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SPECTROPHOTOMETRIC STUDY OF THE THERMODYNAMICS AND KINETICS OF CHARGE-TRANSFER COMPLEXATION OF DIBENZO-18-CROWN-6 WITH IODINE IN CHLOROFORM SOLUTION

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Abstract

The charge-transfer complexation reaction between iodine and dibenzo-18-crown-6 (DB18C6) has been studied spectrophotometrically in chloroform solution at different temperatures. The resulting donor-acceptor complex was formulated as (DB18C6...I^+)I_3^-. The spectrophotometric results, as well as the conductivity measurements, indicated 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 constants at various temperatures and the activation parameters E_a, $\Delta H^‡$ and $\Delta S^‡$ were calculated. The enthalpy and entropy of the complex formation reaction were evaluated from the temperature dependence of the formation constant. It was found that the resulting charge-transfer complex is both enthalpy and entropy stabilized.

Introduction

The formation of charge-transfer complexes (electron-donor-acceptor complexes, EDA) between two neutral molecules involves the transfer of an electron from the highest occupied molecular orbital (HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) of the acceptor. The first theoretical description of such molecular complexes was introduced by Mulliken [1,2]. During the past few decades, the charge-transfer complexation of iodine with a wide variety of donor molecules has been the subject of extensive research [2-8]. Some of these complexes possess very interesting physical properties such as electrical conductivity [5-8].

Macrocyclic polyethers (crowns), first synthesized by Pedersen [9], exhibit remarkable complexing properties toward metal ions of ionic size suitable for fitting inside their cavities. Thus, there has been intensive research on the thermodynamics and kinetics of complexation of these ligands with various cations in a wide variety of solvent systems [10-13]. However, less attention has been paid to molecular complexes of crown ethers with neutral molecules. Recently, increasing interest has been focused on such molecular complexes due to their possible applications in areas such as separation processes, biomimetic receptors and catalysis of chemical reactions [14].

Keywords: DB18C6-iodine complex; Rate constant; Spectrophotometry; Stability; Stoichiometry

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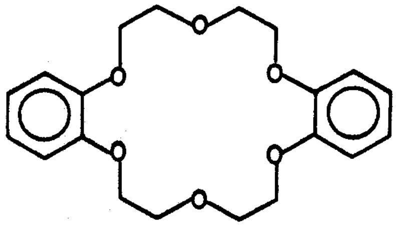

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In recent years, we have been involved in the spectroscopic investigation of molecular complexes of crown ethers with some neutral molecules [15-20]. In this paper, we report the results of a spectrophotometric investigation of the thermodynamics and kinetics of complex formation of iodine with dibenzo-18-crown-6 (DB18C6, I) in chloroform solution.

Experimental Section

The macrocycle DB18C6 (Merck) was recrystallized from reagent grade *n*-heptane and dried under vacuum over P_2O_5. Reagent grade iodine and chloroform (both from Merck) were used without further purification.

All electronic absorption spectra were recorded on a Perkin-Elmer Lambda 15 spectrophotometer and the absorbance measurements were made with a Metrohm 662 probe-type photometer at various temperatures (±0.5°C). Conductance measurements were carried out with a Metrohm 712 Conductivity meter. Specific details are given in the Results and Discussion section.

Results and Discussion

The electronic absorption spectra of I_2, DB18C6 and their mixture in chloroform solution, as well as the spectra of iodine in the presence of the crown ether of varying concentration are given in Figures 1 and 2, respectively. The existence of new bands at 295 and 363 nm of the electronic spectrum of the mixture of I_2 and DB18C6 in chloroform must be associated with a charge-transfer complex, since neither iodine nor the crown ether absorbs significantly in this spectral region. It is well known that the 295 and 363 nm bands are characteristic for the formation of triiodide ion, I_3^-, in the process of complex formation between iodine and different donor molecules [16-18, 20-23]. The observed increase in the specific conductance of iodine from 0.092 to 1.985 µS cm^{-1}, (at 25°C), brought about upon complex formation with the crown ether, further supports the formation of triiodide ion in solution. Moreover, the existence of a well-defined isosbestic point at 495 nm in the spectra of iodine upon titration with DB18C6 (Fig. 2) is further evidence for a simple complexation equilibrium in solution.

