COMPLEX FORMATION OF TMTA14C4 AND IBr IN DICHOLOROMETHANE SOLUTION

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Abstract : A spectrophotometric study concerning the interaction between 1,4,8,11-tetrametyl-1,4,8,11-tetraazacyclotetradecane and iodine monobromide has been made in dichloromethane at 25 °C. The results indicate the formation of $(macrocycle)_2I^+I_3^-$ and Br^+Br^- adducts through equilibrium reaction. The formation constant of the reaction has been calculated by fitting the absorbance–mole ratio data in MATLAB program. Conductometric measurements indicate the formation of free ions adducts. IR spectra of macrocycle and the resulting complex are compared and the effect of complexation on absorption bands is discussed.

Key words: Spectrophotometry, Dichloromethane, TMTA14C4, Crown ether, Iodine monobromide.

Introduction

Interest in the subject of molecular complexes received a strong stimulus in 1949 with the discovery of a new absorption band in the ultraviolet spectrum of solution of I_2 in benzene, which was characteristic of a complex [1]. Not only this obstruction provide a means to study this complex and the many others which show an analogous and characteristic new absorption band, but also its interpretation led to an extension of the Lewis acid–base theory in a quantum– theoretical form which provides the basis for the interpretation of a wide variety of phenomena associated which molecular complexes [2-5]. Since then the field has been extremely active.

Several reviews of the subject have been published since 1950, many of them still useful because of their different and general approach. The first review by Andrews emphasized experimental aspects [6]. The spectroscopic aspects of the subject were discussed by Orgel [7]. Terenin summarized the subject in a well balanced review [8]. McGlynn reviewed the subject from the point of view of theorist, with special emphasis on spectroscopic aspects [9].

In 1992 Izatt et al., reviewed the subject of molecular complexes of macrocycles [10]. The review contains thermodynamic and kinetic data for the interaction of macrocycles with neutral molecules. Several needs in the subject became apparent upon the data compiled in this review. Since then there has been an increasing interest in the study of molecular complexes of crown ethers with different π and σ acceptors [11, 12]. Interest in such molecular complexes has been strongly stimulated by the possibility of application in analytical purposes [13].

We have recently commenced a spectroscopic study of molecular complexes of aza crown ethers [14-16]. In this paper we report the results of spectrophotometric study of the interaction of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane with iodine monobromide in dichloromethane solution.

Experimental

1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMTA14C4) from Fluka company was recrystallized from reagent grade n-hexane and dried under vacuum over P_2O_5.
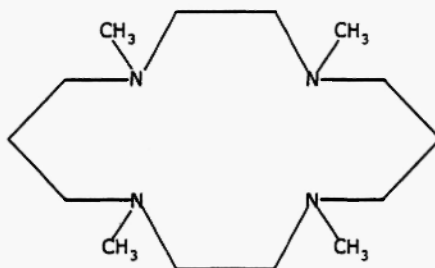
TMTA14C4

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 Methrom 660 conductivity meter in a thermostated cell at 25 ± 1 °C. IR spectra were recorded on a Shimadzu IR spectrometer using KBr pellets.

Results and Discussion

The absorption spectra of 5×10^{-4} of iodine monobromide solution in the presence of varying quantities of TMTA14C4 are shown in Fig. 1. As seen, upon addition of

macrocycle to iodine monobromide solution two new bands are appeared in 290 and 364nm. Also an isosbestic point is formed. The 290 and 364 nm bands are well known bands of triiodide ion [17, 18]. On the other hand, the existence of an isosbestic point is indicative of an equilibrium reaction [19]. Thus it can be concluded that the interaction of TMTA14C4 and iodine monobromide causes the production of triiodide through an equilibrium pathway.

The stoichiometry of the reaction was determined by plotting the absorbance vs. mole ratio [20] and Job methods [20]. The corresponding plots are shown in Figs. 2 and 3, respectively. A break at TMTA14C4/IBr ratio of 0.5 (Fig. 2) and a peak in the X $_{macrocycle}$ = 0.33 (Fig. 3) indicate the formation of a 1:2 macrocycle-IBr complex.

