Asian Journal of Chemistry Vol. 20, No. 3 (2008), 1806-1814

Complex Formation of Tetramethyltetraaza-14-crown-4 with Iodine

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Spectrophotometric and conductometric study concerning the interaction between tetramethyl-tetraaza-14-crown-4 (TMTA14C4) and iodine has been performed in dichloromethane at 25 ºC .The results are indicative of the formation of (macrocycle)$_2$I$^+$. I$_3^-$ sandwich complex through equilibrium reaction. The conductometric data confirm the proposed adduct and show that the products are somewhat as free ions. The stability constant of the complex is obtained by fitting the absorbance *vs.* mole ratio data in MATLAB program. The oscillator strength (f) and the transition probability (μ) of the charge-transfer bands and ionization potential (I_P) of donor have been calculated from the spectral data. IR spectra of pure macrocycle are compared with the corresponding iodine complex and the effect of complexation on absorption bands is discussed. The comparisons of result with the similar ones in chloroform are indicative of the formation of macrocycle. I$^+$. I$_3^-$ in recent solvent. The different stoichiometries in two solvents are assigned to specific interaction between solvent-macrocycle and different physical properties of the solvents.

Key Words: Spectrophotometry, Ttetramethyl-tetraaza-14-crown-4, Dichloromethane, Iodine, Conductometry.

INTRODUCTION

Crown ethers represent interesting class of compounds because of their utility in phase transfer synthetic chemistry[1]. The importance of these ethers is due to their ability to form complexes with various cations of the inorganic salts by metal ion fitting into the cavity of the crown ether and the anion associating to form an ion pair[2,3]. Thus, these compounds can be employed as organic solvents for inorganic salts.

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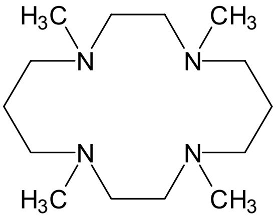
There is increasing interest in the study of charge transfer complex of crown ethers with different π and σ acceptors[4-6]. Among different macrocyclic ligands used for molecular complexation, aza substituted crown ethers show very interesting features. It has been clearly shown that the substitution of oxygen atoms in a crown ether ring by -NH- group results in a drastic increase in the stability of their complexes with iodine[5,7-9] and some π-acceptor molecules[10] over those of ordinary crowns[11,12].

Molecular iodine has been the most studied halogen acceptors. Although there are many reports on molecular charge-transfer complexes between different aliphatic and aromatic amines and iodine in literature[13,14], not much work has been done on similar complexes of aza crown ethers[5,7-9].

In connection with our previous studies made on molecular complexes of crown ethers and their aza derivatives in various solvent[7-9,12,15-19], we report here the results of spectrophotometric and conductometric study of the complexation of TMTA14C4 and iodine in dichloromethane solution. A comparison has also been made with the similar reaction in chloroform.



TMTA14C4

EXPERIMENTAL

The macrocycle TMTA14C4 (Fluka) was purified by recrystallization from reagent grade benzene and dried under vacuum over P_2O_5. Resublimed iodine of analytical grade (Merck) was used as received. Reagent grade chloroform and dichloromethane (Merck) was used without any further purification.

All UV-Vis spectra were recorded on a shimadzu spectrophotometer and the absorbance measurements, at fixed wavelengths, were made with a Shimadzu spectrophotometer. Conductance measurements were carried out with a Methrohm 660 conductivity meter in a thermostated cell at 25 ± 1 ºC. IR spectra were recorded on a Shimadzu IR spectrometer using KBr pellets.

Fresh solutions of iodine and TMTA14C4 were prepared before each series of measurements by dissolving precisely weighted amounts of the components in appropriate volume of solvent. The solutions were discarded after use.

