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Interaction between 1,4,8,11-Tetraazacyclotetradecane with Iodine and Bromine in Chloroform Solution

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A spectrophotometric study concerning the interaction between 1,4,8,11-tetraazacyclotetradecane (CYCLAM) with iodine and bromine has been performed spectrophotometrically in chloroform solution at 25°C. As a helpful guide, the complexation of tetrabutylammonium iodide and tetrabutylammonium bromide with iodine and bromine have also been studied. The results of iodine are indicative of the formation of $CYCLAM^{-}I^{+}I_3^{-}$ through an equilibrium reaction. However, in the case of bromine, the formation of $CYCLAM^{-}Br^{+}Br_3^{-}$ through a non-equilibrium reaction is confirmed. The possible reason for the observation of a non-equilibrium reaction is discussed. The stability constant of the CYCLAM-I_2 complex is evaluated from the computer fitting of absorbance-mole ratio data as log $K_f = 5.32 \pm 0.04$. IR spectrum of CYCLAM has been compared with IR spectra of complexes and the effects of complexation on absorption bands are discussed. The comparison of the conductances of solutions containing complexes with solutions of iodine, bromine or CYCLAM indicate that the complexes are mostly in the form of ion pairs.

Key Words: Spectroscopy, CYCLAM, Iodine, Bromine, Molecular complexes.

INTRODUCTION

During the past few decades, the complexation of iodine with a wide variety of nitrogen containing donating ligands has been studied[1–4]. Recently, there has been increasing attention to the complexes of iodine with macrocycle molecules[5–8]. However, it seems that the bromine complexes have been less mentioned[9]. In addition, there are few comparative reports on both iodine and bromine[9]. Thus, more study in this field is needed. To develop our previous investigations on molecular complexes[10–14], herein, the results of study of interaction between I_2 and Br_2 with 1,4,8,11-tetraazacyclotetradecane in chloroform solution are reported.

EXPERIMENTAL

1,4,8,11-Tetraazacyclotetradecane (Merck) was recrystallized in *n*-hexane and dried in vacuum conditions. Iodine, bromine and chloroform (Merck) were of

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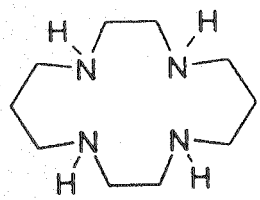
highest purity and used without any further purification. Tetrabutylammonium iodide (TBAI) and tetrabutylammonium bromide (TBABr) (Fluka) were used without any further purification except vacuum drying. All stock solutions were prepared fresh and discarded after use.



1,4,8,11-Tetraazacyclotetradecane

All UV-Vis spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Absorbance measurements were made with a Philips PU875 spectrophotometer at 25 ± 1°C. IR spectra recorded on a Shimadzu IR-470 spectrophotometer using KBr pellets. Solid complex CYCLAM-I_2 on chloroform followed by solvent vaporization. Conductance measurements were carried out with a Metrohm 660 conductivity meter in a thermostated cell at 25 ± 1°C.

RESULTS AND DISCUSSION

The electronic absorption spectra of 4.94×10^{-4} M solution of iodine in the presence of increasing quantities of TBAI are shown in Fig. 1. As can be seen,

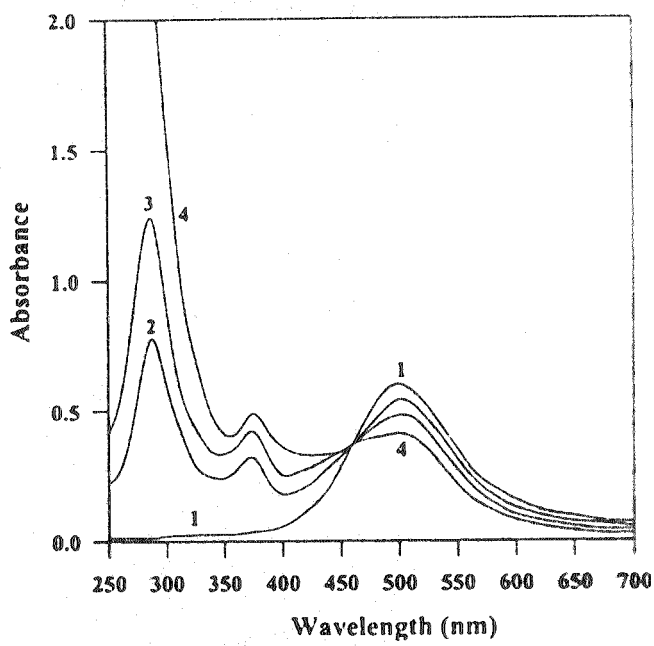


Fig. 1. Absorption spectra of 4.94×10^{-4} M I_2 at mole ratio of TBAI-I_2 :(1) 0.00, (2) 0.09, (3) 0.20 and (4) 0.32

