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Spectrophotometric Studies of Charge Transfer Complexes of 8-Hydroxyquinoline with Iodine in Different Solvents

GETYE BEHAILU YITAGESU [1*] TAMIRU GASHAW Gete[2]
1.College of Natural and Computational Sciences, Department of Chemistry, Wachamo University, Ethiopia
2.College of Natural and Computational Sciences, Department of Chemistry, Wolaita sodo University, Ethiopia

Abstract

The formation of 8-hydroxyquinoline-iodine charge transfer complex was confirmed by UV-Vis spectrophotometric method in carbon tetrachloride, dichloromethane, chloroform, ethanol and methanol. A change in UV-Vis spectrum of iodine is observed upon addition of 8-hydroxyquinolinein these solvents, where as the appearance of new bands support the formation of charge transfer complexes. The spectrum obtained from the complex of 8-hydroxyquinoline and iodine show different absorption bands at different wavelength for different solvents. The ratio of the charge transfer complex formed was determined from Job's Continuous Variation method. The spectrum obtained from the complex of 8-hydroxyquinolineand iodine shows absorption bands at 365 nm for carbon tetrachloride, 360 nm for dichloromethane, 358 nm for chloroform, 355 nm for ethanol and 290 nm for methanol. Parameters like dissociation energy, transition energy of the complex and ionization potential of the donor were calculated from their Λ_{max}. The values of these parameters were found to be increased from the less polar solvent, carbon tetrachloride to the more polar solvent methanol. The complex formed is relatively stable in less polar solvents than more polar solvents.

Keywords: 8-hydroxyquinoline, iodine, UV-Vis spectrophotometer.

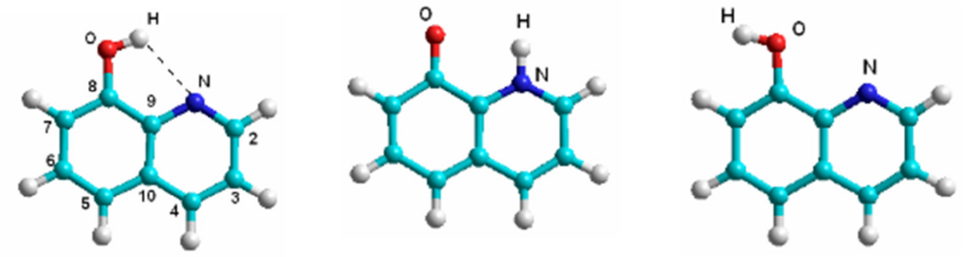
1. Introduction

Charge transfer complexes have recently received much interest in a broad variety of fields like, organic electronics, metal-organic and nonlinear spectroscopy [1-3]. The formation of molecular complexes of the charge-transfer between donors and acceptors plays an important role in many biological fields, such as enzyme catalysis, drug–receptor binding mechanism, and ion transfer through lipophilic membranes; in solar energy storage; in surface chemistry; utilized as organic semiconductors, photocatalysis. All involve complexation between two or more distinct molecules [4-6]. The molecular interactions between electron donors and acceptors are generally associated with the formation of intensely colored charge transfer complexes which absorb radiation in the visible region [7].

Charge transfer complexes involving iodine and a donor molecule with nonbonding electrons have been the subject of extensive research .The study of organic charge transfer complexes formed between the iodine and the donor molecules has played an important role in developing the theories of molecular association. Iodine is σ-type acceptor and has the property of molecular polarizability [8]. It forms a large number of both the weakest and the strongest charge transfer complexes. Most reactions of iodine with benzanthrone derivatives were studied photometrically in chloroform at room temperature [9].

The amount of iodine in the human body is very small. For normal people, the amount is about equal to the size of the head of a pin. That tiny dot of iodine can mean the difference between good and bad health. People who do not have enough iodine can develop serious health problems. At one time, the most common of those problems was a disease known as goiter. Goiter causes a large lump in the neck as the thyroid grows out of control. A goiter tries to make thyroid hormones, but it does not receive enough iodine from the person's diet. So it keeps expanding, trying to do its job [10]. A lack of iodine can cause other problems too. For example, thyroid hormones are needed for normal brain development in an unborn child. They are also needed to continue that development after birth. People who do not include enough iodine in their diet do not develop normally. Today, experts say that low levels of iodine are the leading cause of mental retardation, deafness, mutism, and paralysis. They also say less serious problems can be blamed on low iodine levels. These include lethargy drowsiness, clumsiness, and learning disabilities [11].

