

## Spectrophotometric Study of Charge-transfer Complexes of Iodine with Tetrabutylammonium Halides in Chloroform Solution

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### Abstract

The Complex formation reaction between iodine with tetrabutylammonium halides (TBAX) has been studied spectrophotometrically in chloroform solution at 25°C. Various aspects of the spectra of iodine in the presence of various concentration of different tetrabutylammonium halides have been discussed in terms of electronic specifications of iodine and halides. In the case of tetrabutylammonium iodide and at high concentrations of iodine, both 1:1 ( $I_3^-$ ) and 2:1 ( $I_5^-$ ) complexes have been formed. Formation constants of charge transfer complexes were evaluated from the computer fitting of the absorbance-mole ratio data and found to vary in the order: TBAI>TBABr>TBACl>TBAF.

### Introduction

Investigation of polyhalide complexes has a long background [1] and various aspects of these complexes have been studied extensively. Examples are molecular orbital study [2], [3], spectrophotometric study in different solvents such as acetonitrile and dichloroethane [4], conductometric study in nonaqueous solutions[5], [6], spectroscopic investigations involving Raman[7], [8], NQR[9], X-ray [9] and far-Infrared studies[10]. Unfortunately, there are some ambiguities about the stoichiometry of polyhalides in solution. Also there is very little thermodynamic data for the complexation of polyhalides. Informations obtained from the investigation of the complexation of  $I_2$  with

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**Key words:** Terabutylammonium halides, Charge-transfer complexes, Iodine, Chloroform,

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crown ethers and some of their aza substituents and some similarities between their spectra and of  $I_3^-$  spectrum conducted us to a spectrophotometric study of the complexation of [11],[14] tetrabutylammonium halides and  $I_2$  in chloroform solution. In this paper we report a spectrophotometric study of charge transfer complexes between different tetrabutylammonium halides and iodine in chloroform solution.

## **Experimental**

### **Reagents**

Tetrabutylammonium iodide (TBAI), tetrabutylammonium bromide (TBABr), tetrabutylammonium chloride (TBACl.H<sub>2</sub>O), and tetrabutylammonium flouride (TBAF.3H<sub>2</sub>O) from Merck and Fluka companies were of the highest purity available and used without any further purification. Both iodine and chloroform from Merck were also used without any further purification.

### **Apparatus**

All UV-Vis spectra were recorded on a Philips PUB700 spectrophotometer and the absorbance measurments were made with a Philips PU875 spectrophotometer at  $25 \pm 0.01^\circ\text{C}$

### **Computation Method**

For the evaluation of the fromation constants of the resulting complexes,  $K_f$ , from the absorbance-mole ratio data, a nonlinear least squares curve fitting porgram KINFIT, was used [15]. The program is based on the iterative adjustment of the calculated values of absorbanee to the observed values by using either Wentworth matrix technique[16] or the Powell procedure[17]. Adjustable parameters are  $K_f$  and  $\epsilon$ , where  $\epsilon$  is the molar absorptivity of iodine.

## Procedure

In order to obtain UV-Vis spectra, 3 mL of a  $\sim 10^{-4}$  M of iodine solution was transferred into a 1.00 cm quartz cell and titrated with a tetrabutylammonium halide solution by a 100  $\mu$ l Hamiltonian syringe [solutions of (TBACl.H<sub>2</sub>O) and (TBAF.3H<sub>2</sub>O) were dried by molecular sieves before use]. Each spectrum was recorded immediately after the titrant addition. The spectra were obtained by varying the tetrabutylammonium halide to I<sub>2</sub> ratio from 0- to maximum value of 0.8. The stoichiometry and K<sub>f</sub> values were obtained from the absorbance-mole ratio data obtained by spectrophotometric titration of 3 mL of  $10^{-3}$ - $10^{-4}$  M of iodine solution with tetrabutylammonium halide in a 1.00 cm glass cell at 508 nm.

