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Synthesis and characterization of charge-transfer complex of α-Naphthol and *p*-Chloranil

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ABSTRACT

In recent years, physical properties of charge-transfer (CT) crystals have been extensively investigated. The CT complex of α-naphthol and p-chloranil was grown by solution growth and microwave techniques and its electrical properties were measured. This CT complex behaves as semiconductors at room temperature. The stoichiometric ratio of donor and acceptor in the CT complex was found to be 1: 1.

Key words: CT complex, α-naphthol, p-chloranil, dc electrical conductivity.

INTRODUCTION

Electron transfer or charge transfer (CT) is one of the most important elementary processes in chemistry. Since Mulliken presented the well-known theory [1-2] of the charge-transfer interaction between electron donor and acceptor, it has been successfully and widely applied to many interesting research subjects[3-4]. One of them is the possible role of CT complexes in chemical reactions [5].

Organic charge transfer solids offer a wide range of materials from insulator to superconductors.[6-7] Charge-transfer (CT) complexes of carbazole, N-ethylcarbazole and 1,n-di(N-carbazolyl) alkanes with p-chloranil (p-CHL) have been investigated by Arslan et al[8]. The synthesis of small-molecular organic conductors and nanowires of TTF-TCNQ have been carried out by selective inducement in a two-phase method by π–π stacking interaction [9]. The phonon dispersions of the two quasi-one-dimensional organic conductors, MNEB(TCNQ)2 and TEA(TCNQ)2 was studied by inelastic neutron scattering for phonons propagating in directions associated with the almost one-dimensional conductivity [10]. DC and AC conductivities have been measured for thin films prepared by evaporation of mixtures of tetrathiotetracene and ortho-chloranil [11].

TCNQ (tetracyanoquinodimethane) as π-acceptor has been used with different phenolic donors like p-aminophenol, α-naphthol, 2, 4, 5-trichlorophenol and p-cresol by Chauhan *et al.* [12] Different types of radical ion salts have also been synthesized using TCNQ molecules[13-15], but no attention has been paid to the use of chloranil as π-accepter for the formation of charge transfer complexes. Therefore, the present work was undertaken using p-chloranil as an accepter and α - naphthol as a donor.

EXPERIMENTAL SECTION

Microwave induced synthesis was carried out in a commercially available domestic microwave oven (Kenstar Model No. 26 EGO). The IR absorption spectra of the molecular complex were observed at room temperature by the use of KBr pellets, with a Bruker TENSOR 27 spectrophotometer. The purity of the compound was checked by TLC using silica gel "G" as absorbent and visualization was accomplished by Iodine. Elemental analysis was carried out on Elemetor vario EL III carbo Erba 1108.

Solution Growth Method

In the solution growth method of synthesis [16], the acceptor and donor solution prepared in dry acetonitrile solvent were mixed in 1 : 1, donor: acceptor ratio, in a hot condition. The mixture was allowed to cool slowly in thermocol box filled with insulating material. After a month or even longer, some black crystals with metallic shine were deposited on the walls of the beaker, which were collected after washing with acetonitrile and recrystallised from methanol.

Microwave Method

In the microwave method, the acceptor and donor solution (in dry acetonitrile solvent) were mixed in 1:1, donor: acceptor ratio and irradiated in microwave oven for 60 seconds (in parts of 10 sec.) at power 80 Watt (240 MHz). The reaction mixture was cooled after every 10 seconds for 5-10 minutes and irradiated again under M.W. A beaker of water was placed as a heat sink in the cavity to absorb the excess heat or energy. Then this mixture was kept for evaporation of solvent.

Characterization

Characterization of CT complex crystals was made by analytical techniques such as elemental analysis and spectral analysis (IR, and UV spectra).

Table 1 : Elemental analysis of α-naphthol (p-chloranil) complex

Method of synthesis	C% Found (Calculated)	H% Found (Calculated)	O% Found (Calculated)	Formula	Melting point (^oC)
Solution growth	48.88 (49.23)	1.98 (2.05)	12.10 (12.30)	$C_{16}H_8O_3Cl_4$	>360
Microwave induced method	48.98 (49.23)	1.99 (2.05)	12.8 (12.30)	$C_{16}H_8O_3Cl_4$	>360

Elemental Analysis
The analytical data of the CT complex are listed in Table 1. The theoretical values of the elements in the CT complex has been calculated assuming 1: 1 (donor: acceptor) stoichiometery. It has been observed that the experimental values are in good agreement with the theoretical values.

