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Spectrophotometric and Electrochemical Study of the Complexation of Iodine with 1,10-Diaza-18-Crown-6 in Acetonitrile Solution

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ABSTRACT: *The complexation reaction between iodine and 1,10-Diaza-18-Crown-6 (DA18C6) has been studied in acetonitrile by spectrophotometric, biamperometric and conductometric techniques. The results are indicative of the formation of $[(CH_3CN)_n I^+ . I_3^-]$ from iodine and acetonitrile, and the formation of DA18C6 $I^+ . I^-$ from DA18C6 and $[(CH_3CN)_n I^+ I_3^-]$. The formation constant of the latter reaction has been calculated from the absorbance-mole ratio data, using the nonlinear least square program "KINFIT". The IR spectra of acetonitrile-acetonitrile iodine complex and DA18C6-DA18C6 iodine complex are compared and the effect of complexation on absorption bands are discussed.*

KEYWORDS: *DA18C6 iodine complex, spectrophotometry, formation constant, conductometry, biamperometry.*

INTRODUCTION

Complexation of iodine with a wide variety of donating ligands has been the subject of extensive research [1-5], but the investigation of iodine complexes with macrocyclic crown ethers and their aza substituents in various solvents is a relatively new field of research [6,7]. In this paper the results of spectrophotometric and electrochemical studies of DA18C6-I_2 complex in acetonitrile solution are reported.

EXPERIMENTAL

1,10-Diaza-18-Crown-6 (DA18C6) from Merck

(Darmstadt, Germany) was used after recrystallization from *n*-hexane and drying under vacuum over P_2O_5 . Reagent grade iodine and acetonitrile (Merck) were used without further purification.

All UV - Vis spectra were recorded on a Perkin-

DA18C6

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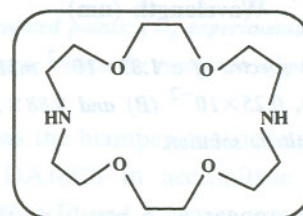
Elemer Lambado2 spectrophotometer and the absorbance measurements were made with a Philips PU87S spectrophotometer at 25±1°C. Conductance measurements were carried out with a Meterohm 660 conductivity meter in a thermostated cell at 25±1°C. Biamperometric measurements were made with platinum electrodes in a thermostated cell at 25±1° C. In order to obtain absorbance-mole ratio data, 3 mL of 2.91 × 10^{-5} M of iodine solution was transfered to a 1.00 cm quartz cell and titrated with a standard macrocycle solution by a 100 mL Hamilton syringe. Similarly, the conductance and *current- mole ratio* data were obtained by titration of 10 mL of 1.77 × 10^{-4} M and 2.25 × 10^{-5} M of iodine with DA18C6 solution respectively. The IR spectra were recorded on a Perkin-Elmer 781 spectrometer using KBr pellets for acetonitrile-iodine, DA18C6-iodine and DA18C6, and NaCl cells for acetonitrile.

RESULTS AND DISCUSSION

The electronic absorption spectrum of iodine in acetonitrile (Fig. 1A) in 200 - 600 nm region shows three bands at 240 , 290 and 364 nm.
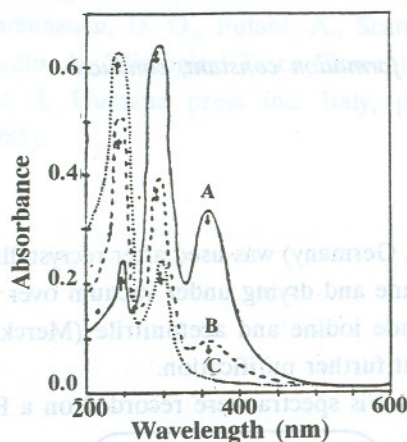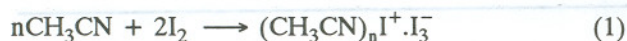

Fig. 1: Absorption spectra of a 1.33×10^{-2} mM iodine in the presence of 0 (A), 0.25×10^{-2} (B) and 0.88×10^{-2} (C) mM DA18C6 in acetonitrile solution.

These bands appear as a result of the following reaction [8,9]

$$nCH_3CN + 2I_2 \longrightarrow (CH_3CN)_n I^+ . I_3^- \qquad (1)$$

The reasons for the occurence of the above reac-

tion are the considerable increase in conductance after addition of I_2 to acetonitrile, the soft-soft interaction of iodine with the cyanide nitrogen [10], and strong interaction of iodine and azamacrocyclic compounds in inert solvents [6,7,11].

