Electrical Behaviour of Some Phthalimide Derivatives and Their Complexes with Transition Metals

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The electrical conductivity of some phthalimide derivatives and their complexes with Co(II), Ni(II), Cu(II), or Zn(II) has been measured in the temperature range 290-435 K. Both the structure of phthalimide molecule and its complexes played an effective role in the conduction process. Conductometric titration and IR spectra were used to characterize the structure of studied samples.

Introduction

The electrical conductivity of several organic compounds is commonly attributed to the presence of closed rings with alternating double and single bonds (delocalized electrons).[1-3] It is increased with increasing the degree of conjugation. At the same time, it is concerned with the charge transfer in the bulk sample, *i.e.*, from a molecule to another molecule and not just around the closed rings. On the other hand, it is found also that the coordination of organic compounds with different transition metals played an important role in the conduction process. Increasing in the conductivity values was observed owing to the inclusion of metal ions into the Π electron delocalization of the organic compound.[1,4] Reduction in the conductivity values of organic compounds was also observed which attributed to the localized bond between metal and organic compound.[2,5]

In view of the above discussion, the present work aims to show the effect of some different organic substituents as well as the complexation with transition metals, such as Co (II), Ni(II), Cu(II) or Zn(II), on the electrical behaviour of phthalimide. Various complexes of phthalimides with nickel,[6] titanium and tin[7] as well as chromium, molybdenum and tungsten[8] were prepared. These complexes were characterized on the basis of spectrometrical and magnetic measurements. Effect of temperature on the stability of phthalimides was studied.[9] N-(n-propyl and n-butyl) phthalimides were found to be thermally stable at about 360°C whereas N-benzyl-phthalimide decomposes smoothly at this temperature.
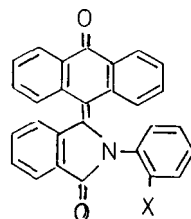
Experimental

All chemicals used in the present work were of the highest
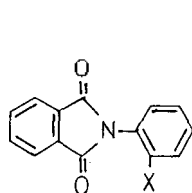
Table 1. Elemental analysis of some phthalimides

Compound	Elemental	% Calcd.	% Found
Compound I	C	70.29	70.34
($C_{14}H_9NO_3$)	H	3.79	3.75
	N	5.86	5.81
Compound II	C	80.95	80.99
($C_{28}H_{17}NO_3$)	H	4.12	4.14
	N	3.37	3.40
Compound III	C	81.10	81.12
($C_{29}H_{19}NO_3$)	H	4.46	4.41
	N	3.26	3.23
Compound IV	C	78.55	78.56
($C_{29}H_{17}NO_4$)	H	3.86	3.83
	N	3.16	3.08
Compound V	C	67.42	67.45
($C_{15}H_9NO_4$)	H	3.39	3.32
	N	5.24	5.20

available purity. 10-phthalyl-9-anthrone was prepared as described previously.[10,11] The product was condensed with the corresponding aromatic amine to N-arylphthalimie anthrone.[12] N-(1') carboxylic phenylphthalimide was also prepared. The elemental analysis is given in Table 1. The phthalimides prepared have the following structures:

The solid metal complexes were prepared by refluxing an ethanolic solution of the ligand (comp. V is taken as a representative sample) and an aqueous solution of Co(II), Ni(II), Cu(II) or Zn(II), in molar ratio 1 : 1, for two hours. The prepared complexes were filtered off, washed with ethanol, then dried *in vacuo*.

To determine the number of crystallized water molecules in the solid, a certain amount of the complex was heated in an oven at 120 °C for five hours. No change in the weight of sample was observed suggesting that the phthalimide complexes are anhydrous.

Complex formation of phthalimide is a precipitation reaction. To determine the stoichiometric ratios of complexes, the conductometric titration method was used. In order to reduce the influence of error due to slow separation of the precipitate with consequent supersaturation of the solution, to removal of titrated solute by adsorption on the precipitate, a dilute solutions in the presence of ethanol were recomme-
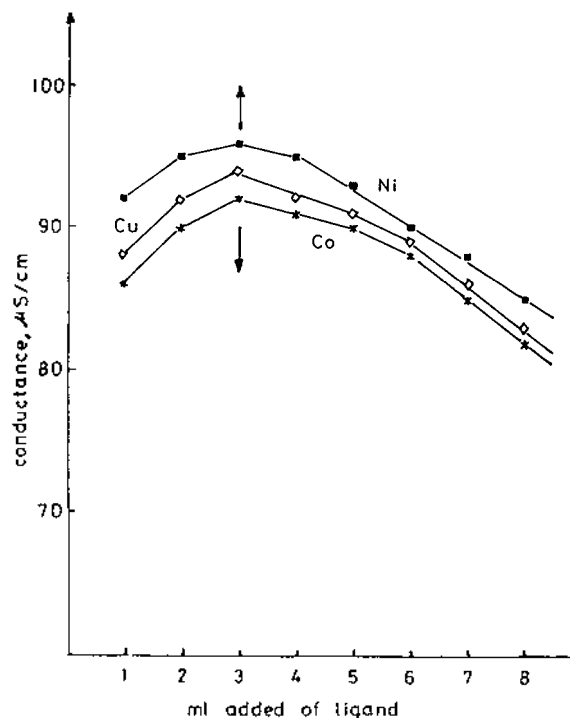

