

Spectroscopic Study of Charge Transfer Complexes of Dibenzo-24-crown-8 (DB24C8) with Iodine in Three Chlorinated Solvents

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ABSTRACT: Charge Transfer (CT) complexes formed between dibenzo-24-crown-8 (DB24C8) as an electron donor with the σ -electron acceptor iodine (I_2) in chloroform, dichloromethane and 1,2-dichloroethane solutions have been studied by different spectroscopic techniques at room temperature. The spectral studies of the complexes were determined by UV-Visible, Fourier Transform InfraRed (FT-IR) Studies on the system showed the time dependence of absorption band of the complexes. The observed time dependence of the charge-transfer band and subsequent formation of I_3^- in solution were related to the slow transformation of the initially formed outer complex to an inner Electron Donor-Acceptor (EDA) complex, followed by fast reaction of the inner complex with iodine to form three iodide ion. Formation constants of the resulting complexes were determined by measuring the absorbance at λ_{max} for a series of solutions with varying excess amounts donor and constant iodine concentration in solvent systems used. The reaction stoichiometry was found to be 1:1 (donor : acceptor) molar ratio for both complexation system by using photometric titration measurements. The formation constant (K_{CT}), molar extinction coefficient (ϵ_{CT}), free energy change (ΔG^0), CT-energy (E_{CT}), were calculated by using the Benesi-Hildebrand method. Stability of the resulting complex in three solvents was also found to vary in the order of 1,2 -DCE > DCM > $CHCl_3$.

KEYWORDS: Charge-transfer complex; Crown ether; Iodine; Spectroscopy.

INTRODUCTION

Charge-Transfer (CT) complexes are formed between electron donors, having sufficiently low ionization potentials, and acceptors, having sufficiently high electron affinities. The transfer of an electron from a donor to an acceptor occurs readily in a CT process [1]. The formation energy of Charge-Transfer (CT) complex depends on the ionization potential of the donor and

the electron affinity of the acceptor [2]. CT interaction was first introduced by Mulliken [3-5] and has been widely discussed by Foster [6]. The photometric methods based on these interactions are usually simple and convenient because of the rapid formation of the complexes. The chemical and physical properties of Charge-Transfer (CT) complexes formed in the reactions of σ - and π - electron

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acceptors with different donors like amines, crown ethers, polysulfur bases, and oxygen–nitrogen mixed bases have been the subjects of many studies both in solution and in solid state [7-9]. The organic electron donors with donor atoms such as nitrogen, sulfur, and oxygen or of mixed donor atoms are well known to form stable CT complexes with a number of σ - and π -acceptors. CT complexation is of great importance in chemical and photochemical reactions, including addition, substitution, condensation [10], molecular self-assemblies [11,12], biochemical and bioelectrochemical energy-transfer processes [13], and drug-receptor binding mechanisms [14-17].

Macrocyclic polyethers, a class of compounds first synthesized by Pedersen [18], macrocyclic polyethers (crowns), exhibit remarkable complexing properties toward metal ions of an ionic size suitable for fitting inside their cavities [19]. These macrocyclic compounds are capable of forming complexes with cations via electrostatic attraction and encapsulation into the cavity [20,21]. Recently, the potential of the complexing ability of these macrocycles toward neutral molecules has been investigated [22]. Although much attention has been paid to CT complexes of macrocyclic donors with σ - or π -electron acceptors [23]. The study of the interaction of iodine with various electron donor to form charge-transfer complexes has attracted considerable interest and growing importance [24]. Some of the CT complexes of iodine show interesting physical properties such as electrical conductivities and some of the complexes have found applications in many forms of electronics and solar cells [25] and some are used for determination of drugs [26]. In continuation of our studies of crown ether molecular complexes [27-30], in the present work, we report the formation of CT molecular complex of dibenzo-24-crown-8 (DB24C8) (Fig.1) with iodine in chloroform, DCM and 1,2-DCE solutions.

EXPERIMENTAL SECTION

Materials

DB24C8 and iodine were obtained from Merck Co. Germany (purity 99 %), were of the highest purity available and were used without any further purification. Chloroform and dichloromethane and 1, 2-dichloroethane (all from Fluka purity 99 %) were used as received.

