

Synthesis and Spectroscopic Studies Of Charge Transfer Complexes as a Combination Models.

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Abstract:

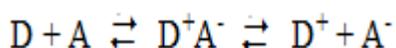
Schiff base of camphor with aniline was prepared. Electron donor-acceptor complexes formed between Schiff base as a donor with 1,4-naphthquinone, 1,4-benzoquinone and 1,8-dihydroxyanthraquinone as a π -acceptors have been synthesized and spectroscopically studied. The UV-Vis spectra of the most complex was shown two types of transition ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$). The Fourier Transform Infrared (F.T.IR) spectrum of the schiff's base-quinone complexes(IA, IB, IC) is shown the stretching of C=N of schiff base in the donor-acceptor complexes show a drastic shift to higher frequencies.

Key words: Charge transfer complex, Electron donor-acceptor, Quinon derivatives.

Introduction

Quinones and their derivatives form a great interest for pharmacologists as it is known as a group of chemotherapy drugs that contain the quinone nucleus. However, due to differences in the structure and the diversity of pharmacological effects that inflammatory and antipyretic properties [Carrier *et al.*,1998] . Naphthoquinones, isolated from plants and microorganisms, are Quinone containing compounds have been widely used for their antitumour and anticancer activity [Benites *et al.*,2011]. radical formation through electron transport with a vital role for the quinone transport

The term charge transfer complex (CTC) was introduced firstly by Mulliken [Mulliken *et al.*,1969,1950]. He 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



Charge transfer complexation is achieved the great importance in biochemical, bioelectrochemical energy transfer process, biological systems and drug-receptor binding mechanism, such as, drug action, enzyme catalysis, ion transfers through lipophilic F *et al.*, [Gutmann *et al.*,1968] were determine drugs based on the charge-transfer(CT) complexes formed with

they show, quinones are not sufficiently studied [Bondarchut *et al.*,2013]. Naphthoquinone derivatives have a wide range of pharmacological properties, they show antibacterial, antifungal, antiviral, insecticidal, anti-

widely used for the treatment of cancerous tumors and parasitic diseases [Arifm *et al.*,1999].

Quinone containing compounds also exert cytotoxicity by The term charge transfer complex (CTC) with a vital role for the quinone (C) ring [Carrier *et al.*,1998].

paramagnetic susceptibility. The charge transfer interactions within a molecular complex consisting of an electron donor D and an electron acceptor A involved a resonance with a transfer of charge from D to A and association constant of the complex decreasing with increasing temperature [Mulliken,1952].

membranes and certain π -acceptors have successfully been utilized in pharmaceutical analysis of some drugs in pure form or in pharmaceutical preparations [Korolkovas *et al.*,1998,Salem,2002, and Elango *et al.*,2010]. Gutmann electron acceptors. Asmaa A. Ibrahim [13] was study the interaction between donor 8-hydroxyquinoline (HQ) and π - acceptor 1,

4-benzoquinone (BQ), consider the BQ is the parent molecule of a class of a heterocyclic biological Systems[Morton,2005]. Most of the organic conductors based on charge-transfer complexes contain a BQ and its derivatives as the acceptor component[Mansour,2005]. 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[Refat *et al.*,2010,Adam *et al.*, 2013, and Elesh *et al.*,2011].

Arshiya *et al.* were used charge transfer concept to offer simple, sensitive method of quantification for drugs. The authors developed quantification methods for nine drugs (Famotidine, Ketorolac tromethamine, Dextromethorphan, Quetiapin, Salmeterol, Sumatriptan, Tamoxifen, Torsemide and Pantoprazole), using *p*-chlor- anilic acid as a chromogen and hence tested them for the formation a charge transfer complexes which is expected to form a basis for the quantification of the drugs. *p*-chloranilic acid forms ion pair complexes with nine selected drugs and the methods are validated, conditions are optimized and applied to analysis of drugs and pharmaceuticals.

aromatic compounds which play a relevant role in

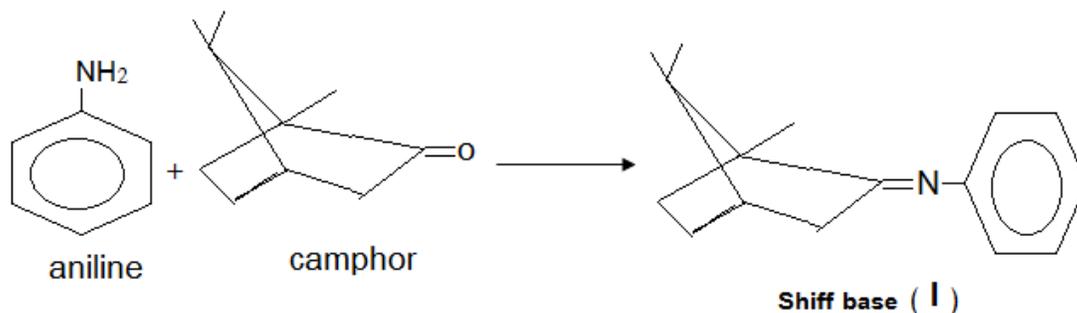
Materials and Measurements

All the chemical materials were supplied from Merck company.

Fourier Transform Infrared Spectrophotometer type FTIR-8400S, Shimadzu (JAPAN) were recorded on the scanning range of $400\text{-}4000\text{ cm}^{-1}$ in pharmacy collage. Ultraviolet/visible spectrophotometer were obtained using a UV-1100 spectrophotometer(USA) in CHCl_3 and ethanol. Both were characterize the chelating behavior of the schiff base – quinone complexes.

Preparation of Schiff base (I) :

(1 mole) (5.07g) of camphor was dissolved in 250 ml benzene, (1 mole) (3.10 g) of aniline was added to above solution. The pH adjusted 7 by drops of concentrated benzene sulphonic acid, the reaction mixture was refluxed for 5 hrs. The pale yellow schiff base was filtered and recrystallized in methylen chloride, yield (85%)(m.p.225 °C) as shows in scheme (1).



