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THESIS ON

SPECTROSCOPIC STUDIES OF ELECTRON DONOR-ACCEPTOR INTERACTION OF 8-HYDROXYQUINOLINE WITH CITRIC ACID IN DIFFERENT SOLVENTS

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Jimma, Ethiopia

SPECTROSCOPIC STUDIES OF ELECTRON DONOR-ACCEPTOR INTERACTION OF 8-HYDROXYQUINOLINE WITH CITRIC ACID IN DIFFERENT SOLVENT

By: Demelash Jado

Advisor: Khalid Siraj (PhD)

Co-advisor: Nathan Meka (MSc)

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Spectroscopic studies of electron donor-acceptor interaction of 8-hydroxyquinoline with citric acid in different solvent.

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A thesis submitted to the School of Graduate Studies Jimma University in partial Fulfillment of the Requirements for the Degree of Masters Of Science in Chemistry.

Approved by Board of Examiners:-

External Examiner	Signature	Date
_____	_____	_____
Internal Examiner		
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Advisor (s)		
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Abbreviations

^{1}HNMR	proton nuclear magnetic resonance spectroscopy
IR	infrared
CT	charge-transfer
8-HQ	8-Hydroxyquinoline
CA	citric acid
EDA	electron donor-acceptor
ED	electron donor
EA	electron acceptor
K_{CT}	formation constant
ε_{CT}	molecular extinction coefficient
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
D^{+}	donor cation
A^{-}	acceptor anion

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Abstract

Charge transfer complex formation between 8-hydroxyquinoline as the electron donor with citric acid as the electron acceptor has been studied spectrophotometrically in ethanol and methanol solvents at room temperature. A new absorption band due to charge transfer complex formation was observed near 320 and 325nm in ethanol and methanol respectively. The stoichiometric ratio of the complex has been identified by Job's and conductometric titration methods to be 3:1. Benesi–Hildebrand equation has been applied to estimate the formation constant and molecular extinction coefficient. It was found that the value of formation constant was larger in ethanol than in methanol. The physical parameters, ionization potential and standard free energy change of the formed complex were determined and evaluated in the ethanol and methanol solvents. The solid complex between 8-hydroxyquinoline and citric acid has been synthesized and characterized by using infrared and proton nuclear magnetic resonance spectrophotometry.

Key words: Charge transfer complex, 8-hydroxyquinoline, electronic absorption spectra.

1. INTRODUCTION

1.1. Charge transfer complexes

Charge transfer phenomenon was introduced first by Mulliken[1]. The term charge transfer gives a certain type of complex resulting from interactions of donor and acceptor with the formation of weak bands and discussed widely by Foster[2]. Mulliken aimed to define a new type of adduct to explain the behavior of certain classes of molecules, which do not conform to classical patterns of ionic, covalent, and coordination of hydrogen bonding components. While such adducts largely retain some of the properties of the components, some changes are apparent, e.g. its solubility, the diamagnetic and paramagnetic susceptibility. Mulliken also showed that the charge transfer interactions within a molecular complex consisting of an electron donor (ED) and an electron acceptor (EA) involved a resonance with a transfer of charge from ED to EA[3].

$$ED + EA \rightleftharpoons ED^{+}EA^{-} \rightleftharpoons ED^{+} + EA^{-}$$

Charge-transfer complexes result from a donor-acceptor mechanism of Lewis acid–base reaction between two or more different chemical constituents. The formation of electron-donor acceptor (EDA) complexes can be rapidly assessed for its validity as a simple quantitative analytical method for many drug substances which can act as electron donors. Charge transfer complexes have been studied exclusively due to their wide application as ion sensors in the field of environmental science and in the determination of drugs based on the charge-transfer (CT) complexes formed with electron acceptors[4-6]. They also can be used as organic semiconductors photo catalysts, dendrimers and in the studying of redox processes[7]. More recently, attention has been given to the isolation and investigation of physical properties of some CT-complexes in the solid states. Some of these complexes show interesting electrical conductivity properties and have found applications in many form of electronics and solar cells[8]. Charge transfer complexation is currently achieve the great importance in biochemical, bioelectrochemical energy transfer process, biological systems, and drug-receptor binding mechanism, for examples, drug action, enzyme catalysis, ion transfers through lipophilic membranes[9].

Recently, many studies have been widely reported about the rapid interactions between different kinds of drugs and related compounds as donors like morpholine, norfloxacin, ciprofloxacin, and sulfadoxine, with several types of σ and π-electron acceptors[4,10] . Charge transfer interactions formed between 8–hydroxyquinoline and acceptors in different solvents has been studied spectrophotometrically[11]. Molecular interactions between electron donors and acceptors are generally associated with the formation of intensely colored charge transfer complexes (CTC) in which absorb radiation in the visible region. Charge transfer complexation is important phenomenon in biochemical and bio-electrochemical energy transfer process. The formation of molecular complexes of the charge-transfer (CT) type between donors and acceptors plays an important role in many biological processes, e.g. enzyme catalysis, drug action, and ion transfer through lipophilic membranes; all involve complexation between two or more distinct molecules. Organic semiconductors of the CT type can find application as cheap sources for the construction of organic solar batteries in virtue of their semiconducting properties[12]. Charge-transfer complexes are known to take part in many chemical reactions like addition, substitution and condensation. These complexes have attracted great attention as nonlinear optical materials and electrical conductors. Electron donor-acceptor (EDA) interaction is also important in the field of drug-receptor binding mechanism, in solar energy storage and in surface chemistry as well as in many biological fields. On the other hand, the EDA reactions of certain π-acceptors have been successfully utilized in pharmaceutical analysis [13].

Charge-transfer complexes were for a long time believed to have an important role in biological systems, e.g. the transfer of charge from one molecule to another. CT interaction is utilized for the assay of different pharmaceuticals and related analyses. Many large biomolecules are good semiconductors. A vast number of organic compounds have been discovered to exhibit significant electrical characteristics. Aromatic heterocyclic compounds represent a very important class of compounds in which the π and n-electrons, at least in principle, can form two types of charge-transfer complexes. The formation of CT complexes between π - and n-donors with σ - and π -acceptors has been investigated. For these wide applications extensive studies on CT- complexes of π-acceptors have been performed [14, 15].

1.2. 8-Hydroxyquinoline (8HQ)

8-Hydroxyquinoline is a white to pale yellow crystal or crystalline powder that is insoluble in water or ether and freely soluble in ethanol, acetone, chloroform, benzene, and aqueous mineral acids. It readily forms stable metal chelates which are soluble in organic solvents depending on the pH of the solution. 8HQ is a mono-protic bidentate chelating agent and has been used for the extraction and analytical determination of metal ions due to the ability to coordinate with metal ions.8-Hydroxyquinoline is an aromatic nitrogen compound characterized by a double-ring structure containing benzene fused to pyridine at two adjacent carbon atoms. (Pyridine is a ring structure compound of five carbon atoms with a nitrogen atom).

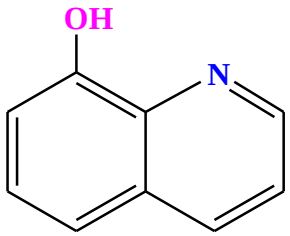

Figure1. Structural formula of 8-Hydroxyquinoline

The heterocyclic aromatic compound, 8-Hydroxyquinoline (8HQ) is often found as an environmental pollutant due to its widespread use in industry, medicine and agriculture. 8HQ in the form of a metal complex, like copper 8-Hydroxyquinoline, Cu $(8HQ)_2$, exhibits fungicidal activity being applied as a pesticide, as a preservative, bactericide and disinfector in different cosmetics. Of increasing importance in display technology is the use of the 8HQ complex compound. Recent pharmacological studies indicate that 8HQ may find an important use as a drug for shortening the course of treatment for both active and latent tuberculosis[16].

8-Hydroxyquinoline is a bifunctional hydrogen-bonding molecule, which in aqueous or alcohol solution simultaneously acts as a donor at the OH site and an acceptor at N-atom. Up on photo excitation the acid/base properties of this molecule change significantly at both sites, rendering OH-group more acidic and the N-atom more basic.

In 8HQ the acidic (H-bond donating) and basic (H-bond accepting) groups of the molecule are relatively close to each other and hence a single solvent can bind to both the sites simultaneously and monomer molecules can also arrange to form dimmers via H-bonding. One might expect tautomerization in H-bond accepting solvents via intra-molecular hydrogen bonding and in all other solvent solutions, there may exist a competition between intra and inter-molecular H-bonding. 8-HQ and its derivatives are capable of forming complexes with many metal ions. 8-HQ has played an important role in organic electroluminescence and was widely introduced in organic electroluminescence cells as emission layer. 8-HQ and its derivatives are also used as insecticides, amoebicides, bactericides and fungicides. Another interesting feature is that some 8-HQ derivatives are expected to exhibit non-linear optical properties[17].

Citric acid is found in nature. Citric acid is the most important organic acid produced in tonnage by fermentation. It is involved in the active sites of bacterial metalloenzymes including aconites, a key enzyme in the citric acid cycle and dinitrogenase in nitrogen-fixing bacteria. It is considered to be a preeminent small molecular weight binder of a number of metal ions. Citric acid is widely used to impart a pleasant, tart flavor to foods and beverages. It also finds applications as a function of additive detergents, pharmaceuticals, cosmetics and toiletries[18].

By considering the above stated applications the present work was designed to carry out spectroscopic studies of electron donor-acceptor interaction of 8-hydroxyquinoline with citric acid in different solvent. This paper would present the results obtained from absorption spectra, IR, ^{1}HNMR and conductivity measurement on the chemical product formed in the reaction of 8HQ, as an electron donor and citric acid as an electron acceptor. And also the aim of this work is to synthesis and characterize the interactions of donor 8-Hydroxyquinoline (8-HQ) with acceptor citric acid in different solvent (ethanol and methanol) at room temperature. The molecular composition of the complex formed was studied using Job's method of continuous variations. The nature and structure of the final product of the complex was characterized to interpret the behavior of interaction using infrared (IR), proton nuclear magnetic resonance (^{1}H-NMR) and electronic absorption spectra. The physical data of synthesized complex were analyzed in terms of formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), standard free energy (ΔG^{o}) and ionization potential (IP).