IR Spectral Study
The IR spectral data of the CT complex are listed below
α-naphthol IR (KBr) cm^{-1} : 3550 (OH str.), 1615,1505,1493 (C=C),2986,2852 (CH_3 str.)and 835 (1,4 disubst.)

p-Chloranil IR (KBr) cm^{-1} : 1685 (C=O) 1605,1510,1473 (C=C) and 745 (C-Cl)

CT complexes IR (KBr) cm^{-1} : 3546 (O-H), 1630.6 (phenyl ring) 2922, 2856 (CH str.), 1675 (C=O) 831.1(1,4 disubtit.) and 732 (C-Cl).

The bands of the donor and acceptor in this complex exhibit small shift in both, the band intensities and wave number values from both of the free molecules. This is normal due to the accepted symmetry and electronic structural changes upon complexation.

^{1}H NMR spectrum
The ^{1}H NMR spectrum of the crystal grown by solution growth method shows a signal for –OH proton at 8.85 ppm. Some doublets due to C_{8H} at 8.05 ppm, C_{5H} at 7.50 ppm C_{1H} at 615 ppm, and C_{3H}, C_{4H}, C_{6H} and C_{7H} at 7.19, 7.33, 7.20 and 7.27 ppm, respectively, as a multiplet were observed.

Electronic spectral study
The electronic absorption spectra of p-chloranil complex contain a charge transfer band (CTB), apart from the absorption bands of donor and acceptor. The appearance of CTB is a characteristics feature of the formation of complex and gives spectroscopic evidence for the formation of a charge transfer complex between α-naphthol and p-chloranil.

The electronic spectra of this complex grown by different methods are quite similar and match satisfactorily with each other. This shows that the similar compounds are formed by different methods used.

On comprising the positions of α-, β- and CT bands in Table 2, it is clear that all the complexes grown by different methods (solution growth and microwave method) of α-naphthol and p-chloranil complex belongs to the category of DA type (Donor- Acceptor type).

Table 2 : Position of α -, β - and charge transfer bands in α -naphthol (p-chloranil) complex

Methods of synthesis	α - Bands (nm)	β -Bands (nm)	CT Bands (CTB) nm
Solution growth	241.0, 239.6	361.4, 364.2, 365.6	362.8
Microwave Method	239.6	277, 240	359.0

Conductivity Measurement

The study of room temperature d. c. electrical conduction behaviour of the charge transfer complex of α-naphthol and p-chloranil was carried out on pellet and the two probe method has been adopted for the conductivity measurements. Keithly's Picoameter, Systronics Twin Power Supply, self made Furnace, Null detector Micro Voltmeter, KTC thermometer and variac, are used as measuring instruments.

The charge transfer complex of α-naphthol and p-chloranil crystals grown by solution growth and microwave methods were used as samples for the present investigation.

- **Solution growth method**

The room temperature conductivity of the α-naphthol (p-chloranil) CT complex pellet observed by two probe method was found be σ_{RT} = 0.0542 x 10^{-6} S cm^{-1} (30^oC). The d.c. electrical conductivity of the α-naphthol (p-chloranil) initially increases with increasing temperature from 303 to 333 K (semiconducting behaviour), then decreases with increasing temperature from 333 to 348 K, (metallic behaviour).

The experimental data of conductivity measurement of α-naphthol (p-choranil) are given in Table (3). These data are graphically represented in figure 1 (as σ v/s T curves) and figure 2 ($\log_{10}$ ρ v/s 1000/T curves).