8-Hydroxyquinoline is an organic compound with the formula C_9H_7NO. It is a derivative of the heterocycle quinoline by placement of an OH group on carbon number 8. 8-hydroxyquinoline (8-HQ) is a conjugated system and a bi functional hydrogen bonding molecule, in protic solvents simultaneously acts as an H donor at the O-H group and as an H acceptor at the N atom [12].



(a) α-8-HQ (b)) β-8-HQ (c) tautomeric form

Figure 1. Structures of 8-hydroxyquinoline

8-Hydroxyquinoline and its derivatives are widely used as chelating reagents in analytical chemistry and radiochemistry for metal ion extraction and fluorometric determination. A quinoline moiety is present in many classes of biologically-active compounds, a number of them have been used clinically as antifungal, antibacterial and antiprotozoic drugs, as well as antituberculotic agents [13].

A qualitative interpretation of solvent shifts is possible by considering the momentary transition dipole moment present during the optical absorption; the difference in permanent dipole moment between the ground and excited state of the solute; the change in ground-state dipole moment of the solute induced by the solvent and the Franck–Condon principle [14].

The identity of charge transfer complex can be determined by UV-Vis, IR, NMR Spectroscopy, Conductometry and Kinetic methods [15]. UV-Vis Spectroscopy is highly sensitive and widely used. The complex formation is identified with a new absorption band in its UV-Vis spectrum [16].The use of spectrophotometers span various scientific fields, such as physics, materials science, chemistry, biochemistry, and molecular chemistry. They are widely used in many industries including semiconductors, laser and optical manufacturing, printing and forensic examination, and as well in laboratories for the study of chemical substances. Ultimately, a spectrophotometer is able to determine, depending on the control or calibration, what substances are present in a target and exactly how much through calculations of observed wavelengths [17].

A variety of electron donating compounds have been reported to yield charge-transfer complexes lead to their utility in the development of simple and convenient spectrophotometric methods. The aim of the present study is to investigate the formation of charge-transfer complex between 8-hydroxyquinoline and iodine using UV-Vis Spectroscopy.

2. EXPERIMENTAL PART

2.1. Apparatus

The apparatus used in this work were shimadzu UV-mini-1240 spectrophometer, volumetric flask, 1cm path length quartz Cuvettes with equal absorption, beaker, standard test tube, analytical balance (model LA 114, Lark, made in China), standard measuring cylinder and standard pipettes and syringes.

2.2. Chemicals

The chemicals used in this work were 8-hydroxyquinoline (India), iodine (Jod DAB, ph.Eur. B.P., ph.Franc. U.S.P), ethanol (ALPHA CHMIKA, 96%w/w), methanol (M.R.P), Carbon tetrachloride (NICE, 99%), Chloroform (LOBA CHEMIE PVT.LTD, 99%), dichloromethane (ALPHA-CHEM, 99.6%) and distilled water (deionized water). All the solvents were selected depending on the solubilty of 8-hydroxyquinoline and iodine.

2.3. Preparation of solutions

8-hydroxyquinoline and iodine sample were finely powdered. An appropriate amount of the 8-hydroxyquinoline (0.1815g) and the iodine (0.3173g) were weighed using analytical balance. The stock solutions (5 mM) in all the solvents (ethanol, methanol, dichloromethane, carbon tetrachloride and chloroform) of both the donor and acceptor were prepared in a 250 ml standard flask. The required amount of solutions of the 8-hydroxyquinoline and the iodine for absorption spectra measurement were prepared from the stock solutions by using dilution law.

2.4. Electronic Spectral Measurements

All UV-Vis spectroscopic measurements were done in different solvents diluted to appropriate concentrations. The UV-Vis absorption spectra of solutions were measured using shimadzu UV-Vis mini -1240 spectrophometer in the wavelength range of 200-800 nm. Using quartz cuvettes of 1.0 cm path length, the absorption of the donor and the acceptor were recorded. The solutions for UV-Vis Measurements were generally prepared by mixing the donor and the acceptor solutions by accurate dilution from stock solutions.