## Results and Discussion

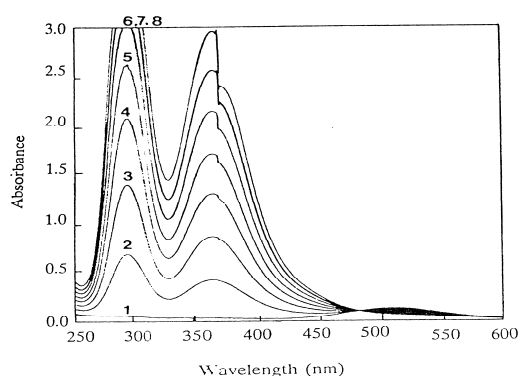
Figs 1-4 show the absorption spectra of iodine solution with a constant concentration in the presence of various concentration of tetrabutylammonium halides. These spectra were obtained by titration of 3 mL of  $1.23 \times 10^{-4}$  M of iodine solution with TBAI (Fig.1), 3 mL of  $5.36 \times 10^{-4}$  M of iodine solution with TBABr (Fig.2), 3 mL of  $5.26 \times 10^{-4}$  M of iodine solution with TBACl (Fig.3) and 3 mL of  $5.36 \times 10^{-4}$  M of iodine solution with TBAF (Fig.4). The halide was added in such a way that maximum ratio of halide to I<sub>2</sub> to remain 0.8. A comparison between the resulting spectra shows that in the case of BrI<sub>2</sub><sup>-</sup> complex (Fig. 2) the 364 nm band has been converted to a shoulder and a profound decrease in the intensity of this band has also been occurred. The intensity of a charge-transfer band and stability of the resulting charge transfer complex for a series of similar donors depend on the variation in the differences in energy between the most stable configuration and the configuration which gives the most intense charge-transfer band [18]. Thus it can be concluded that the orientation and geometry of BrI<sub>2</sub><sup>-</sup> should be different from the others. This is most probably a result of the difference in overlapping of Br<sup>-</sup> orbitals with I<sub>2</sub>, as compared with I<sup>-</sup>, Cl<sup>-</sup> and F<sup>-</sup> ions. Probably BrI<sub>2</sub><sup>-</sup> has a bent geometry and this geometry does not let the formation of 2:1 complex.

The 364 nm band for  $I_3^-$  has been attributed to a  $\pi \rightarrow \sigma^*$  charge transfer transition in which  $\pi$  represents the nonbonding  $5P\pi$  orbital of  $I^-$  and  $\sigma^*$  represents the antibonding  $5P\pi$  orbital of the molecule [19]. If this is true, it is expected that there must be a blue shift in 364 nm band from  $I_3^-$  to  $FI_2^-$ , because of the energy levels of the highest occupied orbitals of  $x^-$  have the sequence:  $5p(I) < 4p(Br) < 3p(Cl) < 2p(F)$ . Since the 364 nm band is fixed in all cases, it cannot be considered as  $\pi \rightarrow \sigma^*$  transition. Whereas it seems reasonable to assign the bands which are located at 290, 279, 264 and 262 for  $I_3^-$ ,  $BrI_2^-$ ,  $ClI_2^-$  and  $FI_2^-$  complexes (Figs.1-4), respectively, as  $\pi \rightarrow \sigma^*$  transitions. An interesting feature of various spectra is a systematic blue shift in their isosbestic points from  $I_3^-$  to  $FI_2^-$ . Which causes by a blue shift in 508 nm band of free iodine during complexation (Mulliken has called this band as a locally excited band)[19]. Such a blue shift in absorption maximum of  $I_2$  has been interpreted as follows:

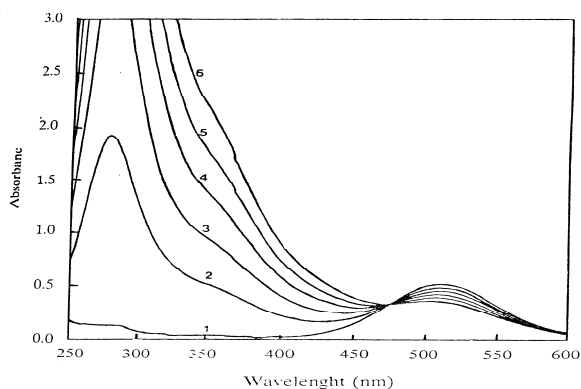
The  $\sigma_u$  MO of iodine is strongly antibonding and therefore large, and its presence in the excited  $I_2$  should considerably increase the effective size of the molecule. When the iodine molecule, paired off with a close partner in a complex, is excited by visible light absorption ( $\pi_g \rightarrow \sigma_u$ ), its suddenly swollen size introduces an exchange repulsion between it and the partner molecule or, one may say, the  $\sigma_u$  electron collides with the partner molecule. This repulsion energy is added to the usual energy of the excited iodine molecule, giving a blue shift in the (vertical, or Franck-Condon peak) absorption frequency.

