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Spectrophotometric Study of the Complexation of Iodine and Iodine Monochloride with 1,4,7-Trimethyl-1,4,7-triazacyclononane in Chloroform Solution

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The interaction between iodine and iodine monochloride with 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN) has been performed in chloroform solution at 25°C. The results of iodine are indicative of the formation of [$TMTACNI^+I_3^-$] through an equilibrium reaction. The stability constant of this reaction has been calculated from the absorbance-mole ratio data, using the nonlinear least square program "KINFIT". In the case of iodine monochloride, the formation of polyhalide, 1 : 4 (as precipitate), 1 : 3 and 1 : 2 macrocyclic to iodine monochloride adducts are confirmed. The formation of 1 : 2 complex was followed through an equilibrium reaction. However, the other adducts were formed through nonequilibrium reactions. The species of [$TMTACNCl^+I(ICl)_n^-$], [$TMTACNCl^+(ICl)_3^-$], [$TMTACNCl^+I(ICl)_2^-$] and [$TATMCl^+I(IC)^-$] are suggested as the possible products.

Key Words: **Molecular complex, Iodine, Iodine monochloride, Chloroform, Spectrophotometry.**

INTRODUCTION

Over the past few decades, reports have appeared from various laboratories concerning the study of complexes of iodine with nitrogen containing macrocycles[1–5]. Some of the resulting charge transfer complexes have revealed very interesting physical properties[6–8]. More recently, some attention has been focussed on the iodine monochloride complexes[9, 10]. However, the latter investigations are much less than the former. Thus, more study in this field is needed. On the other hand, it seems that simultaneous investigation of iodine and iodine monochloride will be more informative and the results of each system will help in the clarification of the other.

We have recently been involved in the study of molecular complexes of macrocyclic compounds[11–15]. In this paper, the results of spectroscopic study of the interaction between 1,3,5-trimethyl-1,3,5-triazacyclononane with iodine and iodine monochloride in chloroform solution are reported.

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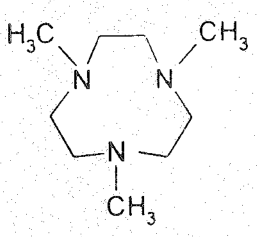
EXPERIMENTAL

Reagent grade iodine (Merck) was sublimed and stored in a desiccator over phosphorous pentoxide before use. Iodine monochloride from Ridel and 1,4,7-trimethyl-1,4,7,-triazacyclononane (TMTACN) from Merck were used as received.



1,4,7-Trimethyl-1,4,7-triazacyclononane (TMTACN)

All UV-Vis spectra were recorded on a Perkin-Elmer Lambda-2 spectrophotometer and absorbance measurements were made with a Philips PU875 spectrophotometer at 25 ± 1°C.

In order to obtain UV-Vis spectra, 3 mL of 4.35×10^{-4} M iodine or 7.5×10^{-3} M iodine monochloride were transferred into 1.00 cm quartz cell and titrated with a concentrated solution of TMTACN by a 100-μL Hamilton syringe. Each spectrum was recorded immediately after the titrant addition. The same procedure was followed for absorbance measurement.

RESULTS AND DISCUSSION

The electronic absorption spectrum of iodine (4.35×10^{-4} M) in the presence of varying concentrations of TMTACN is shown in Fig. 1. The appearance of two bands at 292 and 364 nm is characteristic for the formation of triiodide ion in the presence of complex formation between iodine and different electron pair donor ligands[16–18]. The observation of an isobestic point at 475 nm (Fig. 1) indicates that iodine monochloride and TATACN have an equilibrium reaction[19].

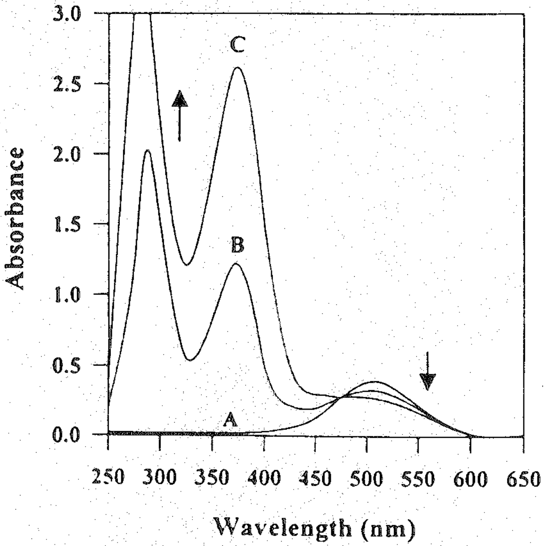


Fig. 1. Absorption spectrum of iodine (4.35×10^{-4} M) at TMTACN/I_2 mole ratios: 0.00 (A), 0.09 (B) and 0.18 (C).

