

Spectrophotometric Study of the Complexation of Bromine with Crown Ethers in Chloroform Solution

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A spectrophotometric study of the complex formation of bromine with 12-crown-4 (12C4), 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), benzo-18-crown-6 (B18C6) and dicyclohexyl-18-crown-6 (DC18C6) has been performed in chloroform solution at 25°C. The results of the 12C4, 15C5, 18C6 and DC18C6 indicate the formation of macrocycle Br^+Br_3^- through equilibrium reactions. In other cases, the formation of macrocycle Br^+Br_3^- and Br^- macrocycle H^+Br_3^- through equilibrium and nonequilibrium reactions were confirmed. Formation constants of the resulting 2:1 (bromine: macrocycle) complexes were determined from the spectroscopic data and found to vary in the order: B15C5, B18C6, 12C4, 15C5, 18C6 and DC18C6. DC18C6 formed the most stable complex. IR spectra of pure macrocycles are compared with the corresponding bromine complexes and the effect of complexation on absorption bands is discussed.

INTRODUCTION

During the past few decades, the complexation of iodine with a wide variety of ligands has been the subject of extensive research [1-7]. More recently, some attention has been focused on the study of iodine complexes with macrocyclic crown ethers in various solvents [8-11]. However, there has been much less attention given to the bromine complexes [12,13]; thus, more study in this field is needed.

In this paper, a spectrophotometric study of molecular complexes of crown ethers with different molecules has been initiated [11,13-16] and the results of a spectroscopic study of the complexation of bromine with some crown ethers in chloroform solutions is reported.

REAGENTS

Reagent grade CHCl_3 , Br_2 , 12C4, 15C5, and tetrabutylammonium bromide (TBABr) from the Merck

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company were used as received. DC18C6 (Merck) and 18C6 (Aldrich) were purified and dried as described previously in [17,18]. B18C6 (from Merck) was recrystallized from reagent grade *n*-hexane and vacuum dried. The structures of ligands are shown in Figure 1.

APPARATUS

All UV-Vis spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer and absorbance measurements were made with a Phillips PU875 spectrophotometer at $25 \pm 1^\circ\text{C}$. IR spectra were recorded on a Shimadzu spectrometer using KBr pellets. The conductometric measurements were made with a Metrohm 660 conductometer with the conductometric cell thermostated at 25°C .

COMPUTATION METHOD

The stability constants of bromine complexes with crown ethers used were evaluated by employing the following equation [19]:

$$[(A/A^\circ) - 1]/C_{\text{Crown}}^\circ = \left(\frac{\epsilon_{\text{Br}_2}}{\epsilon_{\text{complex}}}\right)K_f - K_f(A/A^\circ). \quad (1)$$

In the above equation, A° and A are the values of absorbances of bromine at 450 nm in the absence and in