If the foregoing idea is correct, the "blue shift" should be greater than intimate contact, or overlap, of the partners in the normal state of a complex. (It need not necessarily be quite so closely correlated with the equilibrium constant or even the heat of formation). If so, the following conclusions can be stated: in the methylated benzene complexes at room temperature there is relatively very loose contact and so small blue shift. In contrast, at low temperatures there is closer contact and so there is a moderate blue shift. In the pyridine and the amine complexes contact is relatively intimate even at

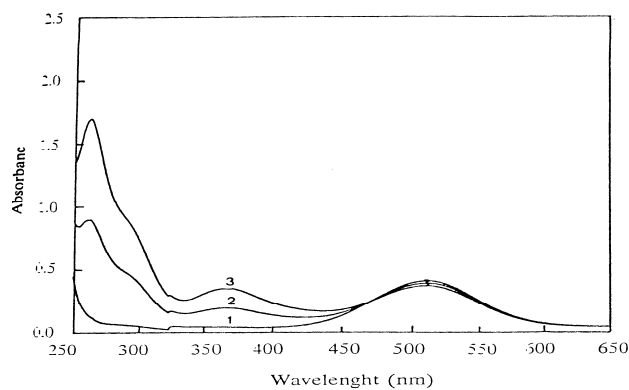
room temperature and so there is large blue shift [18]. According to above discussion, the larger blue shift of  $\text{FI}_2^-$ , relative to the others, can be correlated to the smallest size and highest charge density of  $\text{F}^-$  in the series which causes the more intimate contact or overlap of this anion to iodine. This is because of the fact that  $\text{F}^-$  has the highest polarization effect on  $\text{I}_2$  molecule in the series and thus the perturbation of electronic state of  $\text{I}_2$  by  $\text{F}^-$  is highest relative to the others. It must be emphasized that highest blue shift for  $\text{FI}_2^-$  and lowest  $K_f$  for  $\text{FI}_2^-$  are not in contradiction. Because the former relates to the amount of contact and penetration ability which is highest for  $\text{F}^-$  while the later relates to the amount of electron donation to  $\text{I}_2$  which is the lowest for this anion.



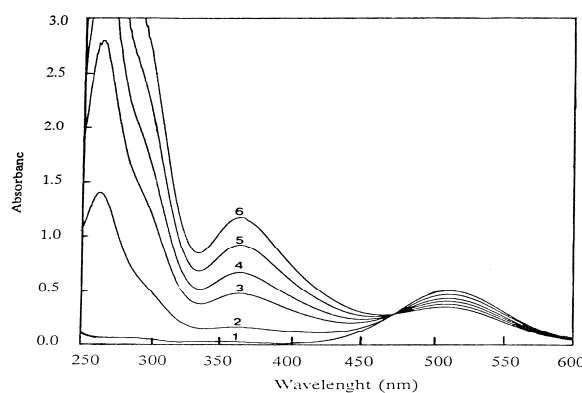
**Fig.1: Absorption spectra of  $1.3 \times 10^{-4}$  M of iodine in chloroform in the presence of varying concentration of TBAI: 1, 0.00M; 2,  $1.4 \times 10^{-5}$ M; 3,  $2.8 \times 10^{-5}$ M; 4,  $4.18 \times 10^{-5}$ M; 5,  $5.58 \times 10^{-5}$ M; 6,  $6.98 \times 10^{-5}$ M; 7,  $8.37 \times 10^{-5}$ M; 8,  $9.77 \times 10^{-5}$ M.**



