



**TRANSFERENCE NUMBER AND ELECTRICAL CONDUCTIVITY
MEASUREMENT OF Fe³⁺ DOPED DIPYRIDINE-POLYVINYL
ACETATE COMPOSITE FILMS.**

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ABSTRACT

Wagner polarization method is a simple and well known method for the transference number measurement of polymer composite films. This paper focuses on the study of transference number (ionic and electronic) conductivity as well as dc electrical conductivity of Fe³⁺ doped dipyridine-polyvinyl acetate (PVAc) composite films synthesized by simple chemical oxidative polymerization method. The values of transference number for the sample synthesized with 10 to 40 wt % FeCl₃ are found to be in the range of 0.5064 to 0.8062. The initial increase in ionic transference number (t_{ion}) with FeCl₃ concentration is due to increase of ion concentration in the composite films, for further increase in FeCl₃ concentration may appear due to decrease in ion mobility. This suggests that the charge transport in Polypyridine-PVAc composite is predominantly due to ions. Also we investigate the effect of temperature on dc electrical conduction in Fe³⁺ doped dipyridine-PVAc composite films in temperature range 308-358 K. The dc electrical conductivity initially increases and reaches to 21.67 x 10⁻¹¹ S/cm for 25 wt % FeCl₃ and then further increase in concentration of oxidizing agent conductivity decreases.

Key words: Composites, Dipyridine, Dc conductivity, Transference number.

INTRODUCTION

Interest in the development of conducting polymers such as polyaniline, polypyrrole, polythiophene, polypyrrodine, etc. has increased during the last decade because of their electrical properties for use in electronic devices. The conductive polymer can be made by filling an insulation polymer matrix with conducting particles such as metal flakes or metalized fibers, by chemical or electrochemical synthesis method to produce intrinsically conductive polymers¹.

Pyridine based polymers have attracted much interest because of their oxidative stability and electron transport properties which make them promising candidates for polymer-based LED applications²⁻⁴.

This paper aims to shed light on some experimental observations of the transference number measurement and temperature dependence of dc conductivity of FeCl₃ doped Dipyrindine-PVAc composite films.

EXPERIMENTAL

Materials

Chemically polymerized Dipyrindine-PVAc composite films were obtained at room temperature by oxidative polymerization by using AR grade FeCl₃ as oxidant and monomer pyridine (E. Merck, Germany) and polyvinyl acetate (PVAc) AR grade (PolyChem Industries, Mumbai).

Preparation of samples

For the preparation of Dipyrindine-PVAc composite films using FeCl₃ as oxidizing agent as well as dopant, a mixed solution of PVAc and methanol (10 : 90) was prepared. In order to make the homogenous solution 1 mole FeCl₃ was added (during this process heat is evolved therefore the process is said to be exothermic) and stirred about 30 minutes. Finally the monomer pyridine was added. Now the homogeneous solution was poured on the chemically cleaned optically plane glass plate to prepared films of the composites. The whole assembly was placed in a dust free chamber maintained at constant temperature. In this manner Dipyrindine-PVAc composite films were prepared by isothermal evaporation technique⁵.

Transference numbers

Wagner polarization method is used for the transference number measurements of the mixed conductors⁶⁻⁷. The change in current has been measured by applying the steady dc potential of 0.1 volt across the silver/graphite electrodes. The conductivity values are obtained from the observed current. The ionic transference number was measured for all prepared films.

Dc conductivity measurements

The thickness of thin films was measured by DIGIMATIC micrometer with least count .001 cm. The dc conductivity σ_{dc} was calculated according to following relation.

$$\sigma_{dc} = \frac{t}{RA} \quad \dots(1)$$

Where, t is the film thickness, A is the sample area and R is the resistance of the film. The measurements were carried out in the temperature range 313-353 K.

