



## Molecular Complexes of Crown Ethers: Part 7. Effect of Surfactant on the Charge-Transfer Complex between Dibenzo-18-Crown-6 and Tetracyanoethylene

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### Abstract

The charge transfer complexes (CTC) of dibenzo-18-crown-6 (DB 18C6) and tetracyanoethylene (TCNE) were studied in the presence of the surfactant Triton X-100. It was found that the stability of the CTC increases with increasing concentration of the donor, acceptor and the surfactant. This suggests that the charge transfer complex is encapsulated in the micelle structure. Results of the effect of time on the complex stability are also presented.

### Introduction

Crown ethers are mainly used as solvent-solvent extractants for a large number of metals [1–3]. Recently the charge transfer molecular complexes between crown ethers containing oxygen such as 15-crown-5, BI5-crown-5, 18-crown-6, and DB18-crown-6 with different acceptors have received increasing attention [4–14].

Different techniques, such as infra-red (IR), nuclear magnetic resonance (NMR) and UV-Visible spectroscopy were used to study the charge transfer between different crown ethers and some acceptors such as tetracyanoethylene (TCNE), and dichloro-dicyano benzoquinone (DDQ).

Oxygen containing crown ethers CE form weak charge transfer complexes (CTC) with electron acceptor (EA) molecules [4–10]. Derwish et al. [9] reported that TCNE interacts with benzo substituted CEs and not with unsubstituted CEs. This is due to the participation of the Ph-OCH<sub>2</sub>CH<sub>2</sub> moiety. The value of  $K_f$  for the complex formed between DB18-C-6 and TCNE is  $2.9 \text{ dm}^3 \text{ mol}^{-1}$  [9, 15].

It was concluded earlier [9] that DB18-C-6 has a rigid structure compared to other crown ethers [16, 17]. This conformation enables the acceptor to approach the plane of the benzene ring in DB18-C-6. DB18-C-6 has two parts, the aromatic ring which is hydrophobic, and the oxygen atoms which are hydrophilic.

Surfactants consists of hydrophilic and hydrophobic parts. Ionic surfactants were found to interact with macrocyclic compounds [18–20], but there are no data concerning the interaction of macrocyclic compounds with the electron acceptor (EA) in the presence of surfactants.

Surfactants have micelle properties, which are affected by the addition of small amounts of electrolytes, nonpo-

lar [21] and polar organic liquids [18, 22–24]. The critical micelle concentration (CMC) [25] results from the hydrophobic interaction between the nonpolar part, which forms the core of the micelle, and a repulsion interaction between the polar head groups.

The aim of this paper is to study the possibility of the micelle structure to encapsulate the CTC thus increasing the charge transfer interaction or to encapsulate one reactant and exclude the other thus decreasing the charge transfer complex interaction. Triton X-100 (iso-octylphenoxy polyethoxy ethanol) surfactant is used throughout this work. This surfactant was chosen because it is neutral and contains no ions that can interact with the crown ether and encapsulate into it.

### Experimental

Dibenzo-18-crown-6 (DB18C6) (Fluka) was of pure grade and used without further purification. Tetracyanoethylene (Aldrich) was recrystallized from chlorobenzene and then sublimed, m.p (198–200 °C). All other chemicals were of high-grade quality (BDH, Fluka). The UV/Vis spectra were recorded on a Perkin-Elmer lambda 2S spectrophotometer, using 1 cm fused silica cells. Dichloromethane (spectrosol, Fluka) was used as solvent.

To ensure that a CMC for Triton was obtained three solvents were used, dichloromethane DCM, dichloroethane DCB and ethanol. The critical micelle concentration CMC of Triton X-100 in different solvents was determined using the conductivity technique. In dichloromethane it was  $2.0 \times 10^{-2} \text{ M}$ , in dichloroethane it was  $2.7 \times 10^{-2} \text{ M}$ , but in ethanol no CMC was found in the concentration range used for the previous two solvents. Surfactant solutions of

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Table 1. Effect of changing the concentration of TCNE, DB18C6, and Triton on the charge transfer complex between DB18C6 and TCNE

