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Interaction of Iodine with Aza-18-crown-6 and Aza-12-crown-4. Kinetic and Spectrophotometric Studies in Chloroform and 1,2-Dichloroethane Solutions

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Interactions of 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (aza-18-crown-6) and 1,4,7-trioxa-10-azacyclododecane (aza-12-crown-4) with iodine have been investigated spectrophotometrically in chloroform and 1,2-dichloroethane solutions. The observed time dependence of the charge-transfer band and subsequent formation of I_3^- in solution were related to the slow transformation of the initially formed 1 : 1 macrocycle·I_2 outer complex to an inner electron donor–acceptor (EDA) complex, followed by fast reaction of the inner complex with iodine to form a triiodide ion, as follows:

$$\text{macrocycle} + I_2 \xrightarrow[\text{fast}]{K_f} \text{macrocycle}\cdot I_2 \text{ (outer complex)},$$
$$\text{macrocycle}\cdot I_2 \text{ (outer complex)} \xrightarrow{\text{slow}} (\text{macrocycle}\cdot I^+)I^- \text{ (inner complex)},$$
$$(\text{macrocycle}\cdot I^+)I^- \text{ (inner complex)} + I_2 \xrightarrow{\text{fast}} (\text{macrocycle}\cdot I^+)I_3^- .$$

The pseudo-first-order rate constants at various temperatures for the transformation process were evaluated from the absorbance-time data. The activation parameters (E_a, $\Delta H^\ddagger$, and $\Delta S^\ddagger$) for the transformation were obtained from the temperature dependence of the rate constants. The stoichiometry and formation constants of the resulting EDA complexes have also been determined. The influences of both the azacrowns' structure and the solvent properties on the kinetics and stability of the resulting charge-transfer complexes are discussed.

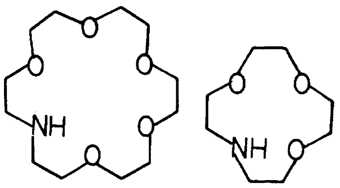
Among the most interesting developments in chemistry has been the synthesis of macrocyclic polyethers.[1,2] These comprise a large group of cyclic compounds which can bind metal ions by entrapment within an electron-rich cavity created by its inward-oriented donor atoms. The intense interest in the macrocyclic ligands centers on the extraordinary stability of their cation complexes and their peculiar ability to selectively bind certain cations in preference to others.[3—5] However, studies on neutral molecule-macrocycle interactions have been far fewer in number than those on cation-macrocycle complexes.[6] Interest in such molecular complexes has been strongly stimulated by the possibility of their applications in such broad areas as separation science, catalysis of chemical reactions, biomimetic receptors and the conversion of chemical reactions into electronic or optical signals.

Iodine has been found to form with a variety of donor charge-transfer complexes whose properties have been thoroughly studied.[7—10] More recently, increasing attention has been paid to the molecular complexes of iodine with macrocyclic crown ethers and their aza derivatives in various solvents.[11—21] The results of these studies have clearly revealed that the substitution of the donating oxygen atoms in a crown-ether ring by NH groups results in a drastic increase in the stability of the iodine complexes[14,15,17,18] over those of ordinary crowns.[11,13,19]

We have recently been involved in a spectroscopic study of the molecular complexes of some azacrown ethers[17,8,20,21] and ordinary crowns[19] in chloroform solution. In this paper we report on the results of kinetic and spectral studies concerning the interaction of I_2 with aza-18-crown-6 (A18C6) and aza-12-crown-4 (A12C4) in chloroform and 1,2-dichloroethane solutions. The structures of the crown ethers used are shown in Fig. 1.

Experimental

The macrocycles A18C6 and A12C4 (both from Fluka) were of the highest purity available and were used without any further purification, except for vacuum drying. Resublimed iodine of analytical grade (Merck) was used as received. Reagent-grade chloroform and 1,2-dichloroethane (both from Fulka) were used without any



A18C6 **A12C4**

Fig. 1. Structure of azacrown ethers.

further purification.