**Fig.2: Absorption spectra of  $5.36 \times 10^{-4}$  M of iodine in chloroform in the presence of varying concentration of TBABr: 1, 0.00M; 2,  $4.13 \times 10^{-5}$ M ; 3,  $3.2 \times 10^{-5}$ M;  $1.23 \times 10^{-5}$ M; 5,  $1.64 \times 10^{-5}$ M; 6,  $1.95 \times 10^{-5}$ M.**



**Fig.3: Absorption spectra of  $4.47 \times 10^{-4}$  M of iodine in chloroform in the presence of varying concentration of TBACl: 1, 0.00M; 2,  $2.09 \times 10^{-5}$ M; 3,  $2.47 \times 10^{-5}$ M.**

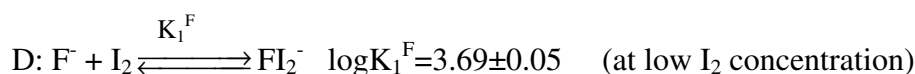
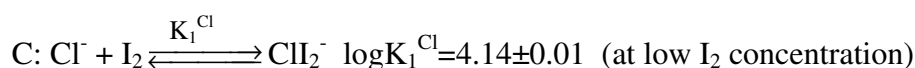
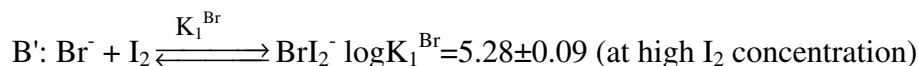
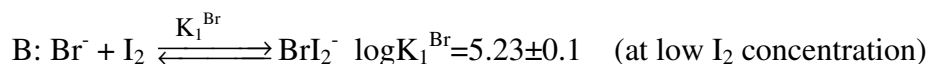
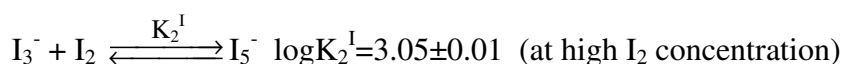
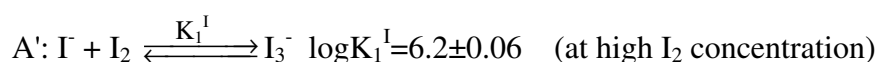
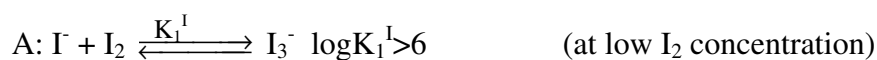


**Fig.4: Absorption spectra of  $3.36 \times 10^{-4} \text{M}$  of iodine in chloroform in the presence of varying concentration of TBAF: 1,  $0.00 \text{M}$ ; 2,  $5.68 \times 10^{-5} \text{M}$ ; 3,  $1.13 \times 10^{-5} \text{M}$ ; 4,  $1.70 \times 10^{-5} \text{M}$ ; 5,  $2.26 \times 10^{-5} \text{M}$ ; 6,  $2.80 \times 10^{-5} \text{M}$ .**

Finally, the UV-Vis spectra of  $\text{ClI}_2^-$  and  $\text{FI}_2^-$  (Figs-3 and 4) show a shoulder at 300 nm which does not exist for  $\text{I}_3^-$  and  $\text{BrI}_2^-$ . This shoulder can be attributed to "contact charge-transfer absorption band" [20] which has similarly been observed for the solution of  $\text{I}_2$  in n-heptane [18,21]. An inert solvent which has normally no charge transfer interaction with  $\text{I}_2$ . A fairly intense charge-transfer absorption band should be possible for donor-acceptor pairs which are merely close or in contact even if no actual molecules of complex are present. That is even if the equilibrium constant for complex formation is zero [20]. The equilibrium constant of chloroform and  $\text{I}_2$  is zero. But it is expected that a suitable contact of  $\text{I}_2$  and chloroform causes the production of contact charge transfer absorption band.

Considering the higher charge density of  $\text{Cl}^-$  and  $\text{F}^-$  relative to  $\text{I}^-$  and  $\text{Br}^-$ , It is expected that the polarization of  $\text{I}_2$  by these ions must be larger than  $\text{I}^-$  and  $\text{Br}^-$  as a result of more electrostatic repulsion between these ions and electronic cloud of  $\text{I}_2$  molecule.