Apparatus and Procedures

Stock solutions of the DB24C8 and iodine freshly

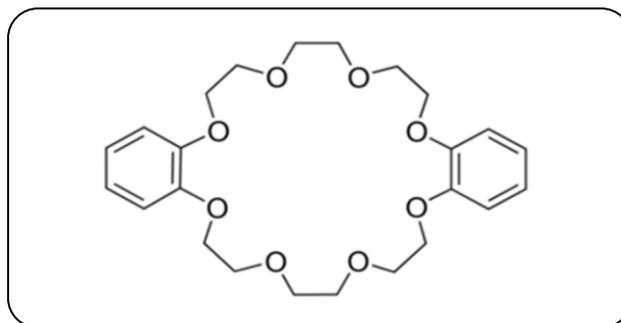


Fig. 1: Dibenzo-24-crown-8 (DB24C8).

prepared before each series of measurements by dissolving precisely weighed amounts of the component in the appropriate volume of solvent. Solutions for spectroscopic measurements were made by mixing appropriate volumes of stock donor and iodine solution and pure solvent. All solutions were kept in the dark except during sampling.

The electronic absorption spectra of the studied CT complex solutions were recorded using a UV-Vis spectrophotometer model Biochrom WPA Biowave II UV-Vis with a pair of matched Quartz cells of 1.0-cm path length. Absorbance measurements as a function of time, at fixed wavelengths, were made with the same instrument. The electronic absorption spectra of the Donor, iodine and their charge transfer complex in chloroform, dichloromethane and 1,2-dichloroethane were recorded in the region 200-800 nm.

The mid infrared spectra of reactant, DB24C8, iodine, and charge transfer complexes were recorded by a spectrum Alpha Bruker FT-IR spectrometer.

RESULTS AND DISCUSSION

Iodine in a solution of chloroform, DCM and 1, 2-DCE displayed an absorption peak at about 500 nm, while the DB24C8 showed no absorption in the 300–700 nm region, mixing the solution of DB24C8 to a solution of iodine in each of three solvents resulted in a change of the absorption peak. The electronic absorption spectra of mixtures of iodine and DB24C8 in chloroform, DCM and 1,2-DCE with an excess amount of iodine were obtained as a function of time at 25 °C (Figs. 2,3 and 4). Sample spectra in DCM are shown in Figs. 2-4. It is evident that upon the addition of DB24C8 to the iodine solution the absorption band at 500 nm which is attributed to the $4\pi \rightarrow 10\sigma^*$ electronic transition in free iodine is

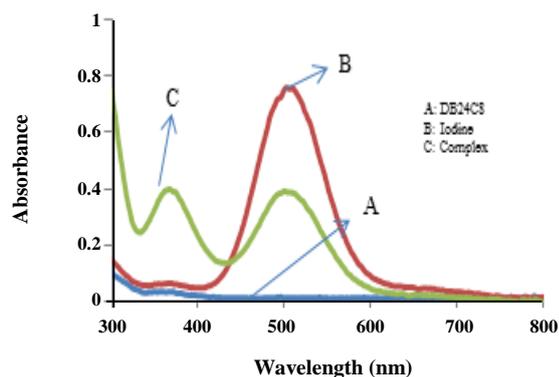


Fig. 2: (A) The absorption spectrum of the DB24C8 ligand, (1×10^{-3} M). (B) iodine absorption spectrum, (1×10^{-3} M). (C) The absorption spectrum of the mixture of DB24C8 and iodine in chloroform at 25°C .

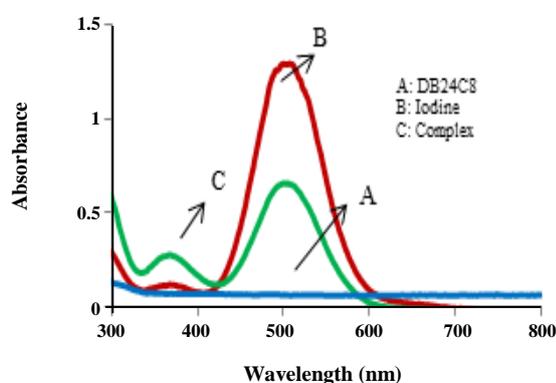


Fig. 3: (A) The absorption spectrum of the DB24C8 ligand, (1×10^{-3} M). (B) iodine absorption spectrum, (1×10^{-3} M). (C) The absorption spectrum of the mixture of DB24C8 and iodine in dichloromethane at 25°C .