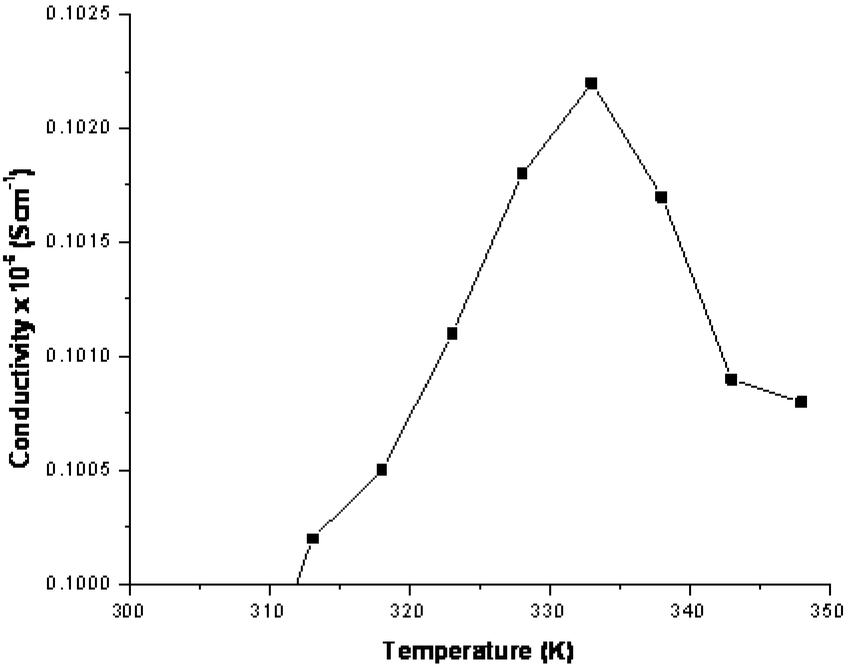

Fig. 1 : Temperature v/s Conductivity

- **Microwave method**

The room temperature conductivity of the α-naphthol (p-chloranil) CT complex grown by microwave method pellet observed by two probe method was found be σ_{RT} = 0.0250 x 10^{-6} S cm^{-1} (30^oC). The d.c. electrical conductivity of the α-naphthol (p-chloranil) initially increases with increasing temperature from 303 to 333 K (semiconducting behaviour), then decreases with increasing temperature from 333 to 338 K, (metallic behaviour) and finally increases with increasing temperature from 343 to 348 K (semiconducting behaviour)