RESULTS AND DISCUSSION

Transference numbers

The ionic transference number was measured for all investigated samples. Fig. 1 (a-d) shows variation of current as a function of time. The total current consists of both ionic current (i_{ion}) and electronic current (i_e). The ionic transference number was obtaining by using standard formula⁸.

$$T_{ion} = \frac{i_{ion}}{i} = \frac{i - i_e}{i} \quad \dots(2)$$

From figure 1 it has been observed that at initial time period all samples shows maximum current (i_{total}) and it start decreasing with increase in time and then it gets saturated. This maximum current (i_{total}) at

the initial stage is due to the flow of both electrons and ions. The exponential decrease in current with time may be due to pile up of the ions at the silver electrode (because of its blocking nature) because of the applied dc potential. Hence the saturated current is only due to the flow of electrons. The values of transference number for the sample synthesized with 10 to 40 wt % FeCl₃ are found to be in the range of 0.5064 to 0.8062. The initial increase in ionic transference number (t_{ion}) with FeCl₃ concentration is due to increase of ion concentration in the composite films, for further increase in FeCl₃ concentration may appears due to decrease in ion mobility. This suggests that the charge transport in polypyridine-PVAc composite is predominantly due to ions. The ion mobility depends on segmental motion of polymer chain⁹.

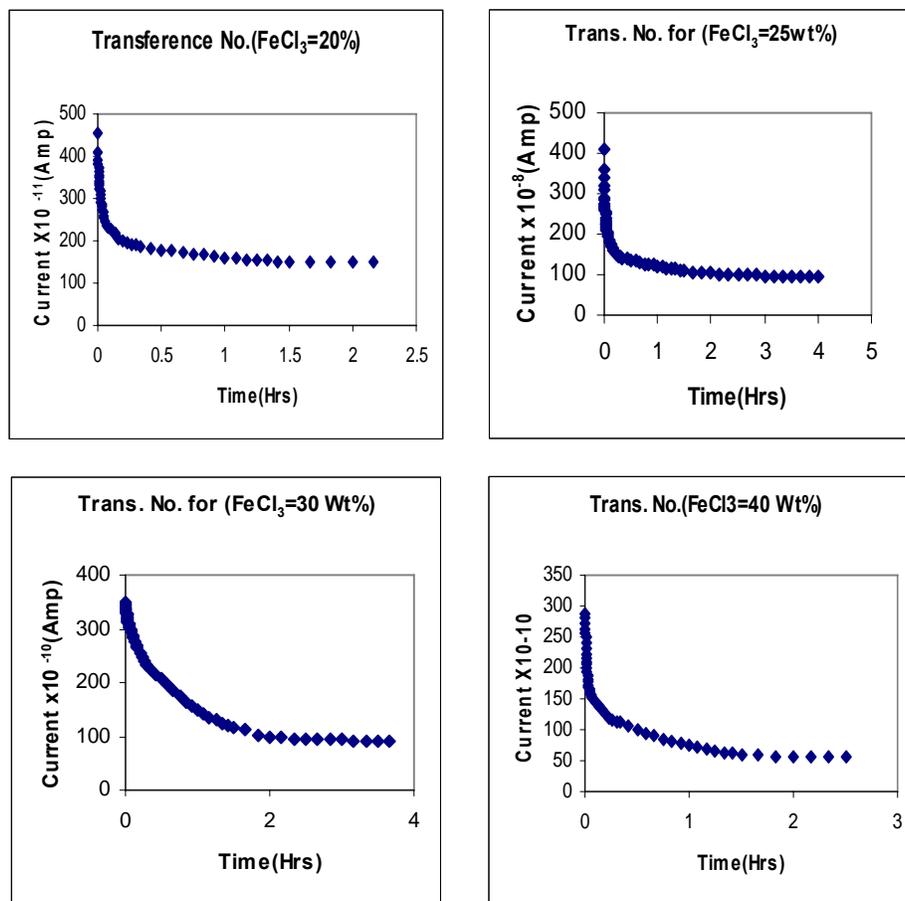


Fig. 1 (a to d): Plots for ionic transference number of dipyrindine-PVAc composite films

Temperature dependence of dc conductivity

Dc electrical conductivity was measured for all dipyrindine-PVAc composite films in the temperature range 313 to 353 K shown in Fig. 2. From plots it is observed that the dc conductivity of all investigated samples depends on temperature. The dc electrical conductivity of these films increases with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the films. As the temperature increases the polymer become soft and the mobility of main chain segment as well as the rotation of side groups become easier. Thus, at higher temperature more and more dipoles are oriented resulting in the higher equivalent surface charge density. Dc conductivity follows Arrhenius equation¹⁰.

