

# D.C. Conduction Phenomenon of Some Rhodanine Azo Complexes

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The electrical behaviour of 5-(4-R-phenylazo)-3-phenyl-2-thioxothiazolidin-4-one compounds and their complexes with  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{UO}_2^{2+}$  was investigated in the temperature range 300–450 K. The conductivities were found to depend on the structure of the compounds and the metal ions. Both the structures of the azo and the complexation process play an effective role in the conduction process. The activation energy,  $\Delta E$ , increases by decreasing the conductivity of the complexes.

The synthesis and properties of azo compounds and their metal complexes have been investigated earlier [1–6]. Complex formation of many organic compounds plays an important role in the field of conduction. An increase in the conductivity values is observed when metal ions are incorporated into the  $\pi$  electron delocalization of the organic compound [7]. However, a reduction of conductivity is noted if a localized bond between metal ions and organic compound is created.

In continuation of the studies of the physicochemical properties of the complexes it seemed to be of interest to prepare 5-(4-R-phenylazo)-3-phenyl-2-thioxothiazolidin-4-ones and their complexes to evaluate their electrical conductivities.

The conductance of a solution at any temperature depends on the ions present and on their concentration. As a result of the complex formation ions of different mobility appear in the solution. Depending on the nature of these ions, an increase or decrease in the conductance occurs [8]. Thus, to show the various possibilities of stoichiometric ratios of complex formation, the addition of ligands to different aqueous solutions containing transition ions was followed conductometrically.

The complex formation can be followed by studying the relationship between the conductance and the volume of the metal ion solution added. The resulting curves characterized by some breaks indicate the presence of different complex species and denote their compositions.

The conductometric titration curves of ligands with  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{UO}_2^{2+}$  ions indicate the probable formation of  $\text{MR} = 1:2$  ( $\text{MR} = n(\text{M}):n(\text{L})$ ) complexes in solution at low concentration of metal ions and  $\text{MR} = 1:1$  complexes at relatively high concentra-

tion of the metal ions. The common behaviour is the increase of the conductance of the solution with the increase of the volume of the titrant. This behaviour can be explained by factors giving the change in conductance:

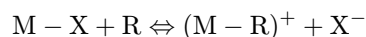
1. The increase of the volume of the metal ions in chelate formation, which is accompanied by the decrease in the value of diffusion coefficient of the particle. The diffusion coefficient is related to the volume of diffusing particle by the Stocks—Emistein equation

$$D_o = K(V_m)^{1/3}\eta$$

where  $D_o$  is the diffusion coefficient of the conductivity species,  $V_m$  is the molar volume and  $\eta$  is the viscosity of the medium.

2. The lowering of the change on the metal ion through covalent bonds formation with the ligand.

3. The replacement of the anions by the ligand as shown below



The 1. and 2. factors lead to lowering of the conduction while the 3. favours increasing the ionic conductivity. Accordingly, the net effect will be the resultant of all these factors depending on the nature of metal ion and the medium.

To identify the structure of complexes, their infrared spectra were measured and compared with the ligand. The main characteristic features of the IR spectra reported are as follows:

1. A strong and broad band at  $3440 \text{ cm}^{-1}$ , assigned to coordinated water molecules, is observed in the spectra of complexes.

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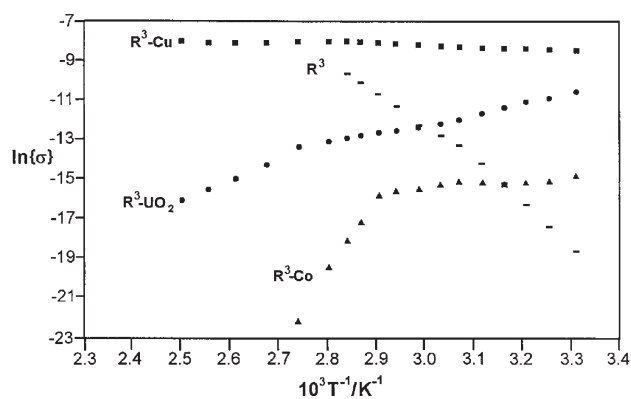


Fig. 1. Arrhenius plot between reciprocal temperature and conductivities for  $R^3$  and its complexes.

