Spectophotometric Study of Charge-transfer Complexes of Iodine with Tetrbutylammonium 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, Spectrophotometr

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 ($TBACl.H_2O$), and tetrabutylammonium flouride ($TBAF.3H_2O$) 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±0.01°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 absorbanece to the observed values by using either Wentworth matrix technique[16] or the Powell procedure[17]. Adjustable parameters are K_f and Є, where Є is the molar absorptivity of iodine.

Procedure

In order to obtain UV-Vis spectra, 3 mL of a ~ 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 µl Hamiltonian syringe [solutions of ($TBACl.H_2O$) and ($TBAF.3H_2O$) were drived 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_2 ratio from 0- to maximum value of 0.8. The stoichiometry and K_f 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 concentaration in the presence of various concentration of tetrabutylammonium halides. These spectra were obtained by titration of 3 mL of 1.23×10^{-4}M of iodine solution with TBAI (Fig.1), 3 mL of 5.36×10^{-4}M of iodine solution with TBABr(Fig.2), 3 mL of 5.26×10^{-4}M of iodine solution with TBACl (Fig.3) and 3 mL of 5.36×10^{-4}M of iodine soluton with TBAF (Fig.4). The halide was added in such a way that maximum ratio of halide to I_2 to remain 0.8. A comparison between the resulting spectra shows that in the case of BrI_2^- 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_2^- should be different from the others. This is most probably a result of the difference in overlapping of Br^- orbitals with I_2 , as compared with I^- , Cl^- and F^- ions. Probably BrI_2^- 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 π ⟶ σ* charge transfer transition in which π represents the nonbonding 5Pπ orbital of I^- and σ* represents the antibonding 5Pπ 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 leveles 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 π⟶ σ* transition. Whereas it seems resonable 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 π⟶σ* 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 σ_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 ($\pi_g \longrightarrow \sigma_u$),its suddenly swollen size introduces an exchange repulsion between it and the partner molecule or, one may say, the σ_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 Franc- 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 FI_2^-, relative to the others, can be correlated to the smallest size and highest charge density of F^- in the series which causes the more intimate contact or overlap of this anion to iodine. This is because of the fact that F^- has the highest polarization effect on I_2 molecule in the series and thus the perturbation of electronic state of I_2 by F^- is highest relative to the others. It must be emphasized that highest blue shift for FI_2^- and lowest K_f for FI_2^- are not in contradiction. Because the former relates to the amount of contact and penetration ability which is highest for F^- while the later relates to the amount of electron donation to I_2 which is the lowest for this anion.

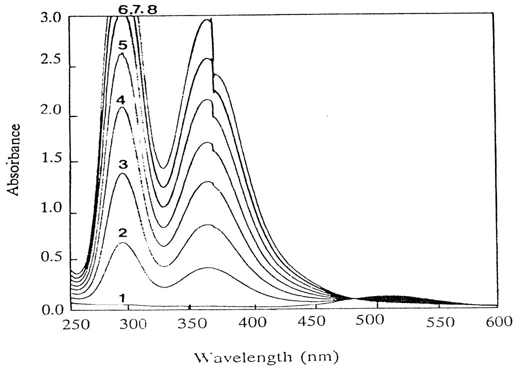


Fig.1: Absorption spectra of 1.3×10^{-4} M of iodine in chloroform in the presence of varing concentration of TBAI: 1, 0.00M; 2, 1.4×10^{-5}M; 3, 2.8×10^{-5}M 4, 4.18×10^{5}M; 5, 5.58×10^{-5}M: 6, 6.98×10^{-5}M; 7, 8.37×10^{-5}M; 8, 9.77×10^{-5}M.

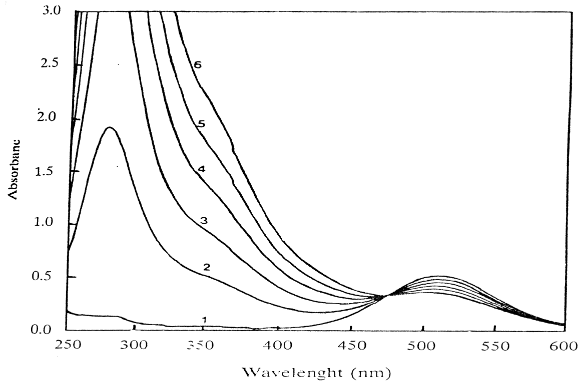


Fig.2: Absorption spectra of 5.36×10^{-4} M of iodine in chloroform in the presence of varing concentration of TBABr: 1, 0.00M; 2, 4.13×10^{-5}M ; 3, 3.2×10^{-5}M;1.23×10^{5}M; 5, 1.64×10^{-5}M; 6, 1.95×10^{-5}M.