The release of triiodide ion into the chloroform solution was found to be a relatively slow process. The time dependence of the absorption spectrum of a mixture of DB18C6-I_2 (20:1) is depicted in Figure 3. The variation of the specific conductance of the mixture with time is also included. It is interesting to note that both absorbance and conductance signals show a uniform pseudo-first-order kinetics for the charge-transfer complexation process. The corresponding ln (absorbance) vs time and ln (conductance) vs time plots are rectilinear in the time period studied.

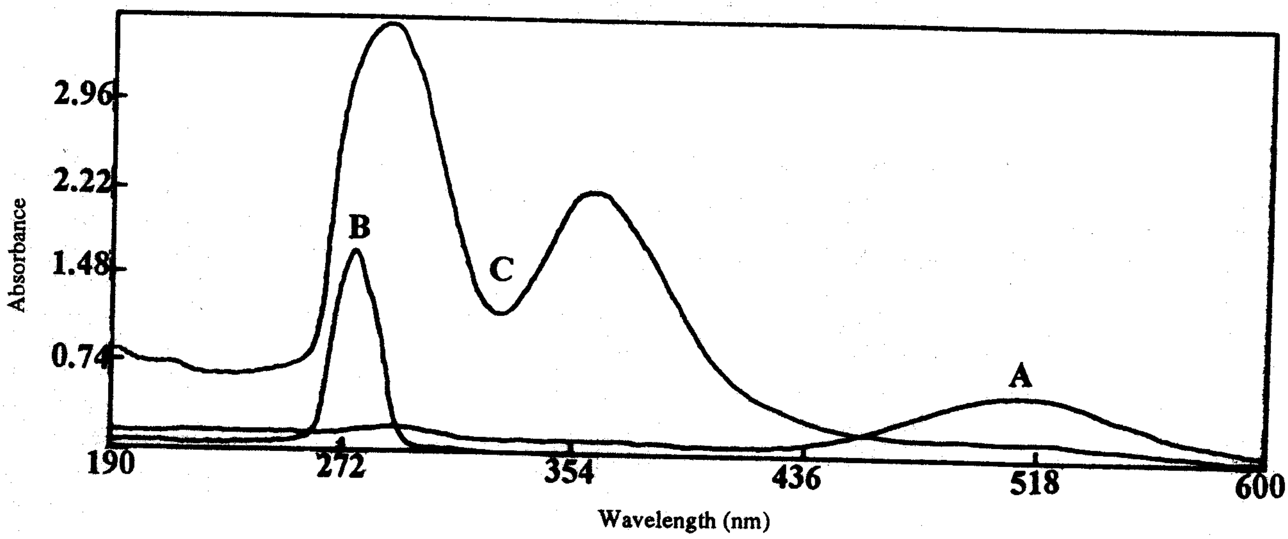

Figure 1. Absorption spectra of iodine (A, 6.1×10^{-4} M), DB18C6 (B, 2.6×10^{-4} M) and their complex (C, 4.1×10^{-3} M) in chloroform