RESULTS AND DISCUSSION

Absorption spectra of 6 × 10^4 M of iodine solution in the presence of varying concentration of TMTA14C4 are shown in Fig. 1. As it can be seen, upon addition of TMTA14C4, the intensity of 510 nm band decreases and simultaneously two new bands are appeared at 290 and 364 nm. An isobestic point is also observed at 460 nm .The 290 and 364 nm bands are well known bands of triiodide ion[20,21]. On the other hand, the existence of isobestic point is indicative of an equilibrium reaction between macrocycle and iodine[22]. Thus it can be concluded that the interaction of TMTA14C4 and iodine causes the formation of triiodide through an equilibrium reaction. The stoichiometry of the reaction was obtained from the absorbance *vs.* mole ratio and Job methods[23]. The corresponding plots are shown in Figs. 2 and 3, respectively.

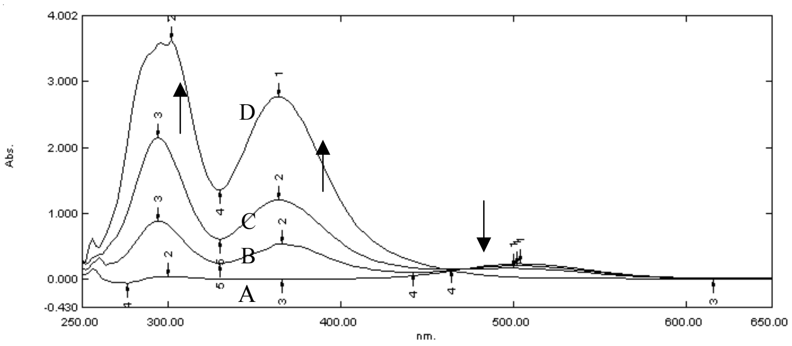


Fig .1. Absorption spectra of 0.0006 M of iodine in CH_2Cl_2 in presence of varying concentration of TMTA14C4. The macrocycle to I_2 mole ratio are A, 0; B, 0.3; C, 0.55; D, 0.85

Both plots clearly confirm 1:1 stoichiometry. This result, beside the spectral evidences (Fig. 1) means that the following reaction is occurred:

$$2 \text{ macrocycle} + 2I_2 \rightleftharpoons (\text{macrocycle})_2 I^+. I_3^- \quad (1)$$

The above reaction indicates that two macrocycle molecules encapsulate each I^+ ion and a sandwich complex is formed (Fig. 4). It seems that the soft-soft interactions plays an important role in the formation of such complex[24]. In fact, upon the location of I^+ in macrocyclic cavity, the proximity to four nitrogen is obtained. However, formation of sandwich complex causes the proximity to eight nitrogen atoms. By increasing the number of donating atoms, the soft-soft interactions will be supported and the stability will be increased.

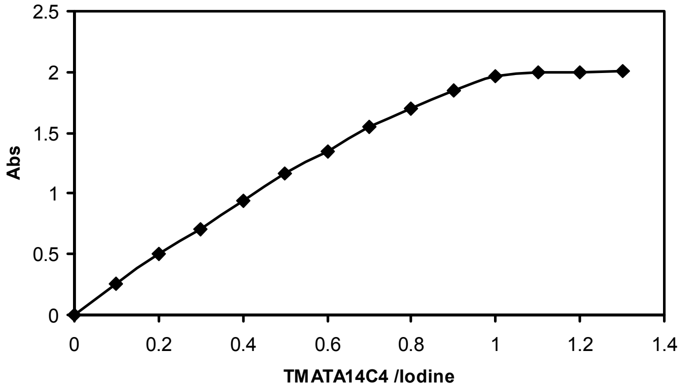


Fig. 2. Plot of absorbance *vs.* TMTA14C4/I_2 in CH_2Cl_2 solution obtained at 364 nm

