CHAPTER 7
CONCLUSIONS
This chapter summarizes the results observed in the present investigation on six charge transfer complexes of pyridine and substituted pyridines with halogen and interhalogens and will highlights the future scope of the work.

**General Conclusions**

The results of the experimental work illustrated in the foregoing chapters lead to the following conclusions.

Six charge transfer complexes pyridine-ICl, 4-methylpyridine-ICl, 3, 5-dimethylpyridine-ICl, 2-bromopyridine-ICl, 3, 5-dimethylpyridine-I\(_2\), 3, 5-dimethylpyridine-IBr were prepared in the solid state. Elemental analyses have confirmed that all the complexes are of 1:1 stoichiometry. From the observed FT-IR frequency shifts of the donors in the complexes indicate that the donor molecules bonded through its nitrogen atom with the acceptor IX (X = I, Cl, Br). Fractional charge transfer from the donors to the acceptors during complex formation was confirmed by the observed downfield shifts of the NMR signals of protons of the donors. Thermal analysis of the CT complexes revealed that the thermal stability of the complexes were not too high. The transformation from outer to inner complex is also indicated by the thermal degradation results. The established monoclinic crystal structure of pyridine-ICl complex is supported by the experimental powder XRD results. The XRD diffraction patterns of 4-methylpyridine-ICl, 2-bromopyridine-ICl and 3, 5-dimethylpyridine-ICl were indexed with the help of ‘Powder –X’ software and monoclinic crystal structure were proposed.
By analysing the experimental impedance spectra, the conductivity and equivalent circuits were evaluated for the complexes at various temperatures. The fitted equivalent circuits were found to be the parallel combination of resistance with either capacitor or constant phase elements (cpe) indicating capacitive nature of materials. The temperature dependence of conductivities of the complexes have been found to follow the Arrhenius law. Frequency dependence of impedance studies revealed the presence of relaxation processes with distribution of relaxation times.

The real and imaginary part of complex permittivity decrease with the increase in frequency. The higher values of dielectric constant at low frequencies are attributed to interfacial and dipolar polarizations within the materials. The variation of loss tangent (tan\( \delta \)) with frequency and temperature is reported. The higher values of losses at lower frequencies are due to the relaxation processes and the losses at higher frequencies are due to conduction. The real part electric modulus (M') increases with the increase in frequency and the imaginary part (M'') electric modulus exhibits an M'' peak at the characteristic frequency. The M'' peak is found to be shifted towards higher frequencies with the increase in temperature.

The frequency dependence of conductivity spectra are characterised by mainly two distinct regions. A low frequency plateau region which is almost temperature independent corresponds to dc conductivity (\( \sigma (0) \) or \( \sigma_{dc} \)). The higher frequency dispersive region is well fitted to the Jonscher’s universal power Law. The value of frequency exponent \( S \) is found to decrease with the rise in
temperature and indicates hopping mechanism of conduction. The values of $\sigma_{dc}$ are extracted from the intercept of the plateau region on the vertical axis and are in good agreement with the dc conductivity obtained by two probe method. In the two probe method (dc technique) dc conductivity of the complexes were calculated from the slope of the current versus potential curves using the pellet dimensions. The linear current-voltage curves indicate the ohmic conduction in the CT complexes under study. The temperature dependence of dc conductivities is found to obey the Arrhenius Law.

Ionic transport numbers are measured by Wagner’s polarisation technique. From the ionic transport number values it is found that the complexes are mixed semiconductors. The ionic transport numbers are found to increase with the rise in temperature indicating more ionization at higher temperatures. However for 4-metylpyridine-ICl complex ionic transport number is observed to decrease with the rise in temperature which is attributed to the discharge of ions at the respective electrodes on repeated electrolysis.

Optical and electrochemical band gaps are measured by diffuse reflectance spectroscopy and cyclic voltammetry respectively. The values of optical band gaps are found higher than the electrochemical band gaps.

**Future Prospects**

We have reported the electrical conducting properties of few CT complexes. Thermal studies indicate comparatively lower thermal stabilities of the complexes. This property of the complexes restricts us for further research works.
on the possible battery application of the materials. However the mechanical strengths of the CT complexes can be improved by making composites of the complexes with various conducting as well as non-conducting cheap materials such as polymers, carbon black, graphite, graphene, graphene oxide or even with materials having metal components. Such composite materials may possess interesting electrical properties and promising device application characteristics. Studies on electrical properties of the positive halogen salts of these CT complexes may be carried out.