Interaction of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone with aza-18-crown-6 and aza-12-crown-4. Kinetic and spectrophotometric studies in chloroform and acetonitrile solutions

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Interactions of aza-18-crown-6 and aza-12-crown-4 with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) have been examined spectrophotometrically in chloroform and acetonitrile solutions. The results indicate immediate formation of an electron donor–acceptor complex, DA [reaction (a)], which is

$$D + A \underset{fast}{\overset{K_f}{\rightleftharpoons}} DA \qquad\qquad (a)$$

followed by two relatively slow consecutive reactions (b). Pseudo-first-order rate constants at various

$$DA \xrightarrow{k_1} [D^+A^-] \xrightarrow{k_2} Product \qquad\qquad (b)$$

temperatures for the formation of the ionic intermediate $[D^+A^-]$ and the final product have been evaluated by computer fitting of the absorbance–time data to appropriate equations. The formation constants of the resulting EDA complexes have also been determined. The influences of both the azacrowns' structure and the solvent properties on the formation of EDA complexes and the rates of subsequent reactions are discussed.

Since the first synthesis of macrocyclic polyethers (crowns),[1] these ligands have drawn considerable attention in both chemistry and biology mostly due to their selective complexation with different metal ions.[2–4] Recently, there has been an increasing interest in the study of the electron donor–acceptor (EDA) interactions between crown ethers and a variety of acceptor molecules.[5–16] Among the different macrocyclic ligands used for EDA complexation, aza-substituted crown ethers show very interesting features. It has been clearly shown that the substitution of the oxygen atoms in a crown ether ring by −NH− groups results in a drastic increase in the stability of their complexes with iodine[9,12–14] and 2,3-dichloro-5,6-dicyano-1,4-benzo-quinone (DDQ)[16] over those of ordinary crowns.[8,9,15]

The primary and secondary amines are known to form both mono- and di-substituted products with chloranil and DDQ.[17–24] The results have indicated the possible participation of π and σ (outer and inner) EDA complexes in the substitution reactions. A major part of the evidence for the participation of outer EDA complexes as intermediates in these reactions has been based on kinetic measurements. The large difference between the rate of disappearance of the acceptor or its amine π complex and the rate of product formation indicated the existence of such intermediates.[17,18] However, such studies on the interaction of π-acceptors and azacrown ethers are quite sparse. To the best of our knowledge, there is only one published report on the complexation of 1,10-diaza-18-crown-6 with DDQ in chloroform solution.[16]

We have recently been involved in the spectroscopic study of molecular complexes of ordinary and aza-substituted crown ethers with iodine[13–15] and some π-acceptor molecules.[12,16] In this paper we report the results of kinetic and spectral studies of interactions of DDQ with aza-18-crown-6 (A18C6) and aza-12-crown-4 (A12C4) in chloroform and acetonitrile solutions.

Experimental

The macrocycles A18C6 and A12C4 (both from Fluka) were recrystallized from reagent grade n-hexane and dried under vacuum. Reagent grade DDQ (Merck) was of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Spectroscopy grade chloroform and acetonitrile (both from Fluka) were used as received.

All UV–VIS spectra were recorded on a Philips PUB700 spectrophotometer and the absorbance measurements as a function of time, at fixed wavelengths, were made with a Philips PU875 spectrophotometer interfaced to a Shimadzu Chromatopac R3A at various temperatures. The conductance measurements were made with a Metrohm 660 conductivity meter. A dip-type conductivity cell, with platinised Pt electrodes, was used. Specific details are given in the Results and discussion section.

Results and discussion

The previously reported spectroscopic and conductometric studies on the interaction of chloranil and DDQ with anilines[17,21] and aliphatic amines[18,19] have provided valuable information towards the existence of an EDA complex in solution, which can act as an intermediate in the final substitution reaction. However, the corresponding rates of product formation are reported[17,18] to be quite fast at room temperature. In contrast, in the preliminary experiments carried out on the interaction of DDQ with A18C6 and A12C4, we noticed that the formation of the final products in chloroform and, especially, in acetonitrile proceeds very slowly.