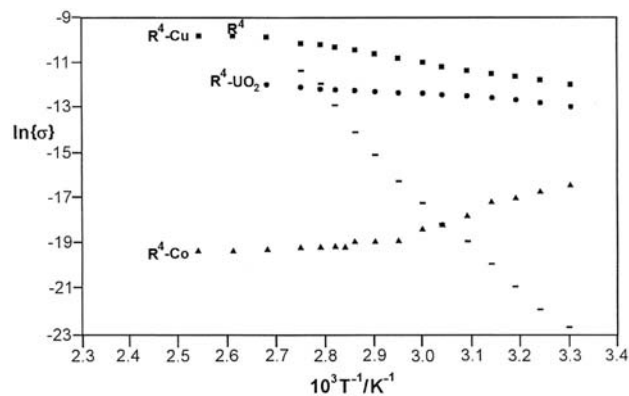


Fig. 4. Arrhenius plot between reciprocal temperature and conductivities for  $R^4$  and its complexes.

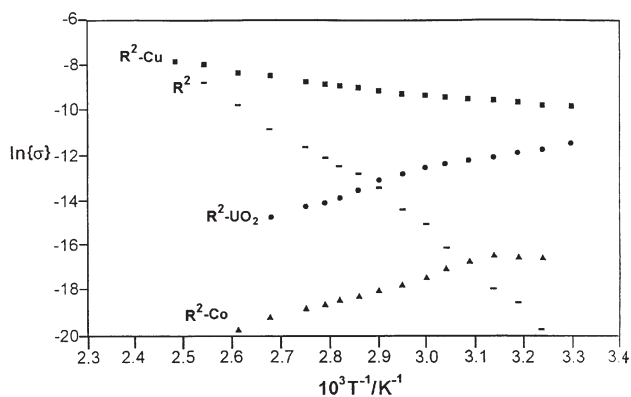


Fig. 2. Arrhenius plot between reciprocal temperature and conductivities for  $R^2$  and its complexes.

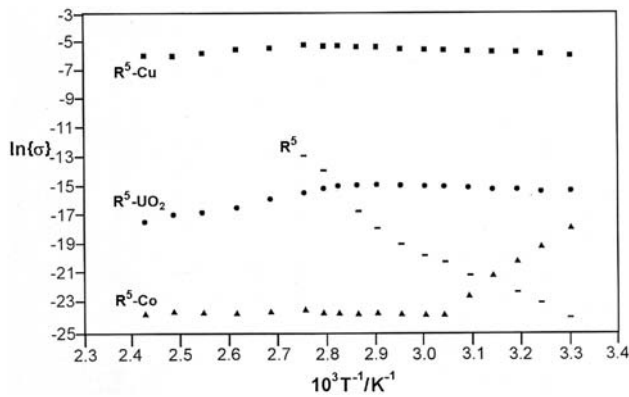


Fig. 5. Arrhenius plot between reciprocal temperature and conductivities for  $R^5$  and its complexes.

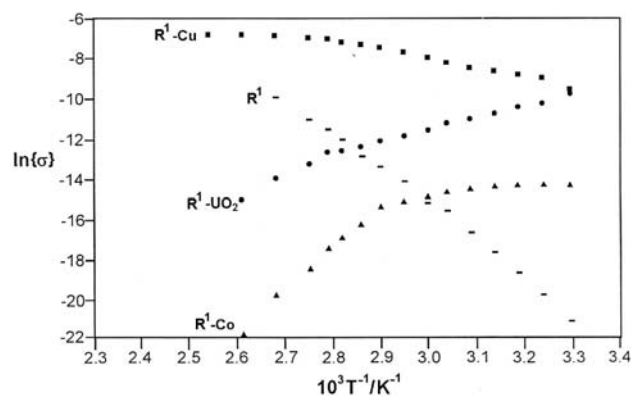


Fig. 3. Arrhenius plot between reciprocal temperature and conductivities for  $R^1$  and its complexes.

2. A weak band at  $3400\text{ cm}^{-1}$  (OH) disappears upon complexing with metal ions. On the other side, another weak band at  $3200\text{ cm}^{-1}$  (NH) is shifted after complexation suggesting that the complexation takes place through the nitrogen atom of azo dye moiety. This is supported by the appearance of a new band of M—N and M—O [1—3].

One of the main characteristics of solid organic

compounds is their electrical conductivity. Almost all conductivity measurements, as shown in Figs. 1—5, specify a relation between  $\ln \sigma$  and  $1/T$  of the straight line form

$$\ln \sigma = f(1/T)$$

These plots are characterized by the following facts:

i) All prepared complexes have low conductivities (Table 1). Studies have suggested that the low conductivity of the complexes is due to the presence of only a small number of free charge carriers that have a small mobility [9]. On the other hand, the complexes could provide a convenient route for the conduction of the charge carriers through chemical bonds rather than tunnelling or charge transfer between molecular species that are not directly bonded [10]. In general, a lower conductivity weakens the conjugation in the chelate rings involved in complex formation. This could be attributed to packing and reduced conjugation [11].

ii) It is apparent that comparison of the electrical conductivities for all complexes shows that the