Fig. 2 shows the plot of absorbance *vs.* TMTACN : I_2 mole ratio[20], obtained at λ_{max} of iodine (508 nm). The plot clearly indicates the formation of 1 : 2 (TMTACN-to-iodine) complex.

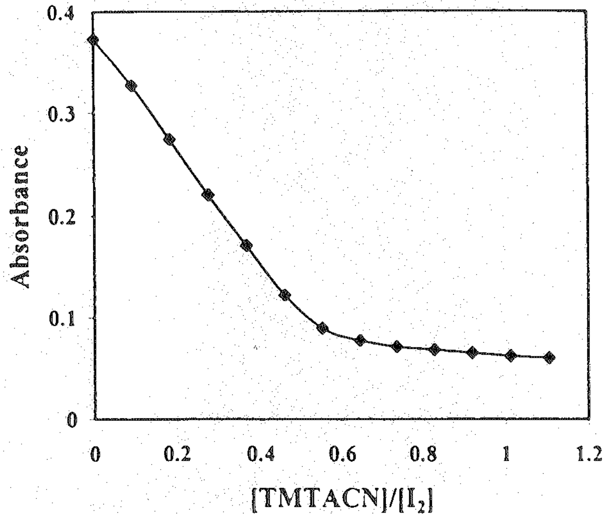


Fig. 2. Plot of absorbance *vs.* TMTACN/I_2 mole ratio at 508 nm

The appearance of characteristic triiodide bands at 292 and 364 nm, the observation of an isobestic point at nm and the confirmation of a 1 : 2 stoichiometry by absorbance-mole ratio method, proves the following equation:

$$\text{TMTACN} + 2I_2 \rightleftharpoons [\text{TMTACNI}^+I_3^-] \quad (1)$$

For the evaluation of the formation constant of the above complex from the absorbance-mole ratio data, the nonlinear least square curve-fitting program KINFIT was used[21]. The program is based on the iterative adjustment of calculated to observed absorbance values by using either the Wentworth matrix technique[22] or the Powell procedure[23]. Adjustment parameters are K_f and ε, where ε is the molar absorption coefficient of iodine.

The observed absorbance of an iodine solution in chloroform at its λ_{max} is given by eqn. (2). The mass balance equations can be written as (3) and (4) and the formation constant of complex as (5).

$$A_{obs} = \varepsilon b[I_2] \quad (2)$$

$$C_{I2} = [I_2] + 2[(\text{TMTACNI}^+)I_3^-] \quad (3)$$

$$C_{\text{TMTACN}} = [\text{TMTACN}] + [(\text{TMTACNI}^+)I_3^-] \quad (4)$$

$$K_f = \frac{[(\text{TMTACNI}^+)I_3^-]}{[\text{TMTACN}][I_2]^2} \quad (5)$$

Substitution of eqns. (3) and (4) into (5) and rearrangement yields (6):

$$K_f[I_2]^3 + K_f(2C_{\text{TMTACN}} - C_{I_2})[I_2]^2 - [I_2] - C_{I_2} = 0 \quad (6)$$

The free iodine concentrations, $[I_2]$ were calculated from equation (6) by means a Newton-Raphson procedure. Once the value of $[I_2]$ had been obtained the concentrations of all other species involved were calculated from the corresponding mass balance equations by using the estimated value of K_f at the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed values for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum-of-squares and the standard deviation of the data. The resulting computer fit of the absorbance-mole ratio is shown in Fig. 3. The good agreement between the observed and calculated absorbances further supports eqn. (1). The log K_f value obtained by this procedure is 5.69 ± 0.01. The high value of the formation constant is indicative of strong interaction between TMTACN and I_2.