1.3. Statement of the problem

The formation of charge transfer (CT) complexes between σ- and π-acceptors with different π- and n-donors has been widely investigated[19-24]. More recently, attention has been given to the isolation and investigation of physical properties of some CT-complexes formed by the reactions of σ- and π-acceptors with different amines, polysulfide bases, crown ethers and oxygen nitrogen mixed bases. Some of these complexes show interesting electrical conductivity properties and have found applications in electronics devices, solar cells, optical devices[8], and also play an important role in many biological systems[4]. To our knowledge, there is no report related to spectroscopic studies of electron donor-acceptor interactions of 8-hydroxyquinoline with citric acid in different solvent at room temperature. Hence the researcher was designed to study the interaction of 8-hydroxyquinoline with citric acid in ethanol and methanol.

1.4. Objectives

1.4.1. General objective

- To synthesis and characterize the charge transfer complex of donor 8-Hydroxyquinoline with acceptor citric acid in ethanol and methanol solvents at room temperature.

1.4.2. Specific objectives

- To synthesis charge transfer complex from 8-Hydroxyquinoline and citric acid.
- To characterize the charge transfer complex using IR and ^{1}HNMR spectroscopic techniques.
- To determine conductivity, solvent effect and physical properties of formed charge transfer complex in ethanol and methanol.

1.5. Significance of the study

The spectroscopic studies of electron donor-acceptor interactions of 8-hydroxyquinoline with citric acid in different solvent would form a new charge transfer (CT) complex. This CT complex would provide information about the structure, CT bands, and electrical conductivity. This information would provide a platform for the further researchers related to the CT complex.

2. REVIEW LITERATURE

The concept of "molecular association" has long been recognized as important in virtually all fields of chemistry. This fact is underscored by the appearance of a plethora of books and reviews devoted to the subject during the past two decades. The concept is that of a relatively electron poor molecule or acceptor (A), interacting in some way with an electron rich molecule or donor (D). The interaction is such that the binding between the components is weaker than a covalent bond. This definition is sufficiently broad so as to take in the extent of both weak and strong interactions between both ionic and uncharged specie[2]. The concept has been utilized in many diverse fields of chemistry. Lewis acid-Lewis base interactions are in principle interactions between donors and acceptors. Inorganic and organo-metallic chemists have used the concept to describe metal-ligand interactions. Ion solvation, ionization equilibria, and catalysis are also fields of chemistry where donor-acceptor interactions play important roles. Organic chemists have applied the terms electrophilic and nucleophilic to acceptor and donor molecules respectively. The literature abounds with such terms as "molecular complexes" "σ and π complexes, and "charge-transfer complexes" which all refer to some sort of donor-acceptor interaction. Modern interest in donor-acceptor complexes has blossomed since the discovery by Benesi and Hildebrand in 1949 of a new absorption band in the electronic spectrum of a solution of benzene and iodine in n-heptane, which did not appear in the spectrum of either component alone[39]. The explanation of this phenomenon was provided by Mulliken in a series of papers published in 1950-1952. His conclusion was that the new band was due to an iodine-benzene complex possessing a 1:1 stoichiometry. A new electronic transition such as that described above is typical of mixtures of donor and acceptor molecules in relatively "inert" solvents (solvents which do not interact to an appreciable extent with either the donor or acceptor component). Thus, if the new band is in the visible region, solutions of colorless donors and acceptors may appear colored. The interaction between the components of the complex was described in the valence bond formulation. The ground state wave function (Ψ_N) and the excited state wave function (Ψ_E) are approximated by[25].

$\Psi_N = a\Psi_0(D,A) + b\,\Psi_1(D^+,A^-)$…… 1

$\Psi_E = a\,\Psi_1(D^+,A^-) - b\Psi_0(D,A)$ ……2

WhereΨ_1 (D^+,A^-) represents the contribution to the bonding of the components from the resonance form where there has been complete transfer of one electron from donor to acceptor, and Ψ_0 (D,A) represents the contribution from all other bonding interactions. For weak molecular interactions the relationship between the coefficients a and b is a >> b, so Ψ_0 is the major contributor in the ground state and $\Psi_1$takes precedence in the excited state[25]. The electronic transition between these two levels is thought to be the origin of the charge-transfer transition. One of the justifications for this theory is the applicability of empirical relationships between the energy of the charge-transfer transition (hv), the ionization potential of the donor (IP) and the electron affinity of the acceptor (E_A).

$Hv = IP - E_A + C$ …….. 3

The constant C represents columbic forces between the donor and acceptor. The values IP and E_A reflect the relative strength of donors and acceptors respectively, strong donors having low IP and strong acceptors having high E_A. Another important consequence of Equations (1) and (2) is that complexes are predicted to have favored orientations, since b (a measure of the amount of charge-transfer) is proportional to the overlap integral between the highest occupied molecular orbital of the donor (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the acceptor. In other words the "charge-transfer" is from the HOMO of the donor to the LUMO of the acceptor, the maximum amount of charge-transfer stabilization of the complex is to be expected when the overlap between these orbitals is greatest[1]. A surprising number of biochemical reactions, such as the solubilization of riboflavin by tryptophan or the synergism between vitamin B_{12} and amino acids in the treatment of megaloblastic anemia are charge transfer (CT) in nature[25]. Charge transfer gives a certain type of complex resulting from interactions of donor and acceptor with the formation of weak band. Charge-transfer interactions within a molecular complex formed from an electron donor (ED) and electron acceptor (EA) as a resonance with a transfer of charge from D to A to form a radical cation and anion, respectively.

Molecular charge-transfer complexes are based on the interaction between two molecular species, namely donor (D) and acceptor (A). The donor molecule has small ionization energy (IP), while the counterpart acceptor molecule has a large electro negativity or electron affinity (EA). When donor and acceptor interact the charge is redistributed among the compound. The donor species oxidizes by the loss of charge and the acceptor is reduced. The result is a charge-transfer salt D_mA_n described by the following reaction:

$$[D_m] + [A_n] \rightarrow [D_m]^{+\delta} + [A_n]^{-\delta}$$

where δ is the charge-transfer ratio, m and n are integers. In some cases, these donor-acceptor interactions mediate the formation of charge transfer crystalline solids in which organic molecules are stacked in homo molecular rows, being the molecular interactions within the chains of π-π character. The molecules pack rather densely in order to maximize the orbital overlapping between neighboring molecules and increase the charge transfer between the donor and acceptor counterparts. This overlap facilitates the mobility of the charge carriers. Hence, the charge transferred among molecules will have a preferential delocalized π character. Therefore, the spatial arrangement of the molecular building blocks is important to determine the directions of charge motion. The overlapping of π molecular orbitals leads to the formation of bands in the organic crystal, whose properties differ significantly from metallic bands. Charge transfer complexes were successfully applied to many interesting studies[26, 27]. The application of charge transfer complexes included the detection of drugs using spectrophotometry based on the appearance of colored complexes formed by the interactions between (π or σ) electron acceptors and using the drugs as donors[28]. Charge transfer complexation is an important phenomenon in biochemical and bio-electrochemical energy transfer process. The electron donor-acceptor interactions have been studied spectrophotometrically in the determination of the drug based on the charge transfer complexes formation with some acceptor[29]. The molecular interactions between electron donors and electron acceptors are generally associated with the formation of intensely coloured charge transfer complexes, which absorb radiation in visible region[30].

8-Hydroxyquinoline (8-HQ) is a long-known molecule which due to its metal-complexation ability is frequently used for analysis or metal precipitation. It is also called oxine, and it is an analytical reagent whose chemical properties towards metal ions have been extensively investigated although, 8-hydroxyquinoline derivatives are endowed with some interesting biological properties. 8-Hydroxyquinoline and its derivatives are widely used as chelating reagents in analytical chemistry and radiochemistry for metal ion extraction and fluorometric determination. 8-hydroxyquinolines are well known because can perform as structurally related subunits in important biomolecules or biochemical process, which show strong cytotoxic and antimicrobial properties, and they represent the main component in some bactericide, fungicide and antimalarial drugs[31]. It is one of the most important chelators for metal ions and has been used extensively in a wide variety of analytical techniques and to constructing highly sensitive fluorescent sensors. Molecules with the quinoid structure constitute one of the most interesting classes of compounds in organic chemistry. The chemistry of quinones is largely dependent on the substituent's being either on the quinonic or on adjacent rings. This is reflected in their chemical reactivity, especially in heterocyclic quinines. Hydroxylated quinones that have one or more hydroxy groups attached directly to the quinone moiety are found in nature in great variety. As most of them exhibit interesting biological activity, there are an increasing number of publications annually about their isolation, characterization and their synthesis in the laboratory.
8-Hydroxyquinoline has a wide variety of uses. 8-hydroxyquinoline and its salts, halogenated derivatives metal complexes have been used as analytical reagents and as antimicrobial agents in medicine, fungicides, and insecticides. It is also used as a preservative in cosmetics and tobacco, a chemical intermediate in dye synthesis and a precipitating reagent for uranium and other radioactive metals in nuclear power plant liquid waste effluent. It is used in nuclear medicine with indium[32].

Citric acid has long been recognized as a universal constituent of plants and animals as well as the human body. Over the past century, it has become the organic acid of choice for industrial consumer products – in the food, pharmaceutical and cosmetic industries as well as being used in a variety of technical applications ranging from textile finishing to waste water treatment.

Citric acid is universally present in today's world, transcending cultural boundaries and serving multiple industries[18]. Citric acid is used in numerous consumer products, from foods to pharmaceuticals and detergents. Commanding over 70% of the world market for fruit acids, citric acid offers formulators a unique combination of benefits: In the food and beverage industry, citric acid is the preferred acidulate due to its high solubility, pleasant tart taste and excellent flavor blending characteristics. Its ability to form complexes with trace metals, citric acid is used as an antioxidant synergist. It stabilizes colour, taste, flavour and vitamins in various food products including processed fruit, potatoes, vegetables, fish and meat products. As a buffering agent, citric acid and its salts help formulators to maintain optimum pH for maximum stability of active ingredients. Citric acid shows the widest buffering capacity (P^H 2.5-6.5) of all organic acids, and therefore can give the food, personal care and pharmaceutical industries the flexibility needed to formulate optimal end products. Citric acid, as well as its sodium and potassium salts, is readily biodegradable and safe for both industry and consumers. These properties underline its utility as a food and pharmaceutical ingredient. Citric acid's unique properties can also be applied over a broad range of industrial applications. The cleaning, construction, textile and paper industries have taken advantage of citric acid's outstanding chelating ability, as well as its non-toxicity, to pioneer new uses for citric acid and citrates. Metal plating, the desulphurization of flue gas, oil recovery or the decontamination of radioactive nuclear reactor materials citric acid is likely to be involved[33, 34].