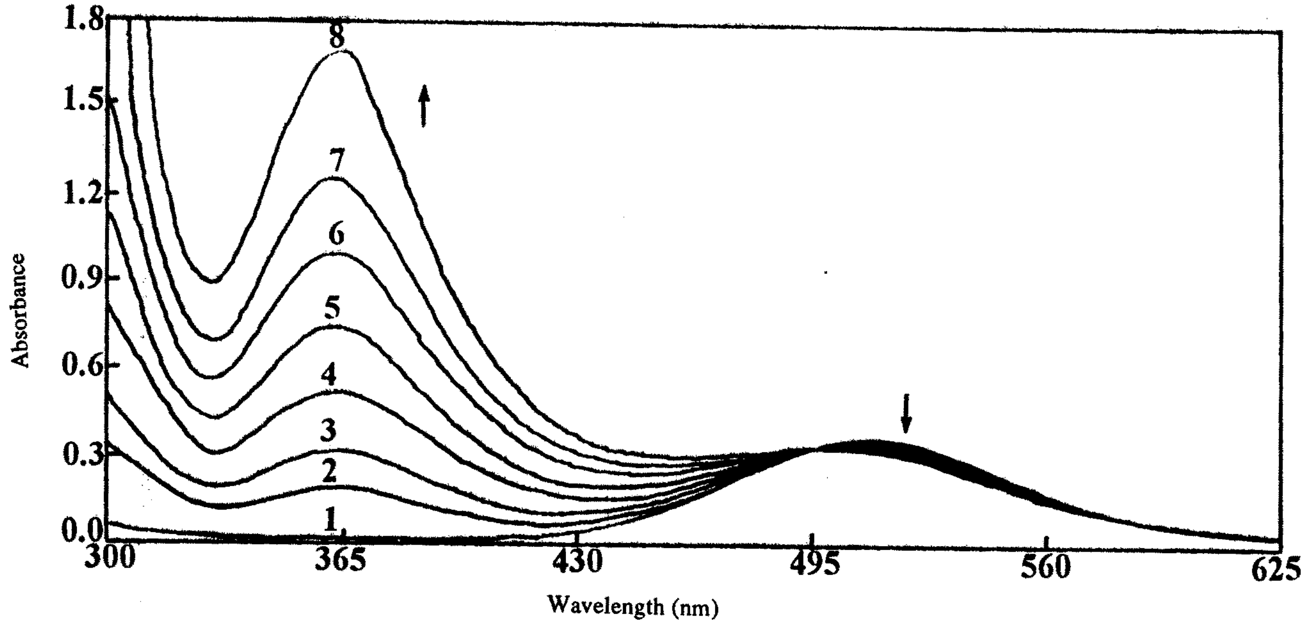

Figure 2. Absorption spectra of 4.0×10^{-4} M iodine in chloroform in the presence of varying concentrations of DB18C6: 1, 0.0 M; 2, 4.62×10^{-4} M; 3, 1.02×10^{-3} M; 4, 1.48×10^{-3} M; 5, 2.03×10^{-3} M; 6, 2.68×10^{-3} M; 7, 3.24×10^{-3} M; 8, 3.80×10^{-3} M

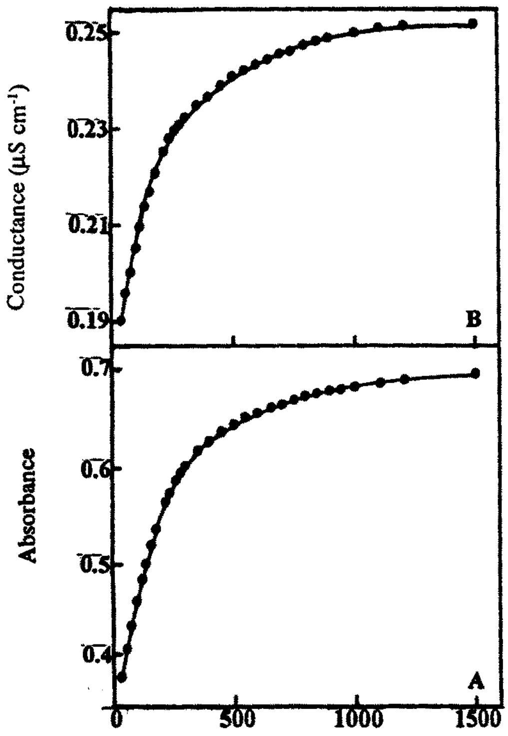

Figure 3. Absorbance vs time (A) and specific conductance vs time (B) plots at 15°C for a 2.60×10^{-4} M iodine solution in chloroform in the presence of excess DB18C6 at $[DB18C6]/[I_2] = 20$

Based on the above-mentioned spectral and conductance behaviors, as well as the previously reported evidence [15-17, 24], it can be reasonably assumed that the formation of triiodide may occur in two steps. The first step involves the formation of a molecular complex in the form of $(DB18C6...I^+)I_3^-$, in which the I_3^- ion exists as a contact ion paired anion, i.e.

$$DB18C6 + 2I_2 \rightleftharpoons (DB18C6...I^+)I^-_3 \qquad (1)$$

Evidence for the formation of such a molecular complex has already been reported [25, 26]. 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 (or solvent separated) triiodide ion into the solution, as

$$(DB18C6 ... I^+)I_3^- \rightarrow (DB18C6...I^+) + I_3^- \qquad (2)$$

The resulting free (or solvent separated) triiodide thus formed has two absorption maxima, one at 295 and the other at 363 nm.