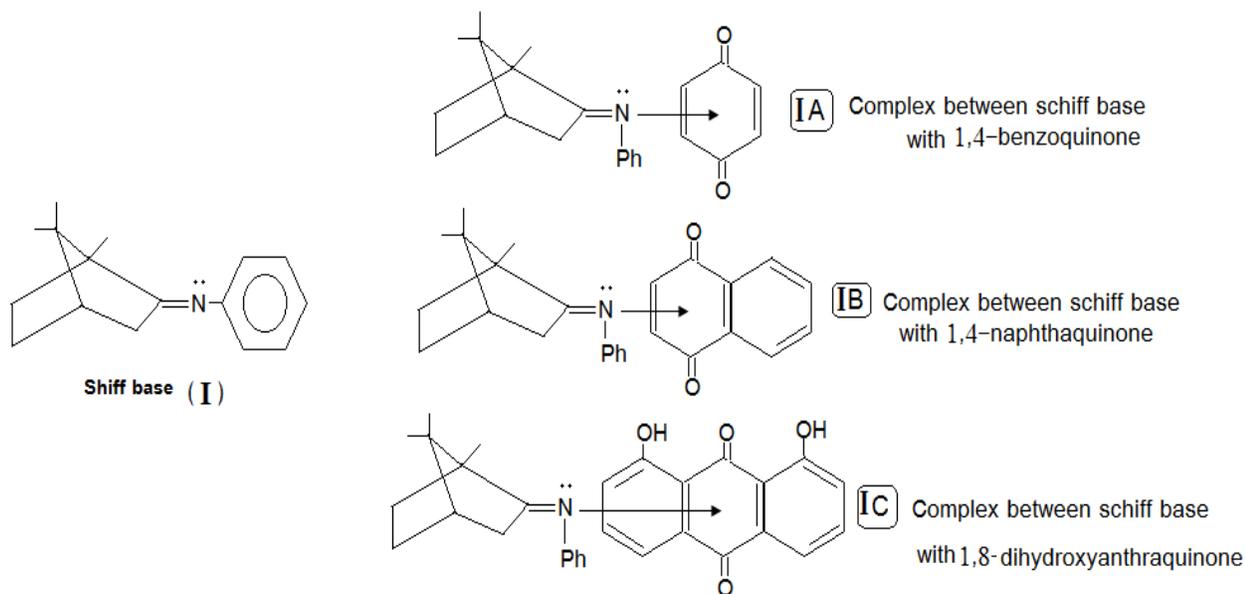
Scheme 1: Chemical reaction of the prepared Schiff base.

Preparation of Schiff base -quinone complexes:

The solid complexes of Schiff base (donor) with acceptor ;1,4-naphthaquinone , 1,4-benzoquinone and 1,8-dihydroxyanthraquinone were prepared by mixing 0.001

mole (0.227 g) of Schiff base dissolved in 20 ml ethanol as a donor, with 0.001 mole (0.158 g, 0.108 g and 0.240 g) dissolved in 20 ml ethanol of each acceptor respectively.

The mixtures were refluxed with stirring for 15 min. The reaction mixture was cold. All the complexes were isolated by evaporation of the solvent except 1,8-dihydroxyanthraquinone complex were precipitate and filtrated off, also the filtrated was shown another product after evaporation of solvent, (Scheme 2). The yield and melting points of complexes are shown in table(1) .



Scheme 2: The chemical structure of the prepared complexes.

Table-1: Show the melting point of Schiff base and complexes.

Compounds	M.p. (°C)	Colour	Yield (%)
Schiff base (I)	225	Pale yellow	85
IA	163	Black	70
IB	oily	Red violet	89
IC _a	188	Orange	95
IC _b	193	Orange	93

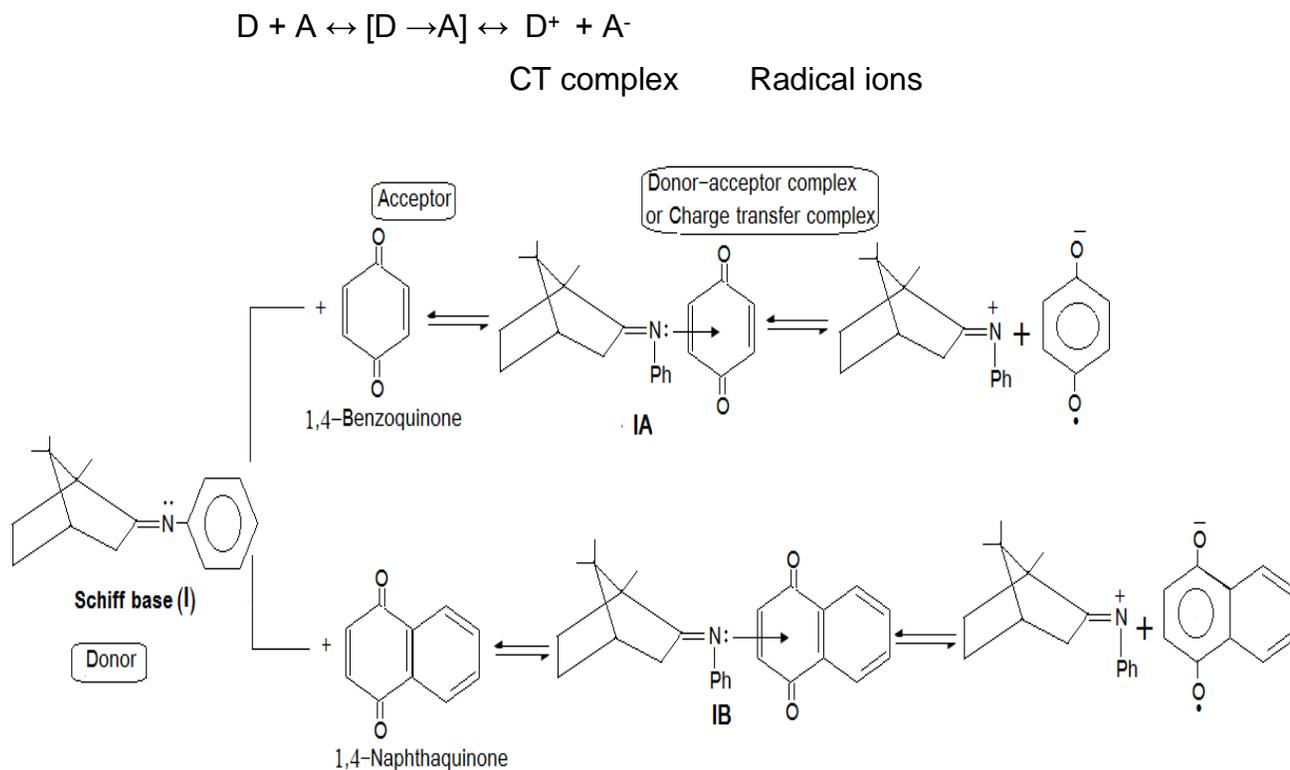
The electronic absorption spectra:

The electronic absorption spectra of all compounds in two solvents chloroform and ethanol was studied. The conc. of 1×10^{-3} M to each compound were prepared and UV-Vis scan range from 200-600 nm Figures (1 and 2) and table (2 and 3) exhibit mainly two bands with $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions due to allowed transition of the electrons between energy levels.

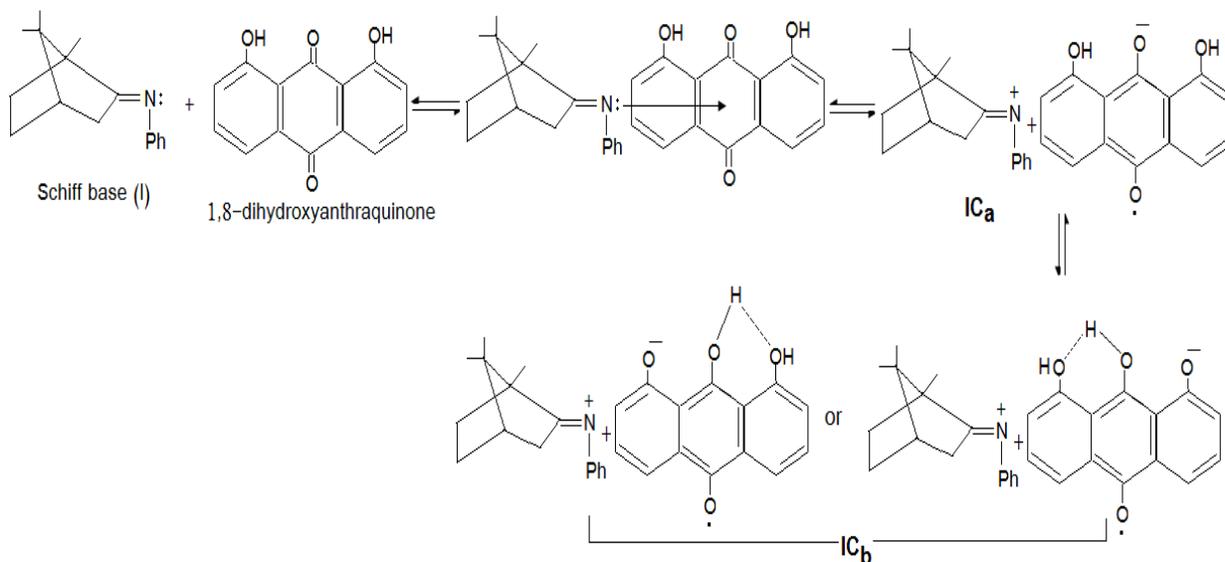
Result and Discussions

These complexes were easily synthesized from the reaction of Schiff base with quinone derivatives. IR and Ultraviolet/visible (UV-Vis.) techniques characterize the Schiff base (I)- quinone complexes.

The donor site participated in CT complexation is the lone pair of electron on N atom of Schiff base (I) [Abraham,2011]. Charge transfer complexes of Schiff base with quinone derivatives were prepared as scheme (3).



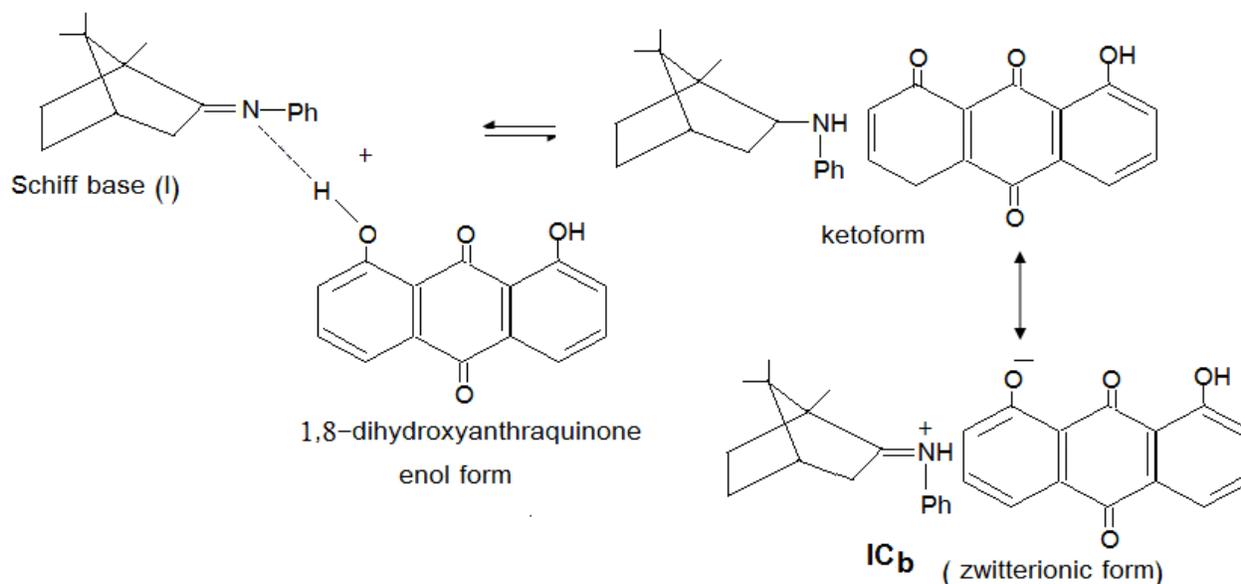
While IC complexes having free OH (hydroxyl) groups display somewhat the expected structure as shown in Scheme 4.