2.5. Determination of stoichiometric ratio of the reactants

The job's method of continuous variation was employed to determine the ratio of 8-hydroxyquinoline to iodine. This was done by varying the concentration of the donor (0.125 mM, 0.25 mM, 0.5 mM ,1 mM ,2 mM and 3 mM which were prepared from 5mM stock solution), while the concentration of the acceptor was kept constant (0.5 mM). The reactions were allowed to proceed for the 30 minutes until some color changes were observed and the absorbance of the resulting solutions were measured. The stoichiometric ratio of donor to acceptor was found to be 1:1 at which maximum absorbance (λmax) was recorded for all solvents used.

3. RESULT AND DISCUSSION

3.1. Spectral characterization of the complex

The solutions of 8-hydroxyquinoline in all the solvents used in the study were colorless, and the solutions of iodine were violet in carbon tetrachloride, dichloromethane and chloroform, deep orange in ethanol and methanol. The absorption spectra of 8-hydroxyquinoline, iodine and the complex in these solvents are shown in (Fig 2 – Fig 6).The change of color is attributed to the formation of charge transfer complex between 8-hydroxyquinoline and iodine. The spectra obtained for the complex shown in table 2 displays main absorption bands at 365, 360, 358, 355 and 290 nm in carbon tetrachloride (Fig 2), dichloromethane (Fig 3), chloroform (Fig 4), ethanol (Fig 5) and methanol (Fig 6) respectively. These bands are characteristics of an intermolecular charge transfer involving the overlap of the lowest unoccupied molecular orbital (LUMO) of the acceptor with the highest occupied molecular orbital (HOMO) of the donor [4].

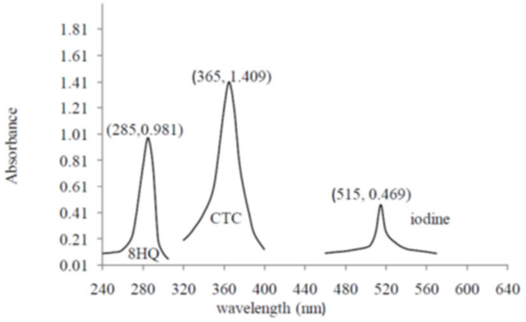


Figure 2.Absorption spectra of 8HQ, Iodine and charge transfer complex in CCl_4

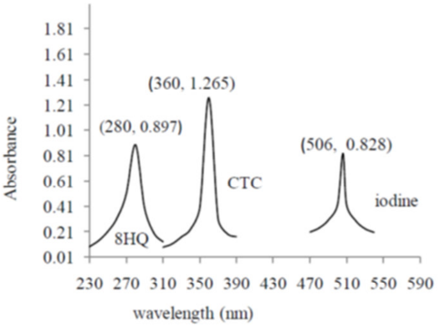


Figure3.Absorption spectra of 8HQ, iodine and charge transfer complex in CH_2Cl_2

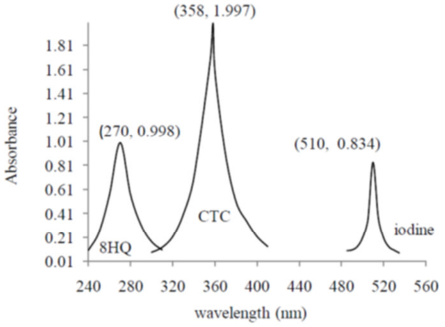


Figure 4. Absorption spectra of 8HQ, iodine and charge transfer complex in chloroform

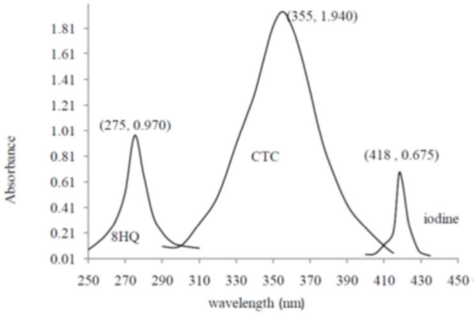


Figure 5. Absorption spectra of 8HQ, iodine and charge transfer complex in ethanol

