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Spectrophotometric Study of the Complexation of Iodine with 1,7-Diaza-15-crown-5 in Chloroform Solution

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Abstract. The complex formation reaction between iodine and 1,7-diaza-15-crown-5 (DA15C5) has been studied spectrophotometrically in chloroform at 25 °C. The resulting 1 : 2 (DA15C5 : I_2) molecular complex was formulated as $(\mathrm{DA15C5}\cdots\mathrm{I}^+)\mathrm{I}_3^-$. The spectrophotometric results, as well as the conductivity measurements, revealed that the gradual release of triiodide ion from its contact ion paired form in the molecular complex into the solution is the rate determining step of the reaction. The rate constant was calculated as $k = (8.8 \pm 0.2) \times 10^{-3}\ \mathrm{min}^{-1}$. The formation constant of the molecular complex was evaluated from the computer fitting of the absorbance-mole ratio data as $\log K_f = 6.89 \pm 0.09$.

Keywords: DA15C5-iodine complex, stoichiometry, stability, rate constant, spectrophotometry.

1. Introduction

During the past few decades, the complexation of iodine with a wide variety of donating ligands has been the subject of extensive research [1–7]. Some of the resulting charge transfer complexes have revealed very interesting physical properties [5–7]. More recently, some attention has been focused on the study of iodine complexes with macrocyclic crown ethers and their aza-substituents in various solvents [8–13]. It has been shown that the substitution of oxygen atoms of crown ether rings by nitrogens causes a very large increase in the stability of their iodine complexes [11, 13] over those of ordinary crowns [9, 10]. It should be mentioned, however, that the size of iodine is too large to form an inclusion complex with the relatively small crown ethers such as 15-crowns.

We have recently reported the spectroscopic study of charge transfer complexes of benzo crown ethers with some π-acceptors in dichloromethane solution [14]. In

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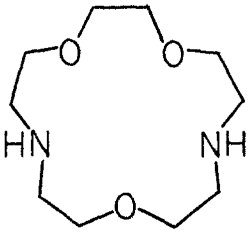
this communication we wish to report the results of a spectrophotometric investigation of the stoichiometry, stability and kinetics of complex formation between 1,7-diaza-15-crown-5 (I) and iodine in chloroform solution at 25 °C.

2. Experimental

1,7-Diaza-15-crown-5 (DA15C5, **I**, Merck) was recrystallized from reagent grade *n*-hexane and dried under vacuum over P_2O_5. Reagent grade iodine and chloroform (both form Merck) were of the highest purity available and used without any further purification.



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All UV-vis spectra were recorded on a Philips PUB700 spectrophotometer and the absorbance measurements were made with a Philips PU875 spectrophotometer at 25 ± 1 °C.

3. Results and Discussion

The electronic absorption spectra of iodine (1.23×10^{-4} M) in the presence of increasing amounts of DA15C5 in chloroform at 25 °C are shown in Figure 1. The resulting DA15C5-iodine complex has strong absorptions at 262 and 390 nm. None of the initial reactants show any measurable absorption in the 250–450 nm region. Interestingly, after about 7 h, the absorption bands at 262 and 390 nm shift to new positions at 292 and 364 nm, respectively (Figure 2B). This latter spectrum resembles that of a 1 : 1 mixture of tetrabutylammonium iodide (TBAI) and iodine in chloroform solution (Figure 2C). It should be noted that the 292 and 364 nm bands are well known to be characteristic for the formation of triiodide ion, I_3^-, in the process of complex formation between iodine and different electron pair donating ligands [9, 11, 12, 15–17].

Figure 3 shows the absorbance vs. DA15C5/I_2 mole ratio plots obtained at the λ_{max} of iodine, 508 nm (Figure 3A), and at 262 nm (Figure 3B). Both plots are clearly indicative of the formation of a 1 : 2 (DA15C5 : I_2) complex in chloroform solution. Moreover, the existence of a well defined isosbestic point at 462 nm in the spectra of iodine upon titration with DA15C5 (Figure 1) is further evidence for a simple complexation equilibrium.