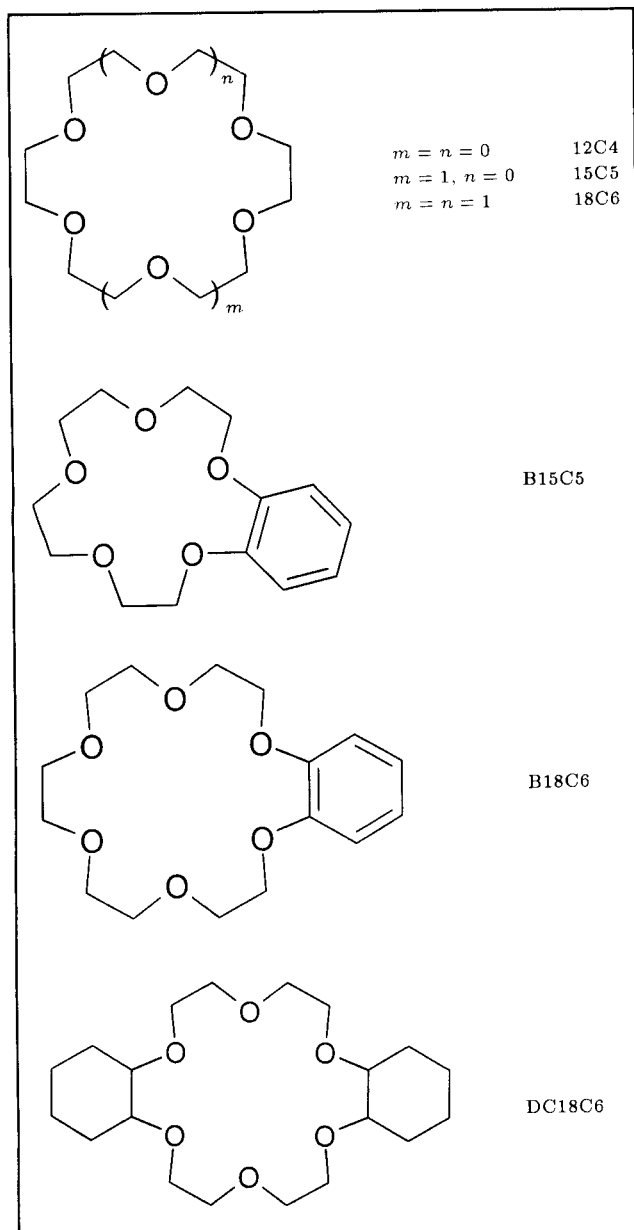


Figure 1. Structure of ligands.

the presence of crown ether, respectively, $\frac{\epsilon_{\text{Br}_2}}{\epsilon_{\text{complex}}}$, is the ratio of molar absorption coefficient of Br_2 to that of the complex, K_f is the complex formation constant and C_{crown}° is the analytical concentration of crown ether. By plotting $[(A/A^\circ) - 1]/C_{\text{crown}}^\circ$ vs A/A° , a straight line will be obtained, the slope of which is equal to $-K_f$.

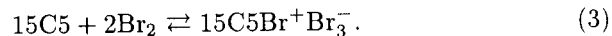
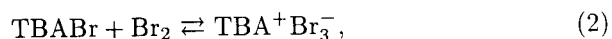
PROCEDURE

In order to obtain the UV-Vis spectra of bromine upon addition of crown ethers, 3 mL of 2.80×10^{-3} or 1.75×10^{-3} M of bromine solution were transferred into a 1 cm quartz cell and the spectra were recorded after the addition of appropriate amounts of crown

ethers. Formation constants were simply obtained from absorbance measurements of 2.59×10^{-3} M (5 ml) of bromine solutions and varying concentrations of crown ethers. The results were fitted in Equation 1. For obtaining IR spectra, a drop of melted crown ether was spread on a KBr pellet. Then, excess bromine was added to the pellet. After evaporation of unreacted bromine, the adduct was used to obtain the spectrum. Conductivity measurements were made for 10 ml solutions that were previously placed in a conductometric cell and thermostated at 25°C .

RESULTS AND DISCUSSION

The UV-Vis spectra of 2.80×10^{-3} M bromine solution, in the presence of varying concentrations of 15C5, are shown in Figure 2. The spectra of bromine in the presence of TBABr are, also, shown in Figure 3. The similarity of spectra indicates that in both cases similar adducts are obtained. The existence of isobestic points proves that the adducts are formed through equilibrium reactions [20]. Obviously, $\text{TBA}^+\text{Br}_3^-$ is the most probable product of the interaction of bromine and TBABr. It can, thus, be concluded that tribromide is the common product of both systems. Tribromide is produced through the following equilibrium reactions:



Because of similarity, the spectra of 12C4- Br_2 , 18C6- Br_2 and DC18C6- Br_2 mixtures are not shown. How-

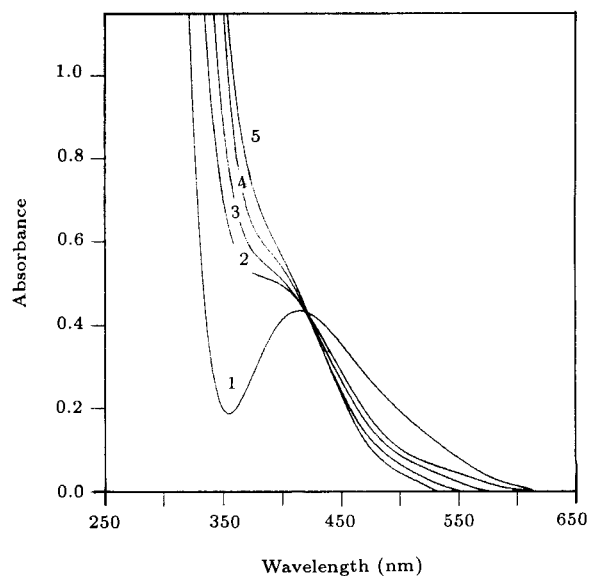


Figure 2. Absorption spectra of 2.80×10^{-3} M of bromine in chloroform in the presence of various concentrations of 15C5: 1) 0.00 M, 2) 1.94×10^{-2} M, 3) 3.67×10^{-2} M, 4) 4.71×10^{-2} M, 5) 7.03×10^{-2} M.