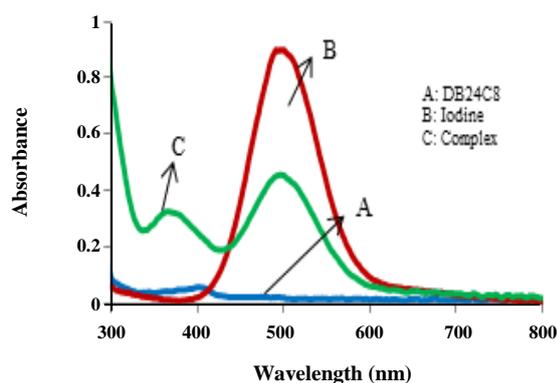
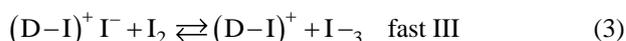
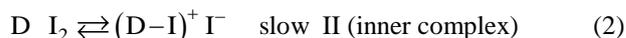


Fig. 4: (A) The absorption spectrum of the DB24C8 ligand, (1×10^{-3} M). (B) iodine absorption spectrum, (1×10^{-3} M). (C) The adsorption spectra of the mixture of DB24C8 and iodine in 1,2-dichloroethane at 25°C .

hypsochromically shifted due to its complexation with the added macrocycle. Therefore, it is reasonable to consider the extent of the blue shift in the iodine band as a measure of the magnitude of the interaction between the donor and iodine molecule. The limiting value of this shift is at about 360-365 nm, which is the characteristic absorption of the I_3^- ions in solution [31].

As seen from Fig. 5, one more absorption band appears at about 290 nm. It should be noted that the 292 nm band is also characteristic for the formation of tri iodide ion, in the process of complex formation between iodine and different electron pair donor ligands [32]. As can be seen from Fig. 5, the intensity of 368 and 299 nm bands increased markedly with the elapse of time. The observed time dependence of the charge transfer band and the subsequent formation of the I_3^- ion in solution are most probably due to a transformation of the initially formed outer complex into an inner EDA complex followed by a fast reaction of the resulting inner complex with iodine to form a triiodide ion, as follows [33,34].



To determine the stoichiometry of the donor-acceptor CT interactions in solution-state, various molar ratios were examined by spectrophotometric titration measurements. These titrations monitored the detectable CT bands during the reactions of DB24C8 with iodine.

Fig. 6. shows the observed absorbance values at a given wavelength of DB24C8-I₂ with increasing $[\text{I}_2]/[\text{DB24C8}]$ molar ratios in DCM at the temperature room. Photometric titration based on the absorption at 368 nm shows a reaction stoichiometry of 1:1 for CT-complex of DB24C8 with iodine. The equilibrium constant (K_{CT}) and molar absorbance (ϵ_{CT}) of the charge transfer complex between iodine and DB24C8 were calculated using Benesi-Hildebrand equation [35].

$$\frac{[\text{A}]_0 [\text{D}]_0 L}{\text{Abs}} = \frac{1}{K\epsilon} + \frac{[\text{A}]_0 + [\text{D}]_0}{\epsilon}$$

Where $[\text{D}]_0$ and $[\text{A}]_0$ are the concentrations of the DB24C8 donor and iodine acceptor molecules, respectively.

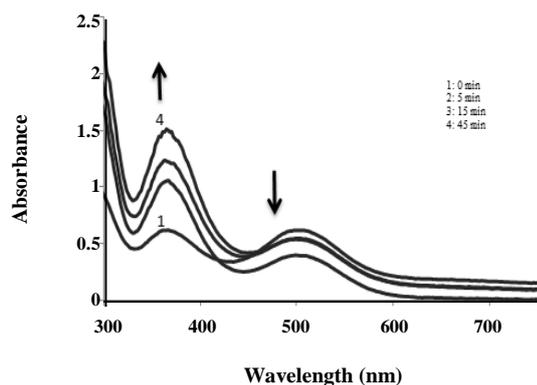


Fig. 5: UV-Vis spectra of a mixture of iodine (1.0×10^{-3} M) and DB24C8 (1.0×10^{-3} M) in DCM solution at 25 °C. (1) Immediately after mixing and at time intervals: (2) 5 min, (3) 15 min, (4) 45 min.

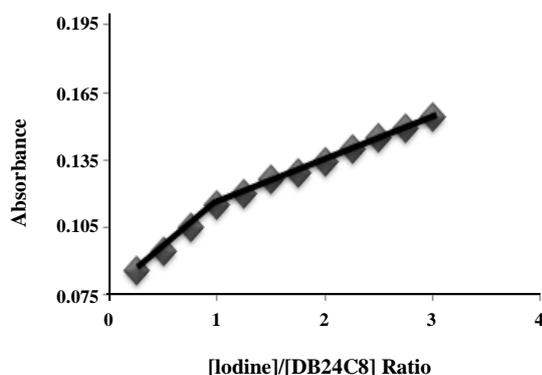


Fig. 6: Spectrophotometric titration curves for the DB24C8 with iodine acceptor in DCM based on the 368 nm absorptions at 25 °C.

