CHAPTER IX

CORRELATION OF DIFFERENT STUDIES
The present work was undertaken to understand the mechanisms taking place in electrical conduction and polarization of pure and DPh doped CA films. Since polarization and electrical conduction are caused by the motion in space of the electrically charged particles of a dielectric, there is a certain affinity between these two phenomena. It will be useful to find some typical differences between these phenomena.

During polarization the charges linked with the definite molecules of matter are brought into motion. These charges cannot leave the confines of a given molecule whereas electrical conduction is caused by the motion (drift) of free charges (carriers) which can move in matter over comparatively large distances and, in limited cases, through the entire thickness of a dielectric from one electrode to the other.

Polarization takes place in all the molecules of a dielectric; it is its bulk property. At the same time, conduction of a dielectric is often and practically fully determined by the presence of a slight amount of impurities (contaminants), and is not attributed to its basic substance. Conduction of a dielectric can appreciably be weakened with purification of its substance. Therefore, when two or several dielectrics which do not interact chemically are mixed, the permittivity of the resultant mixture may be evaluated to a first approximation from the arithmetic rule of mixing. This may prove totally unsuitable
for calculating the resistivity of a dielectric, since even a slight addition of another substance may sometimes reduce by several orders the resistivity of the dielectric. The effect of negligible amounts of impurities on the resistivity of semiconductors may sometimes be much more pronounced.

Thus, the physical picture of polarization of a dielectric may be represented as a negligibly small displacement in space of a very large number of charged particles of matter, and the physical picture of electrical conduction of a dielectric as the motion of a relatively small number of charged particles over relatively large distances.

The displacement of charged particles during polarization may be regarded as an elastic shift of charges. When the effect of the voltage applied to a dielectric is discontinued, the displaced charges may tend to return to their initial positions, which never happens in the phenomenon of electrical conduction.

While the conduction current exists as long as a direct voltage is applied to a dielectric, the displacement current (capacitive current) appears only when the direct voltage is applied or taken off or, generally, when the magnitude of the applied voltage is changed. A capacitive current can exist in a dielectric for a long time only under the action of an alternating voltage. In the presence of a sinusoidal alternating voltage, the conduction current coincides in phase with the voltage, while the displacement current (in a linear dielectric) being
also sinusoidal, is a quarter of a period ahead of the voltage.

**TSDC spectra** are very useful for an understanding of the processes of polarization and for throwing light on conduction mechanisms. Electrical conduction in polymers is governed by trapping levels. Much can be learnt about traps with the help of TSDC spectra.

Temperature dependence of conductivity of an undoped CA film shows an inflection about 90°C. In TSDC spectra of undoped CA films, a peak, namely peak I (β - transition), is observed at 90 ± 1°C and is attributed to the motion of the acetate groups. Peak II (204°C, α - transition) is also observed in TSDC spectra of CA films near the softening point of the polymer, and is characterized by a complex nature.

Activation energy of CA films was calculated by temperature variation of conductivity curve and initial rise method of TSDC (in higher temperature region). The value of activation energy obtained by initial rise method was found to be a bit higher than that obtained from conductivity curve. The most probable cause of this difference may be the formation of surface states. Though the mechanism responsible for the formation of surface states has not been understood yet, the surface states are among the factors which affect the injection phenomenon.
Generally, it is expected that the transient and steady-state conduction should have similar mechanisms. But it is not necessarily so and they may have different mechanisms. Injection of charges and their trapping is the governing mechanism in both types of conduction in doped and undoped CA films.

The presence of significant electrode effect on current-voltage characteristics in CA films in conduction studies suggests the phenomenon of charge injection and formation of space charges. The theoretical values of the coefficients of Richardson-Schottky (RS) mechanism are in fair agreement with the experimental values of the coefficients obtained from $J$ vs. $E^{1/2}$ plots of CA films. Relation $J \propto d^3$ (with $d$ being the thickness of the film) is obeyed by $J - V$ characteristics in the higher field region, and it reveals space charge build-up. TSDC spectra of CA films are markedly affected on changing the film thickness. The intensity of peak II decreases, and it shifts towards higher temperatures with the increase in film thickness.

Pronounced electrode effects were also observed in the transient charging current and on TSDC spectra of CA films.

A clear distinction between charging and discharging transient currents, and the superlinear nature of the isochronal currents against fields are sufficient and reliable evidence in support of the hypothesis of charge injection and trapping in
doped and undoped CA films.

Barker et al. 11 have reported the effect of moisture and ionic conduction in alkali-halide-doped cellulose acetate. The first requisite in applying solid state concepts to biological and biochemical materials is, of course, a proof that the conductivity, if any, is not ionic. Cardew and Bley 12 find that the current through hemoglobin, globin and a number of other biochemically important compounds comes into equilibrium within one minute and is probably not ionic conductivity. A conclusive evidence for a nonionic conduction mechanism in proteins has been adduced by Rosenberg. 13 It appears that the weight of evidence is in favour of electronic conduction unless high percentages of water are present, when protonic conduction becomes paramount. However, it would be expected that proton conduction also would contribute to the current at lower levels of water content. Thus the structure and the chemical identity of the material determine the predominance of the mechanism.