Based on the above mentioned spectral behavior, the formation of triiodide can be reasonably assumed to occur in two steps: The first step involves the formation

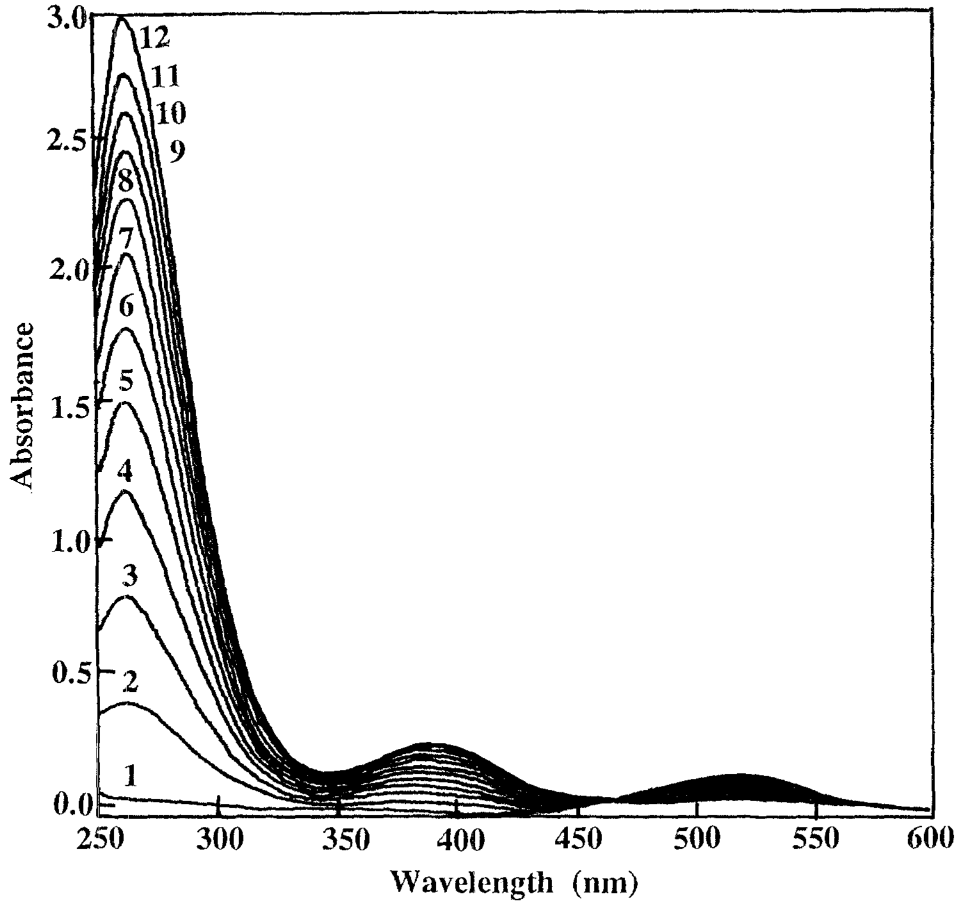

Fig. 1. Absorption spectra of 1.23×10^{-4} M of iodine in chloroform in the presence of varying concentration of DA15C5: 1, 0.00 M; 2, 5.53×10^{-5} M; 3, 1.01×10^{-4} M; 4, 1.43×10^{-4} M; 5, 1.85×10^{-4} M; 6, 2.27×10^{-4} M; 7, 2.55×10^{-4} M; 8, 2.71×10^{-4} M; 9, 2.98×10^{-4} M; 10, 3.17×10^{-4} M, 11, 3.36×10^{-4} M; 12, 3.81×10^{-4} M.

of a molecular complex in the form of $(\mathrm{DA15C15}\cdots\mathrm{I}^+)\mathrm{I}_3^-$ in which the I_3^- ion exists as a contact ion paired anion, i.e.

$$\mathrm{DA15C5} + 2\mathrm{I}_2 \rightleftharpoons (\mathrm{DA15C5}\cdots\mathrm{I}^+)\mathrm{I}_3^- . \qquad (1)$$

Evidence for the formation of such a molecular complex has been reported previously [18]. In the second step, which is actually the rate determining step for the formation of I_3^- ion, the resulting molecular complex is further decomposed to release free triiodide ion (or solvent separated I_3^- ion) into the solution, as

$$(\mathrm{DA15C5}\cdots\mathrm{I}^+)\mathrm{I}_3^- \rightarrow (\mathrm{DA15C5}\cdots\mathrm{I}^+) + \mathrm{I}_3^- . \qquad (2)$$

It can then be concluded that the two absorption maxima at 262 and 390 nm belong to the contact ion paired I_3^-, while the free (or solvent separated) triiodide