**Table 1.** Conductivities Data and Dependence of Activation Energy Values on Temperature

Compound	$\Delta E/\text{eV}$		$\sigma_{(T=40\text{ }^\circ\text{C})}$
	Temp. region I	Temp. region II	$(\Omega\text{ m})^{-1}$
R <sup>3</sup>	1.72	1.47	$8.1 \times 10^{-8}$
R <sup>3</sup> -Cu	0.12	0.12	$2.25 \times 10^{-4}$
R <sup>3</sup> -UO <sub>2</sub>	-0.28	-0.63	$1.46 \times 10^{-5}$
R <sup>3</sup> -Co	-0.20	-2.5	$2.36 \times 10^{-7}$
R <sup>2</sup>	1.53	1.09	$8.94 \times 10^{-9}$
R <sup>2</sup> -Cu	0.33	0.33	$6.57 \times 10^{-5}$
R <sup>2</sup> -UO <sub>2</sub>	-0.38	-0.72	$7.2 \times 10^{-6}$
R <sup>2</sup> -Co	-0.095	-0.86	$6.58 \times 10^{-8}$
R <sup>1</sup>	1.85	1.48	$9.6 \times 10^{-9}$
R <sup>1</sup> -Cu	0.37	0.25	$1.23 \times 10^{-4}$
R <sup>1</sup> -UO <sub>2</sub>	-0.43	-0.37	$1.73 \times 10^{-5}$
R <sup>1</sup> -Co	-0.37	-1.6	$5.3 \times 10^{-7}$
R <sup>4</sup>	1.42	1.93	$7.58 \times 10^{-10}$
R <sup>4</sup> -Cu	0.4	0.32	$9.7 \times 10^{-6}$
R <sup>4</sup> -UO <sub>2</sub>	+0.30	+0.30	$3.37 \times 10^{-6}$
R <sup>4</sup> -Co	-1.02	-0.42	$1.8 \times 10^{-8}$
R <sup>5</sup>	0.57	2.99	$3.1 \times 10^{-10}$
R <sup>5</sup> -Cu	0.3	0.3	$3.7 \times 10^{-3}$
R <sup>5</sup> -UO <sub>2</sub>	+0.001	-0.60	$2.6 \times 10^{-7}$
R <sup>5</sup> -Co	-0.6	-0.10	$8.1 \times 10^{-11}$

adding of metal covers an extensive range of conductivity changes in material matrix. For the cobalt and UO<sub>2</sub><sup>2+</sup> complexes of such series characterized in the low temperature region between 308 and 343 K the D.C. electrical conductivities are higher than that of the free ligand. On the other hand, in the high temperature region between 343 and 493 K, the D.C. electrical conductivities are lower than those of the free ligands. For the copper complex of such series over the same regions the D.C. electrical conductivity is higher than that of the pure ligand for both low and high temperature regions. In other words, the complexes are interaction of the metal orbitals with the ligands to give new molecular orbitals, which are delocalized over the whole molecular complex. It is known that the complexation of organic compounds with transition metals leads to an overlap between *d* orbitals of the metal and  $\pi$  orbitals of the ligands thereby extending electron delocalization.

iii) An abrupt change is observed at a critical temperature  $T_g$  in the temperature interval between 333 and 360 K, corresponding to the glass transition temperature. Glass transition temperature usually is identified by the onset of diffusional motion of large chain segments [12]. The variation of D.C. electrical conductivity with temperature correlated with the mechanism of the processes of conduction. The degree of chemical short-range order in the material initially increases with the increase of the temperature by high

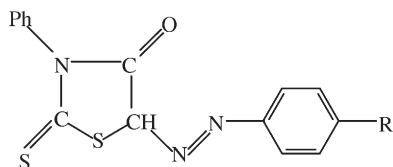
rate due to the growth of small crystallins, and then increases with lower rate with further increase of temperature due to the short thermal degradation of the material.

iv) At room temperature, the measured electrical conductivity of the various rhodanine azo dyes decreases in the order  $\kappa(\text{R}^3) < \kappa(\text{R}^2) < \kappa(\text{R}^1) < \kappa(\text{R}^5) < \kappa(\text{R}^4)$  (Table 1). This behaviour can be attributed to the resonance effects of the various substituents of azo dye compounds studied. In 5-(4-R-phenylazo)-3-phenyl-2-thioxothiazolidin-4-one, there are R<sup>1</sup>, R<sup>2</sup> attached directly to the azo group leading to a high degree of conjugation. But in the R<sup>5</sup> and R<sup>4</sup> a strong electron-withdrawing group is attached to the azo group, making delocalization difficult, where the presence of nitro and/or chloro groups inhibits delocalization sterically. In other words, the electrical conductivity of the various substituents in ligands depends mainly on their degree of conjugation. On the other hand, the conductivity of complexes follows the order  $\kappa(\text{Co}^{2+}) < \kappa(\text{Cu}^{2+}) < \kappa(\text{UO}_2^{2+})$ . This trend depends heavily on the increasing stability of the complexes formed, which increases the number of dislocated electrons.