Both azacrowns used upon mixing with DDQ instantaneously yield a deep red solution, the intensity of which increases within about 20 min at room temperature, and finally becomes yellow very slowly. The final yellow colour of the solution (λ 350 nm) suggests that the final reaction product is 2-chloro-5,6-dicyano-3-azacrowno-1,4-benzoquinone, as previously reported.[21] The IR spectra of the isolated reaction products contain the main bands for both reactants, except that the 3240 cm^{-1} ν_{NH} band of the azacrown ethers has disappeared
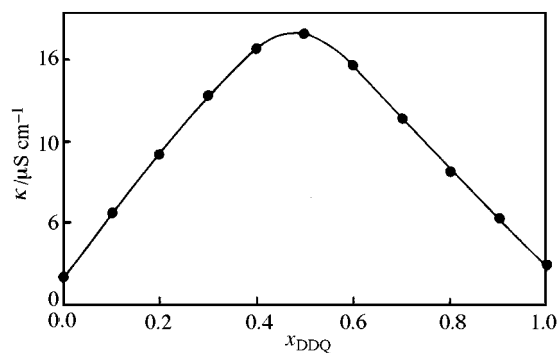
Fig. 1 Conductivity (κ) *vs.* mole fraction (x) of DDQ plot for the A18C6–DDQ system in acetonitrile

and the v_{CO} (1675 cm^{-1}) and v_{CN} (2230 cm^{-1}) stretchings of DDQ show a bathochromic shift to lower frequencies (*i.e.* 1555 and 2200 cm^{-1}, respectively). Such a shift could be indicative of a higher charge density on the carbonyl and cyano groups of the substituted DDQ molecule. Moreover, results of the elemental analysis of the final products agree well with their proposed structures.

On the other hand, the resulting azacrown–DDQ solutions in chloroform and, especially, acetonitrile exhibit appreciable conductivities which may be explained by the possible formation of an EDA complex between the reaction partners in solution.[19–21,25–27] In all cases studied, the conductivity–mole fraction plots yielded a maximum at an azacrown : DDQ molar ratio of 1 : 1. A sample plot is shown in Fig. 1. The increase in conductivity observed upon charge-transfer complex formation is explained by the possibility that the EDA complex formed between the donor, azacrown (D), and acceptor, DDQ (A), may undergo dissociation into an ionic intermediate in solvents of sufficiently high permittivity according to the mechanism shown in reactions (1) and (2).[20,27] The value by which the

$$D + A \rightleftharpoons DA \qquad (1)$$

$$DA \rightleftharpoons [D^+A^-] \qquad (2)$$
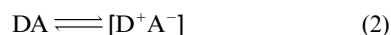
conductivity exceeds that of the base line connecting the conductivities of the pure azacrown and DDQ solutions is a measure of the excess conductivity caused by the formation and subsequent ionization of the EDA complex. As has been suggested, the inner σ complex thus formed may then act as an intermediate in the formation of final products.

In order to obtain further information about the kinetics and mechanism of the interaction of DDQ with A18C6 and A12C4, the electronic absorption spectra of DDQ (3.0×10^{-4} mol dm^{-3}) in the presence of a large excess of the crown ethers (*i.e.* [azacrown]/[DDQ] = 20) were obtained as a function of time in both chloroform and acetonitrile solution. Sample spectra for A18C6–DDQ system in chloroform solution are shown in Fig. 2. Other systems studied show a similar spectral behaviour with time. As seen, while none of the reactants show any considerable absorption in the 430–650 nm range, addition of A18C6 to the DDQ solution results in some absorption bands in this spectral region, presumably due to the formation of a charge-transfer complex which causes the appearance of a deep red colour in solution. Obviously, the spectra recorded for the EDA complex between A18C6 and DDQ are time dependent. The intensities of the different absorptions increase with time for about 20 min, while the general features of the resulting spectra remain unchanged (Fig. 2A). However, after about 20 min, the deep colour of solution begins to disappear slowly and the intensity of the absorption bands in the 430–650 nm region decreases with time whereas the intensity of the 350 nm band continues to increase until the end of the reaction (Fig. 2B).
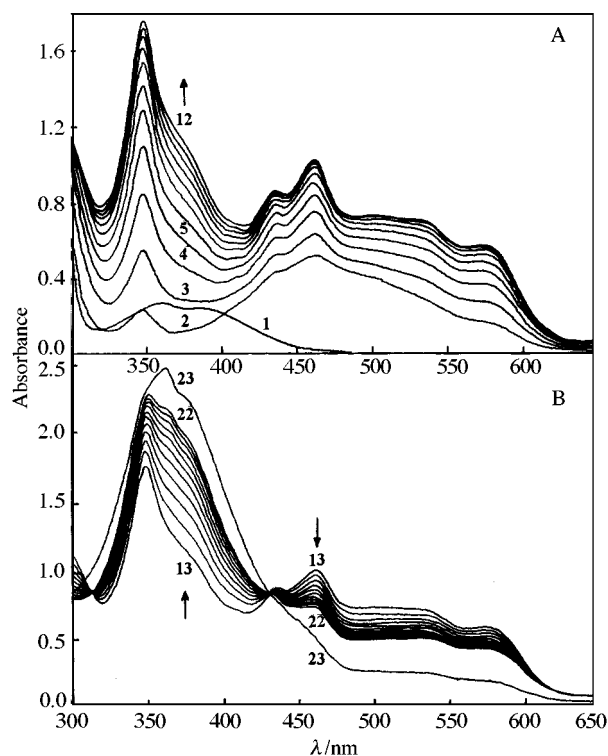