upon addition of TBAI to iodine solution, new bands appeared at 290 and 364 nm. Keeping in mind, that TBAI do not have any absorption in the 290–364 nm region, the 290 and 364 nm bands can be attributed to the adduct of the reaction of TBAI and I_2. Because of confirmation of 1 : 1 stoichiometry by absorbance-mole ratio method (Fig. 2) and the existence of isosbestic point at 457 nm (Fig.

1), the interaction of TBAI and I_2 can be shown by the following chemical equation:

$$TBAI + I_2 \rightleftharpoons TBA^+I_3^- \quad (1)$$

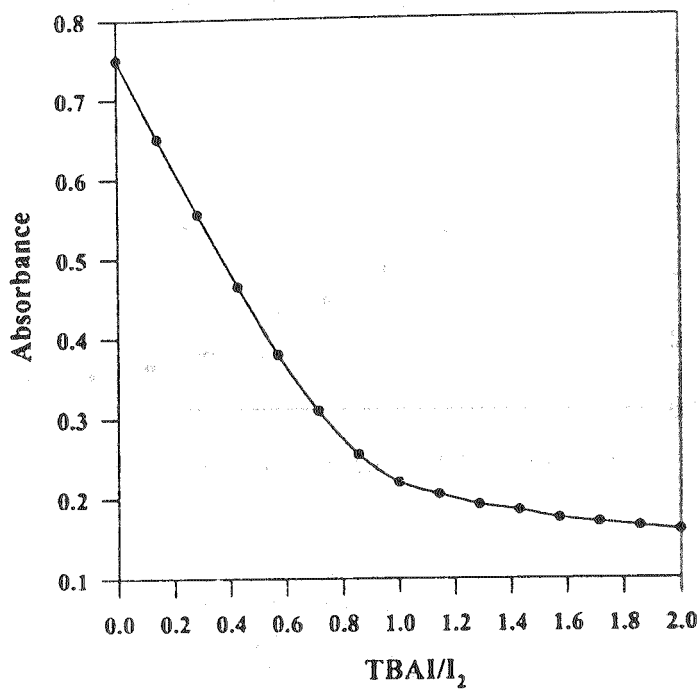


Fig. 2. Plot of absorbance *vs.* mole ratio of TBAI/-I_2 at 510 nm at 25°C

It is interesting to note that the spectra of iodine in the presence of CYCLAM (Fig. 3) are similar to the spectra of TBAI-I_2 mixtures (Fig. 1). So, it can be concluded that identical products are formed in both cases. On the other hand,

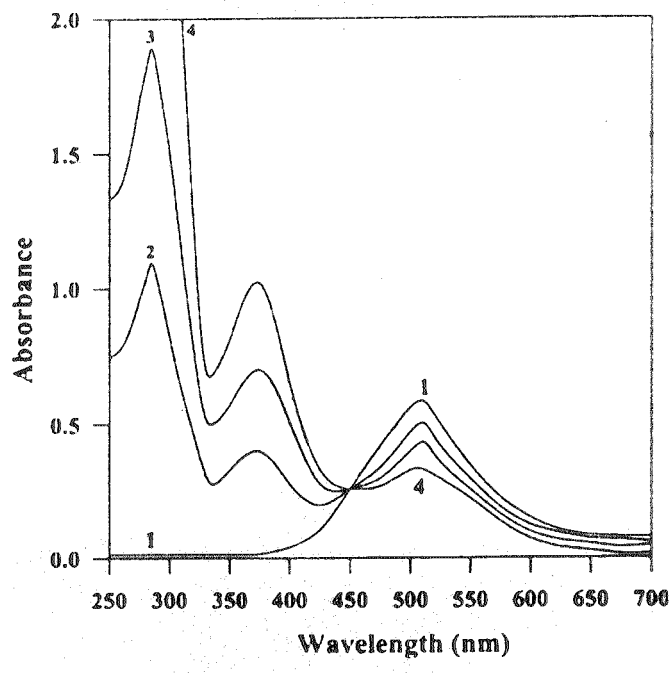


Fig. 3. Absorption spectra of 4.94×10^{-4} M I_2 at mole ratio of CYCLAM/-I_2: (1) 0.00, (2) 0.10, (3) 0.16 and (4) 0.22

