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Spectroscopic Studies on Charge-Transfer Complexation of Iodine with Dibenzo-15-crown-5 and Benzo-12-crown-4 in Chloroform, Dichloromethane and 1,2-Dichloroethane

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The formation of charge-transfer complexation between dibenzo-15-crown-5 (DB15C5) and benzo-12-crown-4 (B12C4) (Donor) and iodine is investigated spectrophotometrically in three chlorinated solvents, chloroform, dichloromethane (DCM) and 1,2-dichloroethane (DCE) solution at 25°C. The change in polarity of the solvent also doesn't affect the stoichiometry of the complexes. Values of formation constants reflect the order of ionization potentials of the donors. The observed time dependence of the charge-transfer band and subsequent formation of I3- ion are related to the slow formation of the initially formed 1:1 Donor.I2 outer complex to an inner electron donor-acceptor (EDAr) complex, followed by fast reaction of the inner complex with iodine to form a triiodide ion, as follows:

Donor + I2 → **Donor**. I2 (outer complex), fast
Donor.I2 (outer complex) → (**Donor**. I+)I- (inner complex), slow
(**Donor** . I+)I- (inner complex) + I2 → (**Donor** .I+)I3-, fast

The pseudo-first-order rate constants for the transformation process were evaluated in different solvent systems. The stability constants of the resulting EDAr complexes were also evaluated and the solvent effect on their stability are discussed. The resulting complexes were isolated and characterized by FTIR and 1H-NMR spectroscopy.

Keywords: Charge-transfer complex; Iodine; Dibenzo-15-crown-5; benzo-12-crown-4; Kinetics; Formation constant; Spectrophotometry; FTIR; ^{1}H-NMR

1. INTRODUCTION

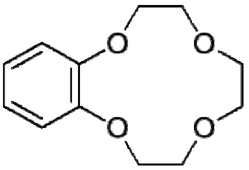
The formation of charge-transfer complex (electron-donor-acceptor complexes, EDA) between two neutral molecules involves the transfer of an electron from the highest occupied molecular orbital (HOMO) of donor to the lowest unoccupied molecular orbital (LUMO) of acceptor. The first theoretical description of such molecular complexes was introduced by Muliken [1,2]. During the past few decades, the charge-transfer complexation of iodine with a wide variety of donor molecules has been the subject of extensive research [1,3,4-8].

Macrocyclic polyethers (crowns), exhibit remarkable complexing properties toward metal ions of ionic size suitable for fitting inside their cavities.Thus, there has been intensive research on the thermodynamics and kinetics of complexation of these ligands with various cations in a vide variety of solvent systems [9-13]. However, less attention has been paid to molecular complexes of crown ethers with neutral molecules.Recently, increasing interest has been focused on such molecular complexes due to their possible applications in areas such as separation processes, biomimetic receptors and catalysis of chemical reactions [11].

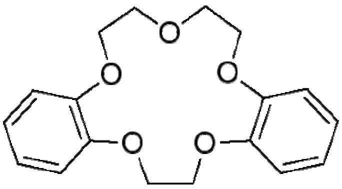
In 1975, HOPKINS *et al*,[14] observed spectroscopic evidence for the formation of molecular complexes between 12-crown-4, 15-crown-5 and 18-crown-6 and iodine in methylene chloride and cyclohexae solutions. They reported that the stabilities of the resulting complexes, which are about the same within experimental error, are two to three times larger than those reported for iodine complexes of monoethers and diethers. In an interesting paper, NOUR EL-DIN reported the formation of 1:1 molecular complexes between DB18C6 and several π-acceptors in methylene chloride solution. He demonstrated that the complex formation is not due to the participation of ether groups in charge transfer bonding but to the Ph-O-CH_2-CH_2 structure.

In recent years, Shamsipur et al have been involved in the spectroscopic investigation of molecular complexes of crown ethers with some neutral molecules [15-17,18-20].

In this research, we report the results of the formation constant and rate constant of complex formation of iodine as a typical σ-acceptor with dibenzo-15-crown-5(DB15C5) and benzo-12-crown-4(B12C4) in three chlorinated solvents, chloroform, dichloromethane and 1,2-dichloroethane solutions.