Fig. 2 UV–VIS spectra of a mixture of DDQ (3.0×10^{-4} mol dm^{-3}) and A18C6 (6.0×10^{-3} mol dm^{-3}) in chloroform at 25 °C: 1, DDQ alone; 2, immediately after mixing; time intervals: 3, 2 min; 4, 4 min; 5, 6 min; 6, 8 min; 7, 10 min; 8, 12 min; 9, 14 min; 10, 16 min; 11, 18 min; 12, 20 min; 13, 30 min; 14, 40 min; 15, 50 min; 16, 60 min; 17, 70 min; 18, 80 min; 19, 90 min; 20, 100 min; 21, 110 min; 22, 120 min; 23, 24 h

Careful examination of the absorption spectra of the azacrown–DDQ systems studied reveals that the spectra are characterized by maximum absorptions at the wavelengths 580, 530 (sh), 500 (sh), 465, 435 (sh), 395 and 350 nm. Such spectral features are in agreement with those reported before for the DDQ$^{\cdot-}$ radical ion.[28–30] The observed increase in the absorption band intensities of the azacrown–DDQ complexes with elapse of time further supports the fact that the EDA complex formed is of the dative-type structure (D^+–A^-) which consequently converts to an ionic intermediate [D^+A^-] possessing the spectral characteristics of the DDQ$^{\cdot-}$ radical ion.[31]

It is worth mentioning, however, that the observed decrease in the intensity of the EDA bands in the 430–650 nm region after about 20 min could be due to the consumption of the ionic intermediate through an irreversible chemical reaction, while the continuous increase of the 350 nm band is indicative of the formation of the final reaction product. Similar to the substitution reactions of different aliphatic[18,32,33] and aromatic amines[17,21,34] and imidazoles[35] with benzoquinone and substituted benzoquinones, it was found that azacrown ethers as cyclic amines are substituted on the DDQ ring (yielding 2-chloro-5,6-dicyano-3-azacrowno-1,4-benzoquinone), although the latter azacrown reactions proceed much slower than the former ones.

The above experimental observations seem to be in accord with the following mechanism, which has been proposed before.[17,18,34,35] The first step involves a very fast equilibrium for the formation of an EDA complex between HNCrown (D) and DDQ (A), which is followed by two relatively slow consecutive reactions as shown in Scheme 1. However, it should be noted that the observation of 'intermediates' does not prove that they are on the reaction pathway, and a scheme such as that shown in Scheme 2 is equally compatible with the experimental observations.
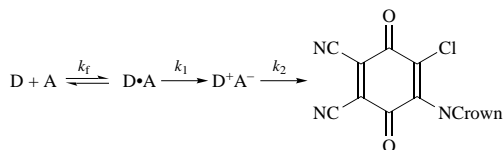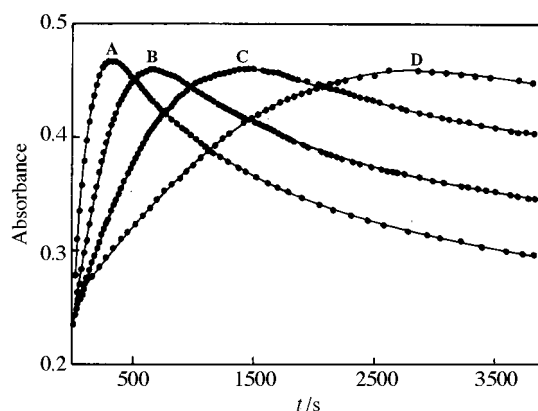
Scheme 1
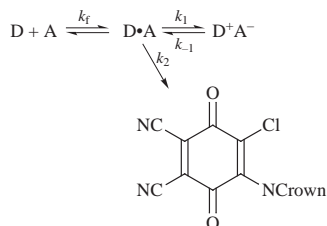
Scheme 2