the absorbance *vs.* CYCLAM/-I_2 mole ratio plot (Fig. 4) indicates the 1 : 2 CYCLAM to iodine stoichiometry. Thus, the interaction between CYCLAM and I_2 can be written by the following reaction:

$$\text{CYCLAM} + 2I_2 \rightleftharpoons \text{CYCLAM}^{-}I^{+}I_3^{-} \quad (2)$$

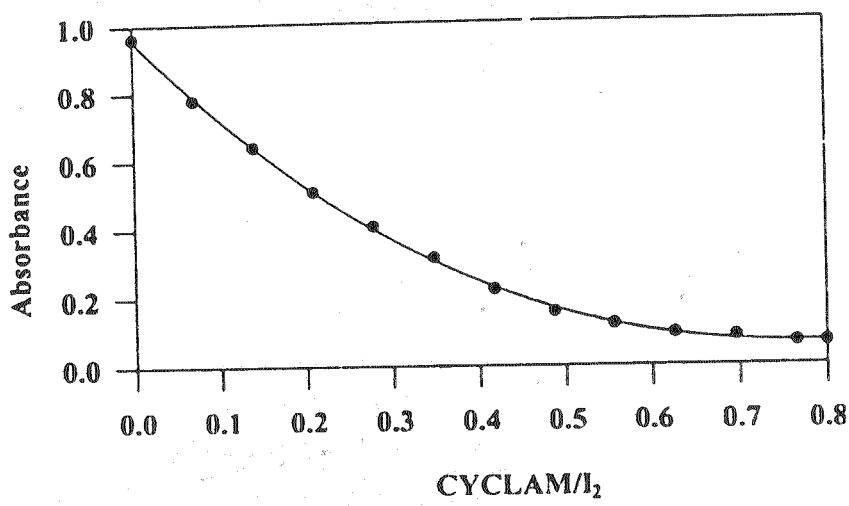


Fig. 4. Plot of absorbance *vs.* mole ratio of CYCLAM/I_2 at 510 nm at 25°C

The absorption spectra of 3.23×10^{-3} M of Br_2 in chloroform in the presence of varying concentrations of TBA-Br and CYCLAM are shown in Figs. 5 and 6, respectively. The similarity of two spectra indicates that in both systems adducts

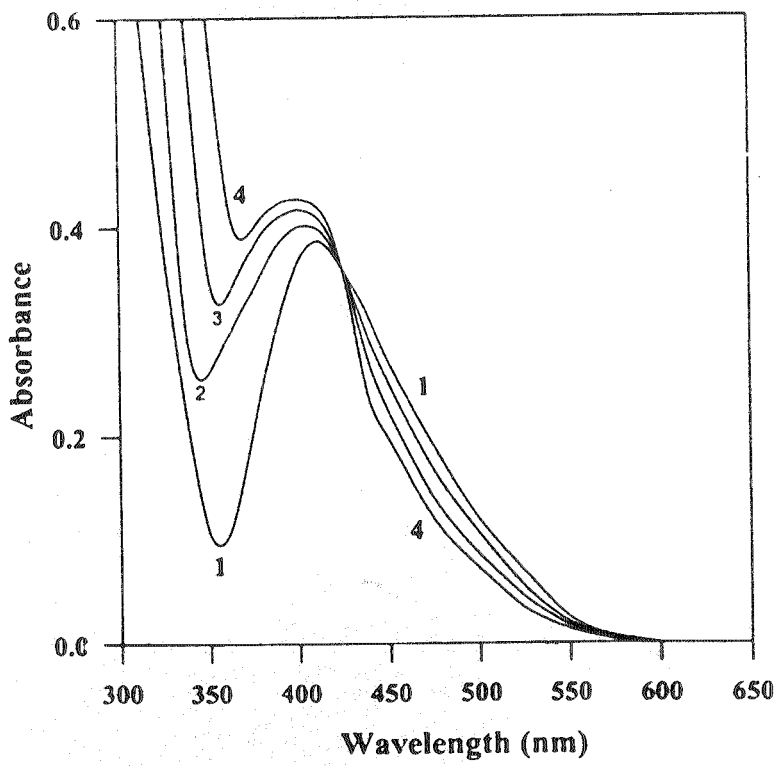


Fig. 5. Absorption spectra of 3.23×10^{-3} M Br_2 at mole ratio of TBABr/Br_2: (1) 0.00, (2) 0.13, (3) 0.23 and (4) 0.31