System DCM	$\epsilon/M^{-1} \text{ cm}^{-1}$
0.006 M DB18C6 + 0.02 M Triton +	0
0.002 M TCNE	$7 \pm 0.5$
0.003 M TCNE	$10 \pm 0.5$
0.004 M TCNE	$13 \pm 0.5$
0.005 M TCNE	$17 \pm 0.5$
0.006 M TCNE	$19 \pm 0.5$
0.006 M TCNE + 0.02 M Triton +	$5 \pm 0.5$
0.002 M DB18C6	$10 \pm 0.5$
0.003 M DB18C6	$14 \pm 0.5$
0.004 M DB18C6	$15 \pm 0.5$
0.005 M DB18C6	$17 \pm 0.5$
0.006 M TCNE + 0.006 M DB18C6 +	$13 \pm 0.5$
0.02 M Triton	$19 \pm 0.5$
0.05 M Triton	$25 \pm 0.5$
0.07 M Triton	$30 \pm 0.5$
0.1 M Triton	$35 \pm 0.5$

Table 2. Effect of changing the concentration of TCNE, DB18C6 and Triton

System in DCM	$\epsilon/M^{-1} \text{ cm}^{-1}$
(R)* = 0.006 M DB18C6 + 0.02 M Triton	
(S)* = 0.006 M DB18C6 + 0.02 M Triton	
S + 0.002 M TCNE	$6 \pm 0.5$
S + 0.003 M TCNE	$10 \pm 0.5$
S + 0.004 M TCNE	$13 \pm 0.5$
R = 0.006 M TCNE + 0.02 M Triton	
S = 0.006 M TCNE + 0.02 M Triton	
S + 0.002 M DB18C6	$10 \pm 0.5$
S + 0.003 M DB18C6	$14 \pm 0.5$
S + 0.004 M DB18C6	$15 \pm 0.5$
S + 0.005 M DB18C6	$17 \pm 0.5$
R = 0.006 M TCNE + 0.006 M DB18C6	
S = 0.006 M TCNE + 0.006 M DB18C6	
S + 0.02 M Triton	$19 \pm 0.5$
S + 0.05 M Triton	$25 \pm 0.5$

\*R = Reference cell.

\*S = Sample cell.

variable concentrations were prepared and the conductivity was measured by a Jenway 4020 conductivity meter.

The molar extinction coefficient,  $\epsilon$ , of the charge-transfer band at 586 nm was roughly calculated from the concentration of dibenzo-18-crown-6 and TCNE. Therefore when both had fixed concentrations,  $\epsilon$  was calculated using the concentration  $6 \times 10^{-3}$  M. When one of the two compounds varied then this concentration was used to calculate  $\epsilon$  (Tables 1 and 2).

## Results and discussion

Figure 1 shows the changes in the conductivity as a function of the concentration of Triton X-100. The CMC obtained in

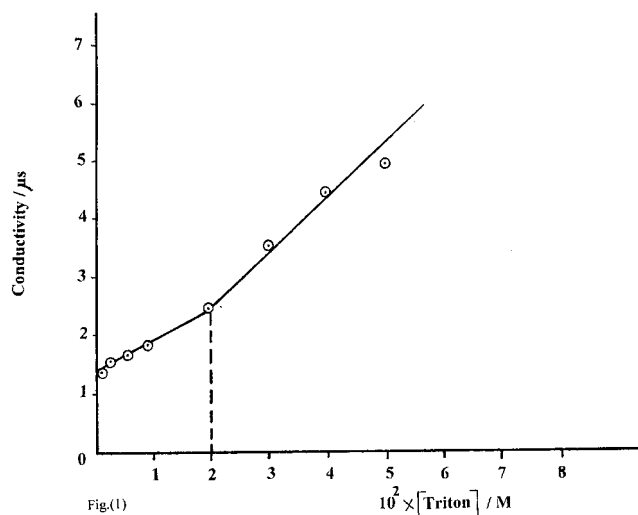


Figure 1. Conductivity vs. concentration for Triton X-100 in DCM.

DCM was  $2.1 \times 10^{-2}$  M. The CMC of Triton X-100 has been determined using other techniques [26] and the value obtained ( $2.1 \times 10^{-2}$  M) was very similar to our value. It seems that the polarity of the solvent has a large effect on the CMC value. In this work we determined the CMC for Triton in three solvents to indicate that we obtained similar values for the CMC in two non-polar solvents with similar properties while no CMC was obtained in ethanol. Other experiments were performed to determine that our procedure is correct. The CMC of Triton was determined using the conductivity method in the presence of a fixed concentration of TCNE ( $6 \times 10^{-3}$  M) and the value was  $1.5 \times 10^{-2}$  M. For the same solutions the CT band of TCNE with Triton was monitored at 399 nm. The absorbance of this band for different solutions were plotted against [Triton] and the value obtained for the CMC was  $1.6 \times 10^{-2}$  M.