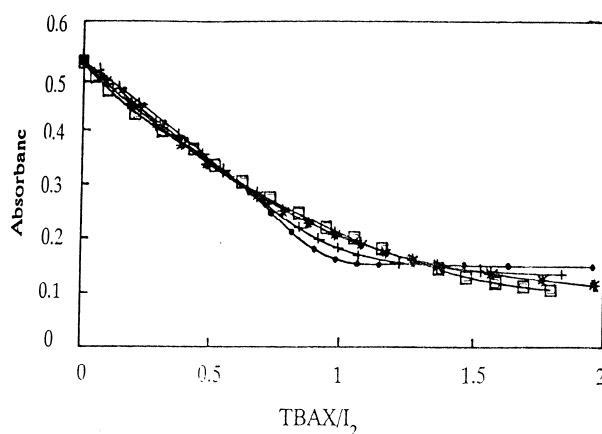
So these ions push the electrons of  $I_2$  toward solvent more effective than the others and result in a better contact of  $I_2$  with chloroform. As a consequence of this effective contact, a shoulder at 300nm due to contact charge-transfer absorption band can be observed for  $ClI_2^-$  and  $FI_2^-$ . Because  $I^-$  and  $Br^-$  are not able to produce such effective contact between  $I_2$  and solvent, similar bands are not observed for them. Final thermodynamic and spectrophotometric results are collected in Table 1. The resulting thermodynamic data correspond to the following equilibria:



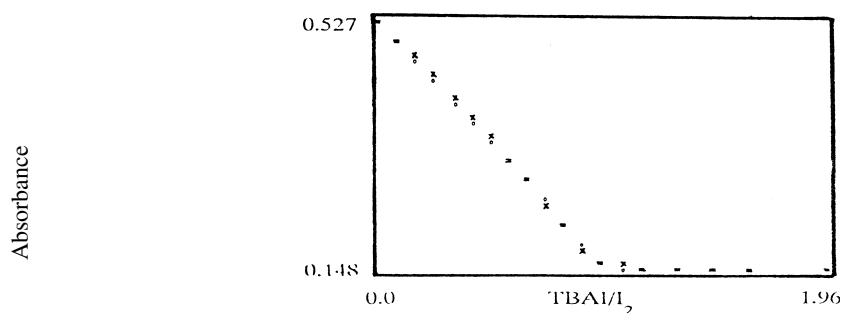
As it is seen (Figs. 5 and 6), at low concentrations of  $I_2$ , only 1:1 ( $I^- : I_2$ ) complex is formed. However at higher concentrations of  $I_2$ , both 1:1 and 1:2  $I^-$  to  $I_2$  complexes are observed (Figs. 7 and 8). Since the 1:2 adducts of  $I_2$  with  $I^-$  (i.e.  $I_5^-$ ) is isolated in the solid state [22], it is not surprising to have such a stoichiometry in chloroform solution. The mole ratio method for  $Br^-$  ion in the presence of iodine at low and high concentrations was also examined. In this case, in contrast with  $I^-$ - $I_2$  system, only a 1:1



adduct was formed. As the other halides have smaller size than  $\text{Br}^-$  [23], the possibility for the formation of 1:2 complexes with iodine are discarded in their cases. Due to the large size of tetrabutylammonium cation and the steric hinderance problems, it is expected that  $\text{I}_5^-$  has a bent geometry, such as that identified in the solid phase [10].

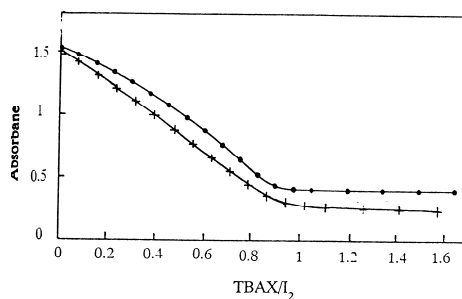


**Fig.5: Plots of absorbance vs. TBAX/I<sub>2</sub> mole ratio. For solutions of  $5.73 \times 10^{-4}$  M of iodine in chloroform obtained at 508 nm: TBAI-I<sub>2</sub> (●), TBABr-I<sub>2</sub> (+), TBACl-I<sub>2</sub> (\*), TBAF-I<sub>2</sub> (□)**

