

Abstract

ABSTRACT

A charge transfer complex is not a stable chemical bond; it is a chemical association of two or more molecules or of different parts of one very large molecule, in which the attraction between the molecules is created by an electron transition into an excited electron* state, such that a fraction of electron charge is transferred between the molecules. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. The present study has been undertaken primarily to get some insight into the understanding of the charge transfer complexes. The studies have been carried out employing spectroscopic techniques viz, multiple charge transfer spectra, UV- Visible, FTIR spectroscopy and ¹H NMR spectroscopy. Formation constant, molar extinction coefficient, transition dipole strengths, ionization potential, free energy and resonance energy of the CT complex have been estimated.

The thesis comprises of five chapters:

The first chapter describes the general introduction to the charge transfer complexes consisting of a brief literature survey on the subject. Important investigations carried out in the field of CT complexes have been critically reviewed. The emphasis in this chapter is towards the existing theory of the charge transfer complexes given by Mulliken and use of Benesi- Hildebrand equation.

The second chapter comprises the spectrophotometric study of the charge transfer complexation of picric acid (2, 4, 6- trinitro phenol) as an electron acceptor with p- nitroaniline as an electron donor in different polar solvents. The interaction of picric acid with p- nitroaniline in different polar solvents such as acetone, ethanol and methanol due to $\pi \rightarrow \pi^*$ transition at room temperature are studied by visible spectral data of CT complex of donor and π –acceptor. The reaction has been studied in both liquid and **solid state**. The effect of polarity of solvent on the formation of CT complexes, absorption spectra of the complexes and other parameters has been studied. Also CT complex was synthesized and characterized by FTIR and comparative studies of physical parameters were carried out as mentioned above.

Formation constant and molar extinction coefficient have been determined by Benesi- Hildebrand equation under condition $[D]_0 \gg [A]_0$

$$[A]_0 / [A] = (1 / K_{CT}\epsilon_{CT}) \times 1 / [D]_0 + 1/\epsilon_{CT}$$

where $[A]_0$ and $[D]_0$ are the initial concentrations of the acceptor and donor respectively. A is the absorbance of the CT complex at λ_{CT} , K_{CT} and ϵ_{CT} are the formation constant molar absorptivity of the complex.

In the third chapter, spectrophotometric and spectroscopic studies of charge transfer complexes of m-nitroaniline as an electron donor with picric acid as an electron acceptor in different polar solvents such as acetone, ethanol and methanol have been studied in order to understand the interactions between picric acid and m-nitroaniline in both **solid state** and solution. The effects of solvents on the formation of CT complex, physical parameters and stoichiometry of CT complex have been studied. Formation constant has been determined by Benesi –Hildebrand equation which has been described previously and other physical parameters mentioned in chapter II have been calculated. Stoichiometry of the CT complex has been determined by straight line method.

Stoichiometry of CT complex is found to be 1:1 in methanol and the K_{CT} values decreases with increasing solvents polarity due to destabilization of dative structure $D^+ A^-$ of CT- complexes in more polar solvent and the dissociation of the complex into D^+ and A^- . The solid CT complex has been characterized by FTIR, and UV-Visible spectra. The spectrophotometric and thermodynamic parameters of the CT complexes were found to be solvent dependent.

As is obvious from the Table 1, λ_{CT} , K_{CT} and ϵ_{CT} vary with change in solvent polarity. These parameters increase significantly from methanol to acetone with decreasing solvents polarity.

Table 1

Data for spectrophotometric determination of stoichiometry, absorption maxima (λ_{CT}), and association constants (K_{CT}), molar absorptivities (ϵ_{CT}), of CTC of PiOH and MNA in acetone, ethanol, and methanol at 298 K

Systems	Temperature (K)	Donor concentration in M	[A] ₀ in M	Absorbance at λ_{CT} (nm)	λ_{CT} (nm)	K_{CT} (l mol ⁻¹)	ϵ_{CT} (l mol ⁻¹ cm ⁻¹)
PiOH/MNA (Acetone)	298	0.01	0.01	1.698	440	729	192
		0.015		1.756			
		0.02		1.798			
		0.03		1.832			
		0.05		1.865			
		0.1		1.895			
		0.2		1.905			
		0.3		1.918			
		0.5		1.932			
PiOH/MNA (Ethanol)	298	0.01	0.01	1.532	445	569	179
		0.015		1.592			
		0.02		1.642			
		0.03		1.689			
		0.05		1.733			
		0.1		1.755			
		0.2		1.772			
		0.3		1.785			
		0.5		1.795			
PiOH/MNA (Methanol)	298	0.01	0.01	1.458	450	470	177
		0.015		1.548			
		0.02		1.593			
		0.03		1.643			
		0.05		1.689			
		0.1		1.732			
		0.2		1.752			
		0.3		1.768			
		0.5		1.785			

The fourth chapter deals with the study on the charge transfer complex of p-toluidine (PTD) as an electron donor with picric acid (PiOH) as an electron acceptor in different solvents. The CT complex has been synthesized and characterized by FTIR, ^1H NMR and electronic absorption spectra. Spectrophotometric studies of CT complex have been carried out in different polar and non-polar solvents such as acetone, ethanol methanol, carbon tetrachloride, chloroform and dichloromethane respectively. The concentration of the donor (PTD) was changed over a wide range from 0.01 M to 0.5 M while concentration of π acceptor PiOH was kept fixed at 0.01 M in each reaction mixture. These produced solution with donor: acceptor molar ratio varying from 1:1 to 50:1. The value of formation constant has been determined by Benesi- Hildebrand equation which has been described previously and other physical parameters mentioned in chapter II and III have been calculated.

