Influence of Salicylic Acid on DC Conduction Behavior of Ethyl Cellulose and Polyvinyl Chloride Polyblends

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Abstract

The electrical conduction mechanism in salicylic acid doped 1:1 Ethyl Cellulose (EC)-Polyvinyl Chloride (PVC) blends was studied by measuring DC conductivity as a function of temperature (303–373 K) and electric field. Thin films were prepared by solution casting technique. The results were analyzed through I-V characteristics, Schottky plots, Richardson plots, Arrhenius plots, Poole-Frenkel plots, and Fowler-Nordheim plots.

The analyzed data indicate that the observed conductivity is primarily governed by Schottky and Richardson's mechanisms. These involve thermionic emission of charge carriers from the electrode into the polymer matrix, with the barrier height lowered by the applied electric field and temperature. Salicylic acid doping significantly enhances conductivity by increasing charge carrier density and mobility. The blends exhibit semiconducting behavior with thermally activated conduction, making them suitable for organic electronic applications.

Key Words: EC- Ethyl cellulose, PVC-polyvinyl chloride, salicylic acid.

I Introduction :

In recent years, polymer composites and blends have gained significant attention in materials science due to their tunable electrical, mechanical, and dielectric properties. Polymer blending offers an effective route to combine the advantageous characteristics of individual polymers while overcoming their limitations. Polyvinyl chloride (PVC) is a widely used polar polymer with a moderate dielectric constant ($\varepsilon \approx 3$), good mechanical stiffness, high chemical resistance, and excellent compatibility with various additives. It is extensively applied in wire and cable insulation, medical devices, and toys. Ethyl cellulose (EC), a weakly polar, thermally stable, and biocompatible polymer, exhibits outstanding film-forming ability, chemical resistance, and compatibility with plasticizers and other polymers, making it suitable for coatings, thickening agents, and waterproof films.

In recent years polymer composites have steadily gained growing importance [1]. They polymer blends are important to the electronic industry for its dielectric properties in the use of capacitors [2]. Various research groups have undertaken extensive studies of the parameters that govern miscibility and have attempted to gain a good knowledge of the thermodynamics of the mixtures [3-5]. The interaction parameters between the two components affect the physical and mechanical properties of miscible systems it determine the nature and the width interface between two immiscible components.

PVC is a commercially available polymer with good dielectric constant [$\varepsilon = 3$] and is good mechanical stiffener [6, 7]. PVC is polar and is used in cable and wire covers, children toys and medical devices [8]. PVC is widely used due to its high electrical and chemical resistance and ability to be mixed with wide range of physical and chemical properties [9].

EC is weakly polar which has excellent chemical resistance and good mechanical properties. It is thermally stable. EC is used for many applications due to its activeness [10]. EC is already extensively used for films thickening agents [11, 12]. It is compatible with other polymers and plasticizers and can therefore be used to make waterproof films. Many researcher reported the electrical conductivity of PVC and EC [13-15].

Bhagyashree K. *et al.* [16] have studied the solid polymer electro light consisting of poly (vinyl chloride) complexed with $CuSO_4$ have been synthesized by solution casting method. The electrical conductivity was evaluated from ac impedance spectroscopy studies in the temperature range 303-363K and the conductivity was found to increase with increasing temperature. The maximum ionic conductivity value 5.1 x 10^{-4} S/cru has been observed for 5 mol% at 363 K using impedance spectroscopy technique.

Zainab *et al.* [17] have reported the effect of filler Content on DC electrical properties of polyvinylchloride filled with magnesium powders has been investigated. The experimental results showed that the DC conductivity of such composites increases suddenly by several orders of magnitude at a critical weight concentration. The D.C. electrical conductivity changed with increasing of temperature. Also the activation energy change with increasing filler concentration.

In the present work we study DC conduction of salicylic acid doped EC/PVC polyblend, to identify the electrical conduction mechanism.