The effect of Triton on the complex formation between DB18C6 and TCNE was studied by the following set of experiments

1. *TCNE and DB18C6*. No absorption was observed for the TCNE or DB18C6 above 400 nm. When they were mixed a new band appeared at 586 nm arising from the charge transfer complex formed between TCNE and the DB18C6. This band was monitored throughout this work.
2. *Triton and DB18C6*. No UV-Visible spectrum was obtained when Triton was mixed with DB18C6 (Table 1). This indicates that there is no CTC between Triton and crown ethers.
3. *Triton and TCNE*. The spectrum of a Triton-TCNE mixture shows a small band at 525 nm with  $\epsilon = 7.0 \text{ M}^{-1} \text{ cm}^{-1}$ . No absorption was observed at 586 nm.
4. *Effect of [TCNE]*. Fixed concentrations of DB18C6 ( $6 \times 10^{-2}$  M) and Triton ( $2 \times 10^{-2}$  M) were mixed. When the mixture attained equilibrium ( $\sim 15$  min), variable concentrations of TCNE were added. The molar extinction coefficient,

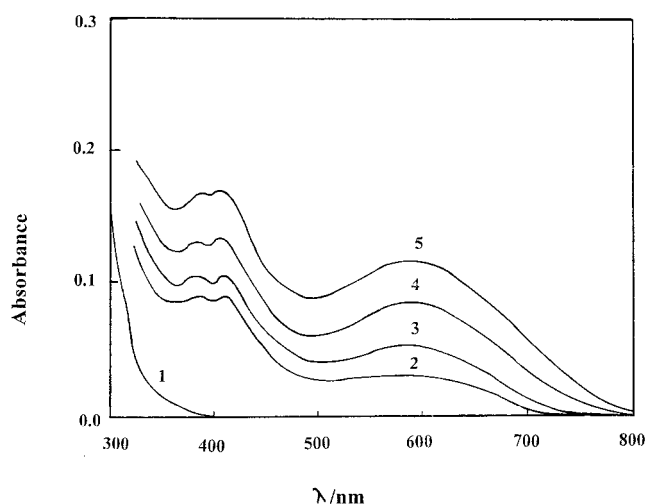


Figure 2. UV-Vis spectra for a mixture of DB18C6 (0.006 M) and Triton (0.02 M) in the presence of variable concentrations of TCNE: (1) 0.0 M TCNE, (2) 0.003 M; (3) 0.004 M; (4) 0.005 M; (5) 0.006 M.

$\epsilon$ , of the charge-transfer band at 586 nm increased from 7 to 19  $\text{M}^{-1} \text{cm}^{-1}$  (Table 1). Figure 2 is a representative diagram.

5. *Effect of [DB18C6]*. TCNE ( $6 \times 10^{-3}$  M) and Triton ( $2 \times 10^{-2}$  M) were mixed and kept constant. After the mixture reached equilibrium (15 min), variable concentrations of DB18C6 were added. The increase in the concentration of DB18C6 led to an increase in the  $\epsilon$  value from 10 to 17  $\text{M}^{-1} \text{cm}^{-1}$  (Table 1).

Experiments 4 and 5 (Tables 1 and 2) show an increase in the absorption when the concentration of TCNE or DB18C6 was increased. Such an increase in absorption was not identical, indicating that the mode of mixing has a small effect.

6. *Effect of [Triton]*. Equal concentrations ( $6 \times 10^{-3}$  M) of the donor and the acceptor were mixed and kept constant. After the mixture attained equilibrium ( $\sim 15$  min), Triton of variable concentrations was added, starting from the CMC ( $2 \times 10^{-2}$  M) to  $1 \times 10^{-1}$  M. The molar extinction coefficient ( $\epsilon$ ) for the charge-transfer band at 586 nm was found to increase from 13 to 35  $\text{M}^{-1} \text{cm}^{-1}$  (Figure 3, Table 1).

Another experiment was performed where varied concentrations of Triton were added to a fixed concentration of DB18C6 ( $6 \times 10^{-3}$  M). No UV-Visible spectra were obtained for those solutions in the range 400–500 nm. This indicated that there is no charge transfer interaction between Triton and DB18C6. Another experiment was performed (Table 1) where different concentrations of Triton were added to a fixed concentration of TCNE ( $6 \times 10^{-3}$  M). It was observed that a new band appeared at 525 nm and blue shifted to 500 nm with increasing Triton concentration and the intensity increased from 5.0  $\text{M}^{-1} \text{cm}^{-1}$  in 0.02 M Triton to 14  $\text{M}^{-1} \text{cm}^{-1}$  when [Triton] reached 0.07 M.