(A)

comp. I : X = OH
comp. V : X = COOH

(B)

comp. II : X = OH
comp. III : X = OCH₃
comp. IV : X = COOH

Figure 1. Conductograms of N-phenylphthalimide with different transition metal cations.

Figure 2. Infrared spectra of N-phenylphthalimide and its metal complexes.

nded.[13] The addition of ethanol causes a reduction of the solubility of the precipitate and there is also less adsorption. 30 mL of 10^{-3} M metal ion solution was titrated against 10^{-2} M ethanolic solution of ligand. A digital conductivity meter 5800-05 solution analyzer, Cole Parmer Instrument Co., was used.

The infrared spectra of different solid complexes were recorded on a Shimadzu spectrophotometer model 440 using KBr disc technique.

Conductivity measurements were made on samples prepared in the form of discs having 6.5 mm radius and 0.4-0.6 mm thickness sandwiched between two parallel copper electrodes. The samples were inserted with the holder vertically into a cyclindrical electrical furnace.[14] Two terminal technique was used by aid of HC-3500 T and Thandar TM 353 multimeters.

Results and Discussion

The conductance of a solution at any temperature depends only on the ions present and their concetration. The addition of a solution to other can affect the conductance if a reaction is occurd.[15] Thus, conductometry can be used to locate the end point of a titration.[16] The conductance of the titrand solution (transition metal cations) is measured after each addition of titrant solution (compound V), and the titration curve of conductance as a function of added titrant is ploted at room temperature, as shown in Figure 1. The change observed with added titrant is attributed to the replacement of metal ions ($\Lambda_o = 55$, 53 and 53.6 for Co^{2+}, Ni^{2+} and Cu^{2+}, respectively) by H^+ ($\Lambda_o = 349.8$). Since H^+ contributes more to the conductance of the solution than transition metal ions
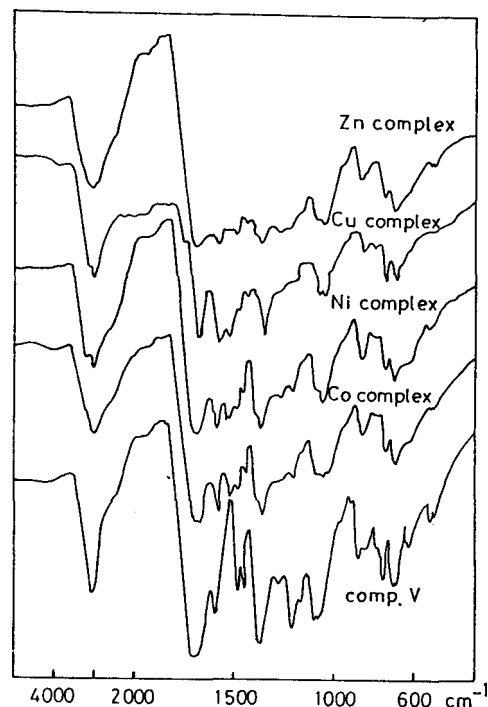
do, the conductance increases with the addition of titrant prior to the end point. After the formation of complex (end point) the conductance no longer increases, since no more H^+ can be evolved. Since the low conducting organic ligand (compound V) is further added after the end point, the conductance decreases. It is clear that the only possible ratio for the formation of phthalimide complexes is 1 : 1.