Interestingly it was found that the addition of DA18C6 to a solution of iodine in acetonitrile caused an isosbestic point, due to reduced intensity of the 290 and 364 nm bands and the increased intensity of 240 nm band (Figs 1B and 1C). As the bands are due to I_3^- (290 and 364 nm) and I⁻ (240), these variations can be attributed to the following equilibrium:

$$DA18C6 + (CH_3CN)_n I^+ . I_3^- \rightleftharpoons DA18C6 \ I^+ . I^- +$$

$$(CH_3CN)_n \ I^+ \ I^- \qquad (2)$$
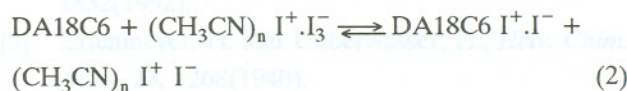
The absorbance vs. DA18C6/I_2 mole ratio plot at 364 nm (Fig.2) clearly shows the formation of a 1:2 (DA18C6/I_2) adduct and further supports the above equation. Besides, since it has been proved in reaction of iodine with azamacrocyclic compounds in inert solvents, I^+ gets inserted DA18C6 cavity and is stabilized by the macrocyclic effect [6,7,12], it is contended that DA18C6 produces strong driving force for the formation of I^+ and promotes this reaction.
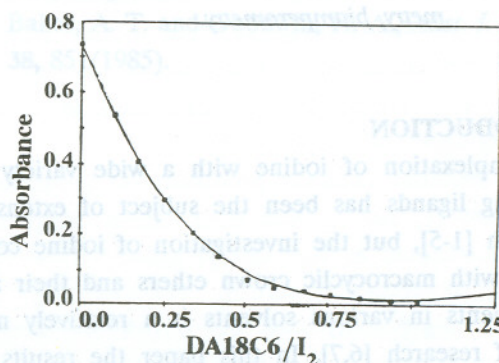

Fig. 2: Plot of absorbance vs. DA18C6/I_2 mole ratio in acetonitrile for a 2.91×10^{-2} mM iodine obtained at 364 nm and 25°C.

Equation (2) is further supported by conductance vs. DA18C6/I_2 mole ratio plot (Fig. 3). As is seen, by addition of DA18C6, the conductance increases as a result of the conversion of one mole of I_3^- to two moles of I⁻ it is interesting that conductometric plot
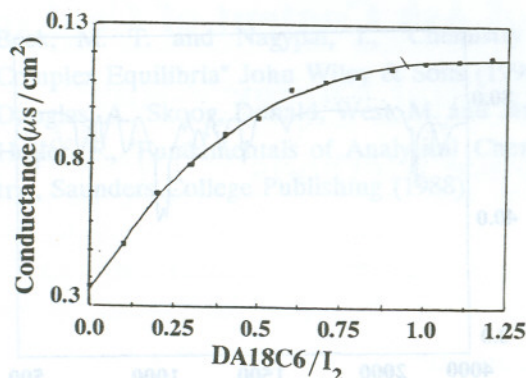
Fig. 3: Plot of conductance vs. DA18C6/I$_2$ mole ratio in acetonitrile for a 1.77$\times 10^{-1}$ mM iodine obtained at 25°C

in accordance with spectrophotometric plot, showing the formation of a complex with 1:2 (DA18C6 : I$_2$) stoichiometry.

The formation constant, K$_f$, in equation (2) evaluated from the absorbance-mole ratio data and using a non-linear least squares curve fitting program "KINFIT" [12]. The program is based on the interactive adjustment of the calculated values of absorbance to the observed values by either the *Wentworth* matrix technique [13] or the *Powell* procedure [14]. Adjustable parameters are K$_f$ and ε, where ε is the molar absorptivity of triiodide ion. The observed absorbance of a solution at the λ_{max} of triiodide is given by

$$A_{obs} = \varepsilon\, b[(CH_3CN)_n\, I^+.I_3^-] = \varepsilon\, b[I_3^-] \quad (3)$$

The mass balance equation can be written as

$$C_I = 2[(CH_3CN)_n I^+.I_3^-] + [DA18C6\ I^+.I^-] + [(CH_3CN)_n I^+.I^-] \quad (4)$$

$$C_{DA18C6} = [DA18C6] + [DA18C6\ I^+.I^-] \quad (5)$$

$$[DA18C6\ I^+.I^-] = [(CH_3CN)_n\ I^+.I^-] \quad (6)$$

The formation constant of the complex is equal to

$$K_f = \frac{[DA18C6\ I^+.I^-][(CH_3CN)_n I^+.I^-]}{[DA18C6][(CH_3CN)_n I^+.I_3^-]}$$

$$= \frac{[DA18C6\ I^+.I^-][(CH_3CN)_n I^+.I^-]}{[DA18C6\ I][I_3^-]} \quad (7)$$

Substitution of Eqs. (4), (5) and (6) into Eq. (7) and subsequent rearrangement yields

$$(K_f - 1)[I_3^-]^2 + (K_f C_{DA18C6} - \tfrac{1}{2}K_f C_I + C_I)[I_3^-] - \tfrac{1}{4}C_I^2 = 0 \quad (8)$$

The triiodide concentrations , [I$_3^-$] were calculated from equation (8) by means of a *Newton-Raphson* procedure. Once the value of [I$_3^-$] 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.