In recent years, organic bulk hetero-junction solar cells have attracted the widespread attention of research institutions and also companies. The joint efforts have lead to devices with almost 100% internal quantum yield, and power conversion efficiencies between 5% and 8%. Nevertheless, for a directed optimization of the solar cell performance, the fundamental aspects of photo generation and energetic have to be better understood. A central role for the function of organic photovoltaic devices is played by the charge transfer (CT) complexes, also called bound polaron pairs, which are the crucial intermediate step between singlet dissociation and free charge generation. There is mounting evidence that the properties of this hybrid state, residing at the hetero interface between donor and acceptor material, governs both, the voltage dependent photocurrent as well as the open circuit voltage.

The photocurrent giving the short circuit current and the fill factor and also the open circuit voltage directly determine the power conversion efficiency of a solar cell. In general, however, a design made to achieve high photocurrents, i.e. where photo generation of free charges is very efficient, might be expected to show a low open circuit voltage and vice versa. In order to increase both, photocurrent and open circuit voltage, at the same time, it is important to gain a detailed understanding of the elementary processes that determine the output voltage and the photocurrent as well as the relation between them. In polymer–fullerene blends useful for photovoltaic energy conversion, usually donor–acceptor systems where both highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the one organic semiconductor (the electron donor) are higher than the electron acceptor. When an isolated molecule absorbs visible or ultra-violet radiation an electronic transition occurs which may result in a considerable intermolecular redistribution of charge. In most organic solar cells, charges are created by photo induced electron transfer. In organic solar cells an electron is transferred from an electron donor material to an electron acceptor material with the aid of the additional input energy of an absorbed photon with energy hv. An electron donor is characterized by a molecular material with a small electron affinity. Vice versa an electron acceptor is a material with a high electron affinity[35] .

3. MATERIALS AND METHOD

3.1. Reagents

8-Hydroxyquinoline, (ACS reagent 99% Sigma Aldrich) and citric acid (crystal LR 99% WARDLE CHEMICALS LTD) of the highest purity were used without further purification. Hexane 95% (UNI-CHEM chemical reagent), Ethanol 97% and methanol 99.99% (Analytical reagent grade) were used without further purification and also distilled water was used throughout the work.

3.2. Instruments used

A Shimadzu model 180 UV-VIS double beam spectrophotometer PG instrument LTD with matched 1-cm quartz cells was used for recording the electronic absorption Spectra measurements at Jimma University, collage of veterinary medicine, Postharvest laboratory. Hanna Research HI 8820N conductivity meter was used for conductance measurements. The IR absorption spectra of the donor 8HQ, acceptor citric acid and its CT-complex were recorded in the frequency range 4000-400 cm^{-1} with spectrophotometer using KBr technique. The ^{1}H-NMR spectra were recorded at NMR laboratory room at Addis Ababa University, Chemistry Department on spectrophotometer using D_2O (Deuterium oxide) and $CDCl_3$ (Chloroform) as a solvent. The ^{1}H-NMR data are expressed in parts per million (ppm). Magnetic stirrer for stirring the complex solution and beam balance to measure weight.

3.3. Preparation

3.3.1. Preparation of Standard Solutions

The stock solutions of donor 8-Hydroxyquinoline (8HQ) at concentration of $5x10^{-4}$ mole L^{-1} were freshly prepared by dissolving accurately weighted amounts in ethanol and methanol in appropriate volumetric flask. In the same way the stock solutions of acceptor citric acid (CA) at concentration of $5x10^{-5}$ mole L^{-1} were prepared in different volumetric flask by dissolving accurately weighted amount in ethanol and methanol solvents.

3.3.2. Synthesis of Complex

The solid CT complex of 8HQ and citric acid were prepared by mixing 3mmol of the donor in ethanol/ methanol (40ml) mixture with 1mmol of acceptor. The mixture was stirred for 3 hours at room temperature which resulted in the precipitation of the solid CT complexes. The resulting complex was isolated as light yellow crystals. The isolated complex was filtered off using filter paper Wathman No.1. The isolated solid CT complex was washed well with little amounts of hexane and dried under vacuum.

3.4. Measurement of conductivity

For conductometric measurement aliquot of 25mL of $5x10^{-4}$M of 8HQ solution was transferred to the beaker and titrated with $5x10^{-5}$M of CA solution at room temperature. The conductance values were recorded and plotted versus the titrant volume in ethanol and methanol.

3.5. Solvent effect

In order to select the suitable solvent for CT complex formation, the reaction of 8-HQ with CA was made in ethanol and methanol solvents. The wavelength of the CT band of the complex and formation constant between 8-HQ and CA was measured in ethanol and methanol solvents.

4. RESULT AND DISCUSSION

4.1. Spectral characteristics of the CT-complexes

The electronic absorption spectra of the donor, acceptors and the resulted CT-complexes were carried out in different solvent such as ethanol and methanol in the region of (450-200 nm) by using Shimadzu model 180 UV-VIS double beam spectrophotometer PG instrument LTD with a 1 cm quartz cell. Illustrative examples of the absorption spectra (Figure 2, 3) of the reaction product of the studied complex formed between 8-Hydroxyquinoline and Citric acid were shown.

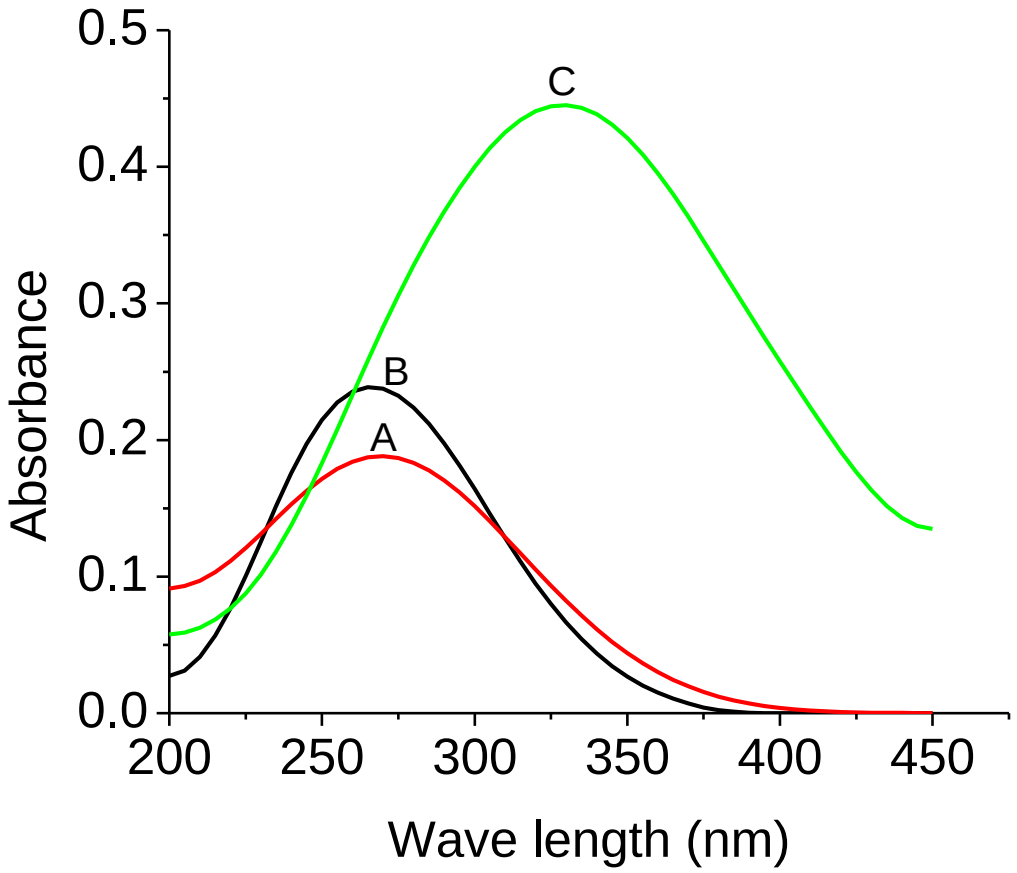

Figure 2. Electronic spectra of: (A) $5x10^{-4}$ mol L^{-1} 8HQ; (B) $5x10^{-5}$ mol L^{-1} CA and (C) CT Complex [$5x10^{-4}$ mol L^{-1} 8HQ + $5x10^{-5}$ mol L^{-1} CA] in methanol.

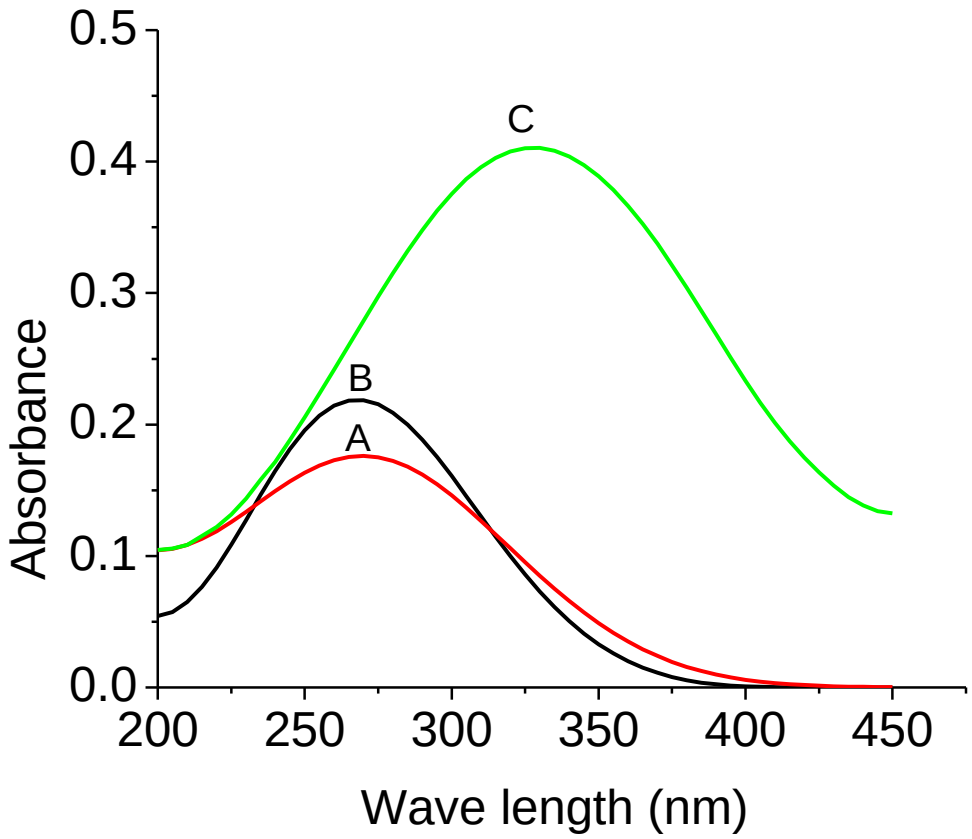

Figure 3. Electronic spectra of: (A) $5x10^{-4}$ mol L^{-1} 8HQ; (B) $5x10^{-5}$ mol L^{-1} CA and (C) CT Complex [$5x10^{-4}$ mol L^{-1} 8HQ + $5x10^{-5}$ mol L^{-1} CA] in ethanol.