II Method of Preparation of EC/PCV polyblend

In the present work isothermal evaporation technique[18-21] has been used as it is best suited to the llaboratory conditions. Ethyl cellulose (EC) and polyvinyl chloride (PVC) were blended in a 1:1 weight ratio and dissolved in a common solvent, tetrahydrofuran (THF). Salicylic acid (SA) was incorporated as a dopant at different concentrations (5%, 10%, 15%, 20%, and 25% by weight). The mixture was continuously stirred and allowed to stand for 3–4 days at room temperature to ensure complete dissolution of both polymers and uniform distribution of the dopant, resulting in a homogeneous and viscous solution.

A clean glass plate measuring 15 × 15 cm was used as the substrate. The plate was thoroughly washed with distilled water followed by acetone to remove any contaminants. For achieving uniform thickness and perfect levelling of the films, the glass plate was placed over a pool of mercury contained in a plastic tray. The prepared polymer solution was carefully poured onto the center of the glass substrate and allowed to spread uniformly in all directions. The entire assembly was then kept in a dust-free chamber at ambient temperature to facilitate slow isothermal evaporation of the solvent. After complete evaporation, the dried films were gently peeled off from the glass substrate and cut into small pieces of suitable sizes for further characterization. The films were subsequently dried in a vacuum desiccator for three days to ensure complete removal of any residual solvent traces.

Polyblend films doped with 5%, 10%, 15%, 20%, and 25% salicylic acid were prepared following the same procedure. However, the detailed results and discussion presented in this study correspond primarily to the 25 wt% salicylic acid doped EC/PVC polyblend. The thickness of the prepared films was measured using a digital micrometer screw gauge (Mitutoyo Corporation, Japan, least count 0.001 mm) and was found to be approximately 56 μm. The polyblend films were sandwiched between gold-plated electrodes in a specially designed sample holder to ensure good electrical contact. The DC electrical properties were investigated by measuring the current–voltage (I–V) characteristics using a Keithley 2400 programmable Source Meter at various constant temperatures.

III Results and Discussion

i) I-V characteristics of Polyblends

The current increases nonlinearly with the applied voltage and does not follow power law (1=kVm, where, k and m are constant).

The possibility of ohmic conduction as well as space charge limited conduction is ruled out from the observed behavior of I-V characteristics. The current in the beginning at low values of voltages increases slowly while it increases at a faster rate at higher values of voltages. Fig 3.1 indicates that (i) the current at a constant temperature increases with applied voltage (ii) the current at constant applied voltage, increases with temperature.

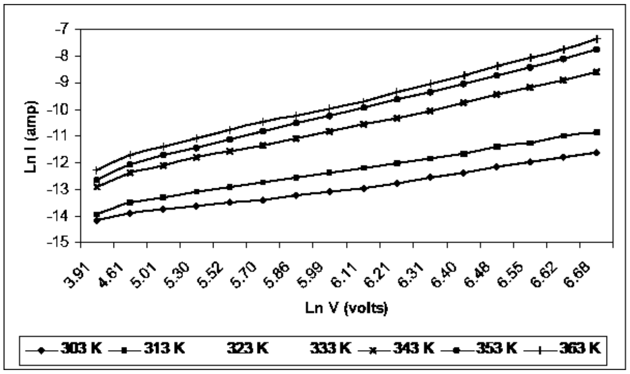

Fig. 3.1 I -V Characteristics of Polyblends

ii) Poole–Frenkel Mechanism

The Poole-Frenkel relation [22] for the current density is given by the eq.3.1,

$$J= B \exp(-\phi/kT+ \beta_{PF} E^{1/2}) \quad \text{.........................(3.1)}$$

Where, $\beta_{PF} = e/ KT (e / \pi\varepsilon_0\varepsilon_r)^{1/2}$ = Constant

and e = electronic charge which predicts a field –dependent conductivity as,

It predicts the field dependent conductivity as eq. 3.2,

$$\sigma = \sigma_0 \ \exp\,[\beta_{PF}\, E^{1/2}/\, 2kT] \ldots\ldots\ldots\ldots (3.2)$$

Which implies as eq. 3.3;

$$\mathrm{Ln}\,\sigma = \mathrm{Ln}\,\sigma_0 + [\beta_{PF}\, E^{1/2}/\, 2kT] \ldots\ldots\ldots\ldots (3.3)$$

So that, the Poole -Frenkel mechanism is characterized by linearity of Logσ $E^{1/2}$ plots with positive slope. In present case 1: 1(EC/PVC) doped with 25% Salicylic acid the log σ Vs $E^{1/2}$plots are linear with negative slope (figure 3.2) indicating the absence of Poole-Frenkel mechanism.