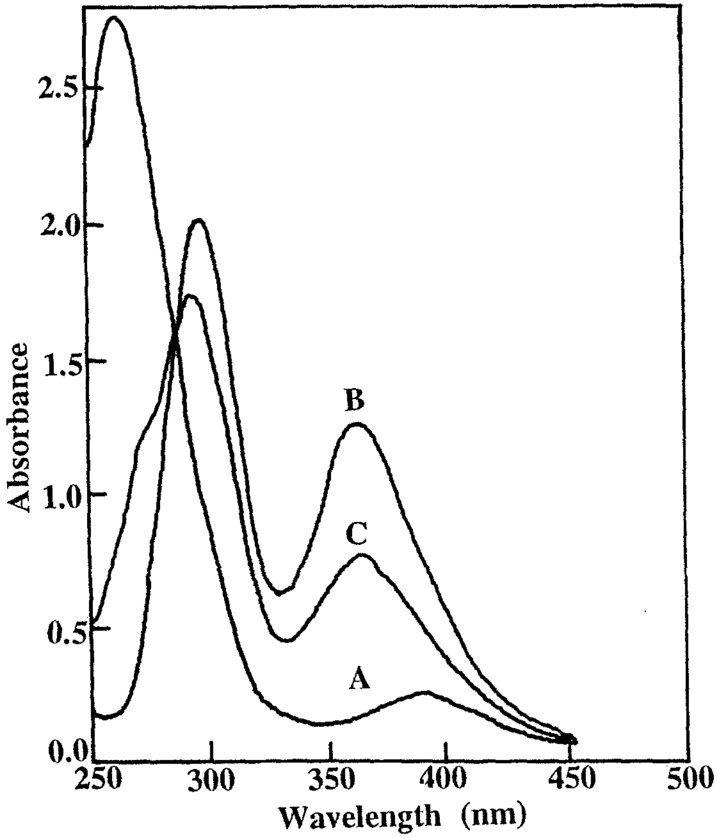

Fig. 2. Absorption spectra of 6.65×10^{-5} M of the DA15C5-iodine complex just after addition of the reactants (A) and after seven hours (B), as well as the absorption spectrum of tetrabutylammonium triiodide in chloroform (C).

ion has two absorption maxima at 292 and 364 nm. The existence of such a two step mechanism for the formation of triiodide ion was further supported by conductivity measurements of a 3.32×10^{-4} M solution of iodine in chloroform before and after addition of DA15C5. Just after addition of the crown ether to the iodine solution (with negligible conductivity) the molar conductance of the solution is 36.4 S cm^2 mol^{-1}; after 7 h the molar conductance increases to 117.5 S cm^2 mol^{-1} indicating the gradual release of I_3^- ion from its molecular complex with DA15C5 into the solution.

In order to investigate the kinetics of triiodide formation, the absorbance of the 364 nm band was monitored as a function of time at 25 °C. The absorbance changes were found to be in accord with a first-order kinetics. The rate constant was calculated by the Guggenheim method using the relationship $\ln(A_\infty - A_t) = -k(t - t_0) + \ln(A_\infty - A_0)$. The rate constant obtained from the slope of the