are the same. However, in the case of CYCLAM-Br_2 (Fig. 6), the isobestic point is not observed, which means that Br_2 and CYCLAM have a non-equilibrium reaction.

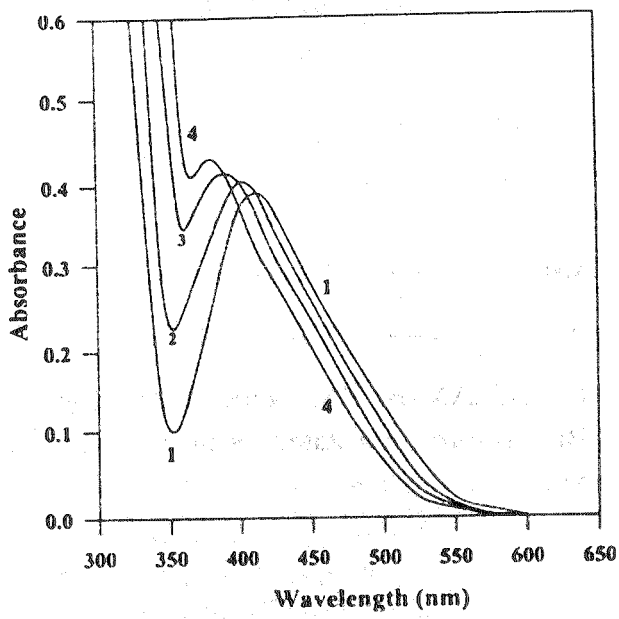


Fig. 6. Absorption spectra of 3.23×10^{-3} M Br_2 at mole ratio of CYCLAM/Br_2: (1) 0.00, (2) 0.11, (3) 0.23 and (4) 0.31

The absorbance *vs.* TBA-Br/Br_2 mole ratio method shows a 1 : 1 TBA-Br to Br_2 stoichiometry (Fig. 7). Thus, the following reaction is suggested for the interaction of TBA-Br and Br_2.

$$TBA\text{-}Br + Br_2 \rightleftharpoons TBA^+Br_3^- \qquad (3)$$

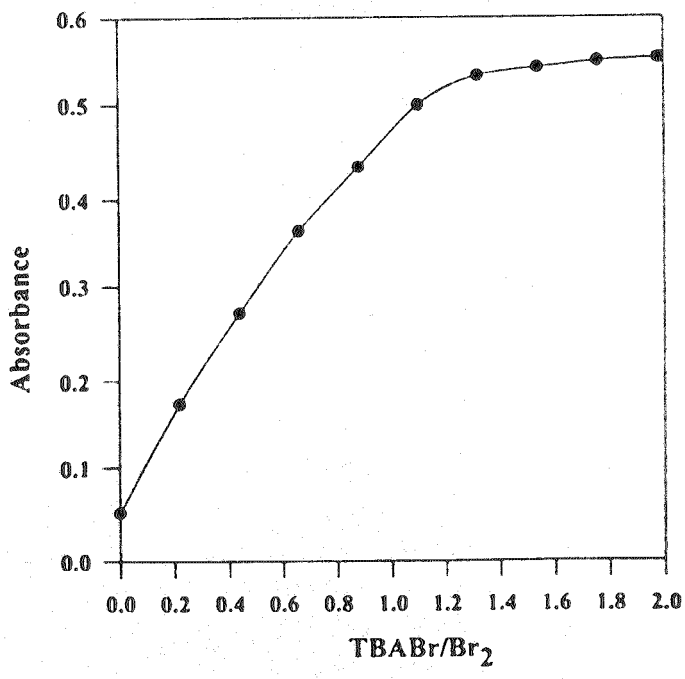


Fig. 7. Plot of absorbance *vs.* mole ratio of TBABr/Br_2 at 375 nm at 25°C

Because of precipitation, the stoichiometry of the reaction between CYCLAM and Br_2 cannot be determined by absorbance-mole ratio method. However, based on the similar spectral behaviour of TBABr-Br_2 and CYCLAM-Br_2 mixtures (Figs. 5 and 6), it can be concluded that CYCLAM and Br_2 interact through the following reaction:

$$\text{CYCLAM} + 2Br_2 \longrightarrow \text{CYCLAM-}Br^+Br_3^- \quad (4)$$

It seems that the non-equilibrium reaction of Br_2 and CYCLAM (eqn. (4)) can be related to the following two step mechanism. This mechanism is similar to the electrophilic addition reaction of bromine to alkenes[15].

$$\text{CYCLAM} + Br_2 \longrightarrow \text{CYCLAM-}Br^+Br^- \quad \text{(Slow step)} \quad (5)$$

$$\text{CYCLAM-}Br^+Br^- + Br_2 \longrightarrow \text{CYCLAM-}Br^+Br_3^- \quad \text{(Fast step)} \quad (6)$$

The formation of CYCLAM-Br^+Br^- intermediate involves the formation of CYCLAM-$Br^{\delta+} \ldots Br^{\delta-}$ as transition state. Because of high charge density of Br^+ and Br^-, it is anticipated that the electrostatic attraction between the cation and anion to be high. This results in much more stability of CYCLAM-Br^+Br^- than that of CYCLAM-Br . . . $Br^{\delta-}$. Consequently, the backward activation energy will be more than the forward one, which leads to a non-equilibrium reaction.

A non-linear least square curve-fitting program KINFIT was used to evaluate the formation constant, K_f, of 2 : 1 complex of I_2 and CYCLAM[16]. The program is based on the iterative adjustment of the calculated values of absorbance to the observed values by using either the Wentworth matrix technique[17] or the Powell procedure[18]. Adjustable parameters are K_f and ε, where ε is the molar absorptivity of iodine.

The observed absorbance of an iodine solution in chloroform at its λ_{max} is given by eqn. (7). The mass balance equations can be written as (8) and (9) and the formation constant of the complex as in (10).

$$A = \varepsilon b[I_2] \quad (7)$$

$$C_{I2} = [I_2] + 2[\text{CYCLAM-}I^+I_3^-] \quad (8)$$

$$C_{CYCLAM} = [\text{CYCLAM}] + [\text{CYCLAM-}I^+I_3^-] \quad (9)$$

$$K_f = \frac{[\text{CYCLAM-}I^+I_3]}{[\text{CYCLAM}][I_2]^2} \quad (10)$$

$$K_f[I_2]^3 + K_f(2C_{CYCLAM}-C_{I2})[I_2]^2 + I^2\text{-}C_{I2} = 0 \quad (11)$$

Substitution of eqns. (8) and (9) and rearrangement yields (11). The free iodine concentration, $[I_2]$, was calculated from equation (11) by means of Newton-Raphson procedure. Once the value of $[I_2]$ had been obtained, the corresponding absorbances (A_{cal}), were calculated from the corresponding estimated value of ε at the current iteration step of the program. Refinement of the parameters is continued until the sum of squares (A_{obs}-A_{cal}) is minimized. The output of KINFIT program comprises the refined parameters, the sum-of-squares and the standard

deviation of the data. The determined log K_f value by this method for CYCLAM-I_2 was 5.32 ± 0.04. The corresponding curve fitting is shown in Fig. 8. The high log K_f value is indicative of a strong interaction between I_2 and CYCLAM.