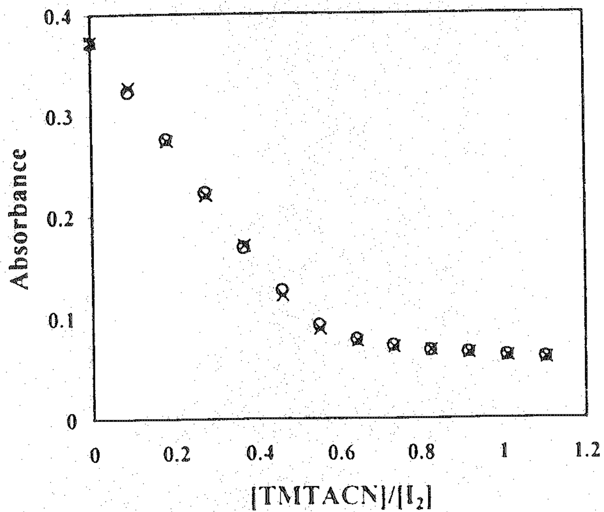


Fig. 3. Computer fit of absorbance *vs.* TMTACN/I_2 mole ratio at 508 nm; (×): experimental points and (O): calculated points

The electronic absorption spectrum of 7.50×10^{-3} M of iodine monochloride in 250–750 nm region is shown in Fig. 4 (A). The spectrum shows a λ_{max} at 350

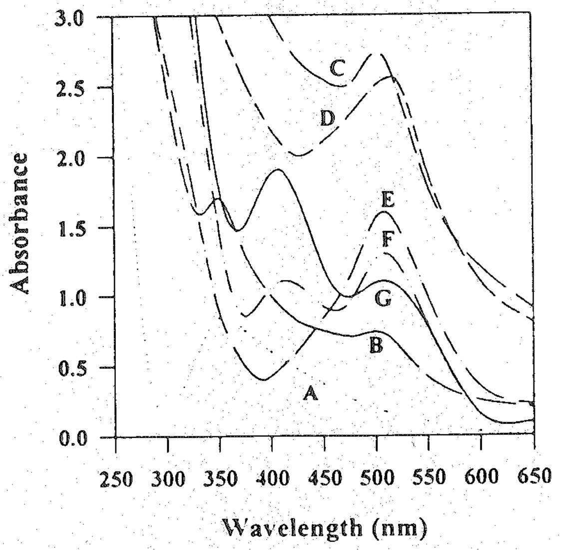


Fig. 4. Absorption spectrum of 7.5010-3 M ICl at TMTACN/ICl mole ratios: 0.00 (A), 0.065 (B), 0.13 (C), 0.26 (D), 0.325 (E), 0.39 (F) and 0.455 (G)

nm and a shoulder at 475 nm. The absorption spectrum of 7.50×10^{-3} M of iodine monochloride in the presence of 4.90×10^{-4} M TMTACN (Fig. 4 (B), TMTACN/ICl = 0.065) clearly shows an increase in the intensity of 350 nm and appearance a distinct band at 500 nm. Upon further addition of TMTACN (9.80×10^{-4} M, TMTACN/ICl = 0.13) the intensity of 500 nm band also increases [Fig. 4 (C)] and as a result of the overlap by a broad band, the 350 nm band disappears. Fig. 4 (D) shows the absorption spectrum of a 7.50×10^{-3} M ICl in the presence of 1.95×10^{-3} M of TMTACN (TMTACN/ICl = 0.26). It must be noticed that a precipitate was observed at this point. So, this spectrum is due to the dissolved portion of the resulting adducting of ICl and TMTACN. Anyway, this spectrum differs from the former (Fig. 4C) in having a λ_{max} at 525 nm.

Interestingly, at higher concentration of TMTACN (2.44×10^{-3} M TMTACN/ICl = 0.325), the precipitate was dissolved. The corresponding spectrum is shown in Fig. 4 (E). As can be seen, the new spectrum shows a λ_{max} at 510 nm and a shoulder at 340 nm. The intensity and the λ_{max} of this spectrum also differs from the previous one [Fig. 4 (D)].

Figs. 4 (F) and 4 (G) show the spectra of 7.50×10^{-3} M ICl in the presence of 2.44×10^{-3} M (TMTACN/ICl = 0.39) and 3.40×10^{-3} M (TMTACN/ICl = 0.46) TMTACN, respectively. Again, this spectrum differs from the previous one [Fig. 4 (E)] in having λ_{max} at 400 and 500 nm. Because of obviousness, the last spectrum of Fig. 4 and new spectra due to solutions containing TMTACN/ICl mole ratios more than 0.46 are shown in Figs. 5 (G) to 5 (J).