Once the donor and acceptor solutions were mixed strong change in color was observed. These changes in colors represent strong evidence of the charge-transfer interactions between the donor and the acceptor. The spectra obtained for CT complex show the new maximum absorption bands at wavelength of 325nm and 320 nm in methanol and ethanol respectively, which are not due to the absorption of any of the reactants and considered to be the results of CT complex formation between the investigated 8-HQ and CA complex. The new, low energy absorptions observed in solvents containing both a donor and an acceptor have been described by Mulliken[1] as charge transfer transitions involving the excitation of an electron on the donor to an empty orbital on the acceptor. The result was in agreement with literature[36].

4.2. Conductivity

For conductometric measurement aliquot of $5x10^{-4}$ mol L^{-1} of 8HQ solution was transferred to the beaker and titrated with $5x10^{-5}$ mol L^{-1} of CA solution at room temperature. The conductance values were recorded and plotted versus the titrant volume in ethanol and methanol.

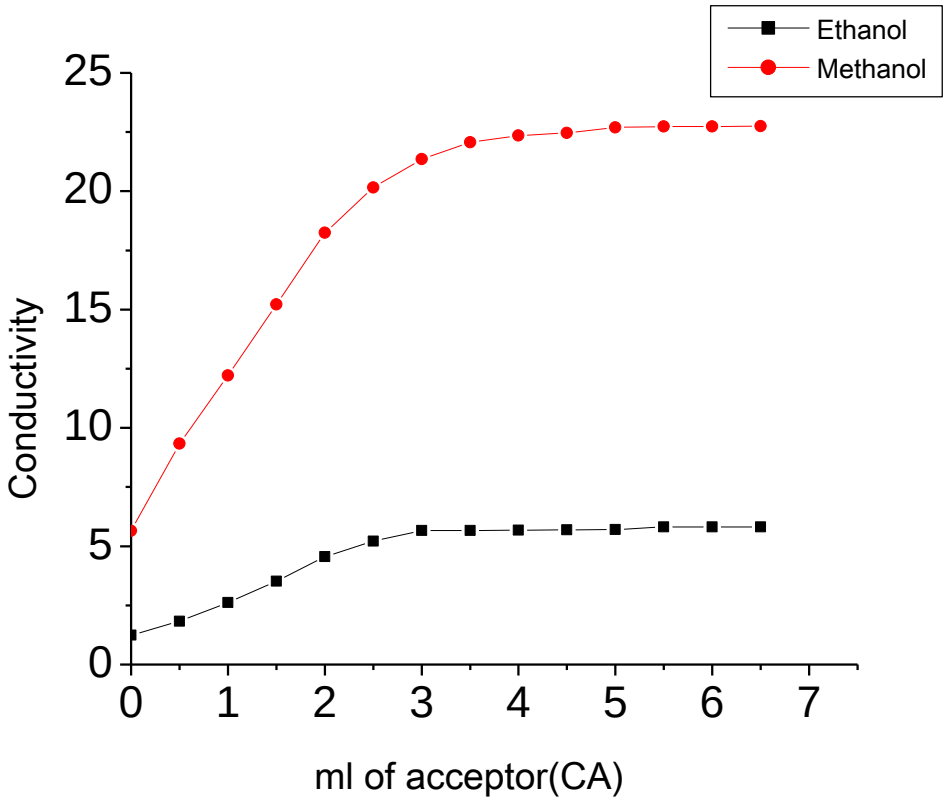

Figure 4. Conductometric titration plots of CT complex in ethanol and methanol.

The resulted charge transfer complex solution exhibit appreciable conductance (Figure 4) which may be explained by possible formation of charge transfer complex between the reaction partners in solution. This result was supported by litratures[37-39]. The greater the polarity of the solvent, the greater would be the formation of ionic species and the conductivity also increases proportionately. It has been observed that the destabilization of the dative structure $D^+ - A^-$ of CT complex in polar solvent is due to dissociation of the complexes into D^+ and A^- [40].

4.3. Stoichiometry of the charge transfer complex

The stoichiometry of the CT complex (Fig.5) formed in ethanol and methanol was determined by applying Job's continuous variation method.

In both solvents the symmetrical curve with a maximum at 0.75 mole fraction indicated the formation of 3:1 (D: A) CT complex.

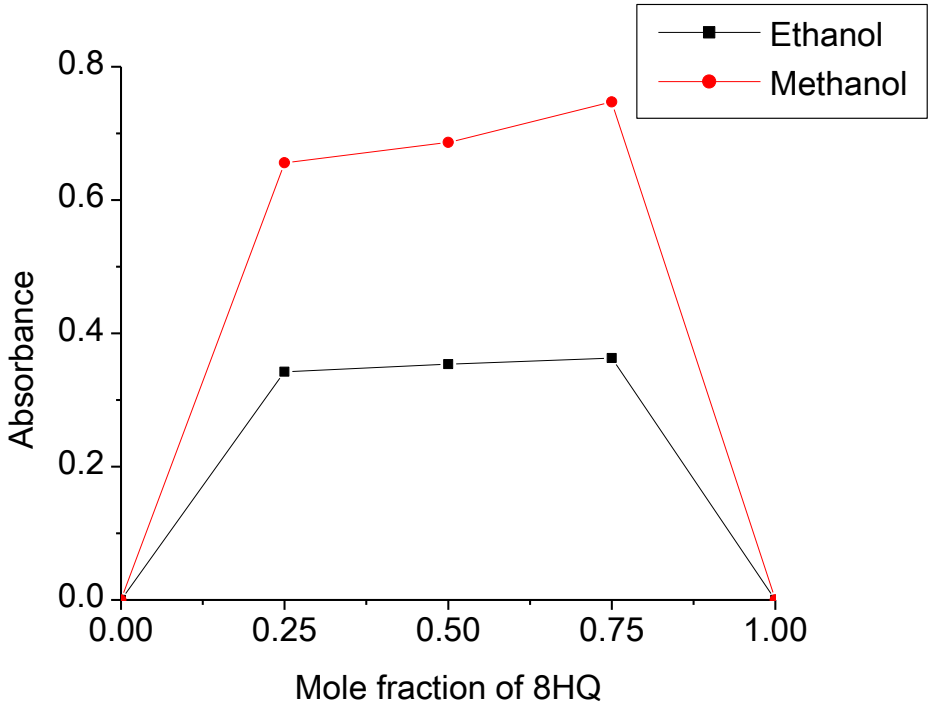

Figure 5. Job's method plots of CT complex in ethanol and methanol solvents.

4.4. Determination of Formation Constants of the CT Complex

Based on the electronic spectra of the intermolecular charge-transfer complex formed from the reactions of 8HQ with CA at various concentrations of 8HQ the values of formation constant (K_{CT}) and molecular extinction coefficient (ε_{CT}) were calculated independently under the condition of [D]>>[A] by using the modified Benesi-Hildebrand equation. The equation derived for this method can be written in the following form[41].

$$\frac{(C_d)^3 Ca}{A} = \frac{1}{K\varepsilon} + \frac{1}{\varepsilon} C_d(9Ca + C_d) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 4.$$

where C_a and C_d are the initial concentrations of the acceptor and the donor respectively, and *A* is the measured absorbance of the detected CT band. It depends on the experimental condition that one of the two component species should be present in large excess.

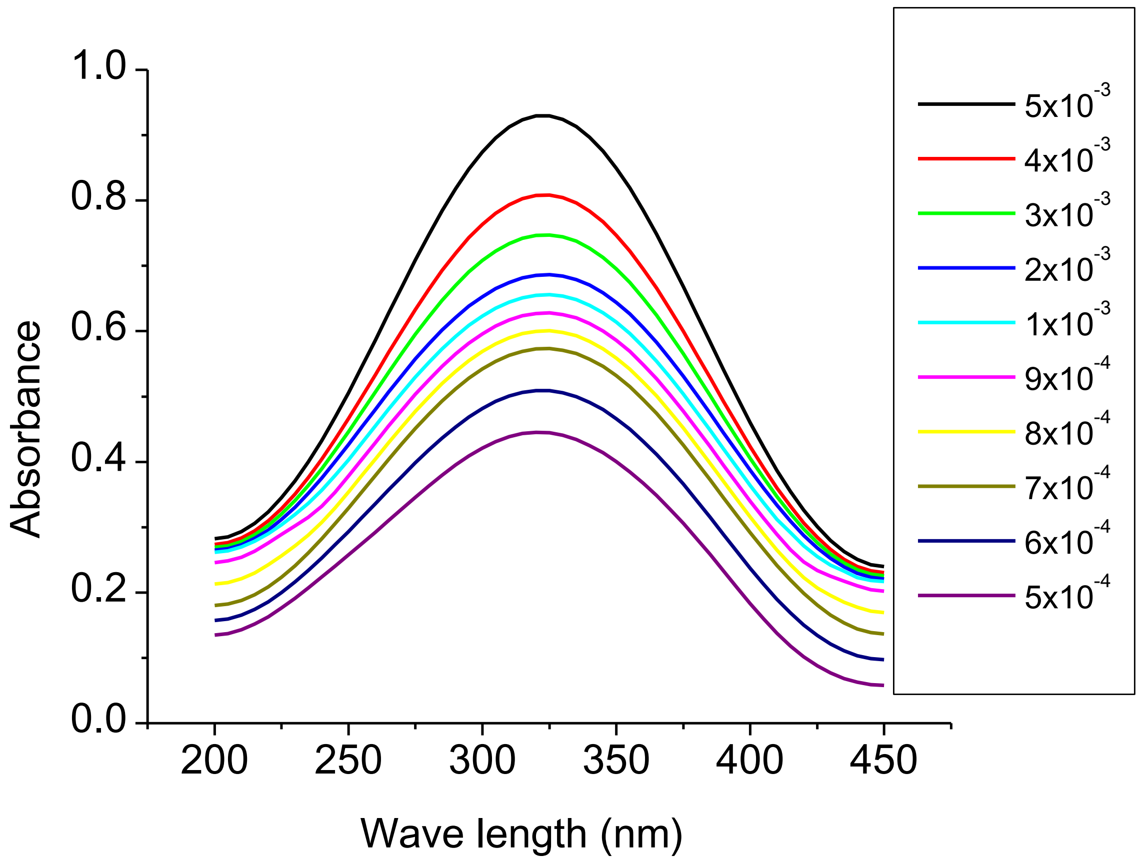

Figure 6. Electronic spectra of CT complex of $5x10^{-5}$ mol L^{-1} CA with various concentrations of 8-HQ from $5x10^{-4}$ to $5x10^{-3}$ mol L^{-1} in methanol.