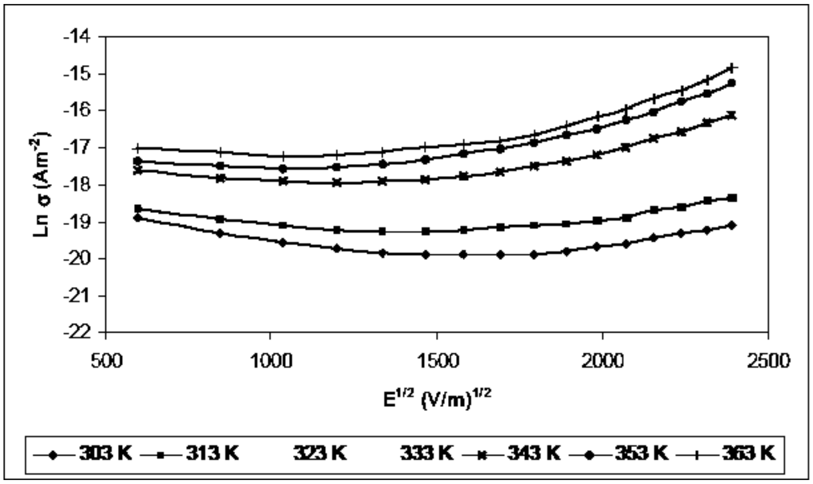

Fig. 3.2 Poole –Frenkel Plot

iii) Fowler– Nordheim Mechanism:

The Fowler -Nordheim Relation [23] for current density J can be expressed by Eq. 3.4

$$\mathrm{Log}\, J/V^2 = \mathrm{Log}\, A - (\phi/V) \ldots\ldots\ldots\ldots (3.4)$$

and the Log J/V^2 vs 1000/v plots are expected to be a linear relation with a negative slope.

In this present case the Log J/V^2 vs 1000/v plots for sample is presented in figure 3.3. Excepting few plots which have strayed away the graph are nearly straight lines with a positive slope indicates the absence of tunnelling current as is suggested by Fowler - Nordheim mechanism.

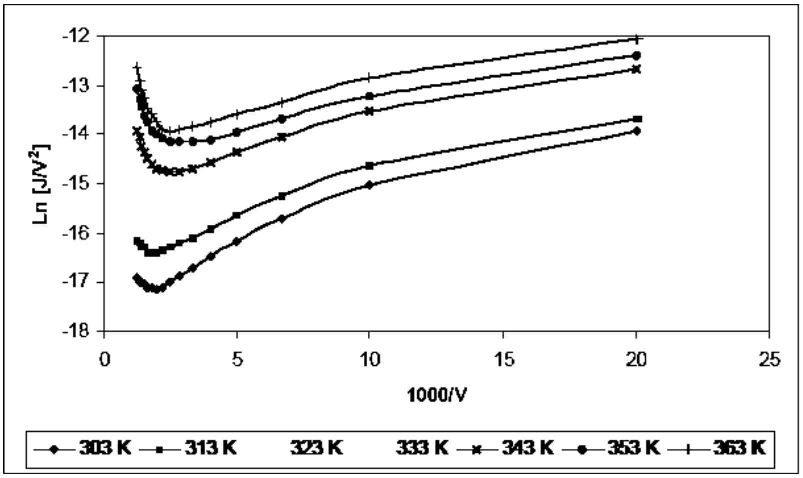

Fig. 3.3 Fowler – Nordheim Plot

iv) Schottky – Richardson Mechanism

The Schottky – Richardson current voltage relationship is expressed by the eq.3.5.,

$$J = A\,T^2 \exp(-x/kT)\exp(\beta V^{1/2})$$

$$\text{or } J = Jo \exp(\beta V^{1/2}) \qquad \text{........................(3.5)}$$

where, Jo = $AT^2\exp(-x/kT)$, is called zero field current density at T K.log J Vs Plot referred to a Schottky Plots should be a straight line with positive slope.