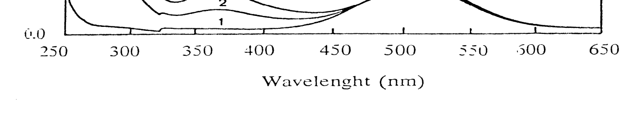


Fig.3: Absorption spectra of 4.47×10^{-4} M of iodine in chloroform in the presence of varing concentration of TBACl: 1, 0.00M; 2, 2.09×10^{-5}M; 3, 2.47×10^{-5}M.

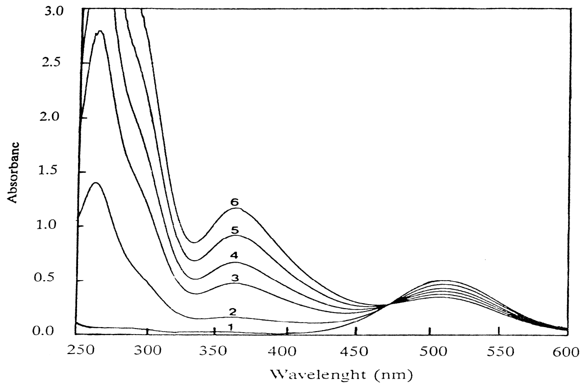


Fig.4: Absorption spectra of 3.36×10^{-4}M of iodine in chloroform in the presence of varing concentration of TBAF: 1, 0.00M; 2, 5.68×10^{-5}M; 3, 1.13×10^{-5}M; 4, 1.70×10^{-5}M; 5, 2.26×10^{-5}M; 6, 2.80×10^{-5}M.

Finally, the UV-Vis spectra of ClI_2^- and FI_2^- (Figs-3and4) show a shoulder at 300 nm which does not exist for I_3^- and BrI_2^-. This shoulder can be attributed to "contact charge-transfer absorption band" [20] which has similarly been observed for the solution of I_2 in n-heptane [18,21]. An inert solvent which has normally no charge transfer interaction with 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 I_2 is zero. But it is expected that a suitable contact of I_2 and chloroform causes the production of contact charge transfer absorption band.

Considering the higher charge density of Cl^- and F^- relative to I^- and Br^-, It is expected that the polarization of I_2 by these ions must be larger than I^- and Br^- as a result of more electrostatic repulsion between these ions and electronic cloud of 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 Table1. The resulting thermodynamic data correspond to the following equilibria:

A: $I^- + I_2 \xrightleftharpoons{K_1^I} I_3^-$ $\log K_1^I>6$ (at low I_2 concentration)

A': $I^- + I_2 \xrightleftharpoons{K_1^I} I_3^-$ $\log K_1^I=6.2\pm0.06$ (at high I_2 concentration)

$I_3^- + I_2 \xrightleftharpoons{K_2^I} I_5^-$ $\log K_2^I=3.05\pm0.01$ (at high I_2 concentration)

B: $Br^- + I_2 \xrightleftharpoons{K_1^{Br}} BrI_2^-$ $\log K_1^{Br}=5.23\pm0.1$ (at low I_2 concentration)

B': $Br^- + I_2 \xrightleftharpoons{K_1^{Br}} BrI_2^-$ $\log K_1^{Br}=5.28\pm0.09$ (at high I_2 concentration)

C: $Cl^- + I_2 \xrightleftharpoons{K_1^{Cl}} ClI_2^-$ $\log K_1^{Cl}=4.14\pm0.01$ (at low I_2 concentration)

D: $F^- + I_2 \xrightleftharpoons{K_1^F} FI_2^-$ $\log K_1^F=3.69\pm0.05$ (at low I_2 concentration)

As it is seen (Figs. 5 and 6), at low concoentrations 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 exmined. 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 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 I_5^- has a bent geometry, such as that identified in the solid phase [10].