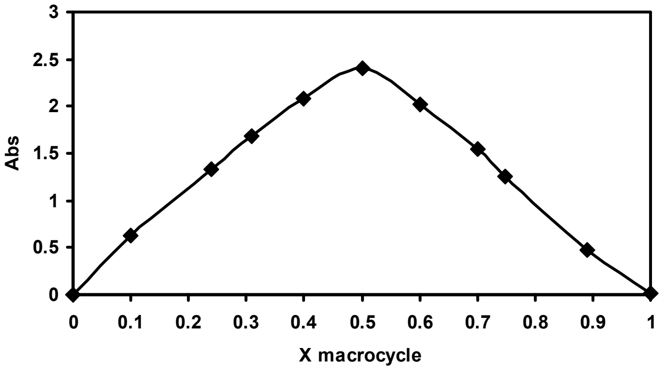


Fig .3. Continus variations plot for TMTA14C4-I_2 obtained at 364 nm

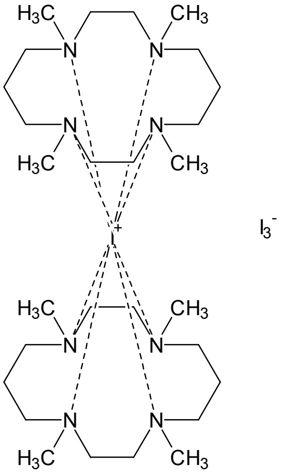


Fig. 4. Formation of 2:2 sandwich complex between macrocycle and iodine in CH_2Cl_2 solution

The conductance values were followed as function of TMTA14C4 mole ratio (Fig. 5). As it can be seen the addition of TMTA14C4 to the solution of iodine in dichloromethane causes steady increases of conductance until the mole ratio of 0.3. This behaviour indicates that the interaction of macrocycle and I_2 produces adducts which are somewhat ionic free. Because of incomplete ionization and some ion pairing, the plateau region do not exactly appear at macrocycle/I_2 = 1.

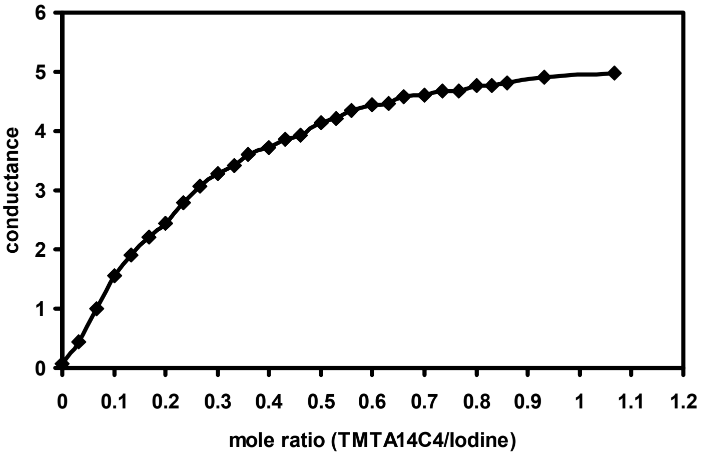


Fig. 5. Plot of conductance vs. TMTA14C4/I_2 obtained in CH_2Cl_2 solution

The formation constant of macrocycle-I_2 was calculated by fitting the absorbance-mole ratio data in MATLAB program. A function is used to final the equilibrium constant that fit the absorbance-mole ratio profiles using the multi parameter minimum search in MATLAB[25] based on the Nelder Mead algorithm[26]. This function uses the modeled equilibrium constant, simulates the absorbance-mole ratio profiles and calculated the difference between the simulated and measured absorbance profiles.

The search algorithm finds the equilibrium constant that result in the best fit between the simulated profiles and the measured absorbance profiles. The resulting computer fit of absorbance-mole ratio data are shown in Fig. 6. As seen, there is a fair agreement between observed and calculated absorbances. The log K_f obtained by the procedure is 5.3 ± 0.1. The high value of formation constant is indicative of strong interaction between iodine and macrocycle.