For the present case, Schottky plot are shown in figure 3.4.1 below. The linear positive slope indicates that Schottky -Richardson mechanism is applicable given sample.

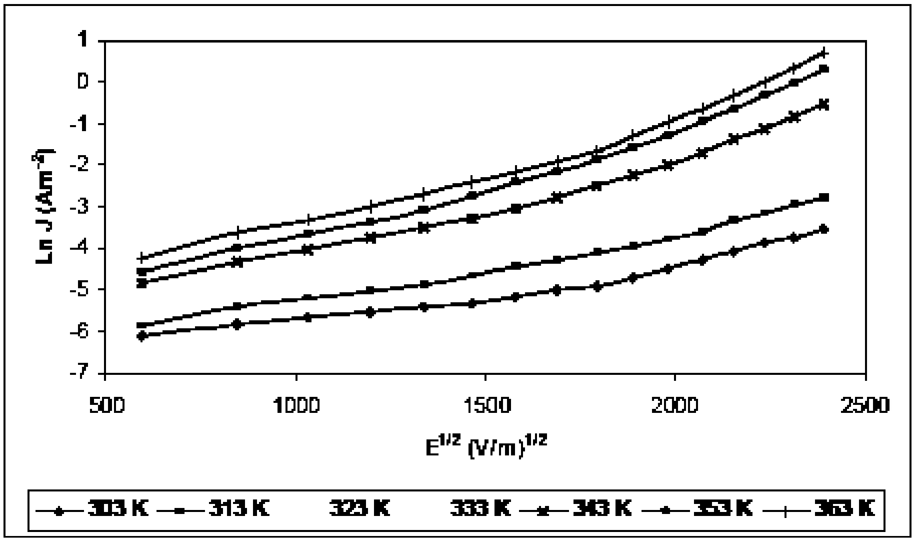

Fig. 3.4.1 Schottky plot

Further, in the case of Schottky – Richardson mechanism the current shows strong temperature dependence but not in case of Poole -Frenkel mechanism. The study of temperature dependence of current density is therefore of great importance.

The temperature dependence of current density is represented plot of ln (J) verses temperature shown in the figure 3.4.2, observed that ln (J) increases almost linearly with change in the temperature. The temperature dependence is great agreement with the Schottky –Richardson Mechanism. Further that the slopes of all the lines are nearly same for all the fields, indicates absence of transition in the temperature range studied.

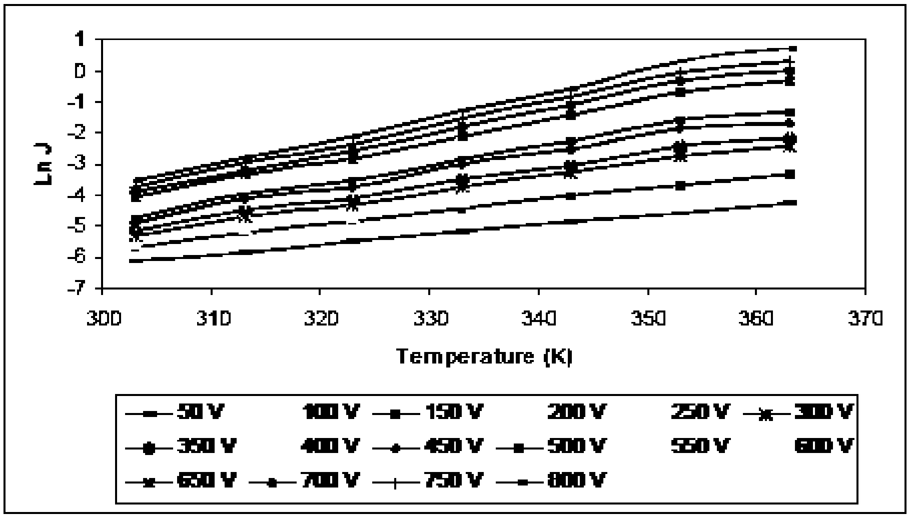

Fig. 3.4.2 Current density log J Vs Temp. Plot

v) Richardson Mechanism :