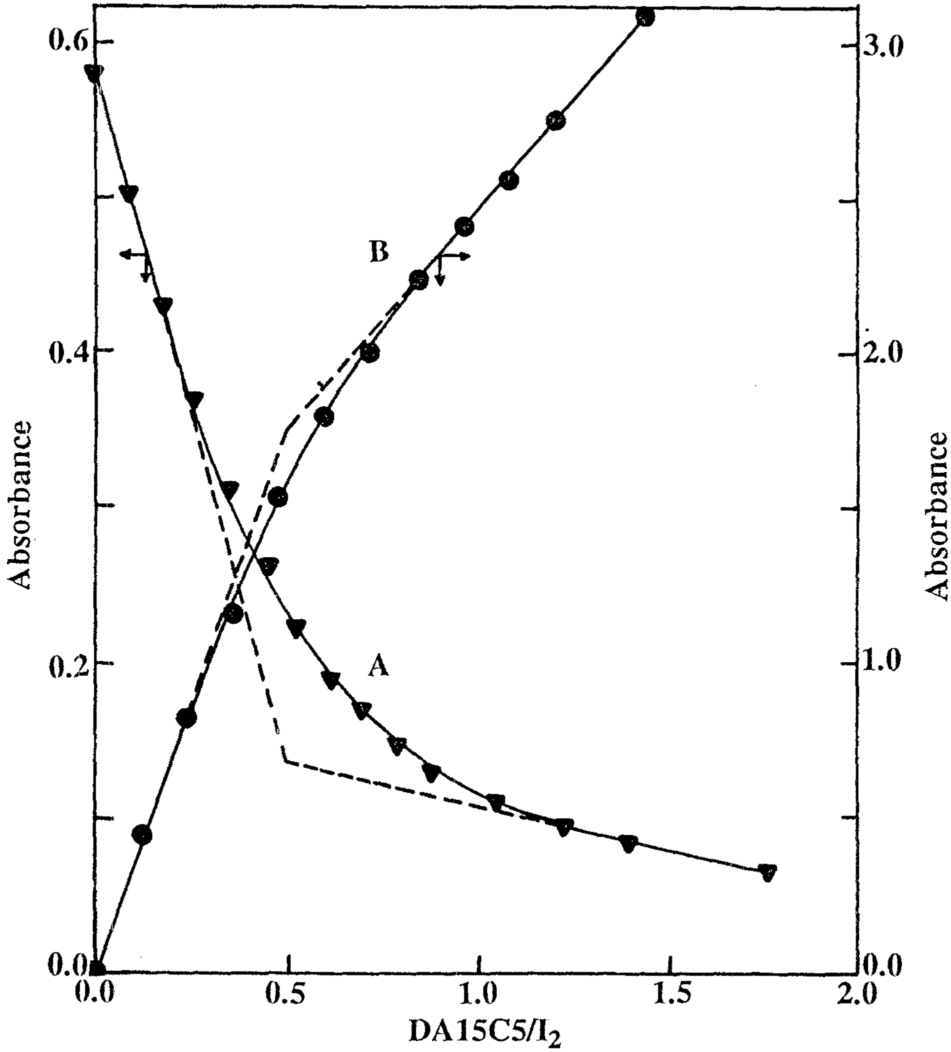

Fig. 3. Plots of absorbance vs. DA15C5/I_2 mole ratio in chloroform solution obtained at 508 nm (A) and 262 nm (B).

corresponding linear $\ln(A_\infty - A_t)$ vs. $(t - t_0)$ plot is $k = (8.8 \pm 0.2) \times 10^{-3}$ min^{-1}.

For the evaluation of the formation constant of the resulting molecular complex, K_f, from the absorbance-mole ratio data, a non-linear least squares curve fitting program KINFIT was used [19]. 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 [20] or the Powell procedure [21]. Adjustable parameters are K_f and ϵ, where ϵ is the molar absorptivity of iodine.

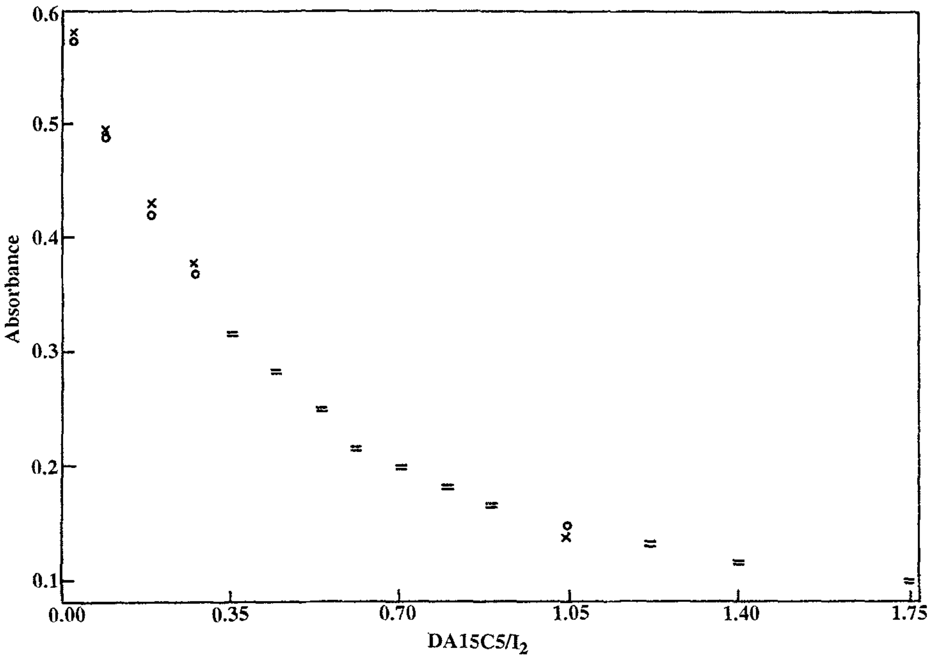

Fig. 4. Computer fit of the absorbance vs DA15C5/I_2 mole ratio plot obtained at 508 nm and 25 °C: (×) experimental point; (○) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

