Fig. 4 Activation energy *E* *vs*. ionic radii of cations

It is apparent that the increase of the charge on the ions causes a decrease in the activation energy, i.e. the conductivity of the complexes increases. The activation energy of the Zn(II) complexes at high temperature is approximatly the same as that of Congo Red. This indicates that the Zn(II) ion which has not unpaired electrons is similar to Congo Red. The Zr(IV) and Th(IV) complexes have the lowest activation energies due to the greater charge on the transition metal ions. At higher temperatures the activation energy of the Zr(IV) complex is lower than that of the Zn(II) complex. The charge of Zr(IV) is greater than

Table 2 Electronic absorption bands, formation constants and phase transition temperatures of Congo Red and its metal complexes

Compound	Visible bands /nm	log k_f for 2:1 (M:L) complex	Phase transition temp./°C
Congo Red dye	342, 496	–	212
$[CrL{\cdot}H_2O]Cl_3$	500, 628	11.30	211
$[FeL{\cdot}H_2O]Cl_3$	522, 668	11.10	233
$[CuL{\cdot}2H_2O]Cl_2$	585	9.22	220
$[ZnL\}Cl_2$	472	8.28	245
$[ZrL{\cdot}H_2O]Cl_4$	552	11.70	293
$[ThL{\cdot}H_2O]Cl_4$	510, 670	10.80	285
$[UO_2L{\cdot}H_2O](CH_3COO)_2$	502, 660	10.30	241

that of Zn(II). This means that the charge of ions plays an important role in the conductivity which increases with increasing ionic charges.

Also, the trend of the conductivities at lower temperatures (50–150°C) depends more on the ionic radius of the cation than on its ligand field strength. Figure 4 illustrates that the activation energy E_1 increases linearlz with increasing ionic radii of the cations (Zn^{++}=0.74, Cu^{++}=0.69, Fe^{3+}=0.64, Cr^{3+}=0.52 °A and Th^{4+}=1.02, UO_2^{++} =0.80, Zr^{4+}=0.79 °A).

The data in Table 1 demonstrate that the thermal activation energies of the 1:1 metal complexes are greater than those of 2:1 (M:L) complexes, i.e. the increase of the proportion of metal ions increases the conductivity of the complex. Also, from the data in Table 1, the thermal activation energies of the two types of complexes, except for the Zn(II) complex, are lower than that of Congo Red. This type of complex is characterized by an increase in conductivity of the organic ligand owing to the binding with a metal ion, in which the π-electron system of the ligand has strong interaction with the valency electrons of the metal which leads to an increase in conductivity.

The apparent formation constants ($\log k_f$) of the metal complexes formed in solution were determined from *pH*-metric titration curves and from a limiting absorbance method [14]. The data of the 2:1 (*M:L*) type which are listed in Table 2, reveal that the stability constants of the complexes follows the order:

$$\mathrm{Zr(IV)>Th(IV)>UO_2(II)\ and\ Cr(III)>Fe(III)>Cu(II)>Zn(II).}$$

These results show that the conductivities of the investigated complexes increase as the stabilities of the complexes increase.

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