The appearance of triiodine ion band (Figure-1) the observation of isosbestic point (Fig. 1), and the confirmation of 1:2 stoichiometry (Figures-2 and 3), indicate that one the following reaction is occurred.
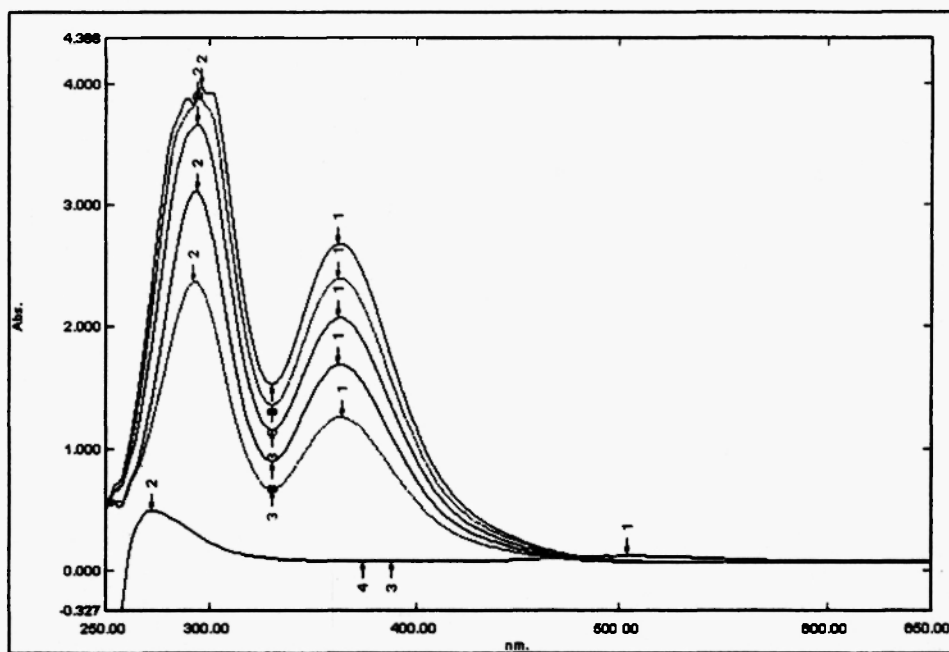

Figure-1 : Absorption spectra of 5×10^{-4} M solution of IBr in the presence of varying concentrations of TMTA14C4.
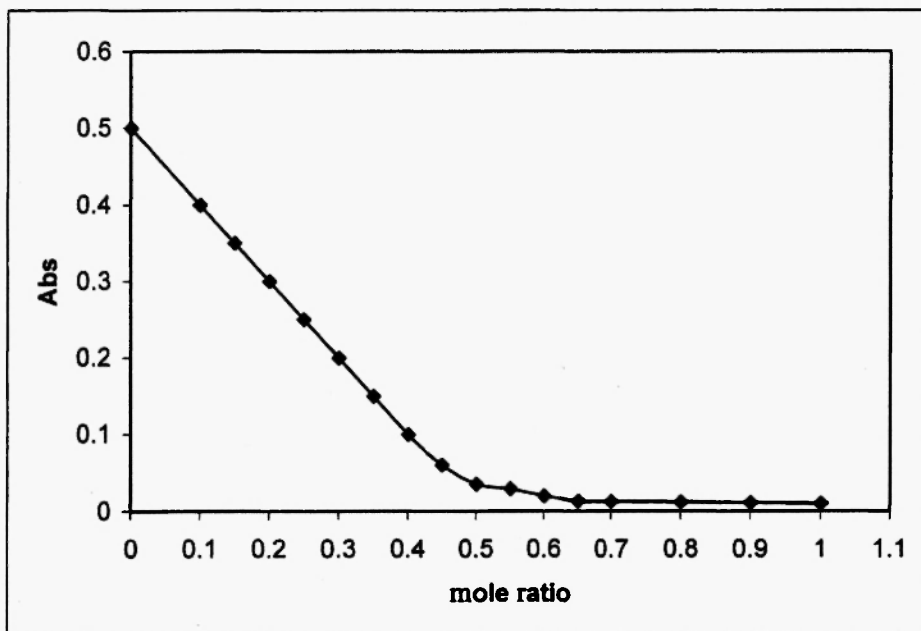
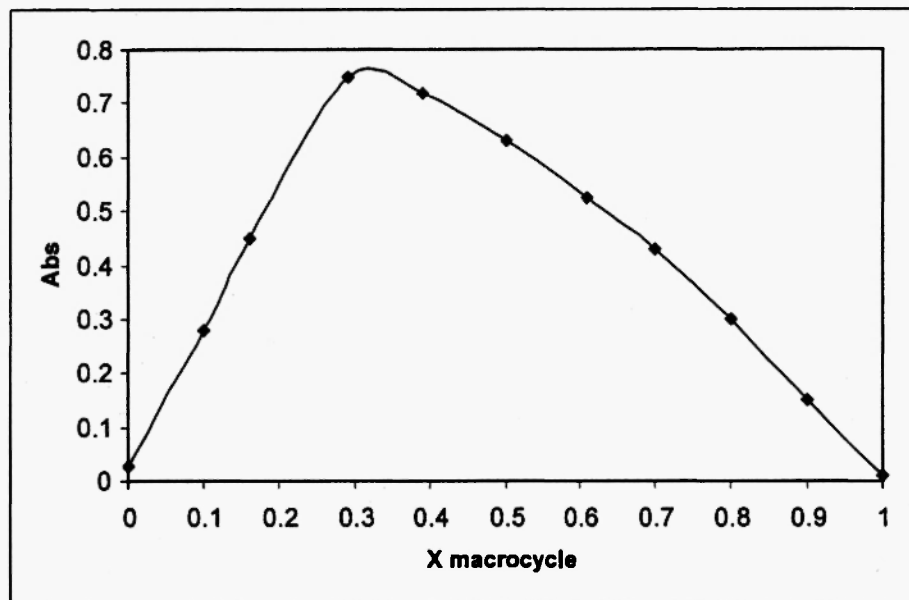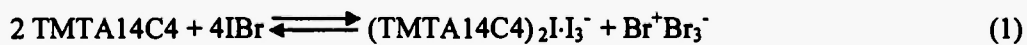**Figure-2** : Plot of absorbance vs. TMTA14C4/IBr at λ = 508 nm.

