

Characterization and Conduction Behaviour in Charge Transfer Materials Based on Ethyl Silicate and Ethyl Dihydrogenborate

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Electrical conductivity of charge transfer materials based on ethyl silicate dimethylsulphoxide with ethyl dihydrogenborate dimethylsulphoxide at various temperatures has been reported. The current voltage curves as a function of time have been obtained to determine the role of ionic conduction in electronic conductors based on charge transfer materials. The apparent activation energies, E_a of the compounds were evaluated. The bulk electrical conductivity of the compound at 1 : 1 molar ratio is found to be in the range of 10^{-4} S cm^{-1} at room temperature. Incorporation of hexakis dimethylsulphoxide-iron(III) perchlorate into the charge transfer material increases conductivity up to 10^{-3} S cm^{-1} range.

Key Words: Conduction, Charge transfer, Ethyl silicate, Ethyl dihydrogenborate.

INTRODUCTION

In recent years the study of semiconductive properties of organic compounds has made much progress. One of the difficulties in the research, the relatively high resistivities of organics as compared with some inorganic semiconductors, might be attributed to the high intermolecular barrier for electronic conduction; forces between the organic molecules are usually of the van der Waals type. Charge transfer (CT) complexes can partially overcome this difficulty. Earlier, Akamatu *et al.*¹ investigated the electrical properties of aromatic hydrocarbon-halogen complexes. Since that time a large number of CT complexes have been prepared for studies of semiconductive properties.

Charge transfer materials usually support electronic conduction. Perylene-bromine complex was the first reported organic conductor exhibiting ionic conduction along with electronic conduction. Mixed conduction in charge transfer materials based on aromatic diamines (benzidine, *o*-toluidine and N,N'-diphenylbenzidine) as electron donor with iodine in different mole ratios has been reported².

In this paper we have reported the synthesis, characterization and conductivity

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studies of molecular complexes, viz., ethyl silicate dimethylsulphoxide (ESD) with ethyl dihydrogenborate dimethylsulphoxide (EBD) and also the charge transfer complexes formed between them. The relative magnitude of ionic to electronic conductivity and activation energy for ESD with EBD showed minimum resistivity at 1 : 1 molar ratio. So, all the experiments are based on this 1 : 1 molar complex. It has been found that the incorporation of hexakis dimethylsulphoxide iron(III) perchlorate, $[\text{Fe}(\text{DMSO})_6][\text{ClO}_4]_3$ (IPD) increases the conductivity of the CT material.

EXPERIMENTAL

Acrylic acid (Merck, AR) was purified according to the procedure adopted by O'Neil³. Commercial grade DMSO (Ranbaxy, AR) was purified⁴ by successive drying over Linde 4 Å molecular sieve and barium oxide, then finally by distillation under pressure. Silicic acid (Ranbaxy), hydrogen peroxide 30% v/v and boric acid (Ranbaxy) were of analytical grade and used without further purification. Ethanol, ether, ferric chloride, ammonia and perchloric acid (Ranbaxy) and calcium chloride were also of analytical grade and used without purification.

Preparation of ESD, EBD and IPD: Acrylic acid (0.10 mol) and silicic acid (0.12 mol) were mixed with 100 mL DMSO in a 500 mL beaker. The mixture was heated at 50°C for about 1/2 h, cooled to room temperature and then treated with 30% H_2O_2 (v/v) slowly for decarboxylation. On freezing the solution, white needle-shaped crystals of ESD were formed. The product was filtered, washed with petroleum ether and then recrystallized several times from acetone and stored over anhydrous calcium chloride.

By following the same procedure EBD were prepared by using boric acid (0.12 mol) in place of silicic acid.

IPD was prepared as reported in the literature⁵.

Preparation of blend of ESD and EBD and blend of ESD, EBD and IPD: ESD (1 mol) and EBD (1 mol) were mixed, ground and then fused together at around 150°C. The blended compound was annealed, powdered and stored over CaCl_2 . In the same way a blend of ESD (1 mol), EBD (1 mol) and IPD (0.15 mol) was prepared.

IR spectra of the compounds were recorded in KBr in 4000–200 cm^{-1} region on a Perkin-Elmer 883 spectrophotometer. ^1H NMR was recorded by dpx 300 spectrophotometer using CDCl_3 as a solvent.