The oscillator strength (f) and the transition probability (μ) of the charge-transfer band[27] have been calculated from the following expressions[28].

$$f = 4.319 \times 10^{-9}\ \varepsilon_{max}\nu_{½} \quad (2)$$

$$\mu = 0.0958\ (\varepsilon_{max}\nu_{½}/\nu_{max})^{½} \quad (3)$$

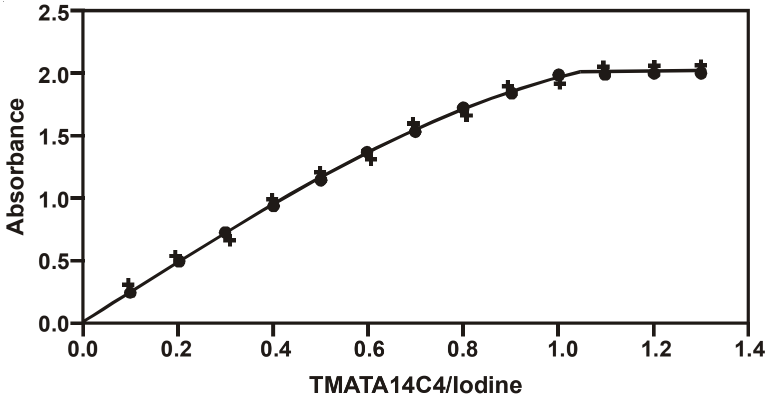


Fig. 6. Computer fit in MATLAB program (•) calculated points, (+) experimental points

In these equations, $\nu_{½}$ is the band width for half-intensity (cm^{-1}), ε_{max} and ν_{max} are the extinction coefficient and wave number at the absorption maximum of the complex, respectively .

The ionization potential (I_p) of the free donor was determined from the CT energies of the CT band of its complex. In the case of iodine as an acceptor, the relationship becomes the following[29].

$$E_{CT} = I_P - 5.2 + 1.5(I_P - 5.2) = 1243.667/\lambda_{CT} \quad (4)$$

The calculated f, μ and I_P are 4.18, 18.0 and 8.2, respectively.

IR spectra of TMTA14C4 and its 1:1 iodine complex are compared in (Fig. 7). Variations of the IR spectra upon complexation have been previously observed for some other charge-transfer complexes[30].

As seen in the TMTA14C4 complex the C-N stretching band at 680 cm^{-1} has been shifted to lower frequencies, indicating the direct involvement of nitrogen in complexation. In fact, the participation of ione pairs of nitrogen atom, lower the charge density on it. These results in a lowering of the force constant and a shift to lower frequencies[31]. On the other hand, the methyl and methylene bending (at 950 and 1100 cm^{-1}) and stretching bands (at 2750 and 2900 cm^{-1}) have been shifted to higher frequencies. Which means that upon complexation, the flexibility of macrocycle is reduced. This is reasonable considering the decrease of vibration freedom of macrocycle in complex than that of free state. In fact, as a result of I^+-TMTA14C4 interactions, the TMTA14C4 is oriented to special directions and the vibrational modes are somewhat restricted[32]. Finally, the appearance of new band in the IR spectrum of complex can be attributed to the $N \cdots I^+$ stretching in the complex[33,34]. As the $N \cdots I^+$ is not a perfect bond, the corresponding IR bond is appeared at lower frequencies.