Fig. 3 Absorbance–time plots for a mixture of DDQ (3.0×10^{-4} mol dm^{-3}) and A18C6 (2.4×10^{-2} mol dm^{-3}) in chloroform solution at different temperatures: A, 45 °C; B, 35 °C; C, 25 °C; D, 15 °C
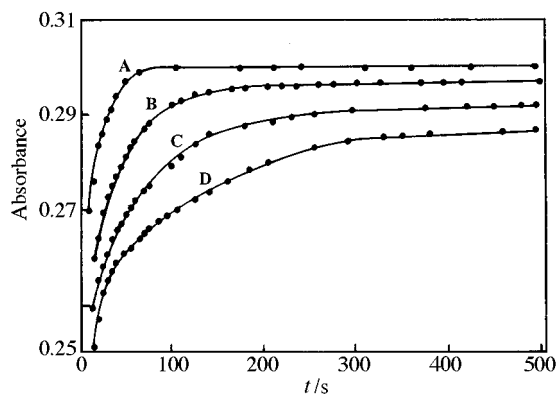

Fig. 4 Absorbance–time plots for a mixture of DDQ (3.0×10^{-4} mol dm^{-3}) and A18C6 (2.4×10^{-2} mol dm^{-3}) in acetonitrile solution at different temperatures: A, 45 °C; B, 35 °C; C, 25 °C; D, 15 °C

In order to investigate the kinetics of production and consumption of DDQ$^{\cdot-}$ radical ions (*i.e.* k_1 and k_2), the absorbance at 463 nm was monitored as a function of time in solutions containing reactants at an azacrown-to-DDQ mole ratio of 80:1 at various temperatures. Sample absorbance–time plots for the A18C6–DDQ system in chloroform and acetonitrile solutions at different temperatures are shown in Figs. 3 and 4, respectively. It is interesting to note that the conductivity–time plots show patterns similar to those observed in Figs. 3 and 4. For example, in the case of A18C6–DDQ in chloroform at 35 °C, production of the DDQ$^{\cdot-}$ radical ions caused a rather sharp increase in solution conductivity for about 15 min. Then, a gradual decrease in conductivity was observed over time, due to consumption of the [D$^+$A$^-$] intermediate to form the final product.
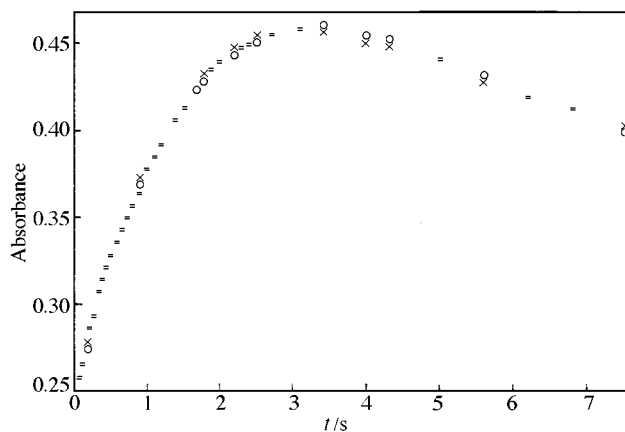

Fig. 5 Computer fit of the absorbance–time plot D in Fig. 3. ($\times$) experimental point; ($\bigcirc$) calculated point; ($=$) experimental and calculated points are the same within the resolution of the plots.