All UV/vis spectra were recorded on a Philips PUB 700 spectrophotometer and absorbance measurements were made with a Philips PU 875 spectrophotometer equipped with a temperature-controlled cell holder. Conductance measurements were carried out with a Metrohm 660 conductivity meter. A dip-type cell made of platinum black with a cell constant of 0.830 cm^{-1} was used. In all experiments, the temperature was kept constant at the desired temperature of ±0.05 °C using a Lo-Temprol 154 thermostat. Specific details are given in the Results and Discussion section.

Results and Discussion

The electronic absorption spectra of mixtures of azacrowns with an excess amount of iodine (i.e. I_2 to crown molar ratio of 10) were recorded as a function of time at various temperatures. Sample spectra for the I_2–A18C6 system in chloroform at 25 °C are shown in Fig. 2. In all cases, the spectrum obtained immediately after mixing iodine with the azacrown ethers resulted in two strong absorptions in the 250—450 nm region, where none of the initial reactions absorb measurably. The first absorption located at 265 nm is presumably a charge-transfer band and the second at 364 nm is the blue-shifted iodine band.[22]

However, as can be seen from Fig. 2, the intensity of the charge-transfer band decreased markedly with the elapse of time, while an intensification of a new band at 293 nm and the band at 364 nm is observed. This latter spectrum resembles that of a 1 : 1 mixture of tetrabutylammonium iodide and iodine in chloroform. It should be noted that the bands at 293 and 364 nm are characteristic for the formation of triiodide ion, I_3^-, in the process of complex formation between iodine and different electron-pair donor ligands.[8,14,15,17—21,23—25] The observed time dependence of the charge-transfer band and the subsequent formation of the I_3^- ion in solution are most probably due to a transformation of the initially formed 1 : 1 macrocycle·I_2 outer complex to an inner EDA complex followed by a fast reaction of the resulting inner complex with iodine to from a triiodide ion:[26,27]

$$\text{macrocycle} + I_2 \xrightarrow[K_f]{\text{fast}} \text{macrocycle}\cdot I_2 \text{ (outer complex)}, \tag{1}$$

$$\text{macrocycle}\cdot I_2 \text{ (outer complex)} \xrightarrow{\text{slow}} (\text{macrocycle}\cdot I^+)I^- \text{ (inner complex)}, \tag{2}$$

$$(\text{macrocycle}\cdot I^+)I^- \text{ (inner complex)} + I_2 \xrightarrow{\text{fast}} (\text{macrocycle}\cdot I^+)I_3^-. \tag{3}$$

The formation and isolation of such a stable (macrocycle·I^+)-I_3^- adduct have been frequently reported in the literature.[11—21]

In order to obtain further information about the kinetics and mechanism of the interaction of iodine with A18C6 and A12C4, the absorbance at 364 nm was monitored as a function of time in solutions of chloroform and 1,2-dichloroethane containing reactants at an iodine-to-macrocycle mole ratios of 20 : 1 at various temperatures. This was done by proper interfacing of the instrument to a personal computer. Sample absorbance-time plots for the A12C4–I_2 system in 1,2-dichloroethane at different temperatures are shown in Fig. 3. It is interesting to note that the conductivity-time plots show patterns similar to those observed in Fig. 3. For example, in the case of A12C4–I_2 in 1,2-dichloroethane at 25 °C, the production of I_3^- ions caused a rather sharp increase in the solution conductivity for about 60 min (see Fig. 4), further supporting the free triiodide ion in solution. The transformation of the outer complexes into the corresponding inner complexes was found to follow a pseudo-first-order kinetics.

All of the resulting rate constants at various temperatures are summarized in Table 1. Using the corresponding Arrhenius plots (Fig. 5) and the Eyring transition-state theory,[28] the activation parameters (E_a, $\Delta H^\ddagger$, and $\Delta S^\ddagger$) were calculated. The results are also included in Table 1. The data given in Table 1 indicate that, in both solvents used, the pseudo-first-order rate constants increase with increasing