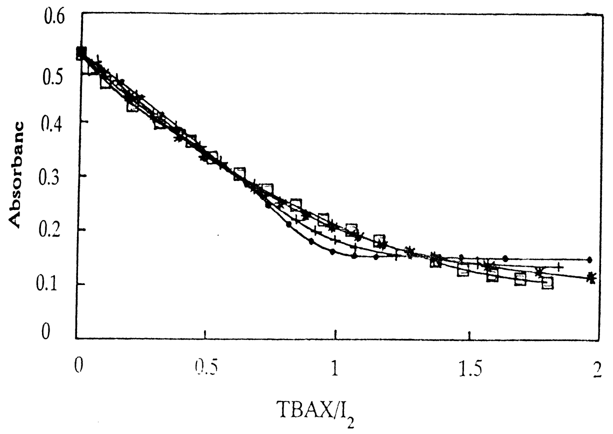
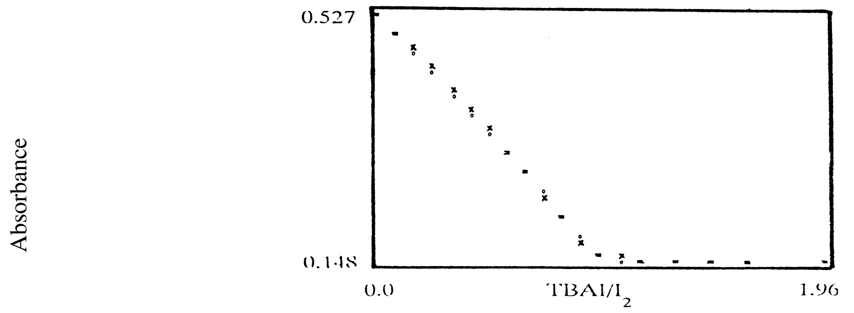


Fig.5: Plots of absorbance vs. TBAX/I_2 mole ratio. For solutions of 5.73×10^{-4}M of iodine in chloroform obtained at 508 nm:TBAI-I_2 (●), TBABr-I_2 (+), TBACl-I_2 (*), TBAF-I_2 ( )



□

Fig.6: Computer fit of the absorbance vs. TBAI/I_2 mole ratio plot for solutions of 5.73×10^{-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.

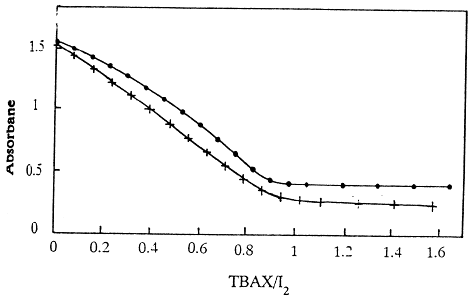


Fig.7: Plots of absorbance vs. TBAX/I_2 mole ratio for solutions of 1.65×10^{-3}M of iodine in chloroform obtained at 508nm: TBAI-I_2 (●), TBABr-I_2(+).

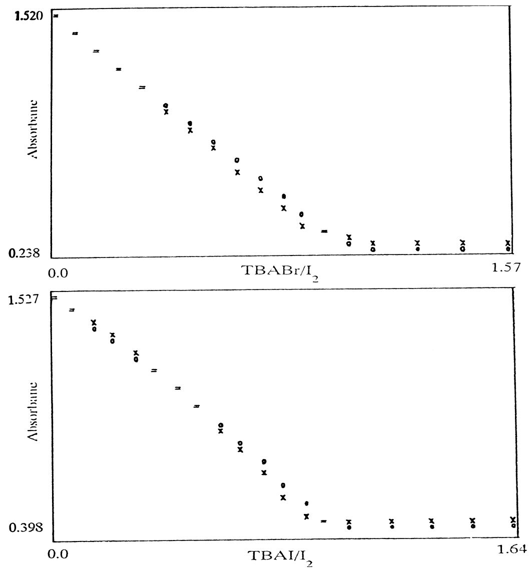


Fig.8: Computer fit of the absorbance vs. TBAX/I_2 mole ratio plots for solutions of 1.63×10^{-3}M of iodine in chloroform obtained at 508 nm and 25°C: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

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]	Λmax(nm)	λ_{IP}[b]
TBAI	L:>6 H:6.2±0.06(K_1) 3.05±0.01(K_2)	290,………, 364	483
TBABr	L:5.23±0.1(K_1) H:5.28±0.09(K_1)	279,….., 364 (sh)	476
TBACl	L: 4.14±0.01(K_1)	264,300(sh), 363.3	470
TBAF	L: 3.69±0.05(K_1)	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- λ_{IP} is the wave-length of the isosbestic point.

Conclusions

Acording 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 $\pi \longrightarrow \sigma^*$ 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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