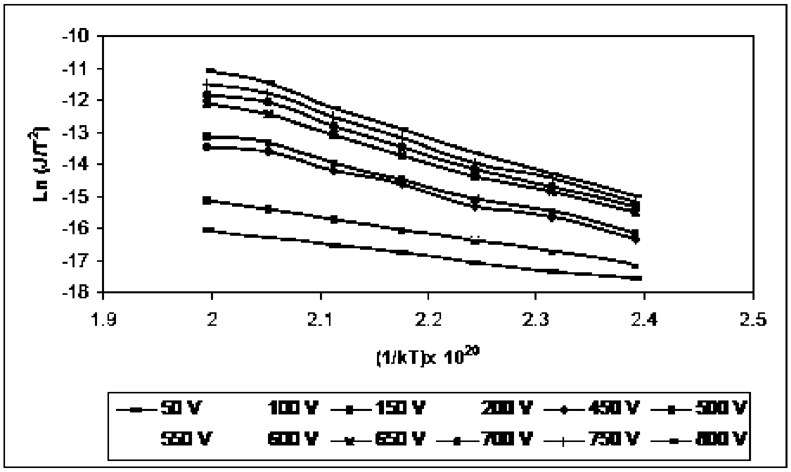

Fig. 3.5 Richardson Plot

The graphs between Ln J/T^2 and 1/kT should be linear with negative slopes.

In our case both of these conditions are satisfied confirming the existence of Richardson Mechanism.

vi) Arrhenius Mechanism

The temperature dependence of conductivity of salicylic acid doped(EC/PVC)thin film was presented in the form of Arrhenius plots the conductivity of polymer is mostly dependent on the temperature. As the temperature increases polymer becomes soft and mobility of the main chain segment as well as the rotation of the side group becomes easier [24]. Thus at higher temperature more & more dipoles are oriented resulting in the higher equivalent surface charge density i,e. as the temperature increases conductivity also increases in accordance with the Arrhenius equation given by relation 3.6.

$$\sigma = \sigma_0 \exp(-Ea/kT) \text{ ....(3.6)}$$

where ,σ_0 - is the pre-exponential factor, Ea- is activation energy and K- Boltzmann constant.

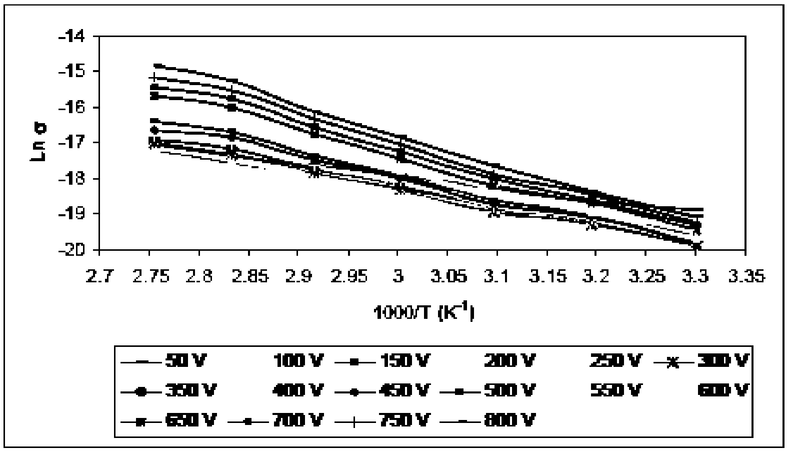

Fig.3.6 Arrhenius Plot

The logσ versus 1/f plots (Fig.3.6) at all values of applied voltages show parallel straight line with a negative slope. From the slope of straight line, the activation energy is calculated and is found to be in the neighborhood of 0.46eV for LTR and 0.54eVfor HTR. This is in good agreement with their ported order of magnitudes [25].

IV Conclusions

From the above discussion, we can draw following inference.

i) At higher field and temperature, Schottky and researcher mechanism are primarily responsible for the observed conduction. Due to the formation of charge transfer complex, there exist a link between the dopant molecules and polymer molecules in amorphous region.

ii) The applied field seems to be insufficient to liberate electrons from the trapping centers (dopant molecules) showing absence of the Poole–Frenkel mechanism.

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