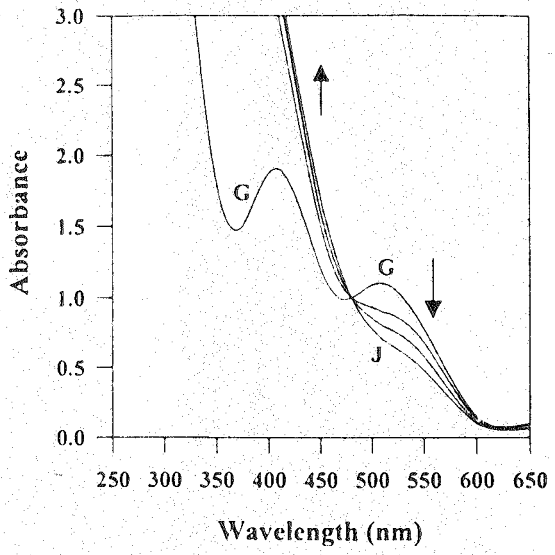


Fig. 5. Absorption spectrum of 7.5010-3 M ICl at TMTACN/ICl mole ratios: 0.455 (G), 0.52 (H), 0.585 (I) and 0.65 (J)

The distinct difference between the spectra of various solutions indicates that different adducts are obtained. The absence and presence of isobestic point (Figs. 4 and 5, respectively) is indicative of nonequilibrium and equilibrium reactions[19]. On the other hand, the complete disappearance of ICl spectrum (Fig. 4) shows that this molecule does not participate in the final equilibrium reaction.

In order to determine the stoichiometry of the resulting adducts the absorbance-mole ratio method at 425 nm and 500 nm was examined (Fig. 6). Both plots show breaks at 0.25, 0.33 and 0.5 points. This is indicative of the formation of 1 : 4, 1 : 3 and 1 : 2 (TMTACN : ICl) complexes, respectively. Also a break at 0.15 can be assigned to the formation of polymer.

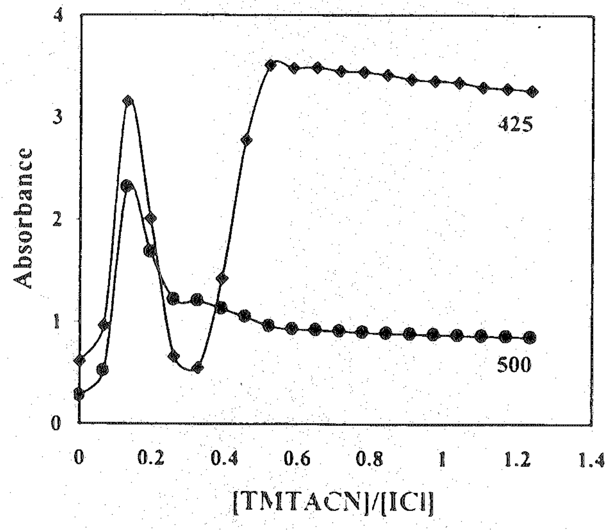


Fig. 6. Plot of absorbance *vs.* TMTACN/ICl mole ratio at 425 and 500 nm

According to the foregoing paragraphs, the following equations are suggested for the interaction between TMTACN and iodine monochloride at different titration steps:

$$\text{TMTACN} + 4\text{ICl} \longrightarrow [\text{TMTACNCl}^+][\text{I(ICl)}_3^-] \qquad (7)$$

$$[\text{TMTACNCl}^+][\text{I(ICl)}_3^-] \longrightarrow [\text{TMTACNCl}^+][\text{I(ICl)}_2^-] \qquad (8)$$

$$[\text{TMTACNCl}^+][\text{I(ICl)}_2^-] \rightleftharpoons [\text{TMTACNCl}^+][\text{I(ICl)}^-] \qquad (9)$$

The above reactions are confirmed by the frequent observation of polyhalides in the reaction between halogens and interhalogens[2, 24–26]. It seems, because of higher diameter of I^- relative to Cl^-,[27] the formation of subsequent adducts in which the I^+ is located in the TMTACN cavity ([TMTACNI$^+$]) and Cl^- is coordinated by ICl molcules to be impossible.

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