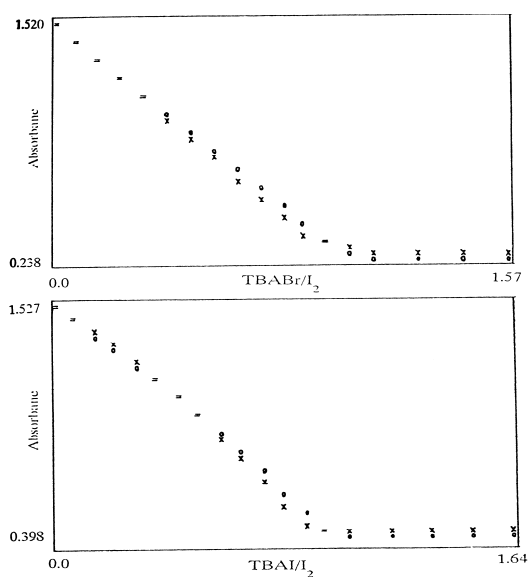


□

**Fig.6: Computer fit of the absorbance vs. TBAI/I<sub>2</sub> mole ratio plot for solutions of  $5.73 \times 10^{-4}$  M of iodine in chloroform obtained at 508 nm and 25°C: (x) experimental point; (o) calculated point; (≡) experimental and calculated points are the same within the resolution of the plot.**



**Fig.7: Plots of absorbance vs. TBAX/I<sub>2</sub> mole ratio for solutions of  $1.65 \times 10^{-3}$  M of iodine in chloroform obtained at 508nm: TBAI-I<sub>2</sub> (●), TBABr-I<sub>2</sub>(+).**



**Fig.8: Computer fit of the absorbance vs. TBAX/I<sub>2</sub> mole ratio plots for solutions of  $1.63 \times 10^{-3}$  M of iodine in chloroform obtained at 508 nm and 25°C: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.**

The values of  $\log K_f$  for 1:1 complexes (Table 1) decrease in the order  $I^- > Br^- > Cl^- > F^-$  which shows that  $I^-$  donates its electron to  $I_2$  the best and  $F^-$  the worst in the series. This is reasonable based on the decreased electronegativity from fluorine to iodine.

**Table 1- Final thermodynamic and spectroscopic results.**

Donor	Log $K_f^a$	$\Delta\lambda_{max}(nm)$	$\lambda_{IP}^b$
TBAI	L:>6 H:6.2±0.06(K <sub>1</sub> ) 3.05±0.01(K <sub>2</sub> )	290,....., 364	483
TBABr	L:5.23±0.1(K <sub>1</sub> ) H:5.28±0.09(K <sub>1</sub> )	279,....., 364 (sh)	476
TBACl	L: 4.14±0.01(K <sub>1</sub> )	264,300(sh), 363.3	470
TBAF	L: 3.69±0.05(K <sub>1</sub> )	262,300(sh), 361	466.3

a- L and H are the values of  $\log K_f$  at low and high concentration of  $I_2$ , respectively.

b-  $\lambda_{IP}$  is the wave-length of the isosbestic point.

## Conclusions

According to the results presented it can be concluded that:

1. The reactions of all of halides with  $I_2$  follows through equilibrium pathway.
2. The spectrum of  $BrI_2^-$  complex (Fig. 2) differs from the other spectra (Figs. 1, 3 and 4). This can be attributed to the difference between  $BrI_2^-$  structure and the other ones.
3. As in all spectra the 364nm band is fixed. So it can not be assigned to a  $\pi \rightarrow \sigma^*$  transition.
4. In the case of  $ClI_2^-$  and  $FI_2^-$  complexes, "contact charge transfer absorption bands" are observed.
5. The  $I^-$  forms both 1:1 and 1:2 complexes. However, the other halides only form 1:1 complexes.
6. The stability of complexes vary in the order of electropositivity of halides.
7. In the spectra of all complexes, "charge transfer absorption bands" are

observed.

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