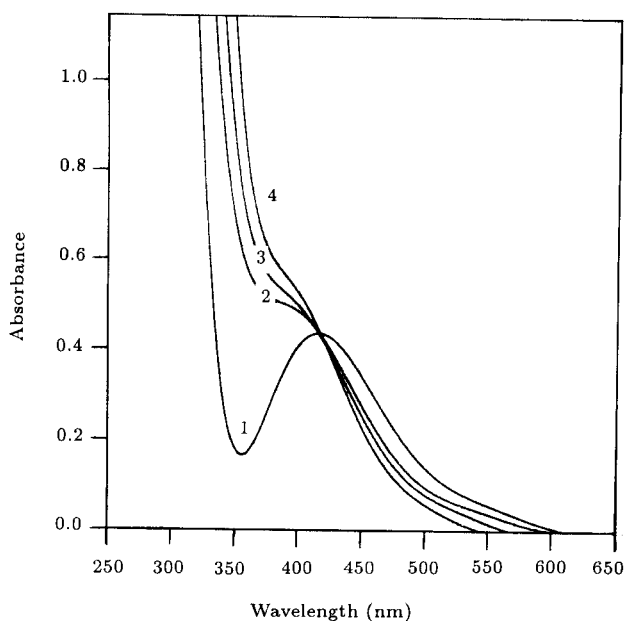


Figure 3. Absorption spectra of 2.8×10^{-3} M of bromine in chloroform in the presence of various concentrations of TBABr: 1) 0.00 M, 2) 5.32×10^{-4} M, 3) 9.24×10^{-4} M, 4) 1.34×10^{-3} M.

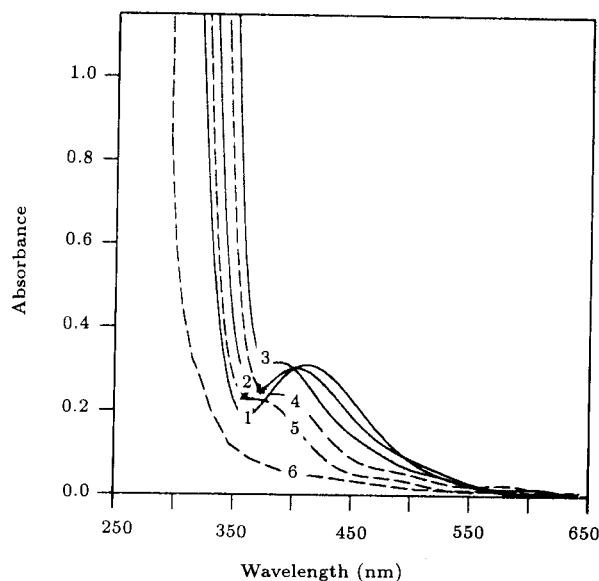
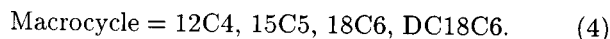
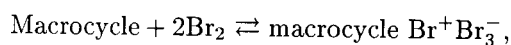
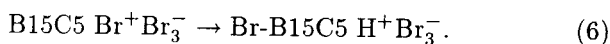
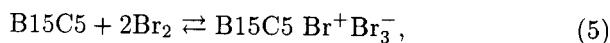


Figure 4. Absorption spectra of 1.75×10^{-3} M of bromine in chloroform in the presence of various concentrations of B15C5: 1) 0.00 M, 2) 1.24×10^{-2} M, 3) 1.76×10^{-2} M, 4) 2.70×10^{-2} M, 5) 3.31×10^{-2} M, 6) 3.73×10^{-2} M.

ever, according to the foregoing discussion, it can be said that these ligands also behave like 15C5 and the following general reaction can be written:



The existence of an isosbestic point in the spectra of B15C5-Br₂ mixtures (Figure 4) is indicative of an equilibrium reaction [20]. Interestingly, at higher B15C5/Br₂ mole ratios, not only the isosbestic point is broken but the bands also shift to the UV region (Figure 4). Such observations can be attributed to the formation of a product through equilibrium reaction and its conversion to another adduct through nonequilibrium reaction. The following reactions are suggested for the two steps:



The accuracy of Equation 5 is confirmed by the comparison of the spectra of B15C5-Br₂ (Figure 4) with that of 15C5-Br₂ mixtures (Figure 2). Equation 6 is acceptable if one keeps in mind that Br⁺ is a highly reactive electrophile and easily participates in electrophilic aromatic substitution reactions [21].

