APPENDIX- II
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Impedance Spectroscopy Study of the AC Conductivity and Dielectric properties of 3, 5-Dimethylpyridine-Iodine Charge Transfer Complex

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ABSTRACT

Solid charge transfer complex of n-donor 3, 5-dimethylpyridine (3, 5-Lutidine) with I\textsuperscript{3}\textsuperscript{-} acceptor iodine was prepared and characterised by using elemental analysis, UV-Vis, FTIR, \textsuperscript{1}H NMR spectroscopy and powder XRD techniques. The electrical parameters of the prepared complex in the pellet form were studied at various temperatures and at wide frequency range by employing AC complex impedance spectroscopic technique. The Nyquist (cole-cole) plots have been successfully explained by employing (RC)(RC)(RC) equivalent circuit corresponding to grain , grain boundary and electrode contributions. The radii of the semicircular arc decrease with increase in temperature which suggests that the material exhibits negative temperature coefficient of resistance (NTCR) behaviour like semiconductors. Dielectric constant, \varepsilon^\prime and dielectric loss, \varepsilon^\prime\prime seems to decrease sharply with increase in frequency. The ac conductivity obeys the power law of frequency.

Keywords: Charge-Transfer complex, Impedance spectroscopy, Dielectric properties.

INTRODUCTION

Charge transfer (CT) or Donor-acceptor complexes are the most important and vastly studied organic species due to their unusual electrical, magnetic and optical properties\textsuperscript{1}. In 1973, the CT complex TTF-TCNQ was reported as organic metal\textsuperscript{2} and after that organic CT complexes have greatly attracted the attention of researchers for several decades, aimed mainly at the discovery of materials with good electrical conductivity or even room temperature superconductivity\textsuperscript{3}. Recently attention has been turned to technologically relevant properties of CT complexes due to their potential in the development of electronic and optoelectronic devices\textsuperscript{4}.

Electrical conduction property of a donor-acceptor complex is mainly influenced by (a) electronic structure of the complex and (b)
Mixed ionic and electronic conductivity study of charge transfer complexes of some substituted pyridines with iodine monochloride (ICl) by AC impedance spectroscopy

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Abstract Mixed ionic and electronic conductivity of three solid charge transfer (CT) complexes of pyridine, 4-methylpyridine (γ-picoline) and 3,5-dimethylpyridine (3,5-lutidine) with ICl (iodine monochloride) are reported. Electrical parameters of the prepared complexes in the pellet form are evaluated at various temperatures and at wide frequency range by employing AC complex impedance spectroscopic technique. Suitable equivalent circuits for the Nyquist plots, which provide the most realistic model of the electrical properties of the CT complexes, have been suggested. Both transport number measurements and impedance spectra reveal that the conduction in γ-picoline-ICl complex is mainly due to ions, in 3,5-dimethylpyridine-ICl complex, it is due to both ions and electrons and in pyridine-ICl complex, it is predominantly due to electrons. The a.c. conductivity measurements of the CT complexes have been carried out in the frequency range of 10⁻¹⁻¹⁰⁵ Hz within the temperature range of 303–353 K. The variation of a.c. conductivity with frequency follows the Jonscher’s universal power law. The temperature dependence of electrical conductivity suggests the semiconducting behaviour of the materials.

Keywords CT complex · Mixed conduction · Impedance spectra · Transport number

Introduction

The intermolecular interaction between electron donor D and electron acceptor A leads to the formation of a new molecular assembly, DA, called charge transfer (CT) complex, first introduced by Mulliken [1, 2]. Organic CT complexes and salts have extensively been investigated in various areas of chemistry and material sciences both from the theoretical and experimental aspects as they exhibit diverse kind of interesting physical properties and functionalities related to optical, magnetic, electrical (super) conductivity and dielectric properties [3, 4]. Since the discovery of the first metallic type CT complex TTF-TCNQ in 1973 [5], attention to organic CT complexes has been focussed for several decades, aimed mainly at the discovery of materials with good electrical conductivity or even room temperature superconductivity [6]. Later on, attention has been turned to technologically relevant properties of CT complexes due to their potential in the improvement of electronic and optoelectronic devices [7].