In order to evaluate the thermodynamic stability of the resulting charge-transfer complex, the absorbance measurements were made at $\lambda = 510$ nm at five different temperatures, of a series of chloroform solutions containing a fixed amount of iodine (2.60×10^{-4} M) with a varying excess concentration of DB18C6 (i.e. $[DB18C6]/[I_2] \geq$

10). It should be noted that only I_2 absorbs light at 510 nm and that the resulting charge-transfer complex has a negligible absorbance at this wavelength. The resulting data were fitted to an easily derived equation [27] which relates the ratio of A_0/A to $[\mathrm{DB18C6}]_0$, where A_0 and A are the absorbances of the iodine solution without and with the presence of the ligand, respectively, and $[\mathrm{DB18C6}]_0$ is the analytical concentration of the ligand added:

$$\frac{A_0}{A} = 1 + K_f[\mathrm{DB18C6}]_0 \qquad (3)$$

According to Equation (3), a plot of A_0/A vs. [DB18C6] will result in a straight line with an intercept of unity and a slope of K_f. The resulting plots at various temperatures are shown in Figure 4 and the corresponding formation constants for the I_2-DB18C6 complex are listed in Table 1.

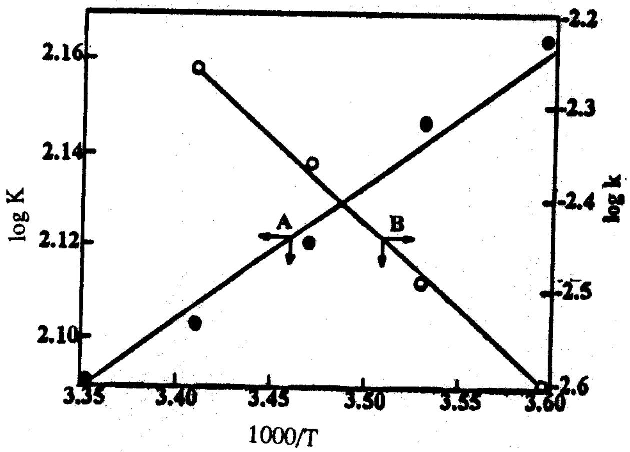

Figure 5. Van't Hoff plot (A) and Arrhenius plot (B) for DB18C6-I_2 complex in chloroform

Plot of log K_f vs. 1/T was linear (see Figure 5); the enthalpy and entropy of the charge-transfer complexation were determined from the slope and intercept of the plot, respectively. The results are also included in Table 1. As is obvious, the resulting complex is both enthalpy and entropy stabilized. Positive ΔS^0 may reveal the stronger solute-solvent interaction of the initial reactants with the low polarity solvent such as chloroform, as compared with that of the resulting polar complex with the solvent molecules. The much lower solubility of the resulting complex than that of iodine and the crown ether in chloroform supports this conclusion.

It is interesting to note that the formation constants obtained in this work for I_2-DB18C6 system are much