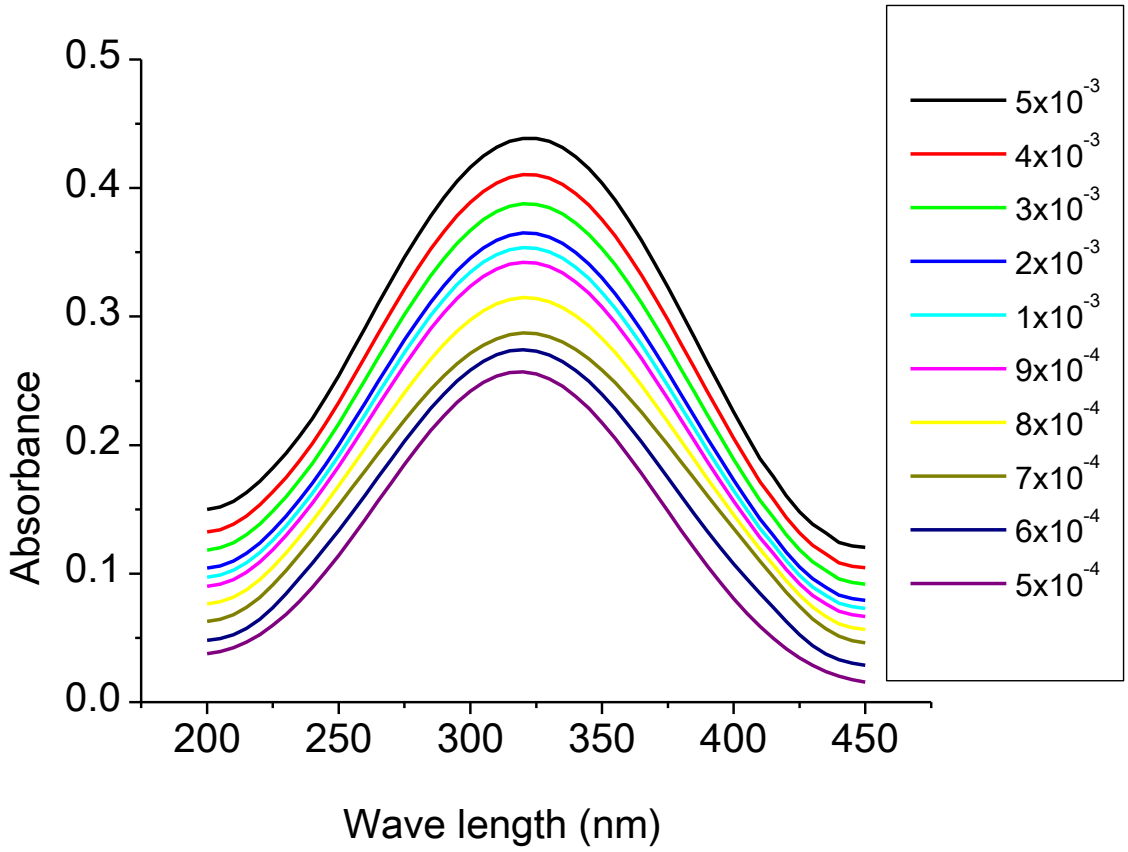

Figure 7. Electronic spectra of CT complex of $5x10^{-5}$ mol L^{-1} CA with various concentrations of 8HQ from $5x10^{-4}$ to $5x10^{-3}$ mol L^{-1} in ethanol.

When the $C_aC_d^3/A$ values for the 3:1 charge-transfer complex is plotted against the corresponding $C_d(9C_a + C_d)$ values, a straight line is obtained with a slope of $1/\varepsilon_{CT}$ and an intercept of $1/K\varepsilon_{CT}$.

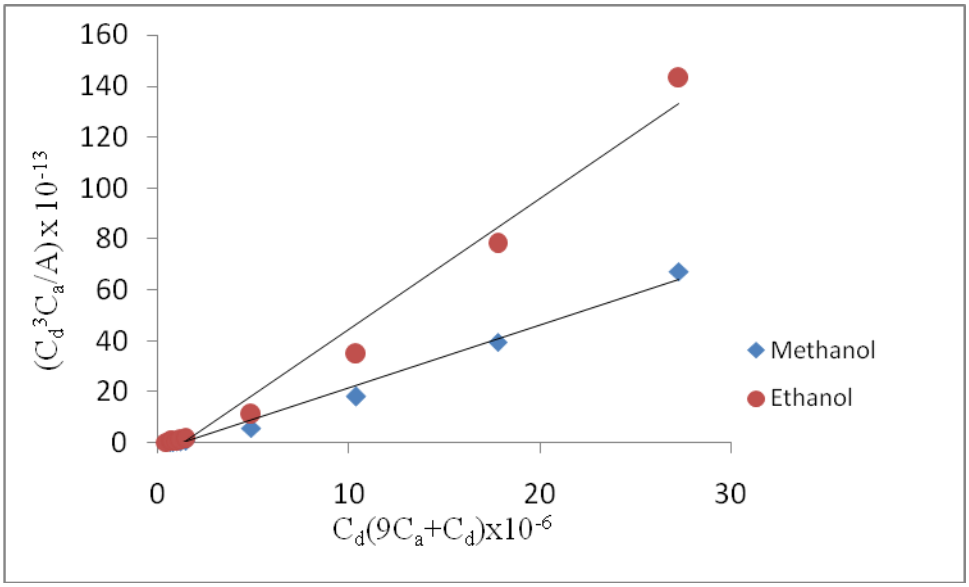

Figure 8. Benesi–Hildebrand plots of CT complex in ethanol and methanol solvents

From figure 8 the K_{CT} and ε_{CT} values associated with the complexes are given in Table1.

Table 1. Absorption maxima, Ionization potential, standard Gibb's free energy change, formation constant and molar extinction coefficient of CT complex in ethanol and methanol.

Solvent	λ_{CT}(nm)	Ip(ev)	ΔG°(KJ/mol)	K_{CT} x10^6	ε_{CT} x10^6
Ethanol	320	10.54	-43.48	7.14	2
Methanol	325	10.46	-33.33	6.67	5

From table 1, one observes the high values of K_{CT} and ε_{CT} in the studied solvents. This confirms the expected high stability of the formed complex in the studied solvents as a result of the high donation power of 8HQ.

4.5. Determination of ionization potentials of the donor

The ionization potential of the donor (IP) of the CT complexes are calculated by using empirical equation derived by Aloisi and Pignataro[42].

$IP\ (eV) = 5.76 + 1.53x10^{-4}x\nu_{CT}$ …… 5.

where ν_{CT} is the wave number in cm^{-1} that corresponds to the CT band formed from interaction between the donor and the acceptor. The electron-donating power of a donor molecule is measured by its ionization potential, which is the energy required to remove an electron from the highest occupied molecular orbital. The ionization potentials of the donor (8HQ) were 10.54 and 10.46 in ethanol and methanol respectively. These values are almost the same in both solvents confirming that IP has limited effect on the stability of the formed complex and solvent independent but in comparison there is strong interaction b/n 8HQ and CA in ethanol than methanol. Moreover the same bonding molecular orbital of the donors overlaps with the same anti bonding molecular orbital of the acceptors. This was supported by litrature[43].

4.6. Determination of standard free energy changes (ΔG°)

The standard free energy of complexation (Δ*G*°) for each complex was calculated from the formation constants using below equation [44].

$$\Delta G° = -2.303RT \log K_{CT} \quad \text{.....6.}$$

Where Δ*G*° is the free energy change ($kJmol^{-1}$), *R* is the gas constant (8.314 $Jmol^{-1}K^{-1}$), *T* is the temperature in K, and K_{CT} is the formation constant of the complex ($Lmol^{-1}$) at room temperature. The obtained value of ΔG° for the CT complex is -33.33 and -43.48 $kJmol^{-1}$in methanol and ethanol respectively; these negative values indicate that the interaction between the donor (8HQ) and acceptor (CA) is exothermic and spontaneous. The negative values of the free energy change suggest the simultaneous production of the formed complex. The values of ΔG^o become more negative as the value of K_{CT} increases. As the bond between the donor and acceptor becomes stronger and thus, the components are subjected to more physical strain or less freedom, the values of become more negative. This is in line with literature [9].

4.7. Effect of solvent

Absorption spectral characteristics (fig.2 above) of the CT complexes of studied 8HQ with CA were carried out in methanol and ethanol solvents at room temperature. However, the most intense absorption was obtained in methanol.

Small shift in the position of both lowest and maximum absorption peaks in each spectra in the solvents were found. The greater the polarity of the solvent, the greater would be the formation of ionic species and the solubility. The experimental results of the CT interaction between 8-HQ and CA in ethanol and methanol solvents show the values of association constants K_{CT} value was larger in ethanol than methanol and also the value of molar extinction coefficient of the complex was larger in methanol and smaller in ethanol. This implies that the K_{CT} values increases from methanol to ethanol with decreasing solvents polarity. Moreover, the increase in K_{CT} values with decreasing solvents polarity may also be due to the fact that CTC should be stabilized in less polar solvent. It means the CTC should be strong in less polar solvent than polar solvent. Ethanol was unsuitable solvent for charge transfer complex due to limited solubility. Methanol gave satisfactory results. This result was in good agreement with litratures[8, 40].

4.8. IR spectral analysis

The infrared spectral analysis has been carried out to understand the functional group present in the crystal, chemical bonding and it provides useful information regarding the molecular structure of the compound. In order to analyze qualitatively the presence of functional groups IR absorption spectra (Fig.9-11) of the electron donor 8HQ, acceptor citric acid and its CT-complex were recorded in the frequency range 4000-400 cm^{-1} with spectrophotometer using KBr technique and the corresponding absorption spectra obtained are shown.