The solid organic CT complexes are one of the most important subclasses of organic semiconductors [8, 9] which often exhibit similar conduction mechanism to inorganic semiconductors where hole and electron conduction layers are typical carriers separated by a band gap. CT complexes exhibiting mixed ionic-electronic conduction have also been reported [10–13].

Although, the electrical conductivity of charge transfer complexes of pyridine analogue with halogens and interhalogens has been reported in literatures [14–16]; however, the detailed studies of frequency dependence a.c. conductivity and complex impedance spectroscopy of these complexes...
UV–Vis spectroscopy and density functional study of solvent effect on the charge transfer band of the n → n* complexes of 2-Methylpyridine and 2-Chloropyridine with molecular iodine

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1. Introduction

Solvatochromism signifies the medium dependence of electronic absorption spectrum of a system. It is an outcome of type of electronic transition and the nature of the chromophore involved [1]. Again the response of the molecular orbitals involved in electronic transition towards the medium is governed by their polarity. Depending on the polarity of the solvent and the corresponding molecular orbitals, energy reshuffling of the molecular orbitals takes place. Energy reshuffling sometimes leads to increase in energy gap between the molecular orbitals involved in transition or it also may lead to decrease in energy gap between them. Either way we obtain a shift of the absorption maximum of the corresponding system in terms of blue shift or red shift [2]. Moreover specific (e.g. hydrogen bonding) and non-specific (dielectric enrichment) interactions between the solute and solvent molecules result in the variation of geometry of the complex which changes the properties like dipole moment, molecular orientation, energy of different molecular orbitals etc. Compounds like everyday life drugs and dyes are medium dependent which makes solvatochromic study very important to understand solution chemistry involved with essential chemicals in different environment [3,4].

Pyridine substitutes, 2-Methylpyridine and 2-Chloropyridine have wide applications in agriculture and medicinal sector [5–7]. They form n → σ* charge transfer complexes with molecular iodine. The charge transfer bands of 2-Methylpyridine-I2 and 2-Chloropyridine-I2 complexes are susceptible to polarity of the solvent medium. A prominent blue shift of these two CT bands is observed in solvents with higher dielectric constant values. Dielectric constant, refractive index and polarizability are bulk properties of solvents. Many other solvent parameters have been assigned which explain the solute solvent interaction at the molecular level [8–13]. Hansen parameter is a 3-dimensional solvent parameter system. In this system solubility parameter is a vector with the components of dispersion forces (\(\delta_d\)), polar forces (\(\delta_p\)), and hydrogen bonding (\(\delta_h\)).
2-Chloropyridine and Iodine monochloride form 1:1 $n \rightarrow \sigma^*$ charge transfer complex which is confirmed by Benesi Hildebrand plot using UV-vis spectroscopy. Multiple Linear Regression Technique (MLRT) shows that 2-Chloropyridine-ICl complex is susceptible to medium effect in reference to different solvent parameters, at both the bulk and molecular levels. Dielectric constant ($\varepsilon$), refractive index ($n$), Hansen parameter, Catalan parameter and Kamlet’s $\pi^*$ values give good linear fit equations between experimental and calculated CT bands with $R^2$ values as high as 1. Polarizability effect on the CT band is examined using Buckingham and Lippert Mataga equation. Formation constant of the complex in different media is found to be linearly dependent on Hansen solubility parameter. Computational analysis defends well the blue shift in polar medium observed for 2-Chloropyridine-ICl. NBO, NRT, and QTAIM analyses explain a shift from ionic character to covalent character in polar medium. It emphasises a stronger donor-acceptor interaction in polar medium and thereby explains the experimentally observed blue shift. A logarithmic relation between the bond lengths of the bridging atoms and dielectric constant is proposed.

1. Introduction

Charge transfer (CT) complexes are formed when electron transfer occurs from one compound to another. The former compound is called the donor (D) and the latter is called the acceptor (A) (Mulliken, 1952, 1956; Mulliken and Pearson, 1969). Appearance of a new band with those of donor and acceptor bands in the electronic spectra of the donor and acceptor together in solution, confirms the formation of a new CT compound which is capable of absorbing in the UV-vis region of the spectrum (Benesi and Hildebrand, 1949). Such bands are thus