The finely powdered materials were converted into pellets by a hydraulic press (Perkin-Elmer) at a pressure of 8 tons. Graphite paste was used as contact electrode⁶. The conduction was evaluated by the standard Wagner polarization technique⁷. The cell SS | Sample | SS (SS = stainless steel) was polarized by a step potential (about 1.0 V) and the resulting potentiostatic current was monitored as a function of time. The t_{ion} was evaluated from the formula

$$t_{\text{ion}} = (i_{\text{T}} - i_{\text{e}}) / i_{\text{T}}, \quad (1)$$

where i_{T} and i_{e} are total and residual current respectively. The impedance (Z) and the phase angle (θ) were measured using HIOKI 3522 LCR HiTESTER in the

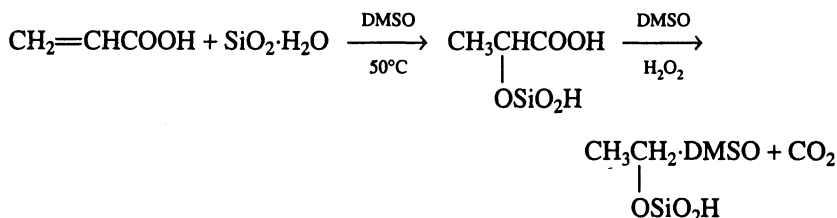
frequency range 1 Hz to 100 kHz, keeping the signal amplitude of 20 mV throughout the experiment at various temperatures ranging from room temperature to 90°C. Electrical conductivities of the compounds were calculated from the value of bulk resistance (R_b) which is defined as the real axis intercept of the impedance plot, from the relation

$$\sigma = t/R_b \cdot A \quad (2)$$

where σ is the electrical conductivity ($S\text{ cm}^{-1}$), t is thickness and A denotes the area of the sample.

RESULTS AND DISCUSSION

Characterization of ESD: The formation of white ESD product was accompanied by vigorous evolution of gases. The gas was identified to be CO_2 by analytical and IR method. The following reaction may take place between $\text{SiO}_2\text{-H}_2\text{O}$, acrylic acid and DMSO for the production of ESD.



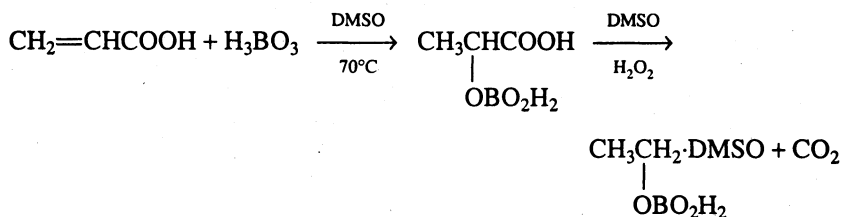
The molecular weight of the compound measured by depression of freezing point method, with benzene as solvent, was found to be 184.2. The compound has sharp melting point at 120°C. By microanalysis, elements present in ESD were found

Calculated: C = 26.09, H = 6.51, S = 17.42%.

Found: C = 26.01, H = 6.43, S = 17.39%.

The characteristic IR bands (cm^{-1}) for ESD (Fig. 1a) appeared at 1120, 3430 due to SiO, SiOH vibration mode respectively⁸. The band at 938 may relate to S=O stretching vibration, indicates presence of DMSO molecule. The bands at 1400 and 420 appeared due to DMSO molecule. In case of ^1H NMR spectrum for ESD the signals observed at 2.6–2.8 and 4.5–4.8 ppm were due to $-\text{CH}_3$ and $-\text{CH}_2\text{O}$ protons respectively (Fig. 2a). A signal at 3.1 was due to DMSO protons.

Characterization of EBD: The following reactions might have taken place between acrylic acid and boric acid to produce EBD.