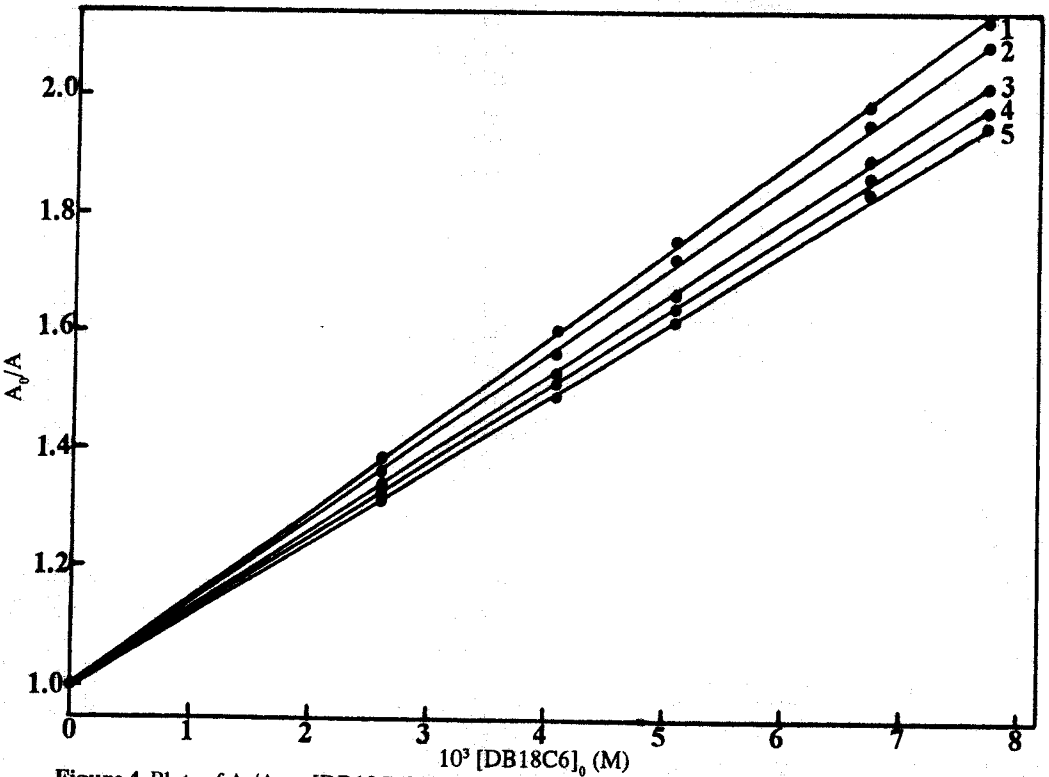

Figure 4. Plots of A_0/A vs. $[\mathrm{DB18C6}]_0$ for a 2.60×10^{-4} M iodine solution in chloroform in the presence of varying concentrations of DB18C6 at different temperatures: 1, 5°C; 2, 10°C; 3, 15°C; 4, 20°C; 5, 25°C

Table 1. Thermodynamic data for the formation of DB18C6-I_2 charge-transfer complex

Temperature (°C)	K_f
5	146.3±0.8
10	140.6±0.4
15	131.6±0.3
20	126.6±0.4
25	123.5±0.5
	$\Delta H° = -6.2 \pm 0.3$ kJ mol^{-1} $\Delta S° = 19 \pm 1$ J mol^{-1} K^{-1}

Table 2. Rate constants at various temperatures and activation parameters for DB18C6-I_2 system in chloroform

Temperature (°C)	$10^3 k (s^{-1})$	
	Spectrophotometry	Conductometry
5	2.50±0.09	2.28±0.13
10	3.25±0.07	3.38±0.13
15	4.37±0.12	4.33±0.11
20	5.42±0.06	5.27±0.10
	$E_a = 35.5 \pm 0.9$ kJ mol^{-1} $\Delta H^{\ddagger} = 33.1 \pm 0.9$ kJ mol^{-1} $\Delta S^{\ddagger} = -175 \pm 3$ J mol^{-1}K^{-1}	

larger than those we [18] and others [21, 28] reported for I_2-18C6 complex. This is most probably due to the increased rigidity of DB18C6, which provides a much better situation for the charge-transfer process, as well as the possible contribution of the benzyl groups in the complex formation with the electron acceptor [15, 29].

In order to investigate the kinetics of triiodide formation, the absorbance (at λ = 405 nm) and the conductivity of a 2.60×10^{-4} M iodine solution in chloroform in the presence of a 20-fold excess of DB18C6 were monitored with time simultaneously, at four different temperatures. This was done by proper interfacing of the instruments to a personal computer. Samples of the resulting absorbance-time and conductivity-time plots at 15°C are shown in Figure 3. As was mentioned earlier, the absorbance and conductivity changes were found to be in accord with a pseudo-first-order kinetics. The rate constants were calculated by the Guggenheim method using the relationship $\ln (S_\infty - S_t) = -k(t - t_0) + \ln (S_\infty - S_0)$, where S is either absorbance or conductivity of solution. The resulting rate constants, obtained from the slopes of the corresponding linear $\ln (S_\infty - S_t)$ vs. $(t - t_0)$ plots, are summarized in Table 2. It is interesting to note that the k values obtained by both absorbance and conductivity measurements are actually the same, within the range of the experimental errors. This supports the two-steps mechanism for the formation of triiodide ion proposed earlier.

Using the corresponding Arrhenius plot (Fig. 5B) and the Eyring transition-state theory [30], the activation parameters E_a, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated. The results are also included in Table 2. The positive enthalpy of activation in going from the contact ion paired form of triiodide ion to its free form (Equation 2) reflects a weaker structure, a poorer overlap and a sloppy geometry for the transition state when it is compared with the initial $(DB18C6...I^+)I_3^-$, while the negative entropy of activation could be due to the penetration of some solvent molecules between the positively-charged species and the triiodide ion to form a kind of solvent separated ion pair, in order to facilitate the release of I_3^- into the solution. Consequently, the more ordered form of the solvent molecules in the transition state results in a large negative $\Delta S^{\ddagger}$ value. Considering the above-mentioned experimental evidence, it seems reasonable to propose the following scheme for the gradual release of triiodide ion from its contact ion paired complex form:

$$(DB18C6...I^+)I_3^- \rightarrow [DB18C6...I^+(CHCl_3)_n I_3^-]^{\ddagger} \rightarrow DB18C6...I^+ + I_3^- \quad (4)$$

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