Figure-3 : Continuous variation plot for TMTA14C4-IBr at λ = 360 nm.

$$2 \text{ TMTA14C4} + 4\text{IBr} \rightleftharpoons (\text{TMTA14C4})_2\text{I}\cdot\text{I}_3^- + \text{Br}^+\text{Br}_3^- \quad (1)$$

$$2 \text{ TMTA14C4} + 4\text{IBr} \rightleftharpoons \text{TMTA14C4I}^+\text{I}_3^- + \text{TMTA14C4 Br}^+\text{Br}_3^- \quad (2)$$

However, the absence of tribromide ion band [21] proves that the equation (1) is right.
The formation constant of macrocycle-I_2 was calculated by fitting the absorbance-

mole ratio in MATLAB program. A function is used to final the equilibrium constant that fit the multi parameter minimum search in MATLAB [22] based on the Nelder-Mead algorithm [23]. This function uses the modeled equilibrium constant, simulates the absorbance-mole ratio portliest and calculates the difference between the simulated and measured absorbance profiles.

The search algorithm finds the equilibrium constant that result in the best feet between the simulated profiles and the measured absorbance profiles. The resulting computer fit of absorbance-mole ratio data are shown in Figure-4. As seen, there is fair agreement between observed and calculated absorbances. The $logK_f$ value obtained by this procedure is 6.30 ± 0.03. It seems that the high stability of macrocycle-I_2 is a strong driving force for the formation of $(macrocycle)_2I^+I_3^-$ (Eqn. 1) instead of macrocycle·$I^+I_3^-$ and macrocycle·$Br^+Br_3^-$ (Eqn. 2). This also origins from the strong soft-soft interaction between I^+ and nitrogen atoms of macrocycle [24].
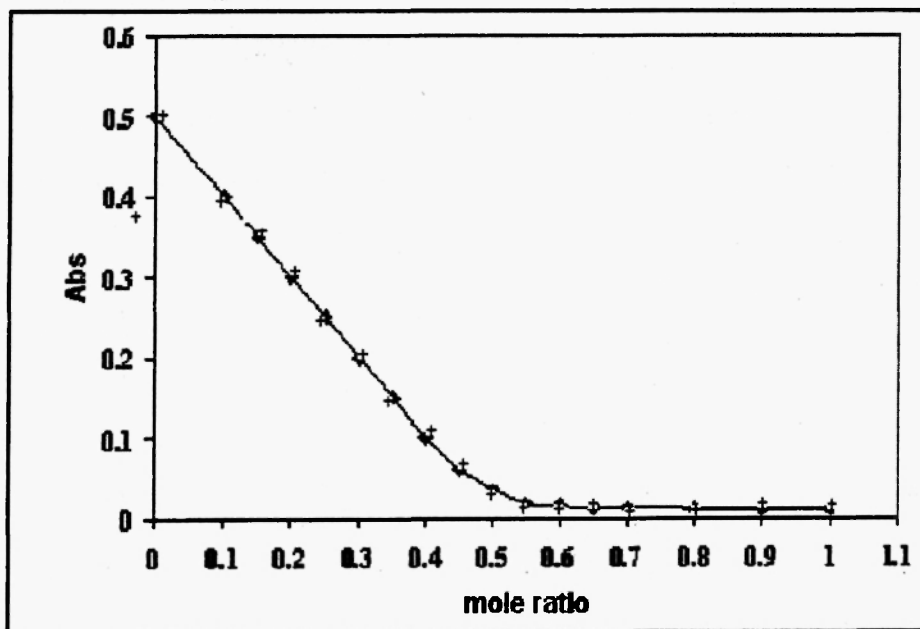