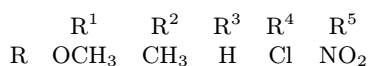
In such conduction mechanism, the apparent activation energies values were obtained from the slope of the Arrhenius plots. The observed conductivities and activation energies can be related to the structures of the complexes as shown in Table 1. For example, in case of R<sup>3</sup>, R<sup>1</sup>, and R<sup>2</sup>,  $\Delta E$  decreases with increasing temperature because the kinetic energy of material chains is sufficiently high to overcome intermolecular association and thus facilitate internal rotation and chain flexibility. In case of R<sup>5</sup> and R<sup>4</sup>,  $\Delta E$  increases with increasing temperature because of the change of conduction mechanism. In the low temperature region the conduction has been attributed to process like electron hopping. In the high temperature region the conduction has been attributed to the breaking of formation of chains. In general, the electrical conduction of a solid organic compound takes place through the movement of charge carriers from one molecule to the other, *i.e.* the conduction takes place through the overlapping of molecular orbitals of neighbouring molecules. Thus, it is expected that the conductance is proportional to the degree of conjugation and coplanarity of substituents. In other words, the conductivities of the halogeno complexes could be compared with each other and with those of their ligands. It is apparent that as the electronegativity increases, the activation energy decreases. For the cobalt and copper complexes of such series of ligands, a remarkable effect was observed. For the same stoichiometry, for any complex in series, as the atomic number increases the activation energy decreases. This indicates that the presence of holes in the system has a little effect on the mobility of charges.

## EXPERIMENTAL

The compounds used in the present study and also their complexes with  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{UO}_2^{2+}$  were prepared and characterized according to Refs. [1–6].



5-(4-R-phenylazo)-3-phenyl-2-thioxothiazolidin-4-one ( $\text{R}^1$ )



Conduction measurements were carried out using YSI model 32X conductivity meter. All measurements were performed at room temperature ( $(25 \pm 0.5)^\circ\text{C}$ ).

The D.C. electrical conduction of the samples was obtained by measuring the resistance of the samples with a type 617 programmable electrometer (Keithly), using the constant current method or V/I method. Such an arrangement can be used for a resistance as low as  $0.1\text{ k}\Omega$  and as high as  $200\text{ G}\Omega$  with the accuracy  $\pm 0.2\%$ . The electrical conduction of the samples was determined using compressed pellets, 14 mm in diameter and 1 mm thick, prepared with the pressure of  $10^7\text{ Pa}$ . The pellet was covered on both sides with a thin layer of a silver paint for conductivity and was mounted between nickel electrodes in a holder. The holder was suspended in a glass jacket, basically similar as described by Jacobs [13]. The cell with the sample was connected to a high vacuum line and outgassed for 24 h to ensure a complete removal of water. The temperature of the sample was measured with the accuracy  $\pm 1^\circ\text{C}$  with a calibrated Ni-NiCr thermocouple inserted inside the cell. The electrical conductivity  $\sigma$  was dependent on the direction of temperature change. The values of activation energies  $\Delta E$  were calculated from the experimental data of conductance by computer least squares fitting to the equation

$$\sigma = \sigma_0 e^{-\Delta E/kT}$$

where  $\Delta E$  is the activation energy,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature.  $\sigma_0$  is the conductivity as defined by  $\sigma_0 = \sigma_{T \rightarrow \infty}$ .

## CONCLUSION

The electrical conductivity of the 5-(4-R-phenylazo)-3-phenyl-2-thioxothiazolidin-4-one compounds and their complexes with  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{UO}_2^{2+}$  is thermally activated depending on the nature of the complexes. For the cobalt and  $\text{UO}_2^{2+}$  complexes of such series characterized, in the low temperature region between 308 and 343 K, the D.C. electrical conductivities are higher than that of the free ligand. On the other hand, in the high temperature region between 343 and 493 K, the D.C. electrical conductivities are lower than those of the free ligands. For the copper complex of such series over the same regions the D.C. electrical conductivity is higher than that of the pure ligand for both low and high temperature regions. The conductivity of complexes follows the order  $\kappa(\text{Co}^{2+}) < \kappa(\text{Cu}^{2+}) < \kappa(\text{UO}_2^{2+})$ . This trend depends heavily on the increasing stability of the complexes formed, which increases the number of dislocated electrons.

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