Electronic conduction, in contrast, should give rise to an approximately time-independent current. This behaviour has been observed in steady-state conduction studies. Recently, Kumar et al. 14 have reported space charge limited currents in pure and iodine-doped cellulose acetate. They also reported that the point of inflection on the conductivity Vs. 1/T curve corresponds to an effective glass transition temperature (T_g) of
pure CA. In the present investigation, a peak (I) is also observed at the temperature of inflection on conductivity vs. $1/T$ curve. Some hypotheses have postulated that conductivity above and below the inflection is respectively ionic and electronic in nature, and yet others are based on the analogy with some other materials, according to which intrinsic conduction exists above inflection, and impurity conduction below inflection.

In the case of ionic migration, the peak position in TSDC is usually field-dependent and saturation (i.e., polarization increasing less than linearly with increasing field strength) may be expected to be reached much sooner than for dipolar processes, since the gradual accumulation of carriers near the electrode rapidly decreases the effective directing field.

In the present investigation, the peak position is field-independent in TSDC study, and $I_m$ and $Q$ for peak II increase superlinearly with $E_p$ in the higher field region. Thus it seems logical to exclude the possible ionic migration in the present investigation.

Incorporation of diphenylthiocarbazone (DPh) in CA exhibits marked changes in conductivity, transient currents and TSDC spectra. These changes have been explained on the basis of the formation of charge-transfer complexes. The infra-red and
the ultra-violet techniques are especially useful when the effects of dopants on the polymer characteristics are to be investigated. The UV and IR spectra are unique to the material under study and are sensitive to any structural changes due to additives.

The steady-state current (at a fixed field) as well as the conductivity of CA films increases after DPh doping up to 25 gl⁻¹, and they begin to decrease with higher concentration. On the other hand, increase in DPh concentration up to 25 gl⁻¹ into CA films results in the decrease of the peak amplitude (Iₚ), peak position (Tₑ) and charge (Q) associated with both the peaks in TSDC analysis. These changes have been attributed to the formation of charge-transfer complexes which can have a four-fold effect: (a) providing conductivity paths through the amorphous regions and thus inter-connecting the crystallites; (b) reducing the barrier at the interfaces; (c) preventing or destroying some of the trapping sites of charge carriers, and (d) enhancing the mobility of dipoles (i.e., side groups)/charge carriers during polarization.

Further increase in DPh concentration, i.e., beyond 25 gl⁻¹, results in a reverse trend, i.e., the steady-state current (at a fixed field) and the conductivity of the CA films decrease and an increase is observed in the values of Iₚ, Tₑ and Q associated with both the peaks in TSDC analysis. These changes have been attributed to the onset of the increase
in heterogeneity of the polymer-plasticizer system, which can increase the trapping sites for trapping of charge carriers during polarization, thus resulting in higher polarization. Due to these additional traps the mobility of charge carriers decreases which results in a decrease in conductivity as well as steady-state value of the current (at a fixed field).

These results indicate that the 25 g l⁻¹ concentration of DPh in CA may be the optimum value at which maximum complex formation is expected.

CA is a hygroscopic polymer and it can absorb the moisture from the surroundings. On heating CA films sandwiched between two like or unlike metallic electrodes, an electric current known as short-circuit current or spontaneous current 'I_s' is generated. A peak around 50°C is observed due to desorption of sorbed moisture. The desorption of moisture at 50°C is confirmed by the thermogravimetric analysis (TGA), Differential thermal analysis (DTA) and more precisely by Differential thermogravimetric curve (DTG). On heating the sample beyond 240°C with the heating rate of 4°C/min, the deacetylation and main chain scission of the polymer may take place.

At higher polarizing temperature, the sharp rise in depolarization current in the temperature region of peak II could be explained in terms of the start of deacetylation and main-chain scission i.e., degradation of CA.
The TSEC does not exhibit the peak (~50°C) which is observed in spontaneous current emission, because of (a) the relatively high temperature (45°C - 50°C) up to which the electrets are cooled during the formation; (b) desorption of sorbed moisture in keeping the specimen for 1.8x10³ sec. at a constant temperature (100°C) during the formation; (c) immediate reheating of the specimen which does not permit it to absorb moisture from the surroundings.

Thus these factors support the presence of the peak at 50°C in spontaneous current emission due to desorption of sorbed moisture as well as its absence in TSEC analysis.

The generation of short-circuit currents and open circuit voltages, however opens a new area of research, the outcome of which might be helpful for the development of a practically useful dry cell composed of plastics.
REFERENCES