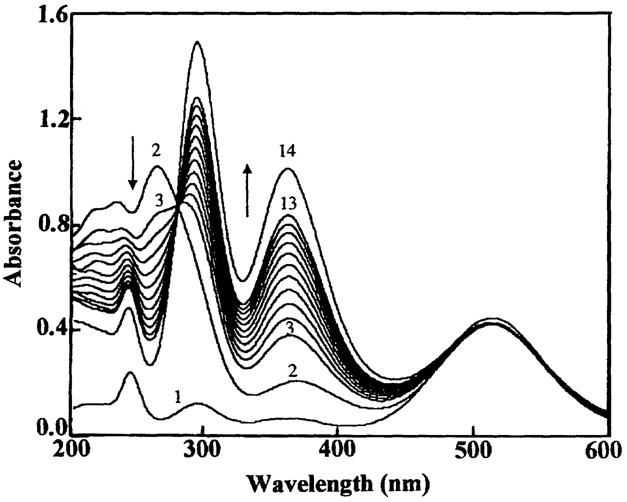


Fig. 2. UV-vis spectra of a mixture of I_2 (5.0×10^{-3} $\mathrm{mol\,dm^{-3}}$) and A18C6 (5.0×10^{-4} $\mathrm{mol\,dm^{-3}}$) in chloroform at 25 °C: 1, I_2 alone; 2, immediately after mixing; time intervals: 3, 20 min; 4, 40 min; 5, 60 min; 6, 80 min; 7, 100 min; 8, 120 min; 9, 140 min; 10, 160 min; 11, 180 min; 12, 200 min; 13, 220 min; 14, 870 min.

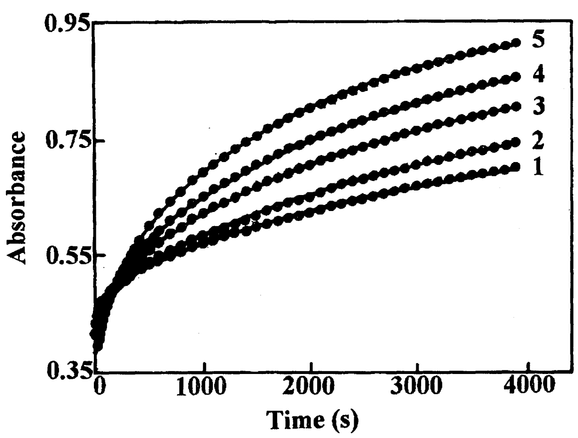


Fig. 3. Absorbance-time plots at 364 nm for a mixture of I_2 (1.5×10^{-3} $\mathrm{mol\,dm^{-3}}$) and A12C4 (7.5×10^{-5} $\mathrm{mol\,dm^{-3}}$) in 1,2-dichloroethane solution at different temperatures: 1, 25 °C; 2, 30 °C; 3, 35 °C; 4, 40 °C; 5, 45 °C.

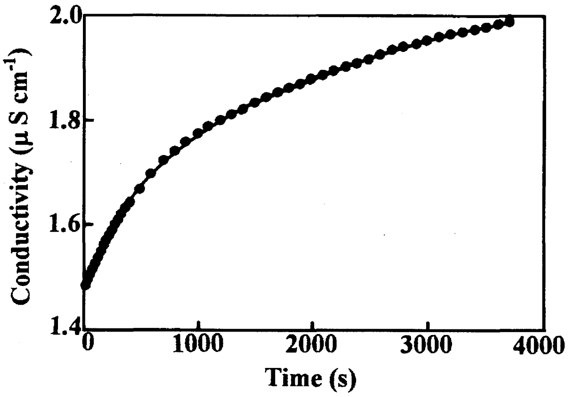


Fig. 4. Conductivity (μS cm^{-1})–time plot for a mixture of I_2 (1.5×10^{-3} mol dm^{-3}) and A12C4 (7.5×10^{-5} mol dm^{-3}) in 1,2-dichloroethane solution at 25 °C.

temperature, the influence of temperature on the A12C4–I_2 system being more pronounced than that of the A18C6–I_2 complex. The much faster transformation of A18C6·I_2 in comparison with the A12C4·I_2 complex could be related to the increased stability of the latter complex over the former one, as will be discussed later. It is noteworthy that the *k* values obtained by the spectrophotometric and conductometric methods at 25 °C for the A12C4–I_2 system in 1,2-dichloroethane are in satisfactory agreement.