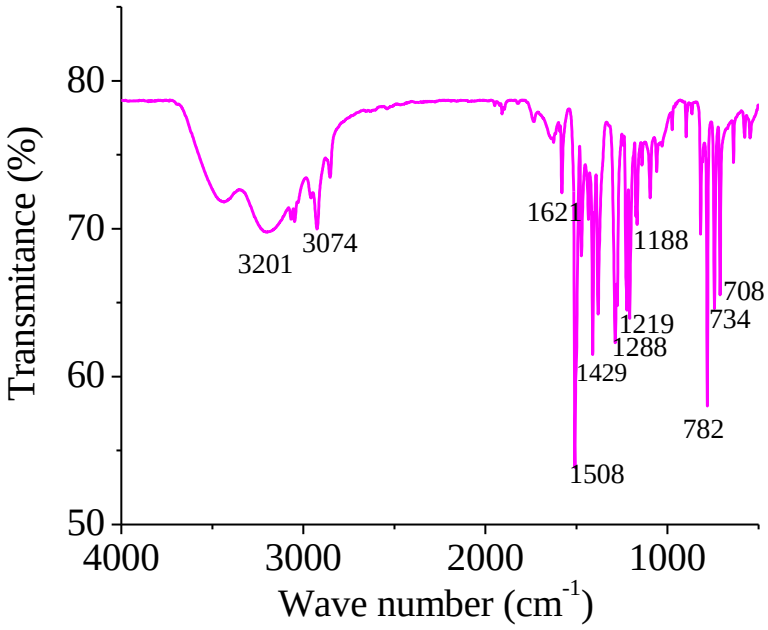

Figure 9. Infrared spectra of 8-hydroxyquinoline.

The IR spectra of 8HQ indicate that the broad band between 3600 cm^{-1} and 3100 cm^{-1} appeared due to the O-H stretching. The characteristic absorption band appeared at 3074 cm^{-1} is assigned to C–H stretching vibration of 8-HQ. The infrared band observed at 1219 cm^{-1} is due to C–O stretching vibration mode. The weak band at 1621 cm^{-1} is responsible for C=N stretching of the ring. The band assigned at 1508 cm^{-1} is attributed to C=C ring stretching vibration. Medium band which observed at 734 cm^{-1} responsible for C=C out of the plane bending in the ring where as weak band observed at 782 cm^{-1}asignd for C=C out of plane bending. The peaks at 1219 and 1288 cm^{-1} are assigned to C-O stretching vibration. The aromatic C-H in plane bending appears at1188 cm^{-1}. The C-H out of plane bending occurs at 708 cm^{-1}. The peak at1429 cm^{-1} is assigned to O-H plane bending.

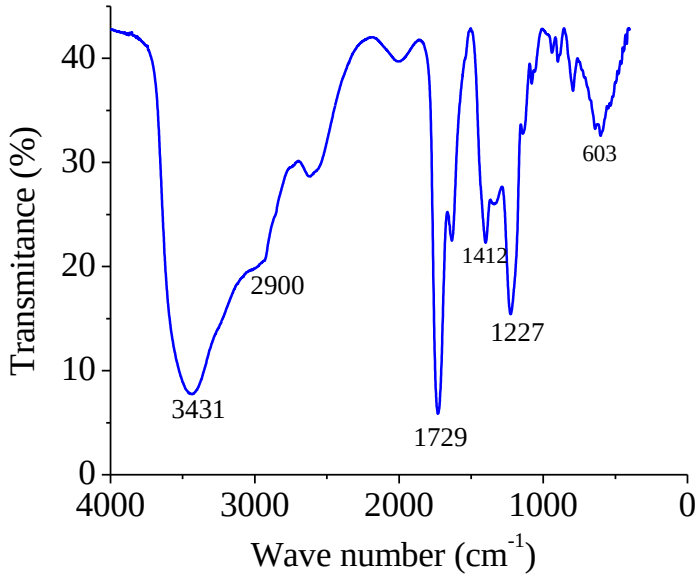

Figure 10. Infrared spectra of citric acid.

The IR spectra of CA indicate that the strong broad band at 3431 cm^{-1} is due to the O-H stretching of the carboxylic acid functionality as well as the alcohol. The medium band at 2900 cm^{-1} confirms the presence of CH_2 group. The strong band at 1729 cm^{-1} is due to the C=O stretching of the carboxylic acid. Weak band which observed at 1412 cm^{-1} responsible for in plan bending where as a very weak band observed at 603 cm^{-1} is due to C=O stretching out of plan bending.

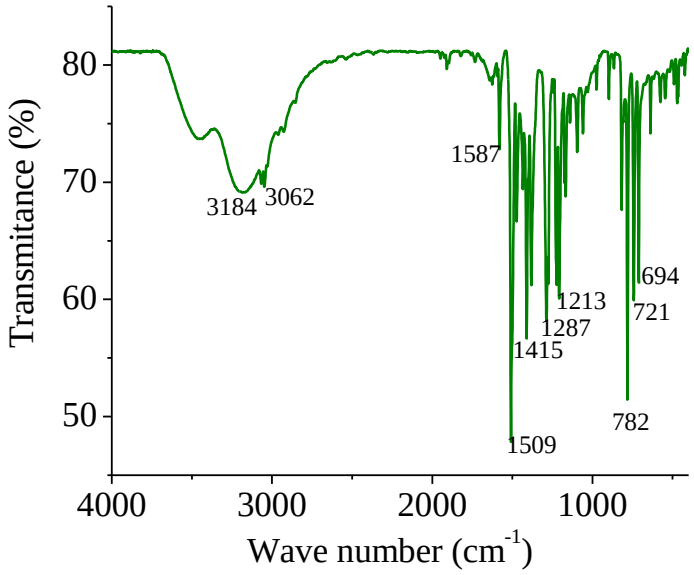

Figure 11. Infrared spectra of charge transfer complex.

Upon complexation, the IR spectrum of O-H was distorted at approximately 4000 and 3000 cm^{-1} due to H-bond formation. This may be interpreted as a result of the formation of intermolecular hydrogen bond between –OH of donor and acceptor molecule. This is a clear indication of the formation of the CT-interactions. Same kinds of results such as shifting wave number values after complexation like the up field shift of C=N to 1587 cm^{-1} and C-H to 3062 cm^{-1} was an indication for the formation of CT complex. And some literatures were support it [9]. The formation of the CT complex is strongly supported by observing the main infrared bands of the reactants, 8HQ, and CA in the product spectra. However, the bands of the donor and acceptor in the complex spectra show small shifts in the frequency as well as some changes in their intensities compared with those of the free 8-HQ (donor) and CA (acceptor). This could be attributed to the expected symmetry and electronic structure changes upon the formations of charge transfer complex.

4.9. ^{1}H-NMR spectra of CT complex and reactants

The ^{1}H-NMR spectra of the donor (8HQ) and the CT complex were measured in $CDCl_3$ whereas the spectrum of an acceptor (CA) was measured in D_2O using spectrophotometer. The chemical shifts of the different types of protons of the donor, acceptor and CT complex were interpreted.

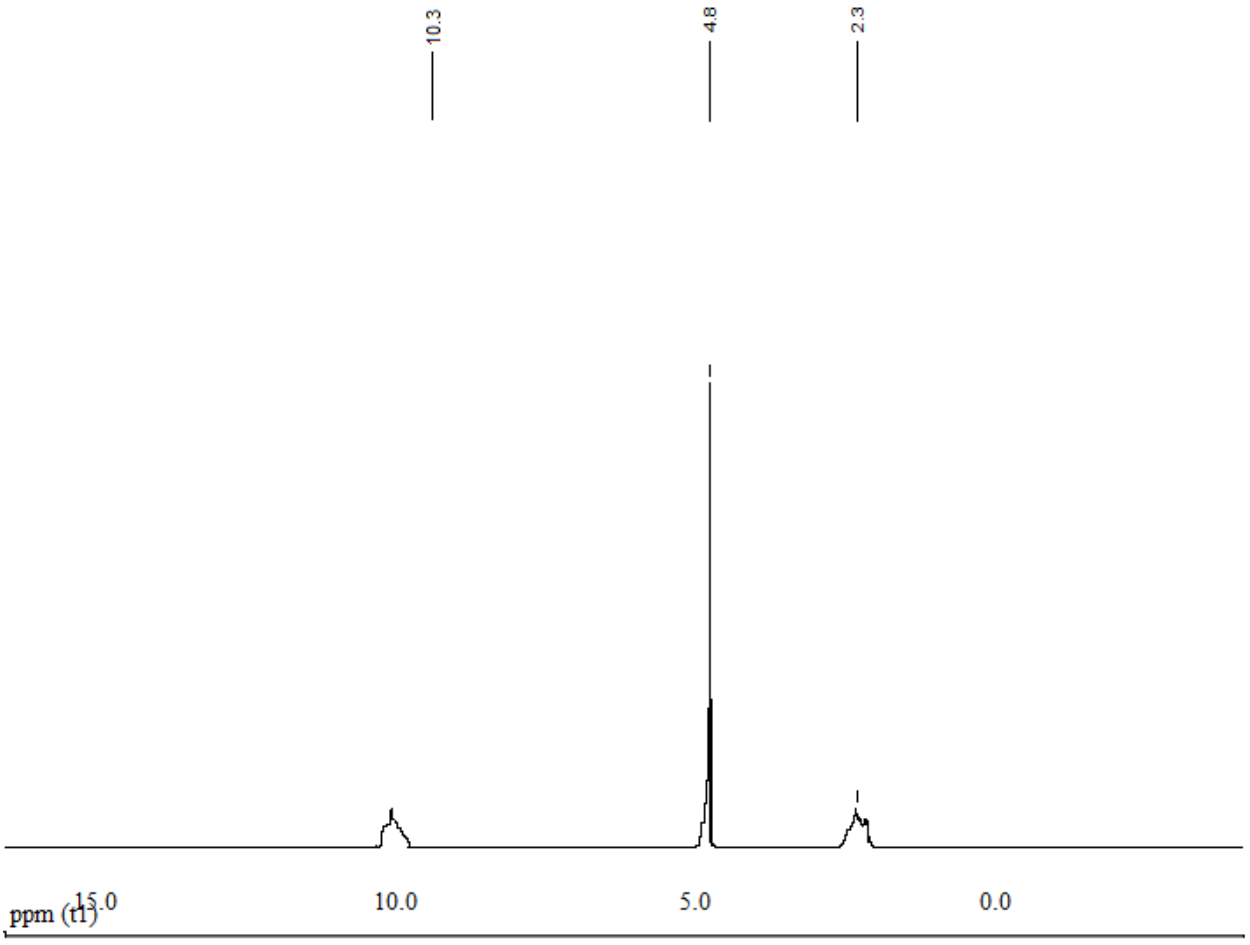

Figure 12: ^{1}H-NMR spectra of citric acid in D_2O.