To identify the particular structure of the complexes under investigation, the infrared spectra of complexes were compared with that of metal free ligand (compound V). The spectra are represented in Figure 2. Although three donor sites on the ligand, namely, the oxygen atom of carboxylic group, nitrogen atom of imide group and the carbonyl group, can be utilized in the complex formation, but the IR results show the following:

a. The IR spectrum of the free ligand shows a sharp and strong band at 3100 cm^{-1} instead of a strong band at 3600-3200 cm^{-1} due to the stretching vibration of OH group. This may be due to the intra-molecular hydrogen bonding between hydroxyl hydrogen and nitrogen of the imide group (staggered form). This is supported by the fact that the characteristic series of bands in the region 3000-2500 cm^{-1} produced by most carboxylic acids[17] were not observed in the spectrum of free ligand. The spectra of complexes show unaltering of the absorption band at 1460 cm^{-1} due to v C-N. The weakening in the intensity of this band after complexation process may be owing to the mass effect of transition metal ions linked to the carbonyl group.

On the other hand, the ligand medium bands observed at 1370-1210 cm^{-1} are ascribed to C-O stretching vibration. These bands were disappeared on complexation suggesting the involvement of carboxylate group in coordination.
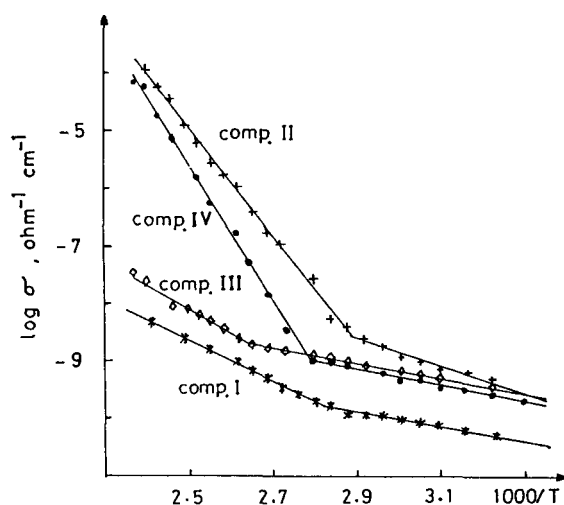
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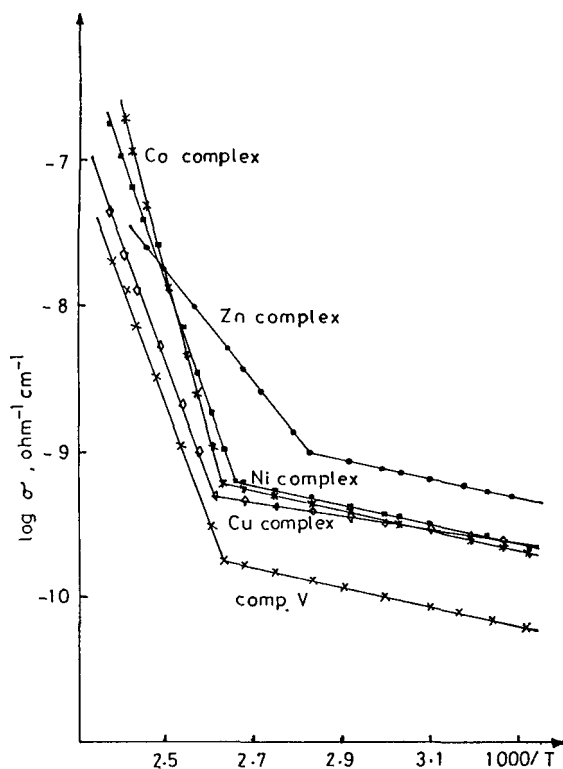**Figure 3.** Electrical conductivity of some phthalimides.

Figure 4. Electrical conductivity of N-phenylphthalimide complexes.

b. A strong and broad band attributed to $\nu\ C=O$ of phthalimide derivative (compound V) was appeared at 1720 cm^{-1}.[18] After the formation of complexes, a blue shift of 30 cm^{-1} was observed suggesting the participation of carbonyl group in the coordination process.

On the basis of the above results, the coordination of phthalimide derivative (compound V) to the central metal atom can be take place through only two donor sites (carbonyl and carboxylate groups), i.e., the ligand is bidentate.

The main electrical property characterizes the solid phthalimide molecule is its electrical conductivity which increases

Table 2. Electrical data of phthalimides at 298 K.