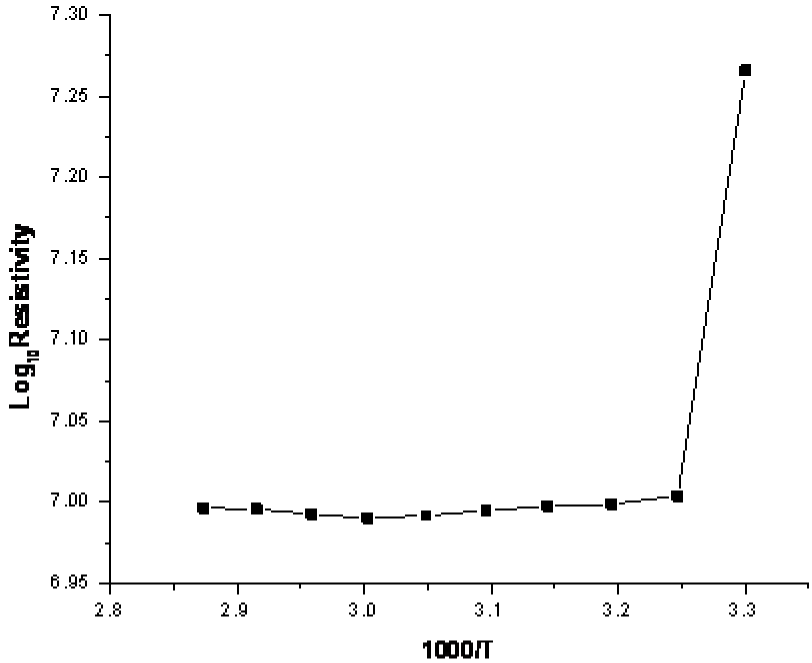

Fig. 2 : 1000/T v/s $\log_{10}$ Resistivity

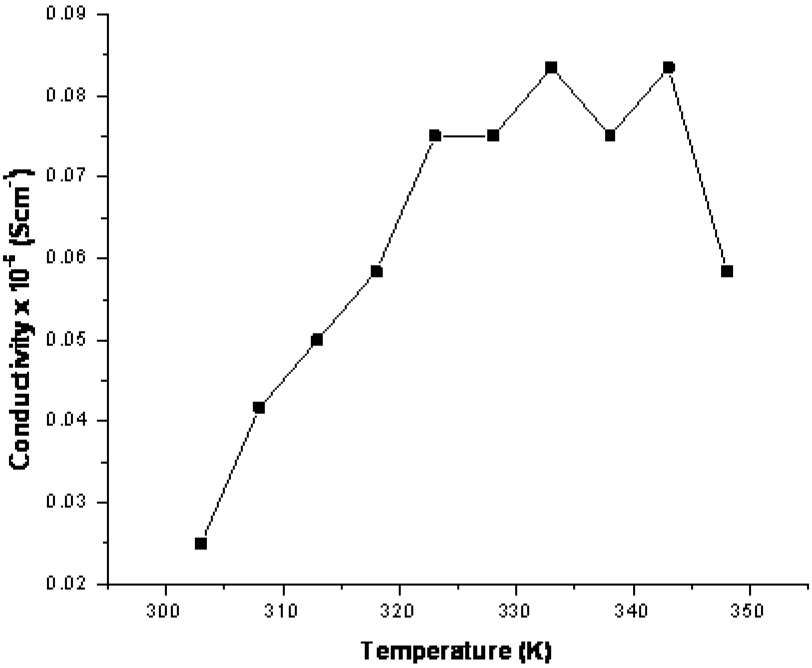

Fig. 3 : Temperature v/s Conductivity

The experimental data of conductivity measurement of α-naphthol (p-choranil) are given in Table (4). These data are graphically represented in figure 3 (as σ v/s T curves) and figure 4 ($\log_{10}$ ρ v/s 1000/T curves).

Table 3 : Room temperature study of α-naphthol: p-chloranil (Solution growth method) Pellet parameters

Room Temperature = 303 K *Voltage = 6.0 volts*
Radius = 0.4535 cm *Variac = 100 volts*
Thickness = 0.647 cm *Pressure = 550 kgf/cm^2*

Temp	Current x 10^6	Resistivity (ρ)(Ωcm) x 10^{-6}	Conductivity(σ) (Scm^{-1}) x 10^6	Log_{10} ρ	1000/T
303	0.0542	18.445	0.0542	7.2658	3.30033
308	0.0993	10.07	0.0993	7.0039	3.24675
313	0.1002	9.9756	0.1002	6.9989	3.19489
318	0.1005	9.9457	0.1005	6.9976	3.14465
323	0.1011	9.8866	0.1011	6.995	3.09598
328	0.1018	9.8153	0.1018	6.9919	3.04878
333	0.1022	9.7801	0.1022	6.9903	3.003
338	0.1017	9.8315	0.1017	6.9926	2.95858
343	0.1009	9.9063	0.1009	6.9959	2.91545
348	0.1008	9.9178	0.1008	6.9964	2.87356

Table 4 : Room temperature study of α-naphthol: p-chloranil (Microwave method) Pellet parameters

Room Temperature = 303 K *Voltage = 6.0 Volt*
Radius = 0.4535 cm *Variac = 100 Volt*
Thickness = 0.647 cm *Pressure = 550 kgf/cm^2*

Temp	Current x 10^6	Resistivity (ρ)(Ωcm) x 10^{-6}	Conductivity(σ) (Scm^{-1}) x 10^6	Log_{10} ρ	1000/T
303	0.15	39.9160	0.0250	7.6011	3.30033
308	0.25	23.9490	0.0417	7.37929	3.24675
313	0.30	19.9580	0.0500	7.30012	3.19489
318	0.35	17.1068	0.0584	7.23317	3.14465
323	0.45	13.3053	0.0751	7.12402	3.09598
328	0.45	13.3053	0.0751	7.12402	3.04878
333	0.50	11.9748	0.0835	7.07827	3.003
338	0.45	13.3053	0.0751	7.12402	2.95858
343	0.50	11.9748	0.0835	7.07827	2.91545
348	0.35	17.1068	0.0584	7.23317	2.87356