The observed absorbance of a solution at the λ_{max} of iodine is given by

$$A_{obs} = \epsilon b[I_2]. \tag{3}$$

The mass balance equations can be written as

$$C_I = [I_2] + 2[DA15C5 \cdots I^+)I_3^-] \tag{4}$$

$$C_{DA15C5} = [DA15C5] + [(DA15C5 \cdots I^+)I_3^-]. \tag{5}$$

The formation constant of the complex is equal to

$$K_f = \frac{[(DA15C5 \cdots I^+)I_3^-]}{[DA15C5][I_2]^2}. \tag{6}$$

Substitution of Equations (4) and (5) into Equation (6) and rearrangement yields

$$K_f[I_2]^3 + K_f(2C_{DA15C5} - C_I)[I_2]^2 + [I_2] - C_I = 0. \tag{7}$$

The free iodine concentrations, $[I_2]$, were calculated from Equation (7) by means of 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 is continued until the sum-of-squares of the residuals between calculated and observed values of absorbance for all experimental points is minimized. The output of the KINFIT program comprises the refined parameters, the sum-of-squares and the standard deviation of the data.

Figure 4 shows the resulting computer fit of the absorbance-mole ratio data. As seen, the fair agreement between the observed and calculated absorbances further support the existence of a 1 : 2 complexation between DA15C5 and I_2 in chloroform solution. The log K_f value obtained by this procedure is 6.89 ± 0.09. It should be noted that formation constants of about the same order have already been reported for iodine complexes with macrobicyclic cryptands in chloroform solution [22].

For comparison, the reported values for log K_f of the molecular complex formed between 15-crown-5 (15C5) and iodine is 0.34 in carbon tetrachloride solution [10] and 0.68 in cyclohexane solution [9]. It is obvious that the substitution of two oxygen atoms of the 15C5 ring with two —NH^- groups causes a tremendous increase (of about six order of magnitudes) in the stability of the resulting complex, most probably due to the strong soft-soft interactions between nitrogen atoms and iodine in solution [23].

References

1. M. Brandon, M. Tamres, and S. Searles: *J. Am. Chem. Soc.* **82**, 2129 (1960).
2. E. M. Arnett and C. Y. Wu: *J. Am. Chem. Soc.* **84**, 1684 (1962).
3. L. J. Andrews and R. M. Keefer: *Molecular Complexes in Organic Chemistry*, Holden-Day (1964).
4. M. Tamres and J. Yarwood: *Spectroscopy and Structure of Molecular Complexes*, Ch. 3., Plenum Press (1974).
5. P. J. Trotter and P. A. White: *Appl. Spectrosc.* **32**, 232 (1978).
6. I. Ikemoto, M. Sakairi, T. Tsutsumi, H. Kuroda, I. Tasumi, and H. Shirakawa: *Chem. Lett.* 1189 (1979).
7. N. Kulevsky and K. N. Butamina: *Spectrochim. Acta* **46A**, 79 (1991).
8. R. M. Izatt, J. S. Bradshaw, K. Pawlak, R. L. Bruening, and B. J. Tarbet: *Chem. Rev.* **92**, 1261 (1992).
9. H. P. Hopkins, D. V. Jahagirdar, and F. J. Windler: *J. Phys. Chem.* **82** 1254 (1978).
10. L. J. Andrews and R. M. Keefer: *J. Org. Chem.* **52**, 2690 (1987).
11. E. M. Nour and L. A. Shahada: *Spectrochim. Acta* **44A**, 1277 (1988).
12. E. M. Nour: *Spectrochim. Acta* **47A**, 743 (1991).
13. W. Hirsch, J. Greenman, and R. Pizer: *Can. J. Chem.* **71**, 2171 (1993).
14. A. Semnani and M. Shamsipur: *Spectrochim. Acta* **49A**, 411 (1993).
15. R. P. Lang: *J. Phys. Chem.* **78**, 1657 (1974).
16. L. Andrews, E. S. Prochaska and A. Loewenschuss: *Inorg. Chem.* **19**, 463 (1980).
17. M. Mizuno, J. Tanaka, and I. Harada: *J. Phys. Chem.* **85**, 1789 (1981).
18. Y. A. Serguchev and T. I. Petrenko: *Teor. Eksp. Khim.* **13**, 705 (1977).
19. V. A. Nicely and J. L Dye: *J. Chem. Educ.* **48**, 443 (1971).
20. W. E. Wentworth: *J. Chem. Educ.* **42**, 96, 162 (1962).
21. M. J. D. Powell: *Comput. J.* **7**, 155 (1964).
22. P. Labbe, R. Le Goaller, H. Handel, G. Pierre, and J. L. Pierre: *Electrochim. Acta* **27**, 257 (1982).
23. R. G. Pearson: *Struct. Bonding* **80**, 1 (1993).