(B12C4)



(DB15C5)

2. EXPERIMENTAL

2.1. Reagents and apparatus

Resublimed iodine of analytical grade (Merck) was used as received. Reagent grade chloroform, dichloromethane and 1,2-dichloroethane (from Fluka) were used without any further purification. 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 600-200 nm using a Shimadzu double beam spectrometer model 2100 using a quartz cell of 1-cm path length. The proton NMR spectra were recorded on a Bruker 500 MHZ FT NMR spectrometer operating at a field of 11.74T using $CDCl_3$ (Merck) as a pure deutrated solvent with tetramethylsilan (TMS) as an internal standard. The mid infrared spectra (4000-400 cm-1) were recorded from KBr discs using a Nicolet FT-IR model 560 spectrometer. The charge transfer complexes in the crystalline form were prepared by dissolving appropriate amounts of the crown ether and iodine in chloroform, as follows. To two solution of DB15C5 (0.032 g, 0.10m mole) and B12C4 (0.022 g, 0.10m mole) in $CHCl_3$ (20 ml), a solution of excess iodine (0.152 g, 0.60 m mole) in $CHCl_3$ (50 ml) was added and stirred for 16h. The formed dark brown precipitate were filtered off, washed two times with minimum amounts of $CHCl_3$ and dried under vacuum over P_2O_5.

3. RESULTS AND DISCUSSION

The electronic absorption spectra of Donor in the presence of an excess amount of iodine in chloroform, dichloromethane and 1,2-dichloroethane were obtained as a function of time at 25°C and the sample absorption spectra of iodine (4.8×10^{-4} M, Fig. 1A and Fig. 1B) in chloroform. As can be seen, in the presence of DB15C5 and B12C4 new bands appears in the 290-450 nm region besides the presence of the iodine band at around 508 nm. None of the initial reactants show any measurable absorption in this region. It should be noted that the bands of 292 and 364 nm are characteristic for the formation of triiodide ion, I_3^-, in the process of complex formation between iodine and different electron pair donating ligands [21,22,23,24-26]. Therefore, the observation of this band can be assigned to the formation of charge transfer complex between DB15C5, B12C4 and iodine.The intensity of the new band increases, whereas that of the free iodine band decreases, as the concentration of the donors are increased.The existence of a well defind isosbestic point at 475 nm is indicative of the occurrence of a simple complex formation equilibrium between iodine and the macrocycle.

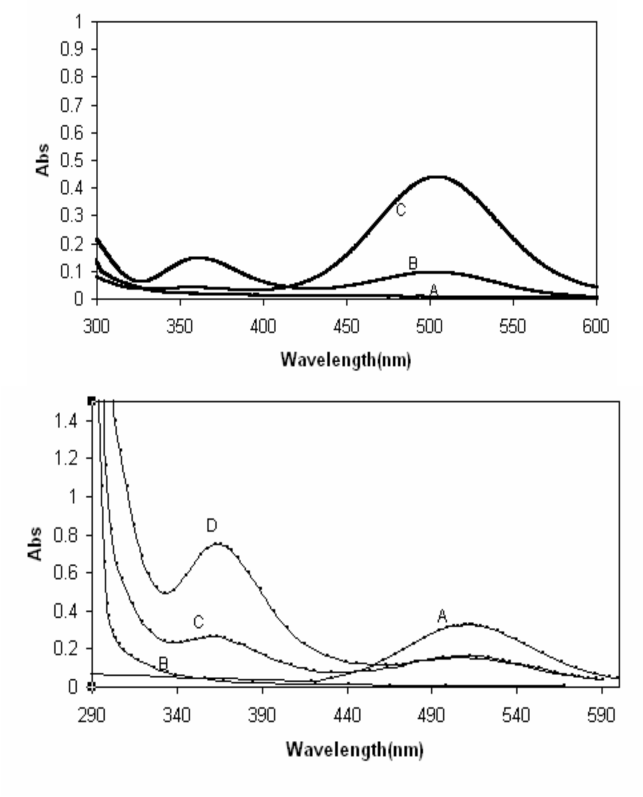


Fig. 1. (A) Absorption spectra of iodine (A, 4.8×10-4M), DB15C5 (B,7.4×10-3M) and their complex (C, after 1min and D, after 2.5 h). (B) Visible spectra of B12C4(A), iodine(C) and iodine-B12C4(B) in chloroform.