Scheme 4 : The charge transfer of IC_b complex.

IC_b complex may be involved in intramolecular hydrogen bonding between free OH groups and N atom of Schiff base, form zwitterionic structure [Helen *et al.*, 2008], Scheme 5.

The electronic absorption spectra of the most products include in the present study in chloroform and ethanol, have two types of transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, Figures (1 and 2),



Scheme 5: The expected charge transfer of IC_b complex.

Table (2 and 3). These spectra indicated that the bands due to localized electronic transitions are slightly influenced by the nature of the solvent used. On the other hand ,the charge transfer band displayed in

general a red shift with increasing the solvent polarity which reflects an increased solvent stabilization of excited state in more polar solvents.

Table-2 : Show UV-Vis spectra of Schiff base with its complex in chloroform.

Compounds	$\lambda_{\max 1}(nm)$	$\lambda_{\max 2}(nm)$
Schiff base	290	415 [*]
IA	285 ^{**}	-----
IB	295 ^{***}	345 and 475
IC _a	285	315 [*] and 430
IC _b	285	315 and 430

*=small broad ** = broad *** = shoulder

Table- 3: Show UV-Vis Spectra of Schiff base with its charge transfer complexes in ethanol.

Compounds	$\lambda_{\max 1}(nm)$	$\lambda_{\max 2}(nm)$
Shiff base	365 ^{**}	465 [*]
IA	350 ^{**} (long peak)	-----
IB	230	290 ^{**} and 390 ^{****}
IC _a	430 ^{**}	-----
IC _b	220 ^{***} and 280 ^{***}	430 ^{**}

*=small broad ** = broad *** = shoulder ****= long broad

Schiff base (I) in ethanol, $\pi \rightarrow \pi^*$ transition in high wavelength and within less transition wavelength in chloroform, display the bands due to the $\pi \rightarrow \pi^*$ transition of the C=N linkage. Within charge transfer complexes, in polar solvent ,were shift the bands to high

wavelength in ethanol compared with chloroform, due to increase the stability of the complexes(zwitter ion form) in polar solvent. this bands is considerably broadened and may be split into other band ,this fact can be attributed to the protonation reaction

The both complexes (IC_a) and (IC_b) are shown two types of transition in chloroform at the same wavelength (285, 315 and 430) nm, but in ethanol IC_a complex is appear as one band at 430 nm associated with very

weak or small band at 335 nm while IC_b complex the band appearance at shorter wavelength are assigned to the absorption of the hydroxyl group.

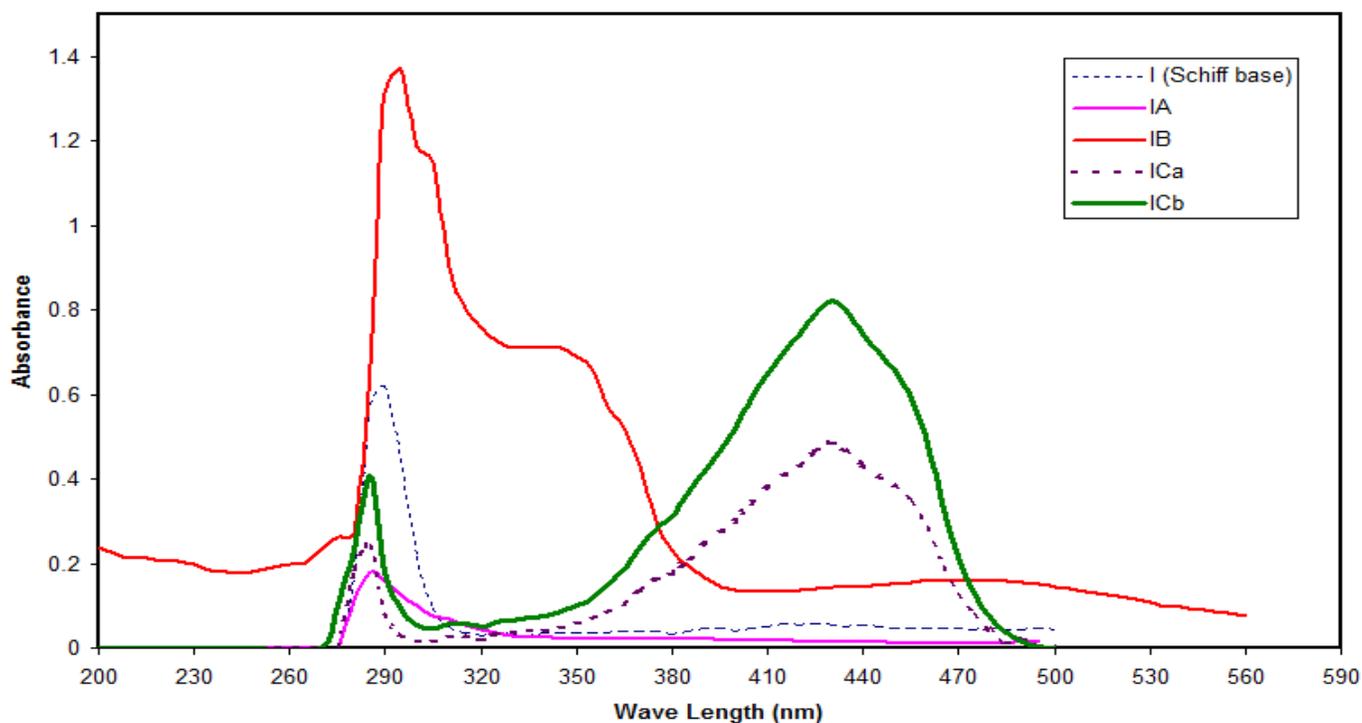


Fig. - 1 : Electronic absorption spectra of Schiff base and its complex in $CHCl_3$.