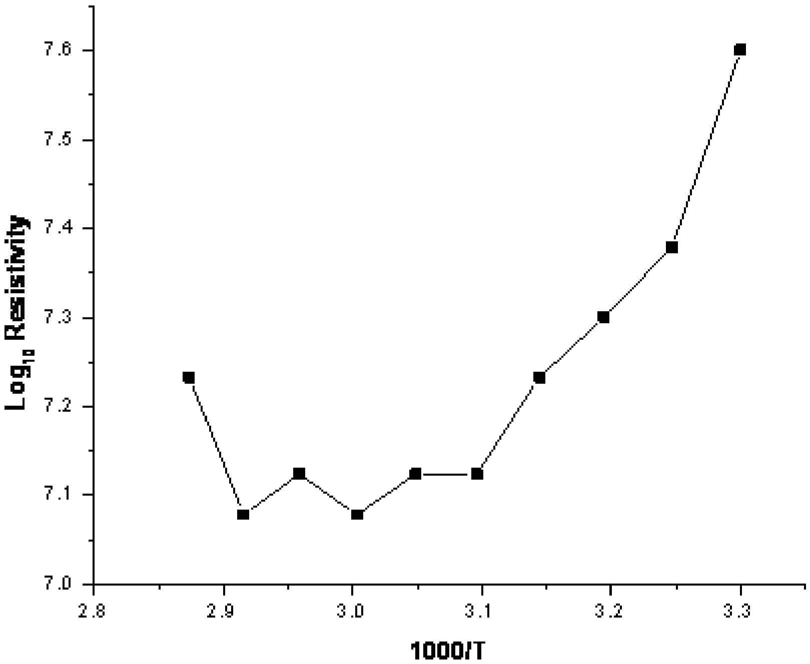

Fig. 4 : 1000/T v/s log_{10} Resistivity

CONCLUSION

On the basis of the results obtained by elemental and spectral analysis in both cases M.W. and solution growth method, it is concluded that a charge transfer complex of DA (donor-acceptor type) is formed with 1: 1 stoichiometry.

The conductivity studies of α-naphthol (p-chloranil) complex indicates that it behave as semiconductors i.e. the conductivity increases with increase in temperature, but on further increasing temperature conductivity decreases thus, the CT complex was found to shows as metallic behaviour.

When the temperature dependent conductivity measurements are performed on the pellet, some small cracks may be developed inside the crystals due to the variation of temperature and current. This may cause small jumps in conductivity, which is observed at certain temperature ranges.

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REFERENCES

[1] M Dakiky; I Nemcova; *Dyes Pigments*, **2000**, 44,181
[2] RS Mulliken; *J. Amer. Chem. Soc.*, **1952**,74, 811.
[3] RS Mulliken; *J. Phys. Chem.*, **1952** ,56, 801.
[4] G Breigreb; Electron - Donor - Acceptor – Complex, Springer- Verlag, Berlin, **1961**.
[5] LJ Andrews; RM Keefer; Molecular Complexes in Organic Chemistry, Holden-Day, Inc., San Francisco, **1964**.
[6] EM Kosower; *Progr. Phys. Org. Chem.*, **1965** 3, 81.
[7] RC Haddon; ML Kaplan; F Wudl; Encyclopedia of Semiconductor Technology (ed.) Wiley Interscience, New York, **1984**.
[8] MR Bryce*; Chem. Soc. Rev.*, **1991 ,** 20, 355.
[9] M Arslan; J Masnovi; R Krafcik; *Spectrochim. Acta Part* A: Molecul. and Biomol. Spectrosc., **2007** ,4, 1063.
[10] H Liu; J Li; C Lao; C Huang; Y Li; L Wang; D Zhu; *Nanotechn.*, **2007**, 18, 495704.
[11] JS Pedersen; KM Carneiro; JS Almeida; J. Phys. C: *Solid State Phys*., **1987**, 20, 1781.
[12] M Samoc; C Gilbert; JB. Webb; DF Williams; *J. Phys. C: Solid State Phys*.,**1980** , 13, 4419.
[13] N Chouhan; ML Kalra; S Kumar; YN Singh; SC Ameta; *Mol. Cryst. Liq. Cryst*.,**2007**, 469, 99.
[14] YN Singh; DP Goswami; ML Kalra; *Int. J. Chem. Sci*.,**2005**, 3, 325.
[15] DP Goswami; ML Kalra; *J. Crystal Growth*, **1994**, 135, 196.
[16] YN Singh; DP Goswami; M Bala; ML Kalra; *Pramana J. Phys*., **1992,** 39, 351.
[17] Y Tomkiewicz; RA Craven; TD Schultz; EM Engler; AR Taranko; *Phys. Rev*.B, **1977,** 15, 1011.