Table 1 shows that the entropies of activation for the transformation of the outer complexes into the corresponding inner complexes are high and negative. The negative $\Delta S^{\ddagger}$ values are indeed what one should expect in reactions involving the ionization of neutral molecules.[29] Since the transformation involves ionization, the activated complex may be an ion pair, stabilized by solvation to a greater extent than the initial outer complex. Consequently, the more ordered form of the solvent molecules in the transition state results in a large negative $\Delta S^{\ddagger}$ value. On the other hand, the positive enthalpy of activation in going from the molecular outer complex to the ionized inner complex reflects a weaker structure, a poorer overlap, and a sloppy geometry for the transition state when it is compared with the initial macrocycle·I_2 complex.

Form the data given in Table 1 it is immediately obvious that, in the case of both macrocycles used, and at all temperatures studied, the *k* values obtained in 1,2-dichloroethane are much larger than those in chloroform solution. There is actually a considerable decrease in the energy of activation along with an increased dielectric constant of the medium; in a more polar solvent, like 1,2-dichloroethane ($\varepsilon = 10.4$), the transformation (2) proceeds much faster than that in chloroform with $\varepsilon = 4.8$. This is in support of the proposed three-step mechanism. In fact, the resulting charged transition states in going from the outer complexes to the inner ones (as the rate determining step of the mechanism) are expected to be more stabilized in 1,2-dichloroethane because of its higher solvating ability and relative permittivity than chloroform.[30]

The stoichiometry of the resulting charge-transfer complexes between A18C6 and A12C4 and iodine were ex-

Table 1. Calculated Rate Constants at Various Temperatures and Activation Parameters for A18C6–I_2 and A12C4–I_2 Systems in Chloroform and 1,2-Dichloroethane Solutions

Macrocycle	Solvent	Temp	k_1	E_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
		°C	s^{-1}	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
A18C6	Chloroform	25	$(9.12\pm0.13)\times10^{-5}$			
		30	$(1.22\pm0.01)\times10^{-4}$			
		35	$(1.54\pm0.02)\times10^{-4}$			
		40	$(2.14\pm0.01)\times10^{-4}$			
		45	$(2.80\pm0.02)\times10^{-4}$	44±1	41±1	−483±5
	1,2-Dichloroethane	15	$(4.16\pm0.32)\times10^{-4}$			
		25	$(7.53\pm0.57)\times10^{-4}$			
		35	$(9.63\pm0.36)\times10^{-4}$			
		45	$(1.66\pm0.06)\times10^{-4}$	33±5	31±3	−201±12
A12C4	Chloroform	25	$(5.70\pm0.10)\times10^{-6}$			
		30	$(7.58\pm0.05)\times10^{-6}$			
		35	$(1.12\pm0.02)\times10^{-5}$			
		40	$(1.86\pm0.01)\times10^{-5}$			
		45	$(2.49\pm0.02)\times10^{-5}$	65±3	61±4	−142±13
	1,2-Dichloroehtane	25	$(1.83\pm0.04)\times10^{-4}$			
		25$^{a)}$	$(2.00\pm0.05)\times10^{-4}$			
		30	$(2.55\pm0.05)\times10^{-4}$			
		35	$(3.77\pm0.08)\times10^{-4}$			
		40	$(5.18\pm0.14)\times10^{-4}$			
		45	$(7.72\pm0.30)\times10^{-4}$	56±2	54±2	−136±5

a) Evaluated from conductance-time data.