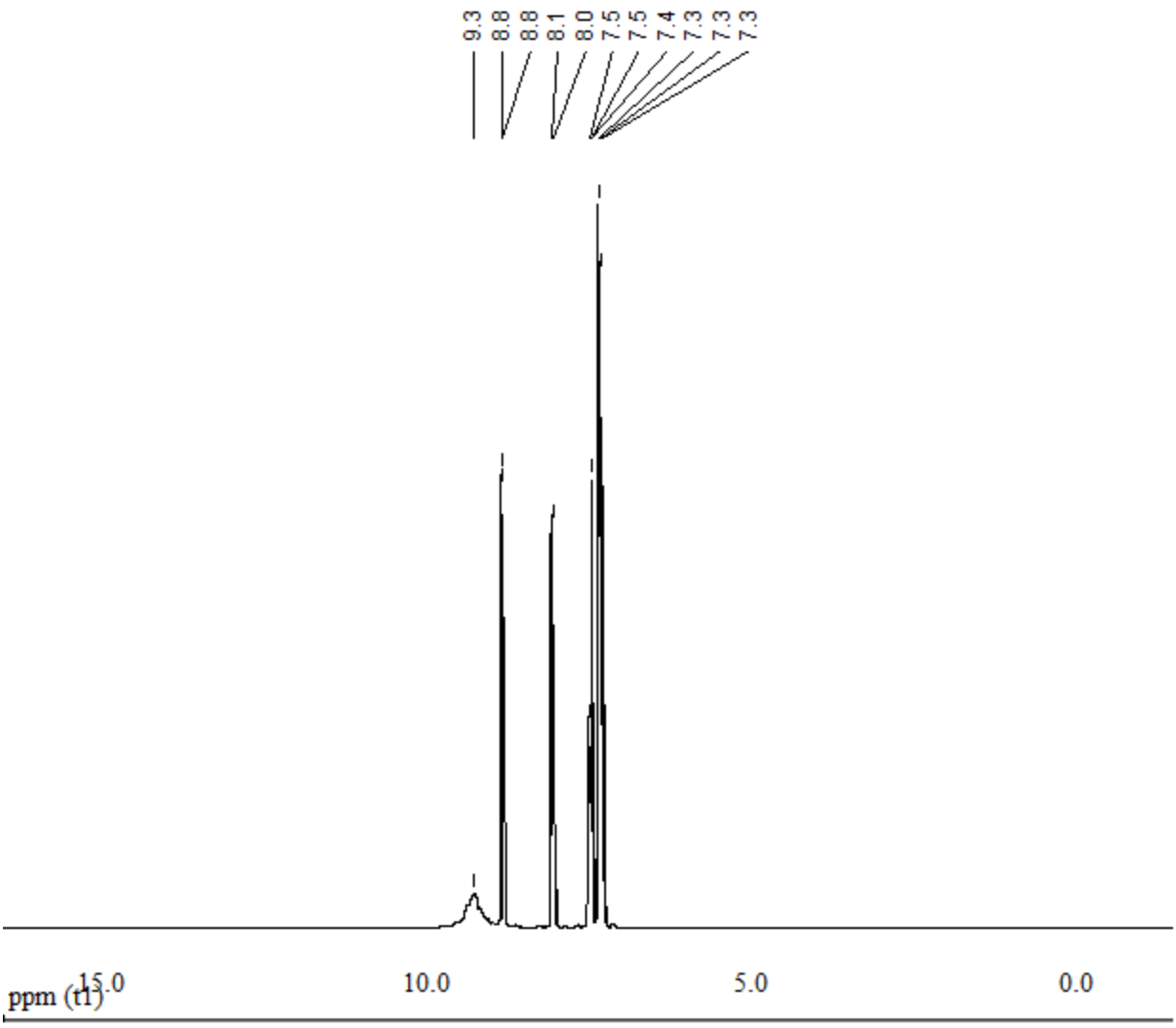

Figure 13: ^{1}H-NMR spectra of 8-hydroxyquinoline in $CDCl_3$.

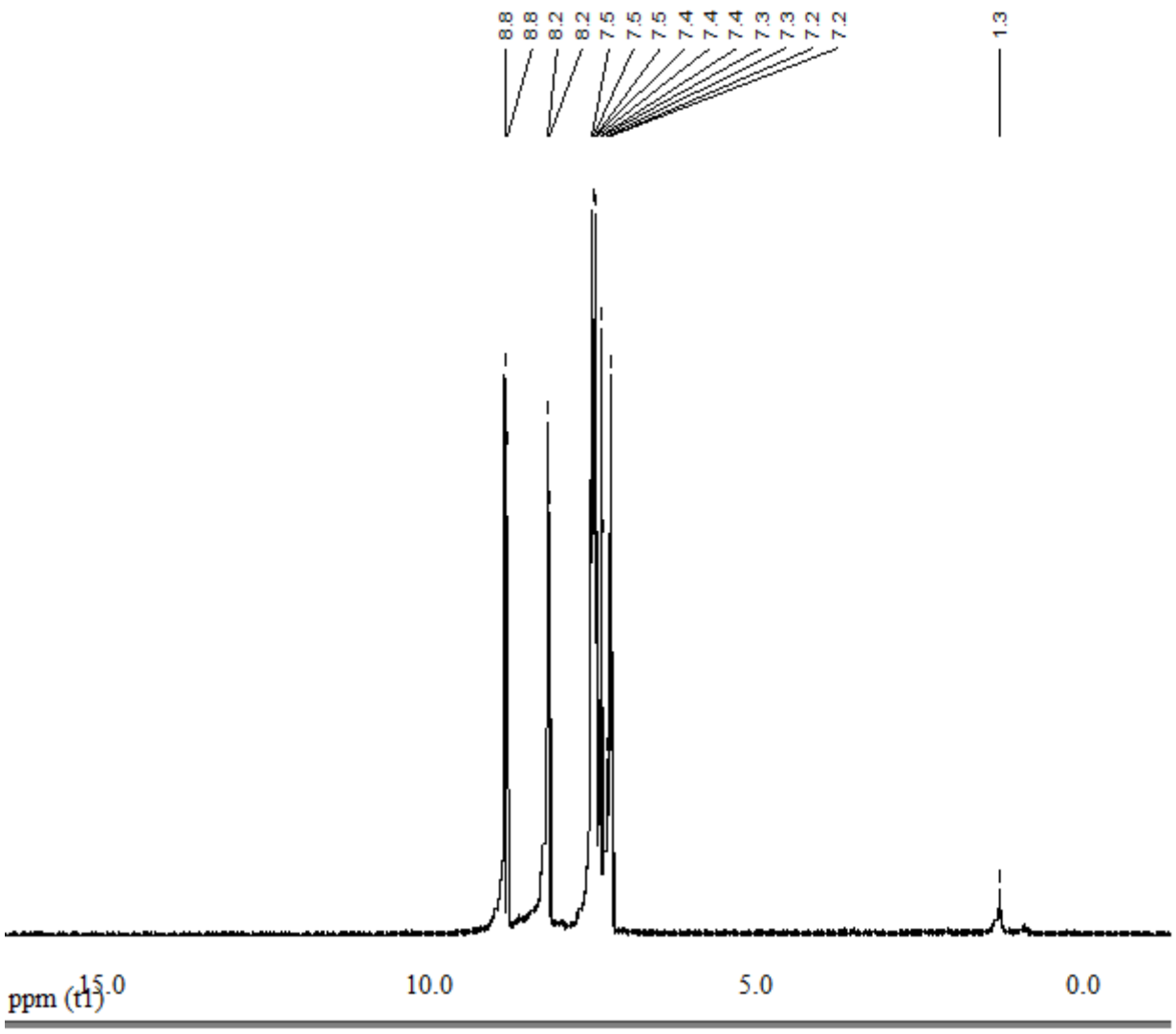

Figure 14: ^{1}H-NMR spectra of charge transfer complex in $CDCl_3$.

The proton transfer from citric acid to the 8-hydroxyquinone was further confirmed by measuring the ^{1}H-NMR spectra of the formed complexes. The 4000 MHz nuclear magnetic resonance (^{1}H-NMR) spectra of the CA and 8-HQ complex were measured in $CDCl_3$ at room temperature and given in Fig.14. The reaction of CA with 8-HQ yielded a new charge-transfer complex, which produced signals at (Fig.14) [$(CA)(8\text{-}HQ)_3$]: δ = 8.8 (d, 1H, C-2), 7.5 (t,1H,C-3), 8.2 (d, 1H, C-4), 7.3 (d,1H, C-5), 7.4 (t, 1H, C-6), 7.2 (d, 1H, C-7) 8-HQ ring protons and at δ 1.3 (s, 4H, CH_2) of citric acid.

It has been found that, the phenolic and citric acid protons (–OH) signals, that are observed at δ 9.3 and 10.3 in the spectrum of the free 8-HQ and CA respectively, disappeared in the spectrum of the CT complex, this indicate the involvement of the -OH group in chelating through the protonation and deprotonation process from the acceptor to donor migration. These changes in the δ (ppm) values of the donors and reaction products strongly support the charge migration from the acceptor acid towards the donor base.

5. CONCLUSION AND RECOMMENDATION

The charge-transfer complexation reaction of 8HQ as electron donor and CA as electron acceptors was studied spectrophotometrically in ethanol and methanol at room temperature. A new charge transfer complex was prepared and characterized through infrared, ^{1}HNMR and electronic spectra. The stoichiometry of the product was found to be 3:1. Benesi-Hildebrand and its modification methods were applied to the determination of formation constant (K_{CT}), and molar extinction coefficient (ε_{CT}). Gibb's free energy change and ionization potential of the resulting CT complex was determined. This charge transfer complex would provide information about the synthesis, solvent effect, and electrical conductivity. The result indicates spectroscopic method would be helpful in improving physical properties.