From Fig. 1, it is obvious that the spectra recorded for the complexes between **Donor** and iodine are time dependent. As seen, the intensity of the iodine band at 510 nm decreased significantly with the elapse of time, while an intensification of new bands at 296 and 364 nm was observed. It should be noted that the absorptions at 296 and 364 nm are well-known characteristic bands for the formation of triiodide ion, I_3^-, in the process of complex formation between iodine and different electron-pair donor ligands [22, 27-39] .

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 CT complex followed by a fast reaction of the resulting inner complex with iodine to form a triiodide ion, as follows [35-37,40,41]:

Donor + $I_2 \rightarrow$ **Donor .** I_2 (outer complex), fas (1)
Donor .I_2 (outer complex) $\rightarrow$ (**Donor .** I^+)I^- (inner complex), slow (2)
(**Donor.** I^+)I^- (inner complex) + $I_2 \rightarrow$ (**Donor**.I^+)I_3^-, fas (3)

In the next step, the electronic absorption spectra of iodine (5.2×10^{-4} M, Fig. 2A and Fig. 2B) in the presence of increasing amount of **Donor** in chloroform were recorded and typical results. As seen, the resulting **Donor**-iodine complex has a rather sharp absorption at 292 nm and a weaker and broader absorption at 360 nm, which are associated with the formation of donor-acceptor molecular complexes between the **Donor** and iodine in solution [22,27-37].

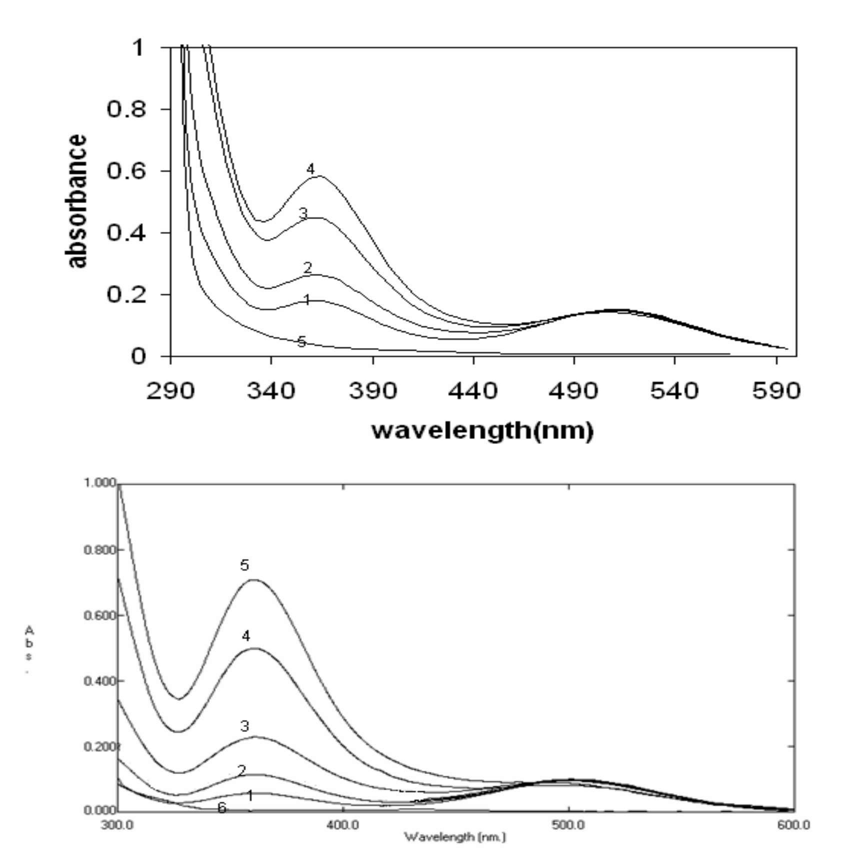


Fig. 2. (A) Absorption spectra of 5.2×10^{-4}M of iodine in chloroform in the presence of varying concentration of DB15C5 at 25 °C. The DB15C5/I_2 mole ratio are: 1, 30; 2, 56; 3, 71; 4, 86; 5, DB15C5 alone. **(B)** Absorption spectra of 5.2×10^{-4} M of iodine in chloroform in the presence of varying concentration of B12C4:1, 2.1×10^{-3} M; 2, 3.1×10^{-3} M; 3, 1.2×10^{-2} M; 4, 2.0×10^{-2} M; 5, 2.8×10^{-2} M and 6, B12C4 (0.04 M).