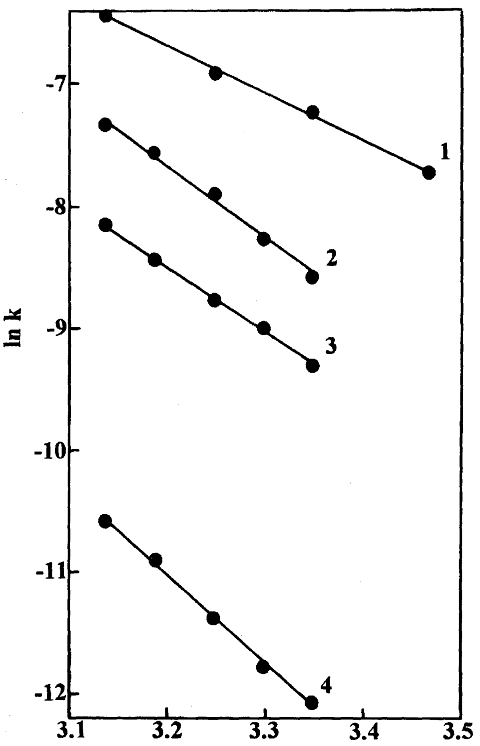


Fig. 5. Arrhenius plots of ln k vs. $1/T$ for different macrocycle–I_2–solvent systems studied: 1, A18C6–I_2–1, 2-dichloroethane; 2, A12C4–I_2–1, 2-dichloroethane; 3, A18C6–I_2–chloroform; 4, A12C4–I_2–chloroform.

amined by the method of continuous variations.[31] Plots of absorbance vs. mole fraction of macrocycles, $X_{\mathrm{macrocycle}}$, for all cases studied are shown in Fig. 6. As can be seen, all continuous variations plots exhibited a maximum at a $X_{\mathrm{macrocycle}}$ value of 0.5, indicating the formation of 1 : 1 charge-transfer complexes in solution.

It is noteworthy that the energy of the blue-shifted band of iodine provides a good measure of the donor–acceptor interaction, as pointed out by Mulliken.[32] Since the blue shift of the I_2 band arises from an increased separation of the σ and σ^* orbitals that occurs during the transfer of charge from the donor to the σ^* orbital of I_2, it is reasonable to expect the extent of the blue shift would be dependent on the amount of charge transferred to the iodine molecule. The blue shift observed for the I_2 molecule in the presence of cyclic amines A18C6 and A12C4 (from 510 to 364 nm) is much larger than that reported for the ordinary amine–I_2 systems.[27] Thus, due to the transfer of more charge from the cyclic amines to the iodine molecule, we expect to witness a largely increased stability of A18C6·I_2 and A12C4·I_2 complexes over ordinary amine·I_2 complexes.

In all cases studied, during the first few seconds after the addition of azacrown to the iodine solution, a rather sharp step-functional increase in the absorbance at 364 nm was observed, as was previously reported (Fig. 7).[33] This initial change in the absorbance (ΔA) upon the mixing of the azacrowns and I_2 was found to increase along with a rise in the azacrown/I_2 mole ratio to reach a constant value at a mole ratio of 1 : 1 (see Figs. 7 and 8). Such a dependence of ΔA on the azacrown/I_2 mole ratio indicates the formation of EDA complexes between the donors and the acceptor used. The corresponding formation constants can be evaluated from ΔA vs. azacrown/I_2 mole ratio as follows.

The macrocycles react with I_2 in solution to form 1 : 1 EDA complexes. The formation constant and the mass-balance equations are given as follows:

$$K_{\mathrm{f}} = [\text{macrocycle}\cdot \mathrm{I_2}]/[\text{macrocycle}][\mathrm{I_2}], \tag{4}$$

$$C_{\mathrm{macrocycle}} = [\text{macrocycle}] + [\text{macrocycle}\cdot \mathrm{I_2}], \tag{5}$$

$$C_{\mathrm{I}} = [\mathrm{I_2}] + [\text{macrocycle}\cdot \mathrm{I_2}], \tag{6}$$

substitution of Eqs. 5 and 6 into Eq. 4 and rearrangement yields,

$$K_{\mathrm{f}}[\mathrm{I_2}]^2 + [1 + K_{\mathrm{f}}(C_{\mathrm{macrocycle}} - C_{\mathrm{I}})][\mathrm{I_2}] - C_{\mathrm{I}} = 0. \tag{7}$$