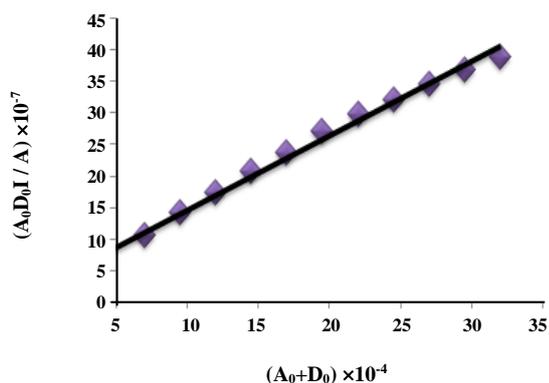


Fig. 7: Benesi-Hildebrand plots of iodine with DB24C8 in DCM.

K_{CT} is the association equilibrium constant and ϵ_{CT} is the molar extinction coefficient of the complex. Fig. 7 shows the Benesi-Hildebrand plots of $[A]_0[D]_0/Abs$ against $[A]_0+[D]_0$ from the data obtained from Fig. 7. A quite satisfactory straight relation obtained showing 1:1 CT complex. The ϵ_{CT} and K_{CT} values were evaluated from the intercept and slope of the linear plot between $[A]_0[D]_0/Abs$ and $[A]_0+[D]_0$. All results are summarized in Table 1.

The association constant, a basic parameter, is a measure of the binding strength between the host (crown ether) and the guest (iodine). It is well known that the value of the association constant depends on temperature and polarity of the solvent. Solvent properties are considered as the major factor influencing the formation constants of crown ether-cation complexes. The reason is that solvent and crown ether molecules compete in binding to metal cations. When the donor properties of the solvent are low, cations are poorly solvated and can easily be complexed by the crown ether. The solvation of crown ethers may also influence the formation constants of the crown-cation complexes [35]. The results (Table 1) show that with increasing polarization of solvent from chloroform to 1 and 2- dichloroethane, the formation of complexes increases. This leads to the process of reducing the number and the dielectric constant from chloroform to 1, 2- dichloroethane is related. By increasing the solvent dielectric constant, the stability of the CT complex in the excited state is higher and thus the constant formation of the complex increases. In strong environmental conditions (high polarity solvent) active energy for the transformation of the outer complex to the inner complex is reduced and the inner complex created is a form of stability for the couple will be the receiver. In solvent 1, 2-dichloroethane, most of the complex transformation stage-DA to the final product it can be seen. The stability constants of complexes are decreased in the order of 1, 2-DCE, DCM and $CHCl_3$. This trend is in agreement with our previous study concerning the solvent effect on the complex formation of dibenzo-15-crown-5 and benzo-12-crown-4 [29] with iodine.

The complexation process in solution could be considered as a series of processes including (i) the guest approaches the host; (ii) desolvation of guest and desolvation of the binding site on the host; (iii) guest enters the cavity on the host resulting in the conformational

Table 1: Formation constants (K_{CT}), molar absorptivities (ϵ_{CT}), for CT complex between iodine and DB24C8 in different solvents at 25 °C.

Solvent	$k_{CT}/1\text{mol}^{-1}$	$\Delta G^0 / \text{J mol}^{-1}$	E_{CT} / eV	$\lambda_{\text{max}} / \text{nm}$	$\epsilon_{CT} / \text{mol}^{-1}\text{cm}^{-1}$
CHCl_3	37.27×10^2	20.37×10^3	3.39	366	2.81×10^2
DCM	43.25×10^2	20.74×10^3	3.37	368	8.44×10^2
1,2-DCE	47.16×10^2	20.94×10^3	3.41	364	8.68×10^2

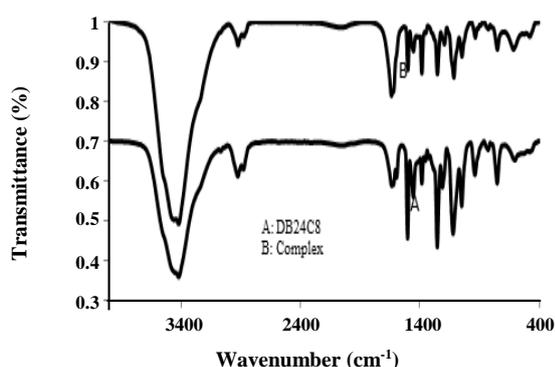


Fig. 8: FT-IR spectra of the (A) DB24C8 and (B) CT-complex.

change of the host; (iv) solvation of the complex. The desolvation process and the motion of both the host and guest usually are considered as main contributors to the entropy term; and the binding force between guest and host and bond breaking and reformation of solvent molecules are considered as main contributors to the enthalpy term.