Figure-4 : Computer fitting of absorbance-mole ratio data in MATLAB program. (+) measured points, (●) calculated points.

The plot of conductance vs. macrocycle/Br_2 mole ratio is shown in (Figure-5). The increasing of conductance upon addition of macrocycle indicates that adduct is ionic. However, the break point of curve is located at TMTA14C4/IBr = 0.5. This means that through the reaction of macrocycle and IBr both ion pair and free ions are formed.
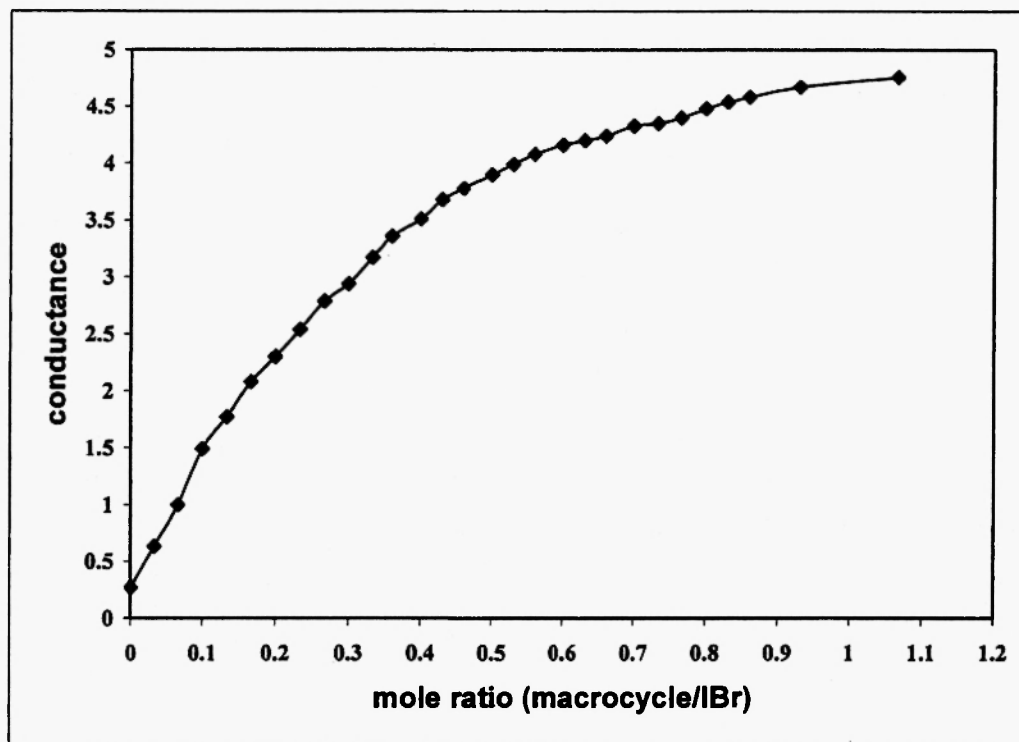
Figure-5 : Plot of conductance vs. TMTA14C4/IBr .