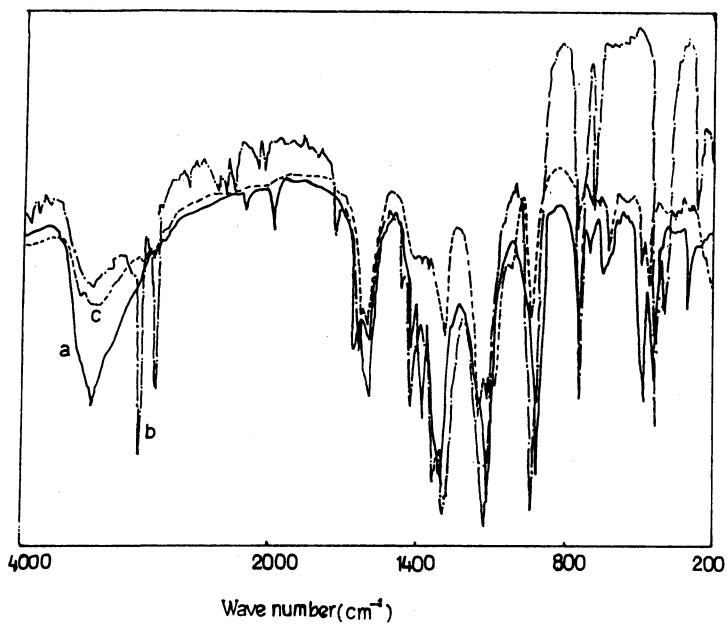


Fig. 1. IR spectrum of (a) ESD (b) EBD (c) ESD/EBD

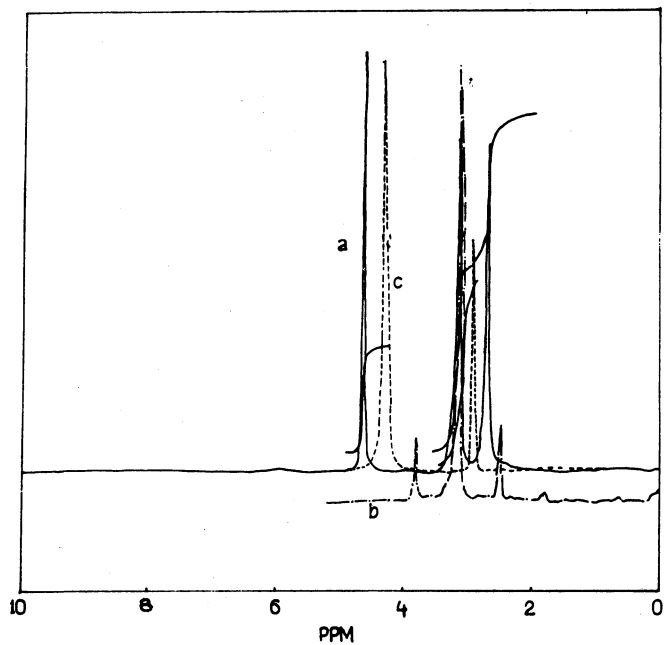


Fig. 2. ¹H-NMR spectrum of (a) ESD (b) EBD (c) ESD/EBD

The molecular weight of the compound measured by depression of freezing point method with benzene as solvent, was found to be 167. The melting point was found to be 106°C. By microanalysis, elements present in EBD were found.

Calculated: C = 28.04, H = 7.78, S = 19.16%.

Found: C = 28.65, H = 7.73, S = 19.04%.

The characteristic IR band for EBD (Fig. 1b) appeared at 1440 and 810 cm^{-1} were due to B—O stretching vibration and bending vibration respectively⁹. The band appeared at 1000–950 cm^{-1} was due to S=O stretching frequency of DMSO molecule. In the ^1H NMR spectra of EBD the signals observed at 1.8–2.3 ppm and 3.8–3.9 ppm were due to CH_3 and CH_2O protons respectively (Fig. 2b). The signal at 3.1 ppm was due to DMSO proton.

Characterization of the charge transfer material: From the IR spectra of ESD/EBD (Fig. 1c) it was observed that the B—O band of EBD at 1400 and 810 cm^{-1} were absent, while Si—O band of ESD shifted from 1120 to 1150 cm^{-1} . From ^1H NMR spectrum (Fig. 2c) it was found that the peak at 4.6 ppm for CH_2 of ESD and EBD disappeared. The DMSO protons shifted from 3.1 to 4.3 ppm and CH_3 protons shifted from 2.6–2.8 to 2.8–3.0 ppm. These results indicate that a proton may be liberated from EBD of the CT complex producing EBD/ESD anion. This is supported by reduction of peak height at 4.6 ppm.

The ac impedance studies on different systems as a function of temperature have been made. Log of conductivity as a function of temperature for ESD, EBD, ESD/EBD and ESD/EBD/IPD are plotted in Fig. 3. It was observed that the formation of charge transfer material increased the ionic conductivity up to

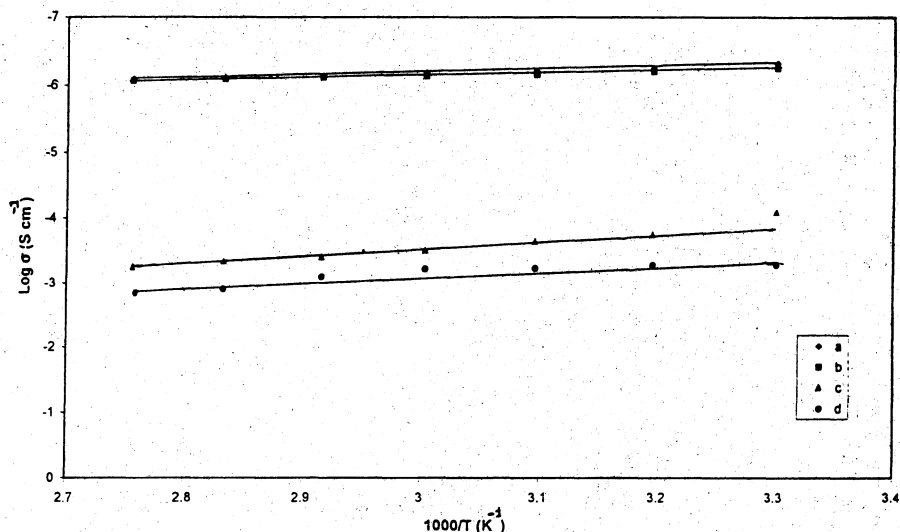


Fig. 3. Plot of log conductivity as a function of temperature

100-fold (Table-1). Higher value was obtained when Fe^{3+} was incorporated. Activation energies of such compounds were calculated in accordance with the Arrhenius expression