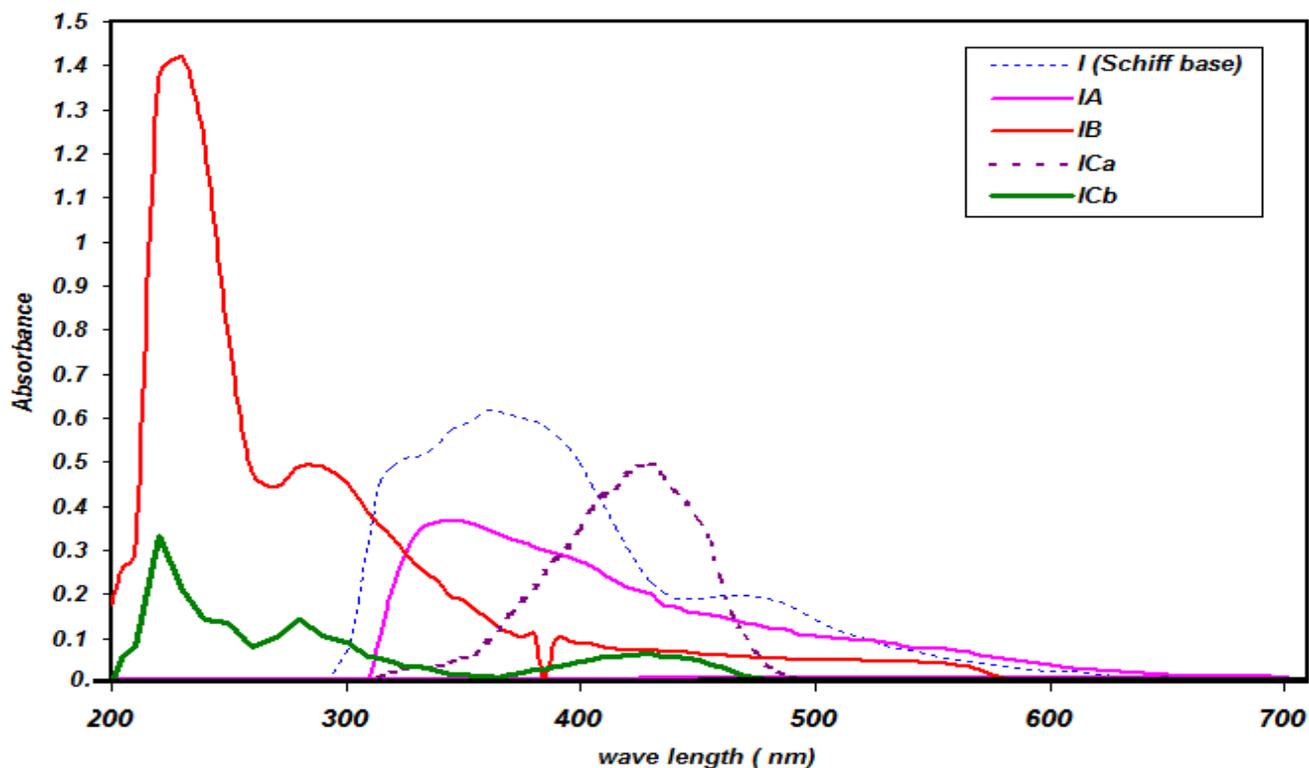


Fig.- 2: Electronic absorption spectra of Schiff base and its complex in ethanol.

IR spectra of the characterized bands of Schiff base (I) and its complexes were represented in Table. 4.

Table -4. The bands of FTIR Spectra of schiff base within its complexes (IA,IB, IC).

Compounds	Streaching Vibration bands (cm ⁻¹)			
	ν CO	ν C=N	ν C=C	ν OH
Schiff base (I)	-----	1623	1573.83	-----
IA	1722.31	1631.67	1494	-----
IB	1721	1632	1570	-----
IC _a	1672.2	1623.95	1461.9	3411.8
IC _b	1722	1631.6	1496.6	3350-3550

The stretching vibration of C=N of Schiff base (I) was detected within region 1623 cm⁻¹

¹.The stretching of C=N in complexes shows shift to higher frequencies which

indicated that interaction placed among the (C=N:) group as donor and π electron in quinine derivatives as acceptor group, may through by donor-acceptor

π - π interactions or electron-donor-acceptor (EDA) complex [Maekawa *et al.*,2002] also may be associated with increased acceptor characterization [Al-Taie *et al.*,2009]. The stretching vibration of carbonyl group in the quinine was overlapping with C=N group within region 1672 - 1722 cm^{-1} . Very weak or no stretching vibration of hydroxyl group in the complexes was shown in 3500 - 3400 cm^{-1} except in the Schiff base-1,8-dihydroxyanthraquinone and 1,4-benzoquinone complexes.

The previous suggestion (scheme 5) which indicate the charge transfer of IC_b complex, from interaction C=N of Schiff base and free hydroxyl group in 1,8-dihydroxyanthraquinone is differ with the result, because IR study does not give band at stretching vibration at 3180 - 3430 cm^{-1} which belonged to NH^+ [Al-Taie *et al.*,2009] but show a strong and very broad absorption band at 3350 - 3550 cm^{-1} of the OH group, broadening of this band indicate that the OH group is involved in hydrogen bonding interaction. The complex ICa show a band at 3411.8 cm^{-1} which can be assigned to stretching vibration of OH group as phenolic structure.