The kinetics of transformation of the outer CT complex into the inner CT complex was followed by the time dependence of the triiodide absorption band at 364 nm, in order to obtain more information about the kinetics and mechanism of the interaction of **Donor** with iodine. The absorbance of solutions containing reactants at a [**Donor**]/[I_2] molar ratio of 20 in all three solvent systems was monitored as a function of time. As is obvious, the transformation of the outer complex into the corresponding inner complex (Eq. 2) found to follow pseudo-first-order kinetics.

The rate constant k was then evaluated based on a simple first-order kinetic model using the following equation:

$$A_t = A_\infty + (A_o - A_t) \exp(-kt) \qquad (4)$$

Where A_o, A_∞ and A_t are the measured at initial and infinite times and time t, respectively. According to Eq 4, the k values can be evaluated from the slope of the resulting linear $\ln(A_\infty - A_t)$-time plots. The rate constants thus calculated for all three solvent systems used are given in Table 1.

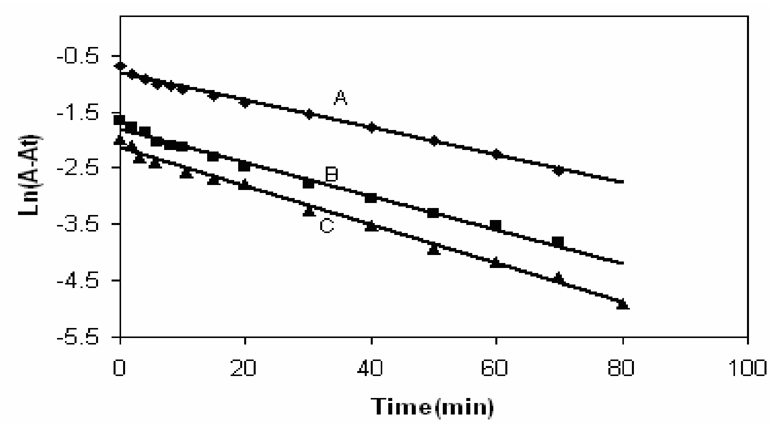


Fig. 3. Plot of Ln(A_∞-A_t) *vs*. time at 364nm for 4.8×10^{-4} M I_2 And 3.11×10^{-2} M DB15C5 mixtures in chloroform(A), Dichloromethane(B) and 1,2-dichloroethane(C).

It is obvious that, the rate of transformation of outer complex to inner complex is in the order of 1,2-DCE > DCM > $CHCl_3$. There is actually a considerable decrease in the energy of activation along with an increased dielectric constant of the medium, in the more polar solvent, like1,2-DCE (ε = 10.3) the transformation proceeds much faster than that in DCM (ε =9.1) and $CHCl_3$ (ε = 4.8). This is in support of the proposed three-step mechanism. In fact, the resulting charged transition states in going from the outer complexes to the inner ones(as the rate determining step of the mechanism) are expected to be more stabilized in 1,2-DCE because of its higher solvating ability and relative permittivity than DCM and chloroform [42]. Formation constants of the resulting 1:1 donor-acceptor complexes were determined employing the blue-shifted iodine bands for a series of solutions with varying excess amounts ligand and constant iodine concentration in all three solvent systems used. The formation constants, K_f, and molar absorptivity, ε_{CT}, of the complex were evaluated using Benesi-Hildebrand equation [43]:

$$[I_2]_o /\text{Abs} = (1/K_f\, \varepsilon_{CT})(1/[\mathbf{L}]_o) + 1/\varepsilon_{CT} \qquad (5)$$