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad \dots(2)$$

Where σ_0 is the pre-exponential factor, E_a is activation energy and k the Boltzmann's constant. For the present composite films, these plots ($\log\sigma_{dc}$ Vs $1000/T$) shows straight lines with negative slope indicating the temperature dependence of conductivity. The values of activation energies have been calculated from Arrhenius plots using the equation (2).

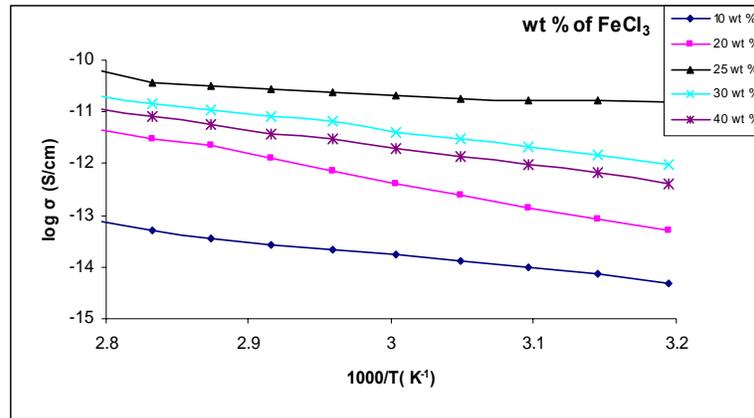


Fig. 2: Temperature dependence of dc electrical conductivity

At any temperature only a fraction of molecules or atoms in the system will have sufficient energy to reach activation energy level of E_a . As the temperature of the system is increased, more molecules or atoms will attain the activation energy level. At high temperature, the activation energy of dipole segmental processes decreases due to disturbance of the cooperative movement of segments. This explains the decrease of activation energy with increase in temperature¹¹. Fig. 3 shows the variation of activation energy with concentration of FeCl_3 . From dc conductivity measurement it is observed that the dc electrical conductivity is maximum for 25 wt. % FeCl_3 .

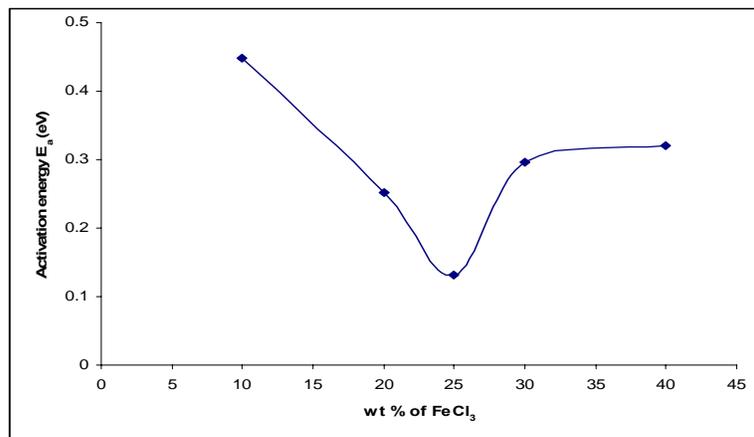


Fig. 3: Variation of activation energy with wt. % of FeCl_3

CONCLUSION

The transference number for the sample synthesized with 10 to 40 wt. % FeCl_3 is found to be in the range of 0.5064 to 0.8062. The initial increase in ionic transference number (t_{ion}) with FeCl_3 concentration is due to increase of ion concentration in the composite films, for further increase in FeCl_3 concentration may appear due to decrease in ion mobility. This suggests that the charge transport in polypyridine-PVAc composite is predominantly due to ions. The dc electrical conductivity of all prepared films is calculated in

the temperature range 313 to 353 K by measuring the resistance of the sample. The dc electrical conductivity of these films increases with increase in temperature, indicating negative temperature coefficient (NTC) of resistance shows the semiconducting nature. As the temperature increases the polymer become soft and the mobility of main chain segment as well as the rotation of side groups become easier. Thus, at higher temperature more and more dipoles are oriented resulting in the higher equivalent surface charge density. The values of activation energies have been calculated from $\log \sigma$ vs $1/T$ plots and found to be in the range 0.131 to 0.448.

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