The observed absorbance change of solution is given by

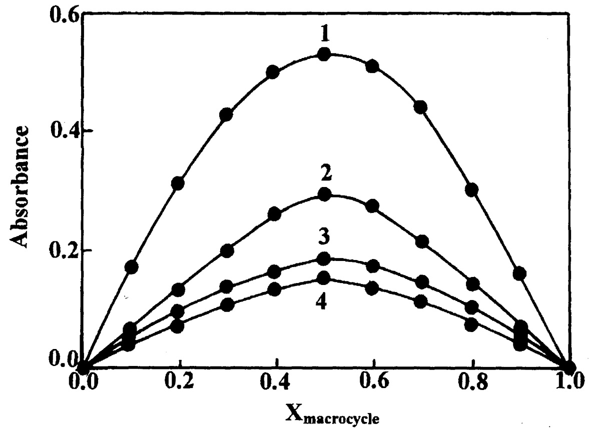


Fig. 6. Absorbance at 364 nm vs. mole fraction of macrocycle, $X_{\mathrm{macrocycle}}$, for different macrocycle–I_2–solvent systems: 1, A18C6–I_2–1,2-dichloroethane; 2, A12C4–I_2–1,2-dichloroethane; 3, A18C6–I_2–chloroform; 4, A12C4–I_2–chloroform.

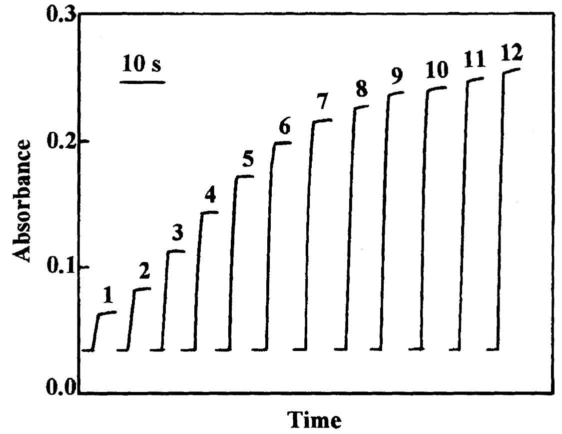


Fig. 7. ΔA vs. time plots at 364 nm for a 1.5×10^{-4} mol dm^{-3} solution of I_2 in chloroform in the presence of varying concentration of A12C4 at 25 °C. [A12C4]/[I_2] mole ratios are: 1, 0.12; 2, 0.25; 3, 0.37; 4, 0.50; 5, 0.74; 6, 0.98; 7, 1.22; 8, 1.46; 9, 1.70; 10, 1.94; 11, 2.40; 12, 2.98.

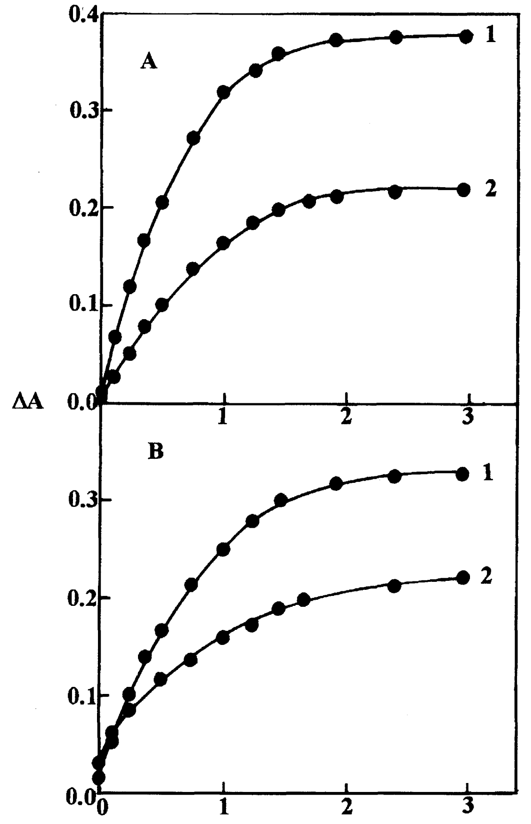


Fig. 8. ΔA vs. [macrocycle]/[I_2] plots for A12C4 (A) and A18C6 (B) in 1,2-dichloroethane (1) and chloroform (2) solutions. The initial concentration of I_2 is 1.5×10^{-4} mol dm^{-3}.

$$\Delta A = \varepsilon_{\text{macrocycle}\cdot I_2}[\text{macrocycle}\cdot I_2]. \tag{8}$$

To evaluate the formation constant from the ΔA vs. $C_{\text{macrocycle}}/C_I$ mole ratio data, a curve-fitting program KINFIT was used.[34] The free acceptor concentrations ([I_2]) were evaluated from Eq. 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 equation 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 the calculated and observed values of the absorbance change for all experimental points is minimized. The output of the KINFIT program comprises the refined parameters K_f and $\varepsilon_{\text{macrocycle}\cdot I_2}$, the sum-of-squares and standard deviation of the data.