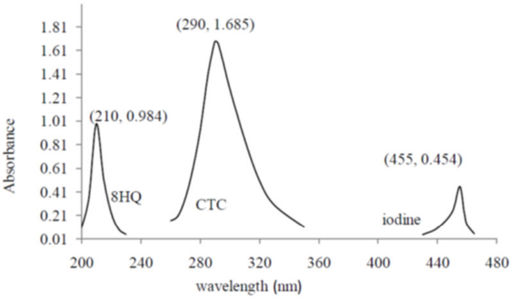


Figure 6. Absorption spectra of 8HQ, iodine and charge transfer complex in methanol

Table 1. Position of Absorption maxima of Donor and acceptor in CCl_4, CH_2Cl_2, $CHCl_3$, CH_3CH_2OH and CH_3OH

System	λmax	Absorbance
8HQ(CCl_4)	285	0.981
8HQ(CH_2Cl_2)	280	0.897
8HQ ($CHCl_3$)	270	0.998
8HQ(CH_3CH_2OH)	275	0.970
8HQ(CH_3OH)	210	0.984
Iodine(CCl_4)	515	0.469
Iodine(CH_2Cl_2)	506	0.828
Iodine($CHCl_3$)	510	0.834
Iodine(CH_3CH_2OH)	418	0.675
Iodine(CH_3OH)	455	0.454
8HQ-Iodine (carbon tetrachloride)	365	1.409
8HQ-Iodine (dichloromethane)	360	1.265
8HQ-Iodine (chloroform)	358	1.997
8HQ-Iodine (ethanol)	355	1.940
8HQ-Iodine (methanol)	290	1.685

8-hydroxyquinoline molecule is relatively electron rich and iodine is a relatively electron deficient molecule, they tend to associate with one another in a weak interaction known as an electron donor- acceptor complex. The new, low energy absorptions observed in solutions containing both a donor and an acceptor have been described by Mullikan [4], as charge transfer transitions involve the excitation of an electron from the donor to an empty orbital of acceptor. In all the systems studied, the absorption spectra are of similar nature except for the position of absorption maxima (λ_{max}) of the complex. The λ_{max} of the complex was found to appear on the shorter wavelength side of the acceptor absorption spectra in all the solvents.

3.2. Stoichiometry of the complex

Job's method of continuous variation [18] was used to determine the stoichiometric ratio of 8-hydroxyquinoline to iodine in the charge transfer complex. These were done by fixing the concentration of iodine to 0.5 mM and varying the concentration of 8-hydroxyquinoline from 0.125 to 3 mM for all the solvents used. The maximum absorbance was recorded when equal volume of 8-hydroxyquinoline and iodine are present in all the solvents. The stoichiometric ratio was found to be 1:1 in all the solvents as shown in table 2.

Table 2. Determination of stoichiometry, and absorption maxima by job`s method in carbon tetrachloride, dichloromethane, chloroform, ethanol and methanol.

System	8HQ Conc.(mM)	Iodine Conc.(mM)	λ_{CT},nm	Absorbance
8HQ-Iodine (carbon tetrachloride)	0.125	0.5	365	1.201
	0.25			1.292
	0.5			1.409
	1			1.326
	2			1.328
	3			1.215
8HQ-Iodine (dichloromethane)	0.125	0.5	360	1.203
	0.25			1.221
	0.5			1.265
	1			1.229
	2			1.218
	3			1.207
8HQ-Iodine (chloroform)	0.125	0.5	358	1.947
	0.25			1.953
	0.5			1.997
	1			1.976
	2			1.968
	3			1.959
8HQ-Iodine (ethanol)	0.125	0.5	355	1.732
	0.25			1.782
	0.5			1.944
	1			1.921
	2			1.852
	3			1.769
8HQ-Iodine (methanol)	0.125	0.5	290	1.543
	0.25			1.569
	0.5			1.685
	1			1.681
	2			1.602
	3			1.587

3.3. Physicochemical parameterization of charge transfer complex

In order to characterize the formation of the complexes between 8-hydroxyquinoline and iodine some physicochemical parameters were estimated to explain the property of the formation of the complexes.