The results obtained in experiment 6 indicated that the band at 586 nm is due to a charge transfer complex between TCNE and DB 18C6. The band intensity of the CTC increased to 35  $\text{M}^{-1} \text{cm}^{-1}$  when the Triton concentration

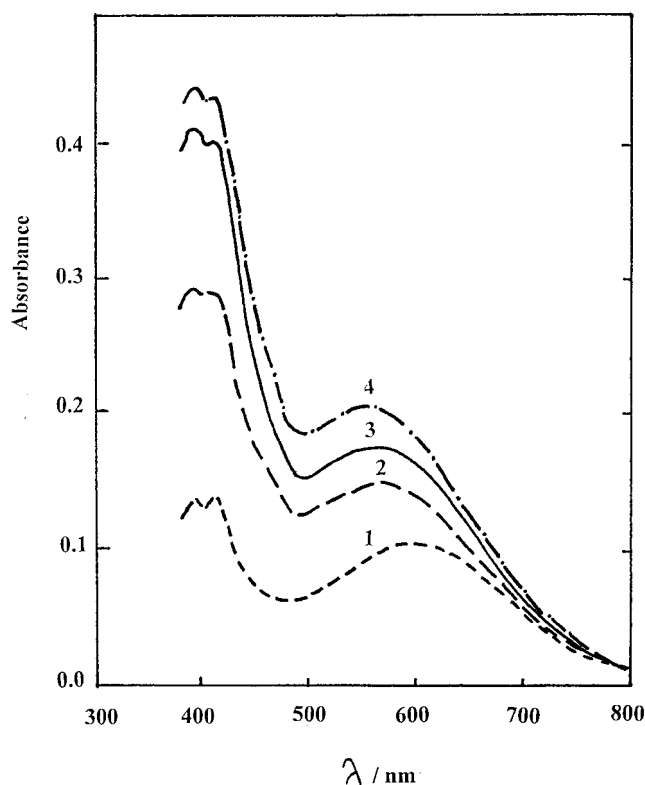


Figure 3. UV-Vis spectra for the TCNE (0.006 M) + DB18C6 (0.006 M) system with variable concentrations of Triton: (1) 0.02 M Triton; (2) 0.05 M; (3) 0.075 M; (4) 0.1 M.

reached 0.1 M. This indicates that Triton has a synergic role in enhancing this CTC and the interaction between TCNE and DB18C6.

Three other experiments parallel to those described above, 4–6, were performed to investigate further the formation of the complex in the presence of Triton.

7. The first experiment involved the mixing of a fixed concentration of DB18C6 ( $6 \times 10^{-3}$  M) and Triton ( $2 \times 10^{-2}$  M) in the sample cell followed by the addition of variable concentrations of TCNE. The reference cell contained the same amounts of DB18C6 and Triton as those in the sample cell (Table 2).

8. The second experiment was carried out where fixed concentrations of TCNE ( $6 \times 10^{-3}$  M) and Triton ( $2 \times 10^{-2}$  M) were placed in the sample cell and variable concentrations of DB18C6 were added. The reference cell in this case contained both the TCNE ( $6 \times 10^{-3}$  M) and Triton ( $2 \times 10^{-2}$  M) (Table 2).

9. The third experiment was performed by mixing TCNE ( $6 \times 10^{-3}$  M) with DB18C6 ( $6 \times 10^{-3}$  M) in the sample cell followed by the addition of variable concentrations of Triton. The reference cell contained both the TCNE ( $6 \times 10^{-3}$  M) and DB18C6 ( $6 \times 10^{-3}$  M) (Table 2).

These experiments confirm that what we observe is indeed due to the charge transfer complex and any  $\epsilon$  value related to the fixed reactants in the sample cell will be cancelled by a similar  $\epsilon$  value to those reactants present in the reference cell.

It was found from experiments 7–9, that the molar extinction coefficient of the charge-transfer complex formed between TCNE and DB 18C6 in the presence of Triton increased with increasing concentration of the added reagent. It was also observed that the  $\epsilon$  values of the CTC obtained from experiments 7–9 were very similar to those obtained from experiments 4–5 (Tables 1 and 2). This would indicate that Triton plays a significant role in enhancing the interaction between the donor and the acceptor molecules.

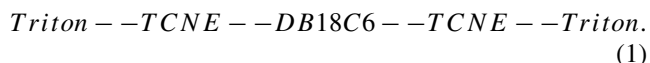
Experiments 7–9 indicate clearly that the absorption at 586 nm (Table 2) is due to the CTC formed from the interaction of TCNE with DB18C6 in the presence of Triton which plays a synergic role in increasing this interaction.