B18C6 behaves like B15C5, but the corresponding spectra are not shown.

The formation constants of the resulting molecular complexes of bromine with the crown ethers were

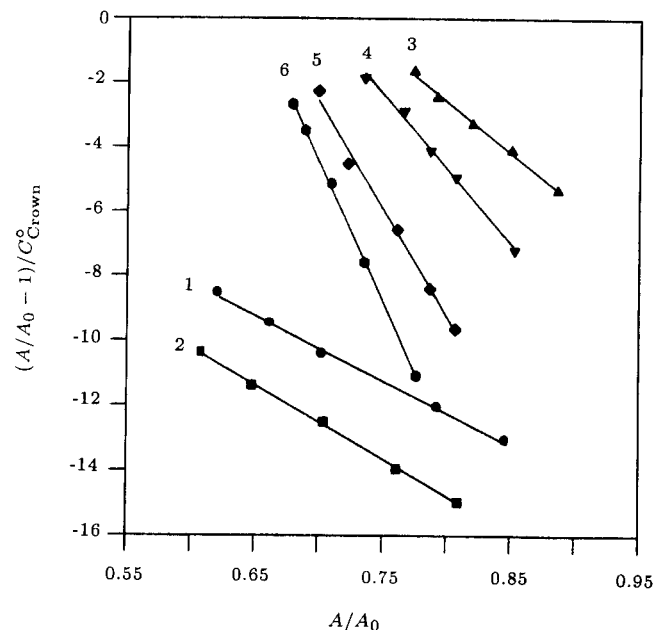


Figure 5. Plots of $[(A/A^0) - 1]/C_{\text{Crown}}^0$ vs A/A^0 for bromine complexes with: 1) B15C5, 2) B18C6, 3) 12C4, 4) 15C5, 5) 18C6, 6) DC18C6.

evaluated at 25°C by absorbance measurements (at 450 nm). The results obtained present a linear relation between $[(A/A^0) - 1]/C_{\text{Crown}}^0$ and (A/A^0) . All the resulting plots are shown in Figure 5 and the calculated K_f values are given in Table 1. The corresponding reported values for iodine complexes are also included for comparison [16].

Table 1. The formation constants, K_f , of different crown ether-bromine complexes in chloroform solution at 25°C.

Crown Ether	Cavity Size ^a (Å)	K_f	
		Br ₂	I ₂ ^b
12C4	1.2-1.5	30.4 ± 0.1	0.84 ± 0.02
15C5	1.7-2.2	44.8 ± 0.5	0.55 ± 0.02
18C6	2.6-3.2	63.7 ± 0.7	1.31 ± 0.09
DC18C6	2.6-3.2	84.3 ± 0.3	2.5 ± 0.1
B15C5	1.7-2.2	18.5 ± 0.5	—
B18C6	2.6-3.2	22.4 ± 0.1	—

a. Data taken from [22].

b. Data taken from [16].

The data given in Table 1 clearly indicate that the stabilities of the molecular complexes of bromine with crown ethers used vary in the following order: DC18C6 > 18C6 > 15C5 > 12C4 > B18C6 > B15C5. There are at least three important parameters influencing the stability of the resulting complexes:

- i) The cavity size of crown ether,
- ii) The number of donating oxygen atoms available,
- iii) The nature of substituents on the macrocycle ring [17,18].

The diameter of Br⁺ is much smaller than the cavity of the smallest crown ether [22,23]. It seems, therefore, that cavity size does not play an important role and the resulting complexes are presumed to be without inclusion, in which the lone pairs of electrons on the ether oxygens are oriented toward Br⁺ cation. On the other hand, the second and third factors play the main role. In fact, the higher stability of 18C6, in comparison with 15C5 and 12C4, is a reflection of the increased number of donating oxygen atoms, as well as their proper spacial positions. The existence of two donating cyclohexyl groups on the 18C6 ring can pump electrons into the ligand ring and increase the basicity of oxygen atoms [6]. Thus, it is not unexpected to observe the higher stability for DC18C6-Br₂ relative to the 18C6-Br₂ complex.