where $[I_2]_o$ and [**Donor**]$_o$ are the initial concentrations of reactants. Sample linear plots of $[I_2]_o$ /Abs *vs*. 1/[**Donor**]$_o$ are shown in Fig. 4, from the intercept and slope of which the ε_{CT} and K_f values can be evaluated. Such a fair linear relationship in the resulting Benesi-Hildebrand plots is a good evidence for the 1:1 stoichiometry of the charge transfer complexes studied. The calculated ε_{CT} and K_f values are also included in Table 1. It is interesting to note that, as expected by the Mulliken's charge transfer theory[44], the formation constant of the **Donor**-I_2 complex increases with increasing polarity of medium as $C_2H_4Cl_2$> CH_2Cl_2 > $CHCl_3$. The observed trend could be due to the high stabilization of the excited states in more polar solvents, where the charges are more separated than those in the ground state [44, 45].

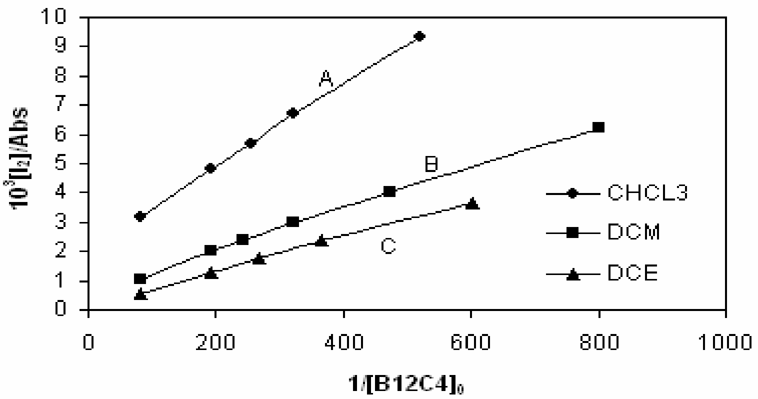


Fig.4. Benesi-Hildbrand plots for B12C4-I2 molecular Complexes in the chloroform (A), dichloromethane (B) and 1,2-dichloroethane (C) solutions.

Table 1. Formation constants $_{(KCT)}$, molar absorptivities $_{(\varepsilon CT)}$ and rate constants (k) for DB15C5-I_2 and B12C4-I_2 complexes at 25°C in chloroform, dichloromethane and 1,2-dichloroethane.

Donor		λ*CT(nm)*	*Log*K_{CT}	*Log* ε_{CT}	10^2 *k*(min^{-1})
DB15C5	$CHCl_3$	364	1.40±0.05	3.71±0.01	2.38±0.12
	$CH_2Cl_{2(DCM)}$	363	1.92±0.04	3.24±0.07	2.54±0.04
	$C_2H_4Cl_{2(DCE)}$	362	2.25±0.07	2.50±0.03	3.05±0.02
B12C4	$CHCl_3$	364	1.68±0.02	3.05±0.01	2.44±0.09
	$CH_2Cl_{2(DCM)}$	362	2.19±0.06	2.70±0.08	2.90±0.06
	$C_2H_4Cl_{2(DCE)}$	360	2.50±0.05	2.48 ±0.03	3.76±0.08

The data given in Table1 revealed that, the K_f value for the B12C4- I_2 is larger than that for the DB15C5- I_2 system. The relatively higher stability of the iodine complex of B12C4 as compared with DB15C5 may be attributed to the more rigid structure of the former ligand which may possibly make the electrons of its donating oxygens more available for the transfer of charge into the LUMO' of I_2 molecule. Moreover, B12C4 has a smaller size(1.2-1.5A°) than DB15C5(1.7-2.2A°); as a result it is expected to be less flexible than DB15C5, consequently, the acceptor molecules probably can easily approach the oxygen atoms of the B12C4 to form the most stable complex. The phenyl group in this case acts as an electron withdrawing group which pulls the electrons from oxygen atoms of the crown ether. The stabilities of the charge transfer complexes with iodine and donating ligands decrease in the order B12C4 > DB15C5.

The infrared spectra of the macrocycle and the isolated solid complexes in the wavenumber range 4000-400 cm^{-1} have been recorded. Tentative assignment of the most important IR-frequencies, that provide structural evidence of these complexes, are listed in Table 2.