A sample computer fit of the ΔA vs. macrocycle/I_2 data is shown in Fig. 9. As can be seen, the fair agreement between the observed and calculated absorbances further supports the existence of a 1 : 1 EDA complexation between the macrocycles and iodine in solution. The $\log K_f$ values obtained by this procedure are given in Table 2. It is seen that, in both solvents used, the K_f values for A12C4–I_2 are larger than those for the A18C6–I_2 system. Such observations could be related to a decreased flexibility of the A12C4 molecule as compared with A18C6. Molecular-mechanics calculations,[35,36] as well as the crystalline structure[37] and spectroscopic investigations,[38] performed on 12C4 and 18C6 molecules have shown that, in the most stable conformation, the heteroatoms of 12C4 are more readily available to the acceptor molecule for the process of charge-transfer, compared with 18C6. This would possibly facilitate the formation of the A12C4·I_2 complex. Moreover, while the I^+ ion having an ionic size of 1.66 Å[39] is too small for the cavity of A18C6 with a size of 2.6—3.2 Å,[40] it possesses a more suitable fitting condition inside the smaller cavity of A12C4 (cavity size = 1.2—1.5 Å).[40]

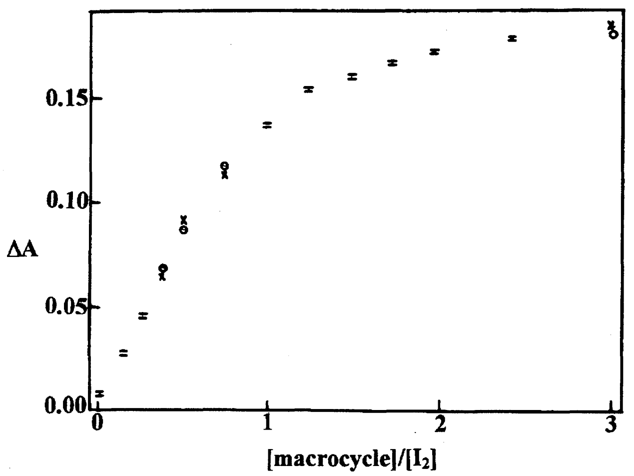


Fig. 9. Computer fit of ΔA vs. [A18C4]/[I_2] in chloroform solution at 25 °C: (×) experimental point; (○) calculated point; (=) experimental and calculated points are the same within the resolution of the plot. The initial concentration of I_2 is 1.5×10^{-4} mol dm^{-3}.

Table 2. Formation Constants of A18C6·I_2 and A12C4·I_2 EDA Complexes in Chloroform and 1,2-Dichloroethane Solutions at 25 °C

Complex	Chloroform		1,2-Dichloroethane	
	$\log K_f$	$\varepsilon_{\text{macrocycle}\cdot I_2}$	$\log K_f$	$\varepsilon_{\text{macrocycle}\cdot I_2}$
A18C6·I_2	4.25 ± 0.16	2290 ± 192	5.01 ± 0.15	5693 ± 183
A12C4·I_2	4.88 ± 0.06	1935 ± 29	5.22 ± 0.13	3240 ± 67

The data given in Table 2 revealed that, in the case of both macrocycles used, the stability of the resulting iodine complexes increases with increasing polarity of the solvent from chloroform to 1,2-dichloroethane. A similar solvent effect on the stability and charge-transition energies of different charge-transfer complexes has been reported in the literature.[41—43] It has been suggested that the observed trend in the stability of the charge-transfer complexes could be due to the high stabilization of the excited states in which the charge is probably more separated than in the ground states.

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