For the pair of consecutive reactions given in Scheme 1, the concentrations of species involved as a function of time, under the pseudo-first-order condition, are given by[36] eqns. (3)–(5),

$$[\text{DA}] = [\text{DA}]_\text{o}\exp(-k_1 t) \tag{3}$$

$$[\text{D}^+\text{A}^-] = [\text{DA}]_\text{o}k_1[\exp(-k_2 t) - \exp(-k_1 t)]/(k_1 - k_2) \tag{4}$$

$$[\text{P}] = [\text{DA}]_\text{o}(1 + \{[k_2\exp(-k_1 t) - k_1\exp(-k_2 t)]/(k_1 - k_2)\}) \tag{5}$$

where $[\text{DA}]_\text{o}$ = initial concentration of the EDA complex, and it is assumed that $[\text{D}^+\text{A}^-] = [\text{P}] = 0$ when $t = 0$. The absorbance of the reaction solution at time t is given by eqn. (6), where ε_DA,

$$A_\text{t} = \varepsilon_\text{DA}[\text{DA}] + \varepsilon_\text{D}^+\text{A}^-[\text{D}^+\text{A}^-] + \varepsilon_\text{P}[\text{P}] \tag{6}$$

$\varepsilon_\text{D}^+\text{A}^-$ and ε_P are the molar absorptivities of species DA, [D$^+$A$^-$] and P, respectively. The substitution of eqns. (3), (4) and (5) into (6) and rearrangements results in eqn. (7). The

$$A_\text{t} = [\text{DA}]_\text{o}((\varepsilon_\text{DA} - \varepsilon_\text{P})\exp(-k_1 t) + \{k_1(\varepsilon_\text{D}^+\text{A}^- - \varepsilon_\text{P}) \times [\exp(-k_2 t) - \exp(-k_1 t)]/(k_1 - k_2)\} + \varepsilon_\text{P}) \tag{7}$$

pseudo-first-order rate constants k_1 and k_2 at various temperatures were then evaluated by fitting eqn. (7) to a non-linear least-squares curve fitting program KINFIT.[37] The program is based on the iterative adjustment of calculated to observed absorbance values by using either the Wentworth matrix technique[38] or the Powell procedure.[39] The adjustable parameters are k_1, k_2, ε_DA and $\varepsilon_\text{D}^+\text{A}^-$. A sample computer fit of the absorbance–time data is shown in Fig. 5. A fair agreement between the observed and calculated absorbances further supports the occurrence of the reactions between A18C6 and A12C4 and DDQ *via* the two-step mechanism suggested. All the values evaluated for k_1 and k_2 at various temperatures are summarized in Table 1.

The data given in Table 1 indicate that, in all cases studied, the pseudo-first-order rate constants increase with increasing temperature, the influence of temperature on the k_1 values being much more pronounced than that on the k_2 values. It is also obvious that, in the cases of both azacrown ethers used, the k_1 values in acetonitrile solution are much larger than those in chloroform solution. While, an opposite solvent effect is observed on the rates of the second steps of the reactions, k_2; the k_2 values in acetonitrile are much smaller than those observed in chloroform solution. It is interesting to note that the observed solvent effect on the k_1 and k_2 values supports the

Table 1 Calculated rate constants for A18C6–DDQ and A12C4–DDQ systems in chloroform and acetonitrile solution at various temperatures

Ligand	Solvent	$T/°C$	k_1/s^{-1}	k_2/s^{-1}
A18C6	CHCl$_3$	15	$(5.45 \pm 0.42) \times 10^{-4}$	$(1.46 \pm 0.15) \times 10^{-4}$
		25	$(1.39 \pm 0.04) \times 10^{-3}$	$(2.35 \pm 0.10) \times 10^{-4}$
		35	$(3.93 \pm 0.21) \times 10^{-3}$	$(3.09 \pm 0.14) \times 10^{-4}$
		45	$(9.69 \pm 0.41) \times 10^{-3}$	$(4.54 \pm 0.09) \times 10^{-4}$
	CH$_3$CN	15	$(6.40 \pm 0.51) \times 10^{-3}$	a
		25	$(1.00 \pm 0.04) \times 10^{-2}$	a
		35	$(1.84 \pm 0.08) \times 10^{-2}$	a
		45	$(5.82 \pm 0.31) \times 10^{-2}$	a
A12C4	CHCl$_3$	5	$(2.62 \pm 0.14) \times 10^{-3}$	$(1.56 \pm 0.05) \times 10^{-3}$
		15	$(5.35 \pm 0.20) \times 10^{-3}$	$(1.67 \pm 0.02) \times 10^{-3}$
		35	$(1.65 \pm 0.22) \times 10^{-2}$	$(1.88 \pm 0.04) \times 10^{-3}$
		45	$(3.17 \pm 0.88) \times 10^{-2}$	$(2.24 \pm 0.07) \times 10^{-3}$
	CH$_3$CN	5	b	$(6.38 \pm 0.27) \times 10^{-4}$
		15	b	$(7.52 \pm 0.23) \times 10^{-4}$
		25	b	$(9.48 \pm 0.29) \times 10^{-4}$
		35	b	$(1.30 \pm 0.04) \times 10^{-3}$
		45	b	$(1.51 \pm 0.10) \times 10^{-3}$