Solid state CT complex has been synthesized and characterized by FTIR, ^1H NMR and comparative studies of physical parameters were carried out as mentioned above. ^1H

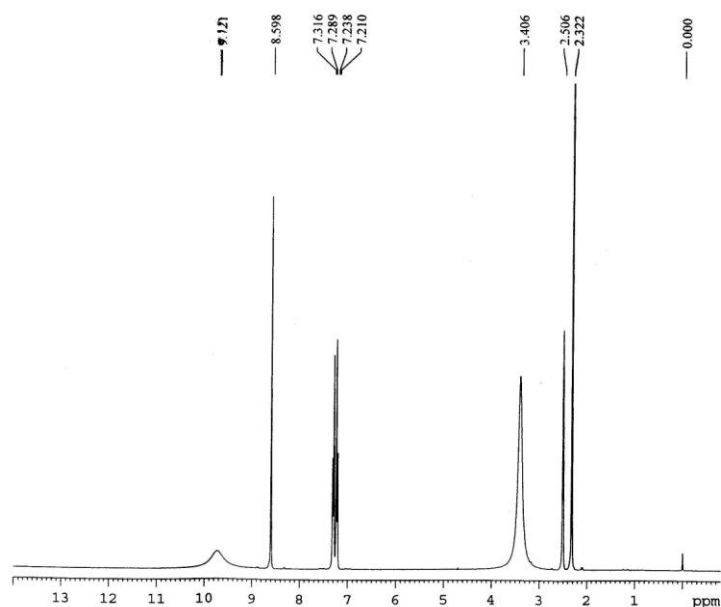


Fig. 1. ^1H NMR Spectrum of CT complex of p-toluidine (donor) and picric acid (acceptor)

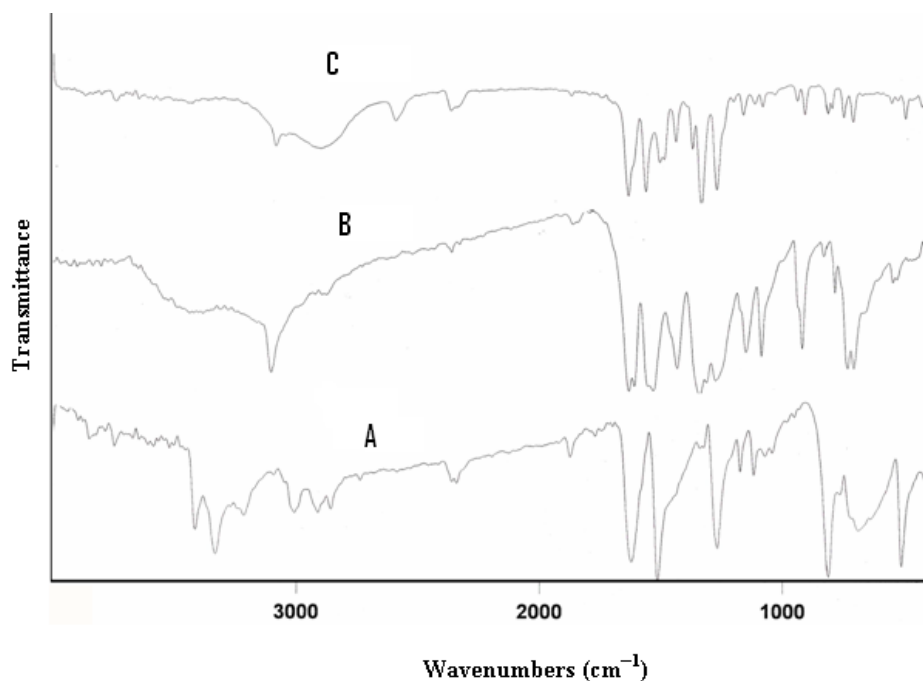


Fig. 2. FT-IR spectra of (A) p-toluidine (donor) (B) picric acid (acceptor) and (C) CT complex.

^1H NMR spectrum of CT complex and FTIR spectra of reactants and CT complex indicate the charge transfer interactions as shown in Figs. 1 and 2 respectively.

The fifth chapter deals with the interaction of 1-naphthylamine and picric acid in both solid state and solution. The interaction between them has been established by the electronic absorption spectra (λ_{CT} has been found to be shifted), FTIR spectra and ^1H NMR spectrum.

FTIR spectral studies suggest the formation of CT complex by observing the main infrared spectral bands of the 1-naphthylamine and picric acid in the product spectrum. However, the position of the most of bands of donor and acceptor in the spectrum of the CT complex show shifts in the frequencies as well as some changes in their intensities. In general, the CTC spectra show the characteristics bands due to various mode of vibrations of the acceptor part, shift to lower wave number while those of the donor part also acquires a counter shift.