To further understand the nature of the interaction between DB18C6 and TCNE in the presence of Triton, the effect of time on the formation and stability of the charge-transfer complex was investigated.

10. *Effect of time on the CTC.* TCNE ( $5 \times 10^{-3}$  M) was mixed with Triton ( $2 \times 10^{-2}$  M) and the solution was left to reach equilibrium. At this stage DB18C6 ( $6 \times 10^{-2}$  M) was added. The spectrum of the reaction mixture was followed for two weeks. It was noticed that the extinction coefficient of the charge-transfer band at 586 nm increased from 17 (first day) to  $19.3 \text{ M}^{-1}\text{cm}^{-1}$  (second day) and then decreased slowly to disappear within two weeks (Figure 4). When the DB18C6 was mixed with Triton then TCNE was added, similar results were obtained.

In a non-polar solvent like DCM it is expected that Triton will form the reverse-micelle structure where the polar part of Triton forms the cavity and the non-polar hydrocarbons form the outer part. Experiments 1–10 suggest the following: In previous papers [5, 14] it was suggested that TCNE interacts with benzo substituted CEs and this interaction is due to the participation of the Ph-OCH<sub>2</sub>CH<sub>2</sub> moiety. Therefore, it is expected here that Triton, which contains an aromatic ring, might also form a charge transfer complex under the present conditions where low concentrations of TCNE and DB18C6 were utilized. Experiments 1–3 indicate that no CT band was observed in the range 550–580 nm. Experiments 4–9 confirm that Triton plays a synergic role in the formation and stability of the CTC between TCNE and DB18C6. Two probable mechanisms for this interaction may be suggested as follows:

I. TCNE and DB18C6 will interact with Triton in a manner shown in Equation (1).



The presence of DB18C6 and TCNE might cause denaturation of the micellar structure of Triton and force its non-polar part to form a cavity around the CTC, thus increasing the

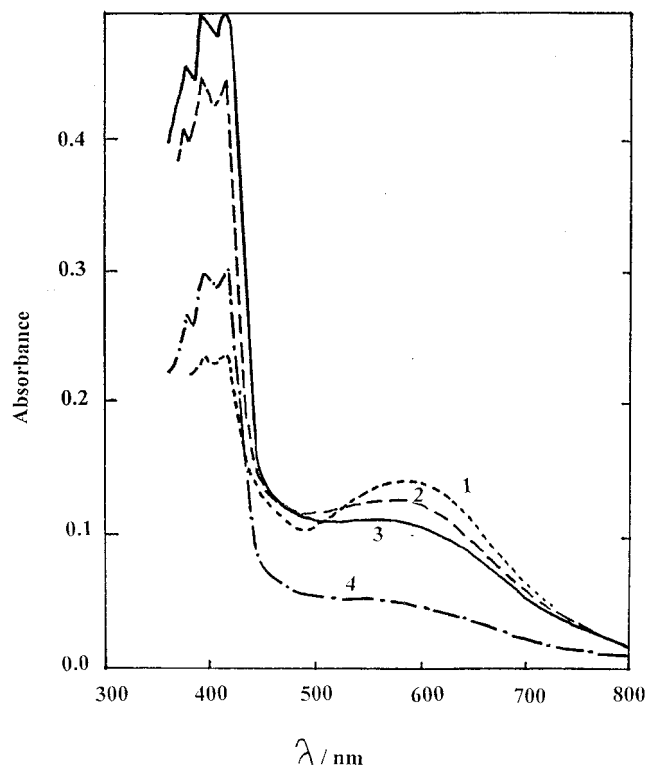


Figure 4. UV-Vis spectra for a mixture of TCNE (0.006 M) + Triton (0.02 M) + DB18C6 (0.006 M) as a function of time: (1) 0.5 h after mixing; (2) 24 h; (3) 48 h; (4) 2 weeks.

interaction between the donor and the acceptor. The TCNE will gradually leave the cavity and interact with the polar side of the Triton leading to the disappearance of the CTC. The evidence for that comes from the decrease in absorbance of the CTC with time (Figure 4).

II. TCNE will be in the center of the polar micellar cavity surrounded by several DB18C6 molecules in a way where one aromatic ring of the CB interacts with TCNE and the other with the polar cavity (Equation (2)).



DB18C6 will leave the cavity to interact with the non-polar side of Triton and consequently the CTC vanishes as time elapses.

Further work is still in progress in our laboratory to better understand the mode of this complex interaction between the donor and acceptor in the presence of Triton.

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