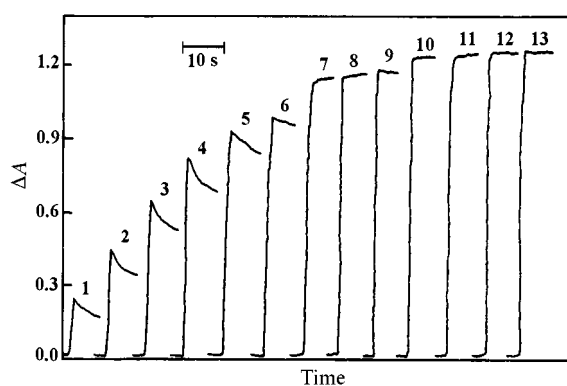^{a} Too slow. ^{b} Too fast.

Fig. 6 ΔA *vs.* time plots for a 3.0×10^{-4} mol dm^{-3} solution of DDQ in chloroform in the presence of varying concentrations of A18C6 at 25 °C. [A18C6]/[DDQ] mole ratios are: 1, 0.2; 2, 0.4; 3, 0.6; 4, 0.8; 5, 1.0; 6, 1.2; 7, 1.6; 8, 2.0; 9, 2.4; 10, 2.8; 11, 3.6; 12, 4.0; 13, 5.0.

proposed two-steps mechanism well. The resulting intermediate complexes are expected to be more stabilized in acetonitrile as solvent because of its higher solvating ability and relative permittivity than chloroform.[40] Consequently, the rate of production of the [D$^+$A$^-$] complex is expected to increase in acetonitrile solution, while the rate of its consumption to the final product should be decreased in this solvent.

It is also noteworthy that, in chloroform solution, both the k_1 and, in particular, k_2 values for A12C4–DDQ are larger than those for the A18C6–DDQ system. A similar trend should also prevail in acetonitrile solution, although some of the rate constants in this solvent are outside the time scales possible for precise determination. Such observations could be related to the decreased flexibility of the A12C4 molecule as compared with A18C6. Molecular mechanics calculations,[41,42] as well as the crystalline structure[43] and spectroscopic investigations,[44] performed on 12C4 and 18C6 molecules revealed 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. In this case, 12C4 most probably adopts a 'square' conformation with the donating atoms in 'side' positions with four identical gauche, gauche, anti-conformations for the individual O–C–C–O units.[42,44] This would possibly facilitate the formation of both the intermediate complex and the final product in A12C4–DDQ system.

In all the examples studied, during the first few seconds after the addition of the azacrown to the DDQ solution, a rather sharp step-functional increase in the absorbance at 463 nm was observed, as was reported previously (Fig. 6).[45] This initial
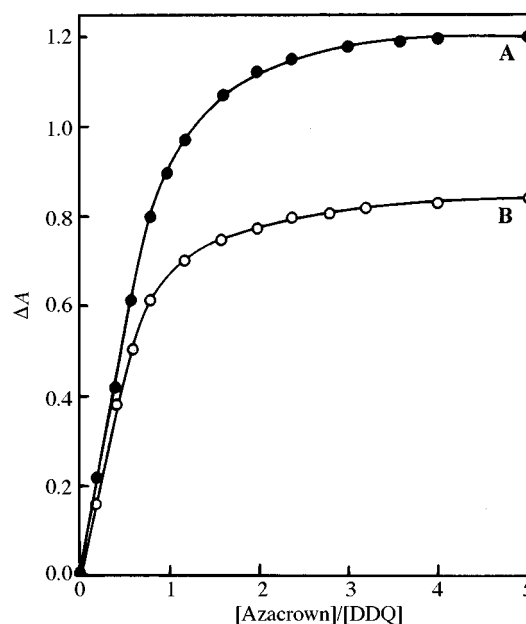

Fig. 7 ΔA *vs.* [azacrown]/[DDQ] plots in chloroform solution at 25 °C for A, A18C6–DDQ and B, A12C4–DDQ systems

change in absorbance, ΔA, upon mixing the azacrowns and DDQ was found to increase with a rise in the azacrown : DDQ mole ratio to reach a constant value at a mole ratio of 1 : 1 (see for example Figs. 6 and 7). Such dependence of ΔA on the azacrown : DDQ mole ratio indicates the formation of an EDA complex between the donors and the acceptor used. The corresponding formation constant can be determined from ΔA *vs.* azacrown : DDQ mole ratio as follows.