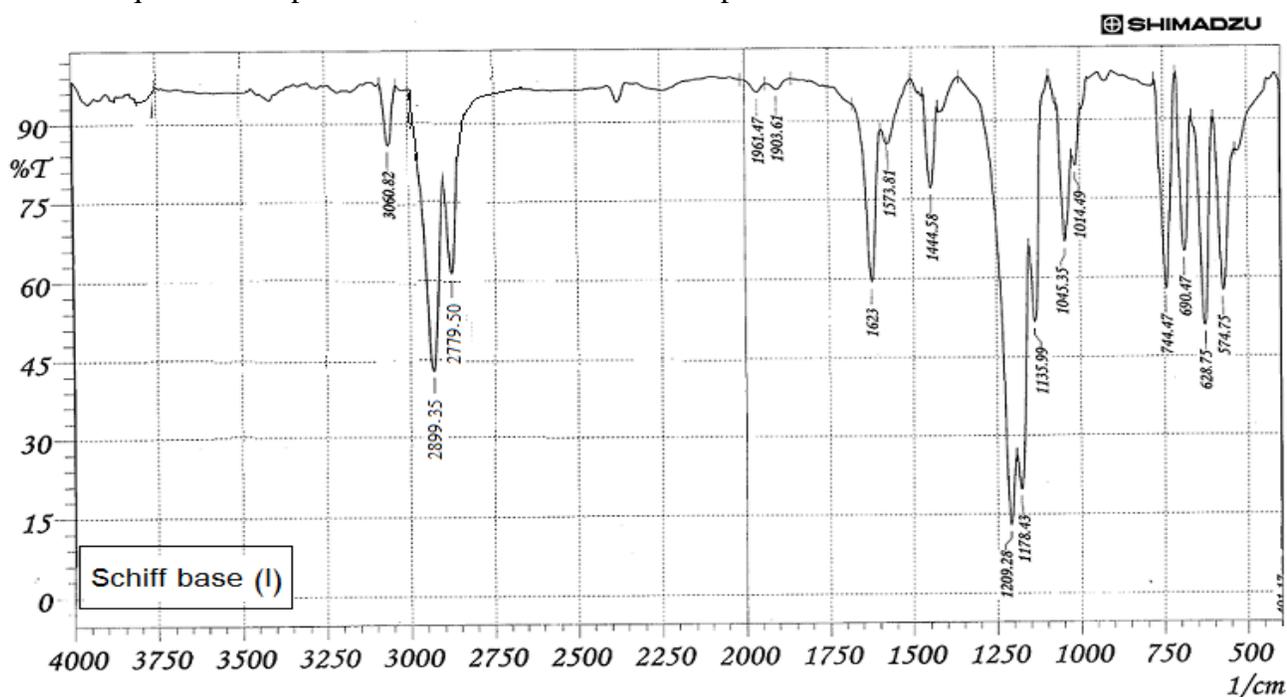


Fig.-3: IR-Spectrum of Schiff base (I).

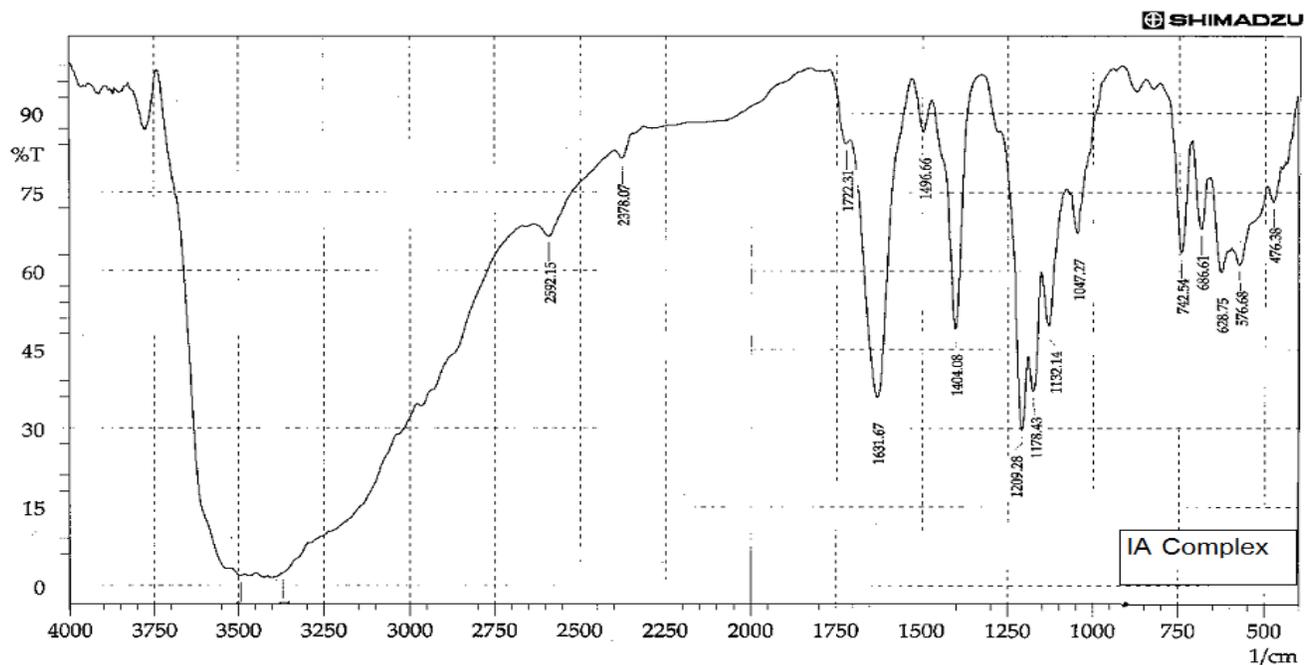


Fig.- 4: IR-Spectrum of Schiff base-1,4-Benzoquinone complex(IA).