Strongly supporting the results obtained from the IR studies. However, other protons of the macrocycle (i.e. –OCH_2- and -OCH_2CH_2O-protons) also show some downfield shifts upon complexation with I_2, although to a much lower extent. The intensity of the bands has been changed (generally decreased). These effects have been observed previously for some other charge transfer complexes [14,28]. The first effect is a result of weakening of some relative weak bands during complexation and the second effect can be attributed to the increasing of the symmetry of molecule during complexation. The methylene stretching of the ethoxy groups of benzo crowns coupled with ring vibration, observed in the 2980-2810cm^{-1} region, show considerable shift upon complex formation. This is probably due to contribution of the ethoxy groups of crown ethers in the interaction with π-acceptors [14].

Table 2. Infrared frequencies (cm^{-1}) and tentative assignments for DB15C5 and B12C4 and theirs charge transfer complexes with iodine.

DB15C5	**[(DB15C5)$_2$I$^+$] I$_3^-$**	**B12C4**	**[(B12C4)$_2$I$^+$] I$_3^-$**	**Assignments**
3424(br)	3420(s,br)	3392(br)	3360(vs,br)	υ (C-H)aliphatic
1593(s)	1645(sh)	1592(s)	1647(sh)	υ (C=C) aromatic ring
1502(vs), 1454(s)	1501(s), 452(m)	503(vs), 1451(vs)	1494(s), 1450(m)	υ (-CH$_2$-)
1122(vs)	1124(s)	1121(vs)	1123(s)	υ (C-O)
2936(m)	2934(w)	2925(m)	2916(w)	couple ethoxy groups with ring vibration

(vs) very strong; (s) strong; (m)medium; (sh) shoulder; (br)broad; (w)weak

From the data given in Table 2 it is obvious that the IR spectra of the resulting molecular adducts contain the main bands of the macrocycle DB15C5 and B12C4, strongly supporting the formation of charge-transfer complexes with iodine [23,24]. As it is seen, the formation of such charge-transfer complexes is associated with some changes in the intensities of the IR bands of the macrocycle such as υ (C=C) and υ (C-O), as well as some measurable shifts in their frequencies to higher values [18]. On the other hand, a comparison of the important IR spectral bands of the free donors with those of the complexes formed with iodine supports the CT complexations. The couple ethoxy groups with ring vibration bands of the free donors are shifted to lower frequencies on complex formation. This behaviour is in accordance with the charge migration from donors to acceptors. Interesting results are obtained from the ^{1}H-NMR spectra of DB15C5 and B12C4 and their I$_2$ complexes .The spectrum of DB15C5 consisted of triplet due to –OCH$_2$- (at about 3.96 and 4.2 ppm), a singlet for - OCH$_2$CH$_2$O- (at about 4.38 ppm) and phenyl-H at about 6.94ppm. The spectrum of B12C5 consisted of triplet due to –OCH$_2$- (at about 3.84 and 4.16 ppm), a singlet for - OCH$_2$CH$_2$O- (at about 3.83 ppm) and phenyl-H at about 7.25 ppm. Protons of the macrocycle show some downfield shifts upon complexation with iodine. The ^{1}H-NMR spectral data of DB15C5, B12C4 and their charge transfer complexes are listed in Table 3.

Table 3. ^{1}H-NMR spectral data of DB15C5, B12C4 and their charge transfer complexes.

	–OCH$_2$-	- OCH$_2$CH$_2$O-	phenyl-H
DB15C5	3.96, 4.2ppm	4.38ppm	6.94ppm
DB15C5-I$_2$	4.10(broad)	4.43(broad)	7.01ppm
B12C4	3.84, 4.16ppm	3.83ppm	6.95ppm
B12C4- I$_2$	4.48, 4.31ppm	3.93ppm	7.02ppm

In low molecular weight aromatic charge transfer complexes the chemical shift of aromatic protons decrease linearly with the degree of complexation. A small effect suggests that such chemical shifts are determined on the whole by ring currents due to the layerin of complexing groups and not by charge transfer. In this case the proton chemical shift for both donor and acceptor are not only numerically alike but also have the same sign, namely an up field shift compared to those of the un-reacted components. One would expect that significant charge transfer would cause a downfield shift of the proton absorptions of the donor in the complex.

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