The resulting computer fit of the absorbance-mole ratio is shown in Fig. 4. The good agreement between the observed and the calculated absorbance further support the Eq. (2). The Log K$_f$ value obtained by this procedure is 5.16 $\pm$ 0.02, while the value obtained by classic method is 4.93+0.11 [15], the high value of formation constant is indicative of strong interaction between I$_3^-$ and DA18C6 and shows high tendency of I$^+$ for location in DA18C6 cavity.
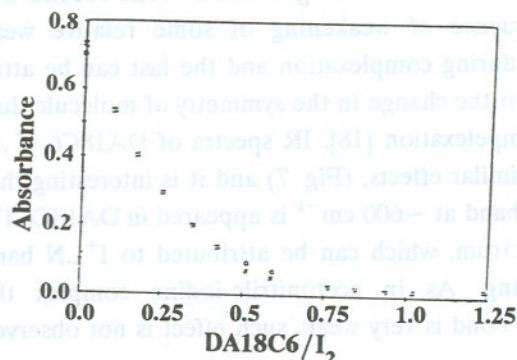

Fig. 4: Computer fit of the plot of absorbance vs. DA18C6/I$_2$ mole ratio obtained at 364 nm and 25°C: (×) experimental points; (O) calculated points; (=) experimental and calculated points are the same within the resolution of plot.

Fig. 5 shows the biamperometric titration curve of iodine with DA18C6 in acetonitrile solution, the curve proves that I$^-$ and I$_2$ act as a reversible couple in acetonitrile medium and has the form of titrations in which analyte is reduced and the reagent is not [16]. Biamperometric plot similar to spectrophoto-metric and conductometric mole ratio plots supports
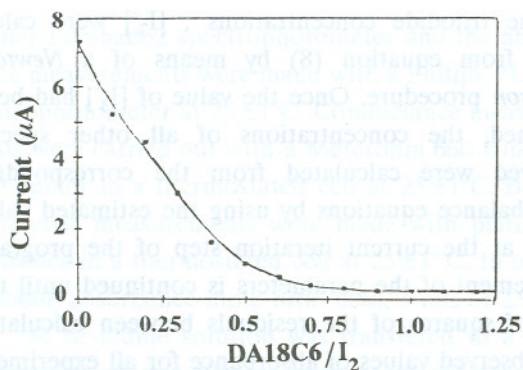
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Fig. 5: Plot of current vs. DA18C6/I_2 in acetonitrile for a 2.25×10^{-2} mM iodine obtained at 25°C (ΔE = 250 mV)

the 1:2 stoichiometry and accuracy of Eq. (2).

The IR spectra of acetonitrile and acetonitrilie - I_2 complex are compared in Fig. 6. It can be seen that: 1) CN stretching frequency has been shifted to higher values, 2) other bands have been shifted to lower frequencies, and 3) the intensity of the bands have been changed. These effects have been observed previously for some other charge transfer complexes [17]. The first effect is a result of electrostatic attraction between nitrogen and I^+ .The second is a consequence of weakening of some relative weak bonds during complexation and the last can be attri- buted to the change in the symmetry of molecule dur- ing compelexation [18]. IR spectra of DA18C6 I^+ .I^- show similar effects, (Fig. 7) and it is interesting that a new band at ~600 cm^{-1} is appeared in DA18C6 I^+ . I^- spectrum, which can be attributed to I^+...N band stretching. As in acetonitrile-iodine complex the similar bond is very weak, such effect is not observed
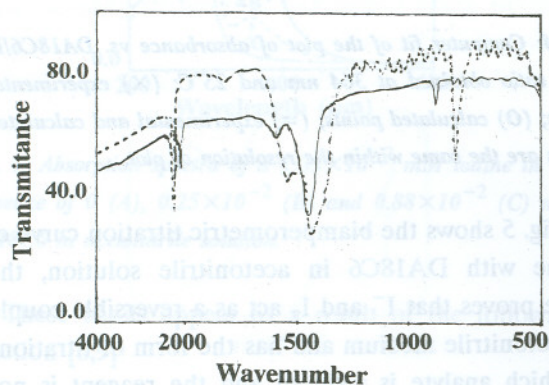
Fig. 6: IR spectra of acetonintrile (-) and acetonitrile-I_2 comlex (...)
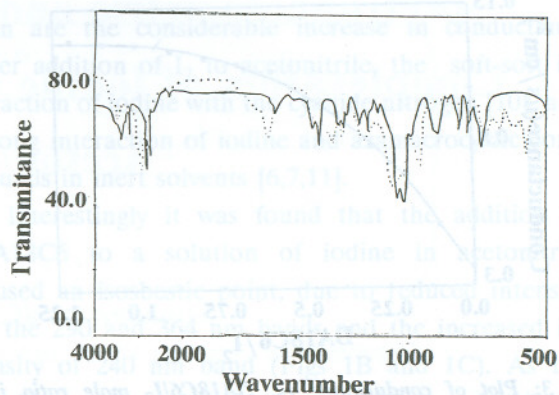
Fig. 7: IR spectra of DA18C6 (-) and DA18C6-I_2 complex (...)

for this system [17,18].

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