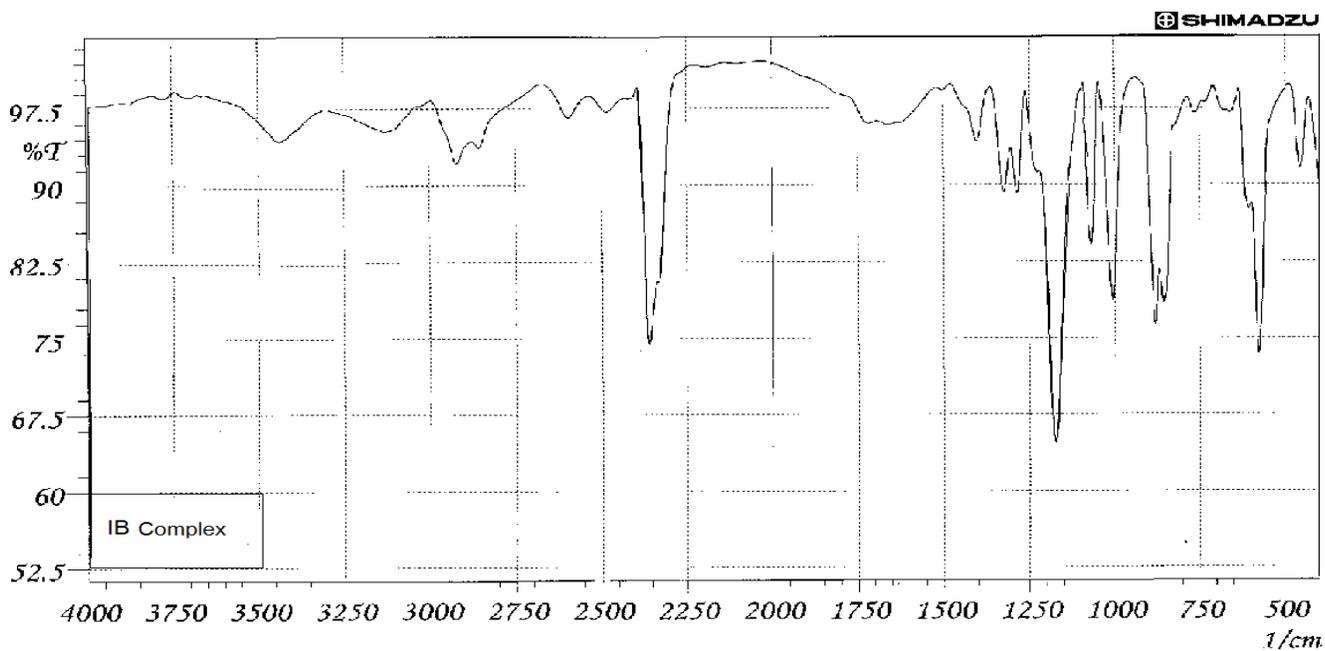


Fig.- 5: IR-Spectrum of Schiff base-1,4-Naphthaquinone complex(IB).

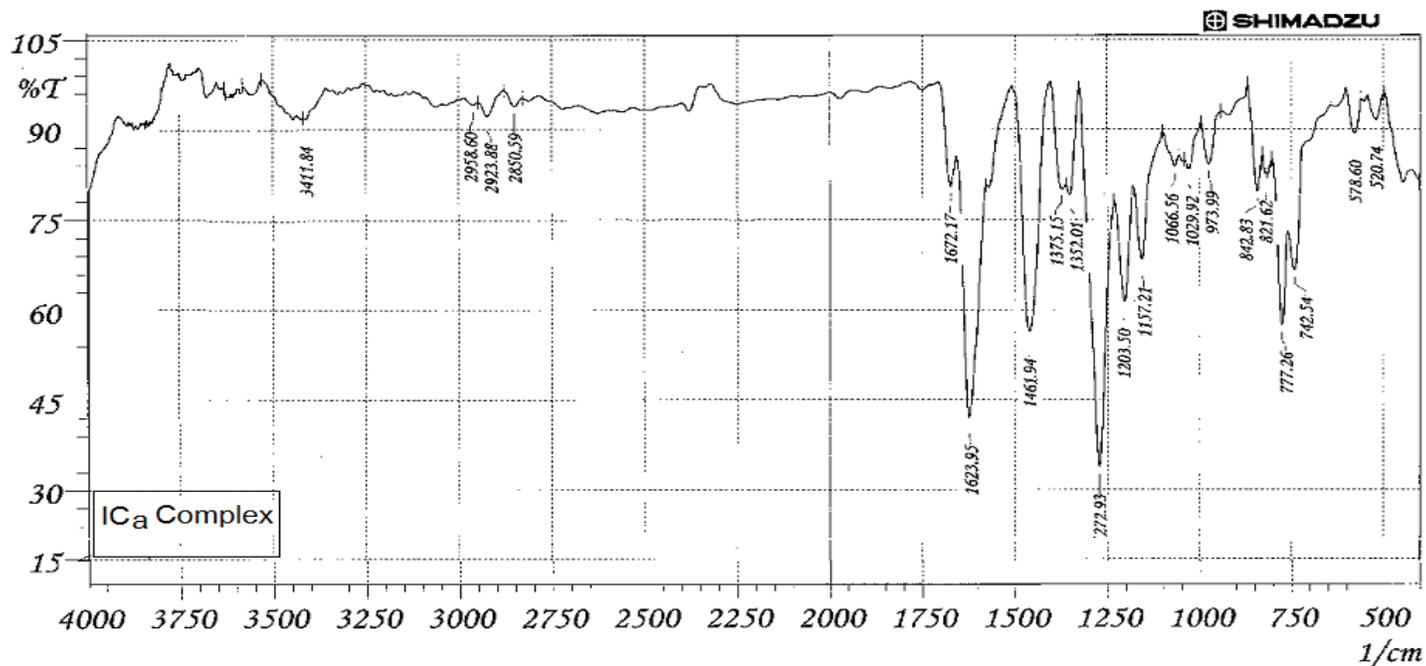


Fig.- 6: IR-Spectrum of Schiff base-1,8-Dihydroxyanthraquinone complex (IC_a).