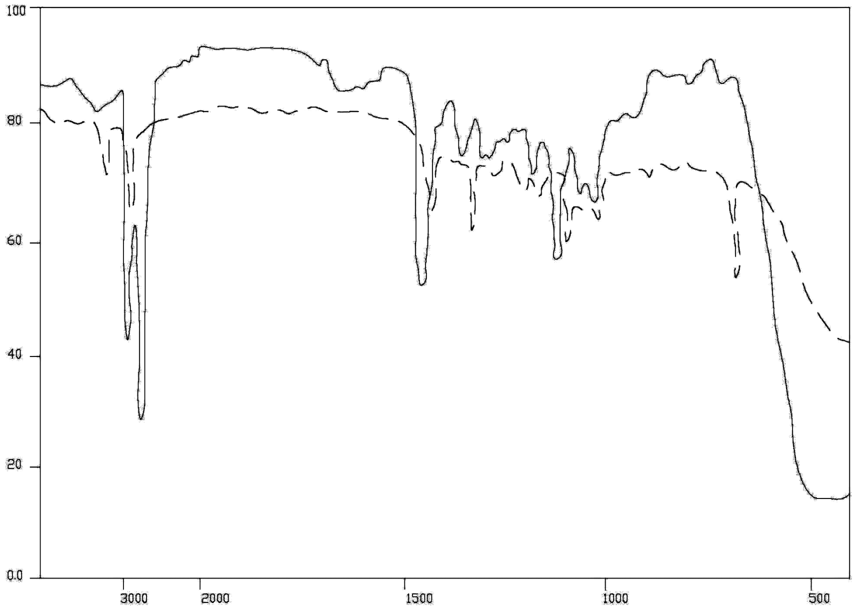


Fig. 7. IR spectra of TMTA14C4 (solid line) and 1:1 TMTA14C4:I_2 complex (dashed line)

The interaction of TA14C4 (*i.e.* a compound with similar structure to TMTA14C4) has been studied in chloroform solution[35]. The plot of absorbance vs. TMTA14C4/I_2 mole ratio in chloroform is also obtained in present work (Fig. 8). Interestingly, both results reveal that 1:2 macrocycle to iodine complex is formed. This means that in contrast to CH_2Cl_2, the complex formation in chloroform, involves the insertion of the I^+ ion in the macrocycle cavity (Fig. 9).

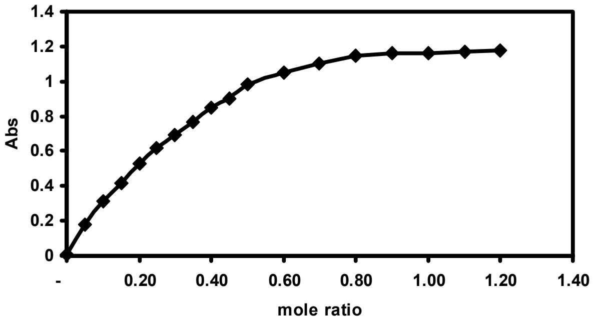


Fig. 8. Plot of absorbance *vs.* TMTA14C4/I_2 in $CHCl_3$ obtained at 360 nm

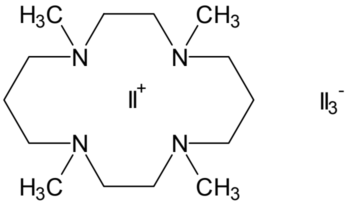


Fig. 9. Location of I$^+$ in the macrocycle cavity in $CHCl_3$ solution

$$\text{Macrocycle} + 2I_2 \rightleftharpoons \text{macrocycle } I^+.\ I_3^- \qquad (5)$$

The different behaviour in two solvents can be related to the combination of specific interaction and different physical properties of solvents. Because of three chlorines in trichloromethane and two chlorine in dichloromethane, the acidity of the former is more than the latter. Consequently, the acid base interactions of solvent-macrocycle in trichloromethane is stronger than dichloromethane. Thus, the competition with I$^+$ is more effective and acid-base interaction suppress the soft-soft ones[24]. The result is formation of inclusion (Fig. 8), instead of sandwich (Fig. 4) complex in chloroform. On the other hand, the dielectric constant of dichloromethane is more than trichloromethane[36]. So, the stability of I$^+$ needs the inclusion by macrocycle. Since, in macrocycle complex, less inclusion occurred, the recent complex is not formed. It should be noted[37] that the ionic radious of it is 0.83 Å, which is considerably less[38] than the cavity size of TMTA14C4 (about 2 Å). Thus, the ion-in-the hole model[3] is of little use. However, the macrocycle twist around the I$^+$ and wrap around complex[39] is formed. This complex facilitates the formation of I$^+$.

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(*Received*: 1 February 2007; *Accepted*: 27 October 2007) AJC-6046