REFERENCES

1. Pearson, W. B., Mulliken, R. S. Structures of Complexes Formed by Halogen Molecules with Aromatic and with Oxygenated Solvents. *J. Am. Chem. Soc.* **1950**, *72*, 600.
2. Foster., R. *Charge Transfer Complexes*. Academic: London, **1969**; Vol. 7, p 576-789.
3. Moamen, S., Refat, M.Y., El-Sayed, A. M. A., Adam, H. A., Saad, H. H. E. Charge Transfer Complexes as a Semiconductor Models: Outline of Spectroscopic Studies on Electron Donor-Acceptor Complexes of Hexane-1,6-diol with Different π-Acceptors. *Int. J. Electrochem. Sci.* **2013**, *8*, 4234 - 4259.
4. Refat, M. S., Ibrahim, O.B., Al-Didamony, H., Abou El-Nour, K.M., El-Zayat, L. Spectroscopic characterizations on the N, N-bis-alkyl derivatives of 1, 4, 6, 8-naphthalenediimide charge-transfer complexes. *J. Saudi Chem. Soc.* **2010**, *4*, 83-97.
5. Khan IM, N. A., Ahmad, A. Semiquantitative determination of some nitrogen compounds by the formation of charge-transfer complexes of diphenylamine with p-dimethylaminobenzaldehyde. *Chinese Chem. Lett* **2010**, *21*, 720-724.
6. Wu DY, Z. L., Liu XM, H. R., Huang,Y.F., Ren, B., Tian, Z.Q. Photon-driven charge transfer and photocatalysis of paminothiophenol in metal nanogaps. *Chem. Commun* **2011**, *47*, 2520-2522.
7. Khan, I. M., Ahmad, A. S. N. Spectroscopic studies of multiple charge transfer complexes of 8-hydroxyquinoline with π-acceptor p-nitrophenol in different solvents at room temperature. *Can. J. Anal. Sci. Spectrosc.* **2009**, *54*, 31-37.
8. Refat, M. S., El-Korashy,S.A., El-Deen, I.M., El-Sayed, S.M. Charge transfer complexes of sulfamethoxazole drug with different classes of accepters. *J. Mol. Struct.* **2010**, *980*, 124-136.
9. Abdel-Majid, A., Adam, M. S., Sharshar, M., Moamen, T., Refat, S. Chemical and Physical Studies on the Reaction Mechanism of Charge-Transfer Complexes Between Narcotic Drugs and Electronic Acceptors. *Int. J. Electrochem. Sci.* **2013**, *8*, 1274 - 1294.
10. Refat, M. S., El-Zayat, L.A., Okan, Z. Y. Spectroscopic characterization Charege transfer complexes of morpholine with chloranilic acid and picric acid in organic media:crystal structure of bis(morpholinium 2,4,6-trinitrocyclohexanolate. *Spectrochimica* **2010**, *75*, 745-752.

11. Khan, I. M., Ahmad, A. Spectrophotometric and spectroscopic studies of complexation of 8-hydroxyquinoline with π acceptor metadinitrobenzene in different polar solvents. *Spectrochim. Acta A* **2009**, *73*, 966-971.
12. Mansour, I. A. Spectral and Electrical Conductance Studies of Charge-Transfer Complexes Derived from 6-Aminoindazole Schiff Bases and Chloro-p-benzoquinone Derivatives. *J. Chem. Pap* **2005**, *59*, 174-177.
13. Amirah, S., AL-Attas, M. M., Maram, H., Basha, T. Spectrophotometric and Conductimetric Studies of Charge Transfer Complexes of Some Pyrimidine Derivatives with Chloranilic Acid as π-Acceptor in Methanol. *World Journal of Chemistry* **2007**, *2*, 16-24.
14. Milica, C., Stević, L. M. I., Gordana Ć. M., Svetlana, M. Stanišić, D. M., Stanković, J. Z. Voltammetric Behaviour and Determination of 8-Hydroxyquinoline Using a Glassy Carbon Paste Electrode and the Theoretical Study of its Electrochemical Oxidation Mechanism. *Int. J. Electrochem. Sci.* **2011**, *6*, 2509-2525.
15. Rakesh, S., Mukesh, P., Sadhana, S., Suresh, A. Synthesis and characterization of charge-transfer complex of α-Naphthol and p-Chloranil. *J. Chem. Pharm. Res.* **2010**, *2*, 98-104.
16. Mooney FS, H. J. G. Lack of proteolytic digestion in the causation of pernicious anemia. *Lancet* **1967**, *290*, 397-399.
17. Naik, L. R., Math, N.N. Photo physical properties of 8-Hydroxyquinoline. *Indian Journal of Pure & Applied Physics* **2005**, *43*, 743-749.
18. Bobtelsky, M., Jordan, J. The structure and behavior of ferric tartrate and citrate complexes in dilute solutions. *J. Am. Chem. Soc.* **1947**, *69*, 2286-2290.
19. El-Mossalamy EH, I. A. Molecular charge transfer complexes of metal ions thiazolylazo compounds with iodine. *Pigment and Reain Technol* **2004**, *33*, 32-38.
20. Sharma, R. P. M., Singh, S., Ameta, R., Ameta, S.C. Synthesis, characterization and electronical conductivity of charge transfer complex of p-toludine and chloranil. *Ind. J. Chem. Technol* **2008**, *15*, 613-616.
21. Aljaber AS, N. E. Spectroscopic investigation of the donor-Acceptor interaction between o-phenylenediamine and tetracyanoethylene in dichloromethane. *Spectrochem. Acta* **2008**, *70*, 997-1000.

22. Al-Qaradawi SY, B. S., Mostafa, A., Nour, E. Synthesis, spectroscopic and thermal investigations of solid charge-transfer complexes of 1,4,7-trimethyl-1,4,7-triazacyclononane and the acceptors iodine, TCNE, TCNQ and chloranil. *Spectrochim. Acta A* **2008**, *71*, 1594-1598.
23. Bazzi HS, S. Y., Al-Qaradawi, S.Y., Mostafa, A., Nour, E.M. Synthesis, spectroscopic and thermal studies of the reactions of the donors piperazine and N,N′-dimethylpiperazine with σ- and π- acceptors. *J. Mol. Struct.* **2008**, *879*, 60-71.
24. Frag EY, M. G., Farag, A.B., Yussof, E.B. Utility of π and σ-acceptor Reagents for the spectrophotometric determination of cefotaxime sodium antibacterial drug via charge transfer complex formation. *Insight Pharm. Sci.* **2011**, *1*, 47-54.
25. Mulliken, R. S. Molecular compounds and their spectra. III. The interaction of electron donors and acceptors. *J.Phys Chem.* **1952**, *56*, 801-822.
26. Refat M S, N. M. Investigation of charge transfer complexes formed between 3,3-dimethylbenzidine (o-toluidine) donor and DDQ, p-chloranil and TCNQ as π-acceptors. *Chinese Sci Bull* **2011**, *56*, 1-8.
27. Pandeeswaran, M. E. Spectroscopic studies on the interaction of cimetidine drug with biologically significant d and π-accepters. *Mol. biomol. spectro.* **2010**, *75*, 1462-1469.
28. Refat, M. S., Yesilel, Z. Spectroscopic characterization of charge transfer complexes of morpholine with chloranilic and picric acids in organic media:crystal structure of bis(morpholinium 2,4,6-trinitrocyclohexanolate). *Spectrochimica Acta* **2010**, *75*, 45-752.
29. Himmi, B. M. B., Kitane, S., Eddaif, A., Alaoui, A., Bouklouz, A., Soufiaoui, M. Study of Zn (II) extraction by 5-azidomethyl-8-hydroxyquinoline experiment and modeling. *Hydrometallurgy* **2008**, *93*, 39-44.
30. Elena, M., Filip, I. V., Constantin, H., Ghirvu, I. Some Aspects of 8-hydroxyquinoline in Solvents. *cta Chemica IASI* **2009**, *17*, 85-96.
31. Davis, H. S., Joist, B. J., Heaton, W., Mathias, C., Sherman, L., Welch M. Scintigraphic detection of atherosclerotic lesions and venous thrombi in man by indium-lll- labelled autologous platelets. *Lancet* **1978**, *1*, 1185-1187.
32. Lamis, S., Adel, M., El-Metwally, N., Hassan, S. B. Synthesis, spectroscopic, thermal and structural investigations of charge-transfer complexes of 4, 40-trimethylenedipiperidine with chloranil, TBCHD, DDQ, TCNQ and iodine. *J. Molec. Struc* **2009**, *933*, 1-7.

33. Carlos, R. S., Luciana, P. S., Vandenberghe, C. R., Ashok, P. New Perspectives for Citric Acid Production and Application. *J. Food Technol. Biotechnol* **2006**, *44*, 141-149.
34. Pandey, A., Soccol, C.R., Rodriguez-Leon, J.A., Nigam, A. Production of Organic Acids by Solid-State Fermentation. In: Solid-State Fermentation in Biotechnology Fundamentals and Applications. *Asiatech Publishers Inc* **2001**, 113-126.
35. Hoppe, H.; Sariciftci, N. S. Organic solar cells: An overview. *J. Materials Research* **2004**, *19*, 1924-1945.
36. Asmaa, A., Ibrahim, A. Spectrophotometric studies of charge transfer complex of 8-hydroxyquinoline with 1,4-benzoquinone. *African Journal of Pure and Applied Chemistry* **2011**, *5*, 507-514.
37. Al-Shuja'a, O. M., Obeid, A.O., El-Shekeil, A.G. Spectral, thermal and DC electrical conductivity of charge transfer complex formed between 5,7-dimethyl-1-oxo-2-phenyl-1H-pyrazolo [1,2-α]pyrazol-4-ium-3-olate and iodine. *J. Macromol. Sci.* **2011**, *5*, 355-364.
38. Yakuphanoglu, F., Arslan, M . Determination of electrical conduction mechanism and optical band gap of a new charge transfer complex. *Solid State Commun* **2004**, *132*, 229-234.
39. Doaa, F., Baamer, E.H., Mossalamy, E.l. Salih, S., Juaid,A.l. Spectrophotometric and Kinetic Studies of Charge Transfer Complexes of Pantoprazole with Chloranilic Acid and DDQ as π-Acceptors. *2nd International Conference on Chemical, Environmental and Biological Sciences* **2013**, 17-18.
40. Benesi, H., Hildebrand, J. A Spectrophotometric Investigation of the Interactionof Iodine with Aromatic Hydrocarbons. *J. Am. Chem. Soc.* **1949**, *71*, 2703-2707.
41. Aloisi, G., Pignataro, S., *J. Chem. Soc. Faraday Trans.* **1972**, *69*, 534.
42. Reem, M. A. Spectrophotometric study of charge transfer complex between 2,6-diaminopyridine and 2,5-dihydroxy-p-benzoquinone. *Physics and Chemistry of Liquids* **2012**, *1*, 1-16.
43. Martin, A. N. J., Swarbrick, A., *Cammarata, Physical Pharmacy*. 3rd ed.; Lee and Febiger: Philadelphia, **1969**; PA, 344.
44. Bazzi, H. S., AlQaradawi, S.Y., Mostafa, A., Nour, E.M. Synthesis, spectroscopic and thermal studies of charge-transfer complexes of 1,4,8,11-tetraazacyclotetradecane-5,7-dioine with iodine,TCNE and DDQ. *J. Mol. Struct* **2010**, *980*, 218-224.