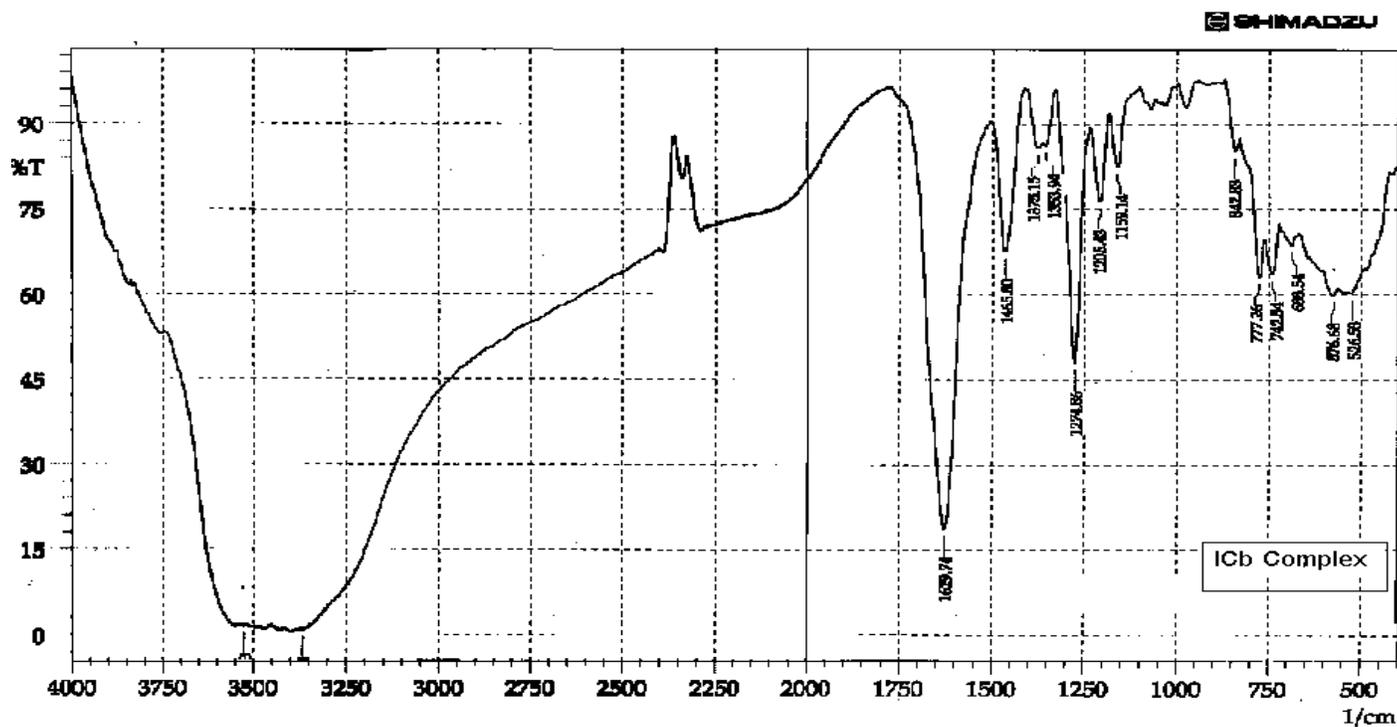
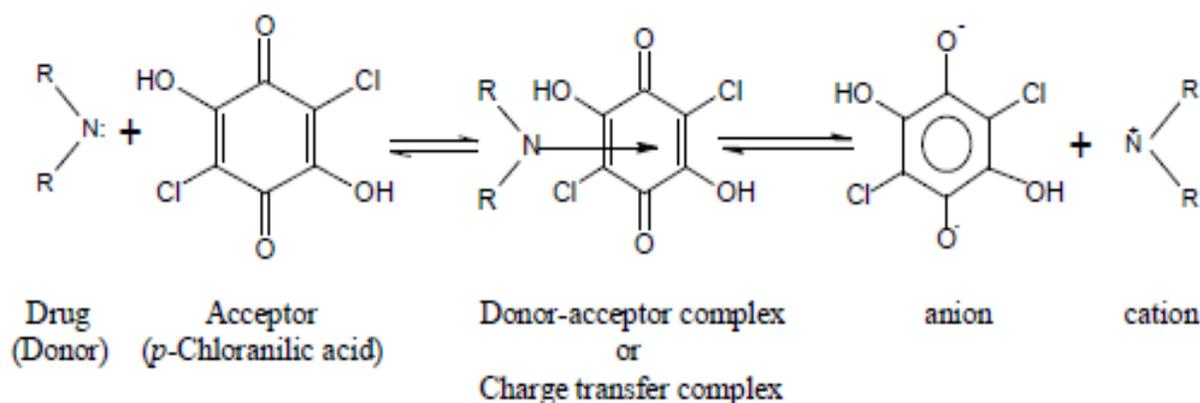


Fig.-7 : IR-Spectrum of Schiff base-1,8-Dihydroxyanthraquinone complex (IC_b).

The above result confirm with the following study, which include using the quinine derivatives as π -electron acceptor for the determination of amino acid and drugs with potential donor ability. The addition of *p*-chloranilic acid to the drugs ,

possessing a lone pair of electron results in the formation of a charge transfer complex of the $n \rightarrow \pi$ type[Mansour,2005. The *p*-chloranilic acid exhibits absorption maximum at 430 nm while its anion at 520 nm as shown in Scheme .6 .



Scheme 6 : Charge transfer complexes of drugs with *p*-Chloranilic Acid.

Conclusion

The donor-acceptor complex between Schiff base and some quinine derivatives were investigated by spectrophotoscopic method. This investigation was shown molar 1:1 ratio. The UV-Vis spectra shows the two types of transition. FTIR spectra was shown distinguish quinine as acceptor and Schiff's base as a donor.

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تحضير ودراسة طيفية لمعقدات تبادل الشحنة كنموذج مركب

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رحيم جميل

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الخلاصة

تم تحضير قاعدة شف من تفاعل الكافور مع الأنلين، كما تم تحضير معقدات أنتقال الشحنة بين قاعدة شف كواهة للإلكترون وبعض مشتقات الكوينون 4,1-نفثاكوينون ، 4,1-بنزوكوينون و 8,1-داي هيدروكسي دراسة المعقدات كمستقبلات للإلكترون π . تم دراسة المعقدات المحضرة (IA, IB and IC) طيفيا باستخدام مطيافية الأشعة فوق البنفسجية والمرئية ومطيافية الأشعة تحت الحمراء. باستخدام مطياف الأشعة المرئية وفوق البنفسجية تم الحصول على نوعين من الانتقالات ($\pi^* \rightarrow \pi$) و ($\pi \rightarrow \pi^*$). كما لوحظ طيف الأشعة تحت الحمراء ان الامتصاص الاتساعي المميز لمعقدات قاعدة شف مع الكوينون لمجموعة (N=C) ذات إزاحة حمراء في المعقدات المحضرة.