FT-IR

The infrared spectra of the DB24C8 and complex of DB24C8-I in dichloromethane it has been shown in Fig 8. These assignments are based on the comparison of the spectra of the DB24C8 and complex of DB24C8-I in dichloromethane. The spectra of DB24C8-I complex are different from DB24C8. The FT-IR spectra show some changes in band intensities and in some cases shifts in the frequency wavenumber values. This observation strongly supports the charge transfer interactions between the DB24C8 and iodine.

In the spectrum concerning complexes, small variations in vibrational quantities and their severity are observed in comparison with the spectrum of ligands. Which confirms the formation of load transfer complexes. Also, some strips are down to the lower frequency, this effect can be considered as a result of weakening some of the links during complexization. All results are summarized in Table 2.

From the data given in Table 2 it is obvious that the IR spectra of the molecular adducts contain the main band of the macrocycle DB24C8, supporting the formation of CT complexes with iodine. As seen in the DB24C8-I complex, the C-O stretching band at 1116.12 cm^{-1} shifted to a lower frequency, in fact, electron donating ability of oxygen lowers the charge density on it. This results in a lowering of the force constant and shifts to lower frequencies. On the other hand, a comparison of the important IR spectral the CT complexation. A couple of ethoxy groups with ring vibration band of the free donors are shifted to lower frequencies on complex formation. The methylene stretching of the ethoxy groups of benzo crown coupled with ring vibration is observed in the 2921 cm^{-1} region. Small but noticeable changes were observed in the ethoxy groups with ring vibration band of the free donor. On the other hand, the $\nu(\text{C}=\text{C})$ of the macrocycle L show small shifts on complexation with iodine. These changes are as expected [36].

In Table 3, a number of different epoxy crowns have been formed in different solvents and in the presence of different detectors, forming stable consonants. According to obtained spectroscopic data, the effect of different solvent on crown ether it is different because the circumferential conditions are different. In the presence of a high-polarity solvent, the activation energy will be reduced to transform the outer complex to the internal complex, and the resulting inner complex will form a more stable form. The functional group are also among the factors that influence the stability of the load transfer complex. The presence of a lethal electron group like the nitro group reduces the complex stability of the complex. The complexes studied in this study have good stability due to the presence of an electron group and large ring sizes.

CONCLUSIONS

The interaction of the crown ether dibenzo-24-crown-8 with iodine has been studied in CHCl_3 , DCM and

Table 2: FT-IR wavenumber and tentative band assignment for DB24C8 and CT-complex of DB24C8-I in dichloromethane.

DB24C8	DB24C8-I	Assignment
3418.88 (s,br)	3418.86 (s,br)	ν (C-H) aliphatic
1637.81 (m)	1635.59 (m)	ν (C=C)
1503.11 (vs)	1500.74 (m)	Aromatic ring
1455.30 (m)	1454.29 (w)	ν (-CH ₂ -)
1122.65 (vs)	1116.12 (m)	ν (C-O)
2924.43 (m)	2921.98 (w)	Couple ethoxy group with ring vibration

Table 3: Comparison of obtained stability constant of crown ether in this study with several other crown ethers.

Complex	Solvent	λ_{\max} (nm)	$\log k_{CT}$ (mol ⁻¹)	0
AM15C5-I ₂ [37]	CHCl ₃	364	3.9	3482
AM15C5-I ₂ [37]	1,2-DCE	364	4.9	7403
NB15C5-I ₂ [27]	CHCl ₃	363	1.41	1125
NB15C5-I ₂ [27]	CH ₂ Cl ₂	362	1.9	2500
B15C5-I ₂ [27]	CHCl ₃	362	1.6	1545
B15C5-I ₂ [27]	CH ₂ Cl ₂	361	1.9	3176
B15C5-DDQ [38]	CHCl ₃	592	6.88	1657
DB24C8-I ₂ (In this work)	CHCl ₃	366	3.57	281
	DCM	368	3.63	844
	DCE	364	3.67	868

1,2-DCE at room temperature. The charge transfer absorptions and far infrared of the formed charge-transfer complex were recorded and discussed. The observed time dependence of the charge-transfer band and subsequent formation of I₃⁻ in solution were related to the slow transformation of the initially formed 1:1 DB24C8: I₂ outer complex to an inner Electron Donor Acceptor (EDA) complex, followed by fast reaction of the inner complex with iodine to form a triiodide ion. The values of the formation constant, K_{CT}, for each complex is evaluated from the Benesi-Hildebrand equation. Stability of the resulting complex in three solvents was also found to vary in the order of 1,2-DCE > DCM > CHCl₃.

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Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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