$$\sigma = \sigma_0 e^{-E_a/kT} \quad (2)$$

where σ is the conductivity, σ_0 is a pre-exponential factor, k is the Boltzmann constant, T is the absolute temperature and E_a is the apparent activation energy. The activation energies found for the compounds ESD, EBD, ESD/EBD and ESD/EBD/IPD were 0.0520, 0.0312, 0.3900 and 0.0650 eV respectively. A little bit of higher values for the ESD/EBD were observed in comparison with other three compounds.

TABLE-1
TEMPERATURE DEPENDENCE OF CONDUCTIVITY OF
ESD, EBD, IPD, ESD/EBD AND ESD/EBD/IPD

Temperature (°C)	Conductivity (S cm^{-1})			
	ESD	EBD	ESD/EBD	ESD/EBD/IPD
30	4.74×10^{-7}	5.63×10^{-7}	8.20×10^{-5}	5.20×10^{-4}
40	5.69×10^{-7}	6.24×10^{-7}	1.80×10^{-4}	5.25×10^{-4}
50	6.11×10^{-7}	6.97×10^{-7}	2.25×10^{-4}	5.80×10^{-4}
60	6.54×10^{-7}	7.26×10^{-7}	3.05×10^{-4}	5.98×10^{-4}
70	7.19×10^{-7}	7.61×10^{-7}	3.80×10^{-4}	7.91×10^{-3}
80	7.73×10^{-7}	8.05×10^{-7}	4.50×10^{-4}	1.24×10^{-3}
90	8.04×10^{-7}	8.64×10^{-7}	7.04×10^{-4}	3.56×10^{-3}

The relative magnitude of ionic conductivity to electrical conductivity was determined from Fig. 4. The ionic transport number was found to be 0.97 for ESD/EBD and 0.40 for ESD/EBD/IPD. Therefore the major mechanism of conduction in ESD/EBD was ionic. Obviously electron transfer from Si to B takes place resulting in the formation of a CT complex in ESD/EBD from which protons may be liberated due to cleavage of the bond between oxygen and hydrogen showing ionic conduction. The relatively large value of activation energy (0.062 eV) may be due to the thermal activation energy for ionic conduction². The blend ESD/EBD/IPD showed more electronic than ionic conduction. In this case the electron transfer process may become more rapid due to the formation of a coordinate complex between Fe^{3+} and CT complex due to $\pi\pi$ - $d\pi$ interaction¹⁰. An extended π bond may be formed between the coordinated ligands in the octahedral complex and Si by interaction of metal d orbital, π orbital of the ligand and the $3p$ orbital of the Si, which facilitates electron transfer.

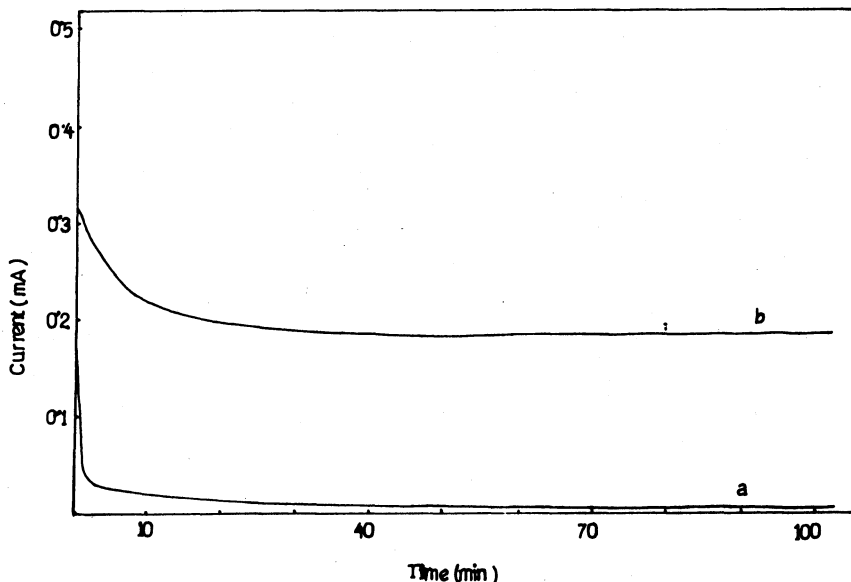


Fig. 4. Current vs. time plot of (a) ESD/EBD and (b) ESD/EBD/IPD

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