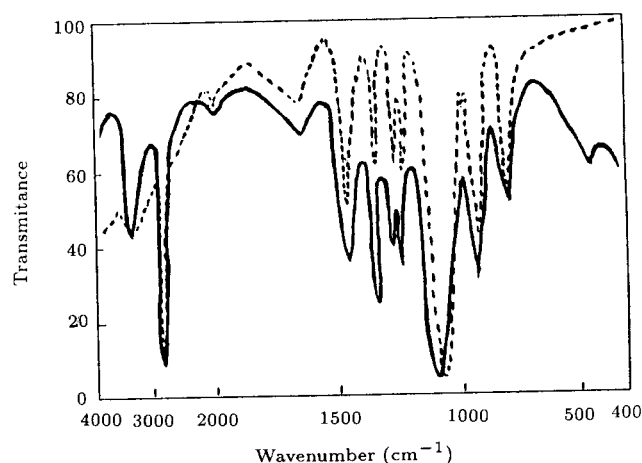
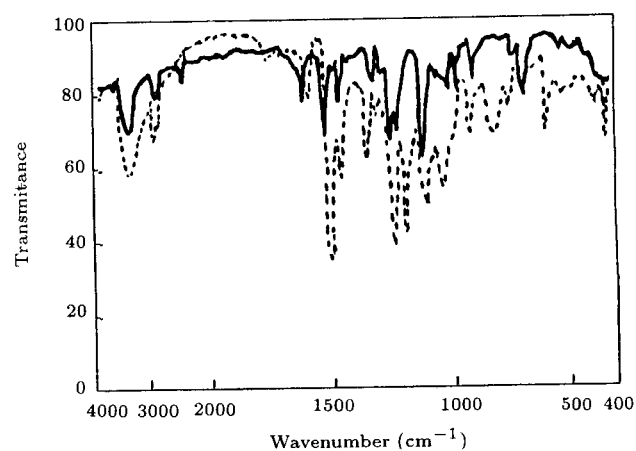
The addition of the benzo group to 15C5 or 18C6 lowers the stability (Table 1). This behavior would be caused by some combination of the electron withdrawing property of the benzo groups, which weakens the electron donating ability of the oxygen atoms of the ring, as well as the reduced flexibility of the ligand, which prevents the macrocyclic molecule from wrapping itself around the cation [17]. The net result is a weaker cation ligand interaction.

As can be seen from Table 1, the bromine complexes are markedly more stable than the iodine complexes. This would be due to the higher charge density of macrocycle Br⁺ and Br₃⁻ relative to macrocycle I⁺ and I₃⁻. The result is the higher electrostatic

attraction between the ions in bromine complexes compared to that of iodine complexes. This causes an increased stability in the former, relative to the latter, complex [24].

Figures 6 and 7 show the sample IR spectra of 18C6, B18C6 and their bromine complexes. Variations of the IR spectra upon complexation have been previously observed for some other charge transfer complexes [11,25]. As seen in the 18C6-Br₂ complex, the C-O stretching band at 1110 cm⁻¹ shifted to lower frequencies, indicating the direct involvement of oxygens in complexation. In fact, the electron donating ability of oxygen lowers the charge density on it. This results in a lowering of the force constant and a shift to lower frequencies [26]. On the other hand, in B15C5, the vibration frequency of the benzene ring at 735 cm⁻¹ shows a drastic shift. This means that the benzene ring has an important contribution in complex formation and confirms the previously suggested reaction (Equation 6).

The conductance of CHCl₃, 1.2 × 10⁻³ M bromine

**Figure 6.** IR spectra of 18C6 (solid lines) and 18C6-Br₂ complex (dashed lines).**Figure 7.** IR spectra of B18C6 (solid lines) and B18C6-Br₂ complex (dashed lines).

in CHCl_3 , 10^{-2} M 18C6 and 1.2×10^{-3} M bromine in the presence of 1.0×10^{-2} M 18C6, are measured. The determined values are 1.28, 1.28, 10.0 and 12 μS , respectively. The small increase in the conductance during complexation shows that the complex is mainly ion pair and there is little free ion in the solution.

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