Compound	σ (Ω^{-} cm^{-1})	E (eV)	W (eV)	n (cm^{-3})	μ (cm^{2}V^{-1}s^{-1})
comp. I	3.39×10^{-11}	0.28	0.30	4.52×10^{20}	4.69×10^{-13}
comp. II	2.24×10^{-10}	0.48	0.51	1.86×10^{17}	7.53×10^{-9}
comp. III	2.40×10^{-10}	0.27	0.30	6.67×10^{20}	2.25×10^{-14}
comp. IV	1.58×10^{-10}	0.26	0.29	9.85×10^{20}	1.00×10^{-12}
comp. V	6.03×10^{-11}	0.16	0.18	4.85×10^{22}	7.77×10^{-15}
Co complex	2.04×10^{-10}	0.13	0.15	1.56×10^{23}	8.17×10^{-15}
Ni complex	2.24×10^{-10}	0.12	0.15	2.31×10^{23}	6.06×10^{-15}
Cu complex	2.34×10^{-10}	0.09	0.12	7.43×10^{23}	1.97×10^{-15}
Zn complex	4.68×10^{-10}	0.10	0.12	5.03×10^{23}	5.82×10^{-15}

with rising the temperature according to the relation,

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

E represents an ordering activation energy of the conduction process. Different phthalimides and transition metal complexes investigated were followed over the temperature range 290-435 K. Figures 3 and 4 demonstrate the variation of the logarithmic conductivity values as a function of reciprocal absolute temperature. The electrical data are listed in Table 2.

The observed conductivity values at room temperature of different phthalimide derivatives follow the order:

comp. II>comp. III>comp. IV>comp. V>comp. I

To explain this behaviour, it is known that in the light of resonance theory of conjugated system, compounds of type (A) (comp. I and V) show only one acting conjugated system while those of type (B) (compounds II, III and IV) show two acting conjugated systems. Consequently, the presence of anthracene moeity (type B) increases the aromaticity, i.e., the resonance. This leads to increase the mobility of Π electrons of compounds II, III and IV compared to those of compounds I and V.

On the other hand, in view of the mesomeric and inductive effects of the substituents OH, OCH$_3$ and COOH, it is known that the first two groups are electron donor, whereas the last group is an electron acceptor. Therefore, the presence of OH and OCH$_3$ groups increases the electron density on the conjugated phthalimide leading to increase its electrical conductivity in relative to the presence of COOH group which withdraw the electron cloud from such system.

Figure 4 shows the effect of complexation with different transition metals on the electrical conductivity of N-phenylphthalimide (compound V). The conductivity of the metal free ligand is equal to 6.03×10^{-11} ohm^{-1} cm^{-1}. After complexation, it will increase by about one order of magnitude higher than that of the ligand. The increasing in conductivity follows the order from cobalt to zinc complexes. This increment is attributed to the overlap between the electrons in the antibonding Π-orbitals of σ-donor/Π-donor ligand (N-phenylphthalimide) and the empty d-orbitals of the different transition metal cations used.[19] It leads to delocalization of the Π electronic charge on the phthalimide molecule. Furthermore, the formation of complexes lowers the activation

energy needed for the conduction process explaining the relatively high conductivity of complexes investigated.

A phase transition was observed which attributed to the change in the mechanism of conduction from electronic to ionic, *i.e.*, from band to hopping conduction.[20] In this sense, there is a clear rising in the activation energy value from 0.1-0.4 eV at low temperature to about 2.0 eV at high temperature.

In order to illustrate the mechanism of conduction of N-phenyl-phthalimide and its complexes, the mobility of charge carriers, μ, must be determined using the relation

$$\sigma = n \, e \, \mu$$

where e is the electron charge and n is the charge carrier density. The last term can be calculated from the relation

$$n = 2\left(\frac{2\Pi m^- \, kT}{h^2}\right)^{3/2} e^{-E/kT}$$

where m^+ is taken as the rest mass of an electron. It is clear that all the studied compounds are characterized by very low mobility which is smaller than 10^{-9} cm^2/V.s., in addition to the fact that the mobility increases with temperature.

The conduction in solid organic compounds takes place by the transport of charges from a molecule to other through the overlapping of neighboring molecules. For a broad intermolecular potential barriers, the overlap is poor and the band width is narrow. In this case, the charge carriers can jump from one molecule to the neighboring molecule.[21] With the assumption of jumping or hopping mechanism, the mobility of charge carriers is very low.[22] This model is in a good agreement with the obtained electrical data.

In view of hopping mechanism, the conductivity is a function of temperature and is given as

$$\sigma = \frac{C}{T} \exp(-W/kT)$$

C is a constant and W is the activation energy of hopping conduction. From the difference between W and E, the activation energy of mobility was calculated. It is found in the range of 0.02-0.03 eV.

It is clear that the conductivity of phthalimides depends not only on the formation of metal complexes, but also on their structure as well as the degree of conjugation.

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