3.3.1. Transition energy of charge transfer band

The transition energy is one of the physicochemical parameter of the complex and calculated using equation (1) [19].

$$E_{TC}\ (\mathrm{eV}) = h\nu_{CT} \ \ldots\ldots\ldots\ldots \ (1)$$

Where E_{TC} is the lowest transition energy in electron volts, h is Planck's constant and ν_{CT} is the wave number of the absorption peak of the charge transfer complex in cm^{-1}. The transition energy was found to be 3.407 eV in carbon tetrachloride, 3.455 eV in dichloromethane, 3.474 eV in chloroform 3.503 eV in ethanol and 4.289 eV in methanol. The transition energy increases with increasing solvent polarity. If the transition energy lower then it is easy to excite the electron from the ground state to the excited state of the complex [20].

3.3.2. Ionization energy

The ionization potentials I_D in eV of the donor can be calculated using the experimentally determined λ_{max} of the CTC from Eq. (2) [19].

$$h\nu_{CT} = aI_D + b \ \ldots\ldots\ldots\ldots \ (2)$$

Where a and b are constants and their values are 0.89 and -5.15 respectively. The calculated values of I_D for the 8-hydroxyquinoline - iodine system are: 9.615 eV in carbon tetrachloride, 9.669 eV in dichloromethane , 9.69 eV in chloroform , 9.719 eV in ethanol and 10.605 eV in methanol and they are shown in Table 3.

Table 3. Transition energies ($h\nu_{CT}$) of complex, ionization potential (I_D) of the donor and dissociation energy (W) of the CTC in different solvents.

System	$h\nu_{CT}$ (eV)	I_D (eV)	W(eV)
8HQ-Iodine (carbon tetrachloride)	3.407	9.615	2.928
8HQ-Iodine (dichloromethane)	3.455	9.669	2.934
8HQ-Iodine (chloroform)	3.474	9.690	2.936
8HQ-Iodine (ethanol)	3.503	9.719	2.938
8HQ-Iodine (methanol)	4.289	10.605	3.036

3.3.3. Dissociation energy

Further evidence for the nature of charge transfer interaction in the present systems is the calculation of the dissociation energy (W) of the charge transfer excited state of the complex in different solvents. Hence the dissociation energies of the complex were calculated from their charge transfer energy (E_{CT}), Ip, and electron affinity (E_A =2.8) of the acceptor using the empirical relation given in Eq. (3). [20]

E_{CT} (eV) = $I_D - E_A - W$……………………………………………………………… (3)

Thus, the acquired values of W of charge transfer excited states of the complex in different solvents were tabulated in table 4.

3.4. Solvent effect on charge transfer complex formation

One way of investigating the behavior of charge transfer complex is to vary the solvents. The unique property of a medium is the complex interaction between solvent and solute because polarity of solvent can affect stability of the complex. The experimental measurements of electronic transitions of charge transfer complex in different solvents provide valuable information about the mechanism of their formation. The solvent interferes with interactions between the donor and acceptor within the solvated complex [10]. In the present investigation, the blue shift occurred in the charge transfer complex was caused by a polarity change from using carbon tetrachloride to methanol. Therefore, the data reported in the present studies show that 8-hydroxyquinoline interacts more strongly with iodine in carbon tetrachloride than the other four solvents.

The charge transfer bands are shifted to lower wavelength with increasing solvent polarity. So it seems that the ground state is more polar than excited state and the ground state is stabilized by polar solvents [10]. This polar salvation increases with solvent polarity and this causes additional energy required to go to excited state. This explains the blue shift in the complex formation. However, it is difficult to decide unequivocally whether the observed effects are due to dielectric effects or specific interactions [22].

4. Conclusion

Charge transfer complexation between 8-hydroxyquinoline and iodine occurred with a 1:1 stoichiometry, with maximum absorption at 365,360,358, 355 and 290nm in carbon tetrachloride, dichloromethane, chloroform, ethanol and methanol respectively. All these absorption spectra of the complex matched neither the donor nor the acceptor spectra. Both the shift in absorbance and colour change are evidences for the formation of charge transfer complex between 8-hydroxyquinoline and iodine. Generally the blue shift was observed in all the solvent. However; the shift was more in polar solvents than non polar solvents. The complex formed was found to be relatively more stable in less polar solvents than more polar solvents. The average value of physicochemical parameters was increased from non polar to polar solvents.

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