When the azacrowns used react with DDQ in solution a 1 : 1 EDA complex is formed, as given by Scheme 1. The formation constant and mass balance equations are given by eqns. (8)–(10). Substitution of eqns. (9) and (10) into eqn. (8) and

$$K_f = [DA]/[D][A] \qquad (8)$$

$$C_A = [A] + [DA] \qquad (9)$$

$$C_D = [D] + [DA] \qquad (10)$$

rearrangement yields eqn. (11). The observed absorbance

$$K_f[A]^2 + [1 + K_f(C_D - C_A)][A] - C_A = 0 \qquad (11)$$

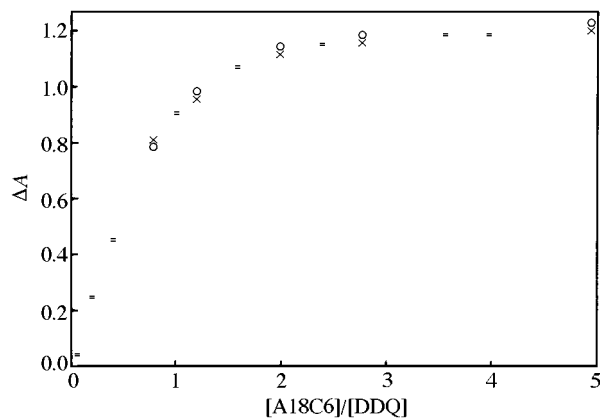**Fig. 8** Computer fit of the ΔA *vs.* [A18C6]/[DDQ] mole ratio in chloroform solution at 25 °C; (×) experimental point; (○) calculated point; (=) experimental and calculated points are the same within the resolution of the plot

Table 2 Formation constants of A18C6–DDQ and A12C4–DDQ EDA complexes in chloroform and acetonitrile solutions at 25 °C

	$\log K_f$	
Complex	Chloroform	Acetonitrile
A18C6–DDQ	4.82 ± 0.04	3.72 ± 0.03
A12C4–DDQ	5.12 ± 0.13	4.84 ± 0.09

change of solution at 463 nm is given by eqn. (12). For evalu-

$$\Delta A = \varepsilon_{DA}[DA] \qquad (12)$$

ation of the formation constant from the ΔA *vs.* C_D/C_A mole ratio data, the curve fitting program KINFIT was again used.[37] The free acceptor concentrations, [A], were calculated from eqn. (11) by means of a Newton–Raphson procedure. Once the value of [A] 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 change for all experimental points is minimized. The output of the KINFIT program comprises the refined parameters K_f and ε_{DA}, the sum-of-squares and the standard deviation of the data.

A sample computer fit of the ΔA *vs.* C_D/C_A data is shown in Fig. 8. As seen, the fair agreement between the observed and calculated absorbances further supports the existence of a 1:1 EDA complexation between A18C6 and DDQ in chloroform solution. The $\log K_f$ values obtained by this procedure are given in Table 2. As seen, in the case of both azacrowns used, the stability of the resulting EDA complexes with DDQ is higher in chloroform solution, a solvent of low relative permittivity (ε 4.8), than in acetonitrile with much higher relative permittivity (ε 37.5).[40] This can be explained based on the fact that the EDA complexes formed are of the dative structure, so that an increased polarity of the medium can lead to dissociation of the dative-type molecular structure owing to the expected high dipole–dipole or dipole-induced dipole interaction along the same direction.[31,46] Thus, it is not surprising to have observed the highest stabilities in chloroform solution. On the other hand, in both solvent systems used, A12C4 forms a more stable EDA complex with DDQ than A18C6. As was mentioned before, such observations could be related to the increased rigidity of A12C4 as well as its more convenient conformational arrangement for the process of charge-transfer in the A12C4–DDQ system.[42,44]

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