IR spectra of TMTA14C4 and TMTA14C4-IBr complex are compared (Figure-6). As seen , upon complexation, (i) the CH_3 and CH_2 bending (at 1450 cm^{-1} and 1600 cm^{-1}) and stretching bands (at 2800 cm^{-1} and 2950 cm^{-1}) are shifted to higher frequencies, (ii) the C-N stretching band at 1120 cm^{-1} is shifted to lower frequencies and (iii) a new band is appeared at 650 cm^{-1}. The first effect can be attributed to the rigidness of macrocycle through complexation [25]. The second effect is a result of direct involvement of nitrogen atoms of macrocycle in complex [26], and the last effect origins from the N...I^+ stretching in the complex [27].
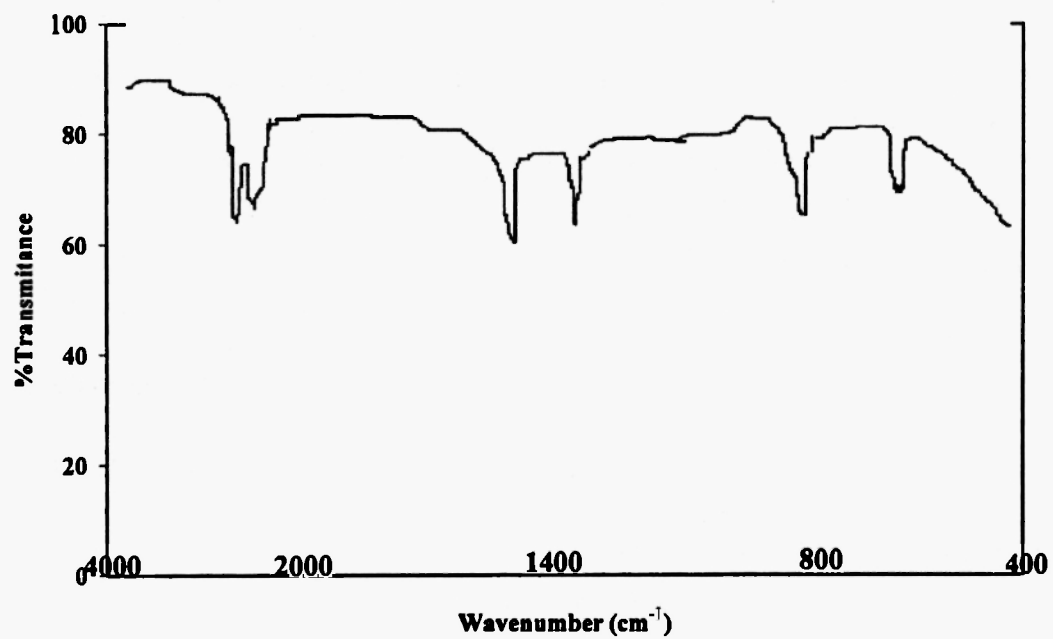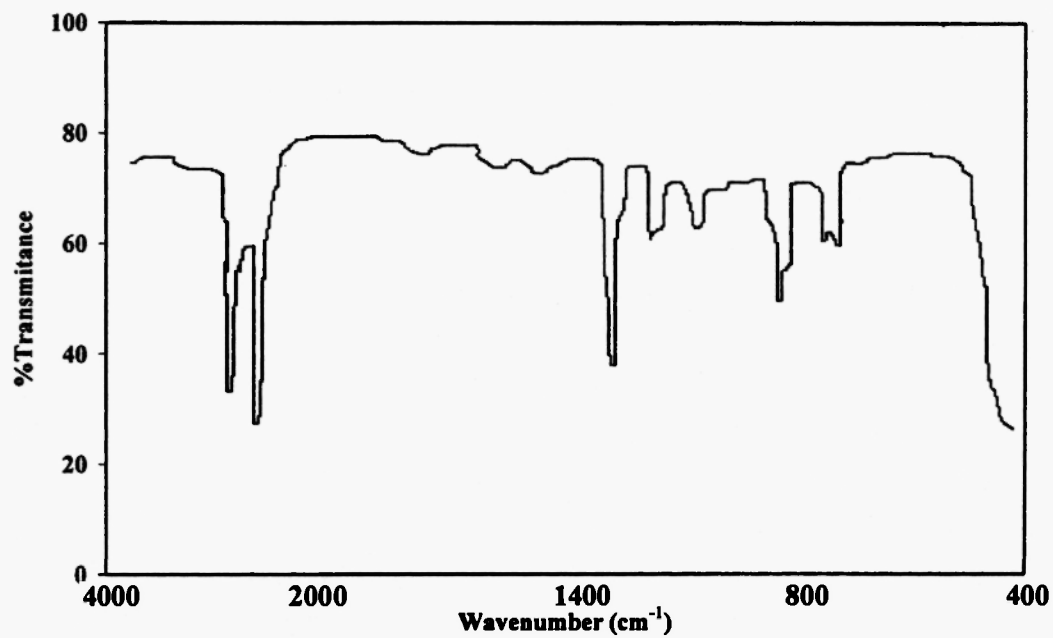
Figure-6 : IR spectra of TMTA14C4 (up) and TMTA14C4-IBr complex (down).

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