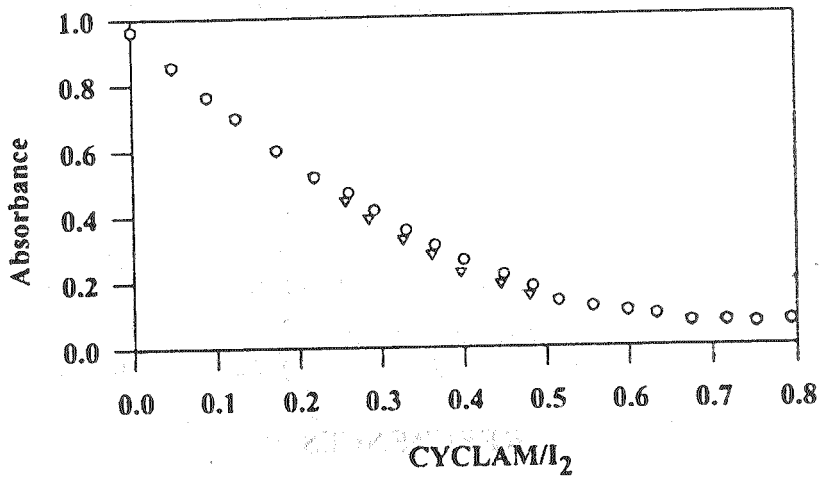


Fig. 8. Computer fit of the plot of absorbance *vs.* CYCLAM/-I_2 mole ratio obtained at 510 nm and 25°C: (∇) experimental points; (○) calculated points

The IR spectra of CYCLAM and 1 : 2 CYCLAM-I_2 complex are compared in Fig. 9. As can be seen, the absorption bands of CYCLAM have been affected by complexation. The greatest changes are (1) the decrease in the band intensities, (2) appearance of new band at 675 cm^{-1} and (3) the shift stretching frequency of C—N from 1120–1100 cm^{-1}. Similar effects have been observed for some other molecular complexes[20]. The first effect can be related to the increasing of the symmetry of CYCLAM upon complexation. This also originates from the orientation of nitrogen atoms toward I^+[21]. The second is an interesting effect, which is due to vibration of N···I^+. As the N···I^+ band is very weak, the corresponding bands have appeared at low frequencies[21, 22]. The third effect results from the direct involvement of nonbonding electrons of nitrogen atoms with subsequent weakening of C—N band and shift to lower frequency[23].

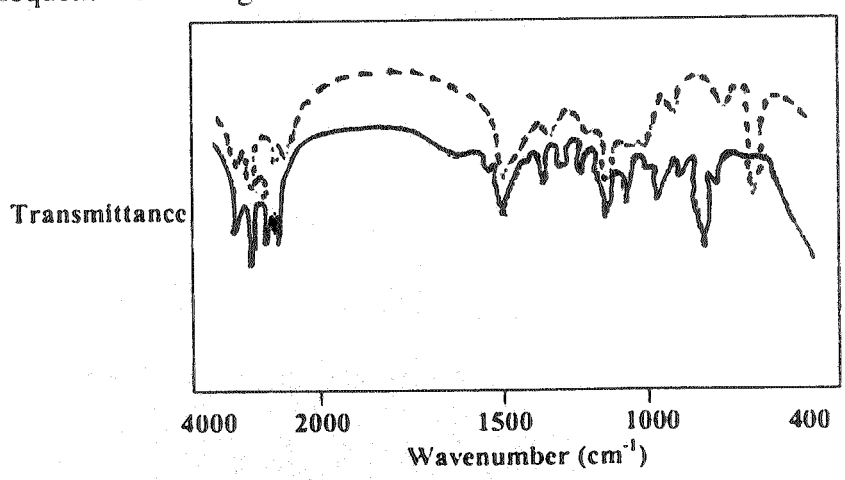


Fig. 9. IR spectrum of CYCLAM (——) and CYCLAM-I_2 complex (·····)

The above effect was also observed in the complex of CYCLAM-Br_2. However, because of similarity the corresponding spectra are not shown.

The conductances of pure $CHCl_3$ and solutions of 1.75×10^{-4} M of I_2, 1.64×10^{-4} M of Br_2, 3.12×10^{-4} M of CYCLAM, 1.74×10^{-4} M of I_2 in the presence of 3.12×10^{-4} M CYCLAM and 1.64×10^{-4} M of Br_2 in the presence of 3.12×10^{-4} M of CYCLAM in chloroform were measured. The determined values are 1.27, 1.28, 10.38, 13.2 and 12.1 $\mu S/cm^2$, respectively. The small increase of conductance during complexation means that the complexes are mainly in the form of ion pair and there is little free ion in the solution. It must be noticed that in our previous works, the existence of free ion in the complexes of I_2 and Br_2 with some crown ethers has been reported[11, 12]. The absence of free ion in this study can be assigned to the non-inclusion of Br^+ and I^+ by macrocycle ring. In fact, the conductometric data indicate that the nitrogen atoms are somewhat direct toward Br^+ and I^+ during the complexation. In contrast to crown ethers the inclusion of Br^+ and I^+ by macrocycle ring does not occur.

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