



Spectroscopic Study of Charge-Transfer Complexes of Some Dicyclohexano-Crown Ethers with Π -acceptors in Dichloromethane Solution

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Abstract. A spectrophotometric study was conducted on solutions of dicyclohexano-18-crown-6 and dicyclohexano-24-crown-8 with some Π -acceptors in methylene chloride at 25 °C. The spectroscopic data indicate the formation of a charge-transfer complex. In contrast to previous results, our study shows that the Ph-O-CH₂ structure is not essential for the formation of charge-transfer complexes. The formation constants (K_f) were calculated and the effect of KCl and NaCl salts on the formation and stability of the complexes is discussed.

Key words: charge-transfer complexes, crown ethers, Π -acceptors, formation constants, UV-visible spectra, salt effect

1. Introduction

Since their synthesis by Pedersen [1], crown ethers have received ever increasing attention as an extractant for alkali and alkaline earth metals [2–4]. Most of the work has been concentrated on the complexing properties of the crown ethers. Their selective metal binding properties make them useful ligands in the study of the coordination chemistry of metallic ions for synthetic and analytical purposes [5]. However, little work has been done on the molecular complexes of crown ethers with some Π -acceptors. Recently, several published studies [6–10] reported the formation of 1:1 molecular complexes between some dibenzo-crown-ethers with different Π -acceptors such as tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), Chloranil (CHL) and 7,7,8,8-tetracyanoquinodimethane (TCNQ). The above studies demonstrated that the formation of a charge-transfer complex requires the participation of the Ph-O-CH₂ group in the crown ether.

It was of interest to us to examine the necessity of the phenyl group in the formation of charge transfer complexes. In this paper we wish to report a spectroscopic study of the charge transfer complexes between dicyclohexano-18-crown-6 (DC18C6) and dicyclohexano-24-crown-8 (DC24C8) with tetracyanoethylene

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(TCNE) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in dichloromethane solution at 25 °C in the absence and presence of NaCl and KCl.

2. Experimental

TCNE (Fluka) was recrystallized from chlorobenzene and then sublimed m.p (198–200 °C). DDQ (Fluka) was recrystallized from benzene-chloroform mixture m.p (213–215 °C). Reagent grade NaCl and KCl were used without further purification except for vacuum drying over P₂O₅ for 72 h. Dicyclohexano-18-crown-6 (DC18C6) and dicyclohexano-24-crown-8 (DC24C8) were used without further purification.

All UV-visible spectral measurements were carried out on a DMS spectrophotometer-100 by using 1 cm fused silica cells. The donor concentration was varied within the range 1.2×10^{-2} – 4.8×10^{-2} M while the acceptor concentration was kept constant at 1×10^{-3} M.

The effect of salt was studied by adding solid salt to the crown solution, then adding the acceptor. The Benesi-Hildebrand [11] Equation (1) is used to calculate the molecular complex formation constant and the molar absorptivity (ϵ) for A + D → AD

$$\frac{[A]_0}{\text{Abs}} = \frac{1}{K_f \cdot \epsilon \cdot b} \cdot \frac{1}{[D]_0} + \frac{1}{\epsilon b}, \quad (1)$$

where $[A]_0$ is the initial concentration of acceptor, $[D]_0$ is the initial concentration of donor, Abs is the absorbance of is solution and b is the cell thickness, Equation (1) is valid under the condition $[D]_0 \gg [A]_0$. The reported K_f values are the average of four to five results obtained in different experiments.

3. Results and Discussion

A new band in the visible region of the spectrum appearing after mixing solutions of crown ethers with the acceptors in methylene chloride [9], was taken as an indication of a charge-transfer (CT) complex since both donor and acceptor alone did not absorb in this region.

Surprisingly, when dicyclohexano-18-crown-6 (DC18C6) or dicyclohexano-24-crown-8 (DC24C8) solution was mixed with a solution of TCNE or DDQ, a color develops and the solution mixture gives new bands in the visible region which must be associated with the formation of charge-transfer complexes. Five different runs gave the same observations. Figures 1 and 2 show the spectra of solutions with the new bands appearing in the visible region.

The above results clearly indicate that the Ph-O-CH₂ group is not essential for the formation of a charge-transfer complex as previously published [6–10] and the crown ethers such as DC18C6 and DC24C8 can form charge transfer complexes with Π -acceptors, especially those with low ionization energy.

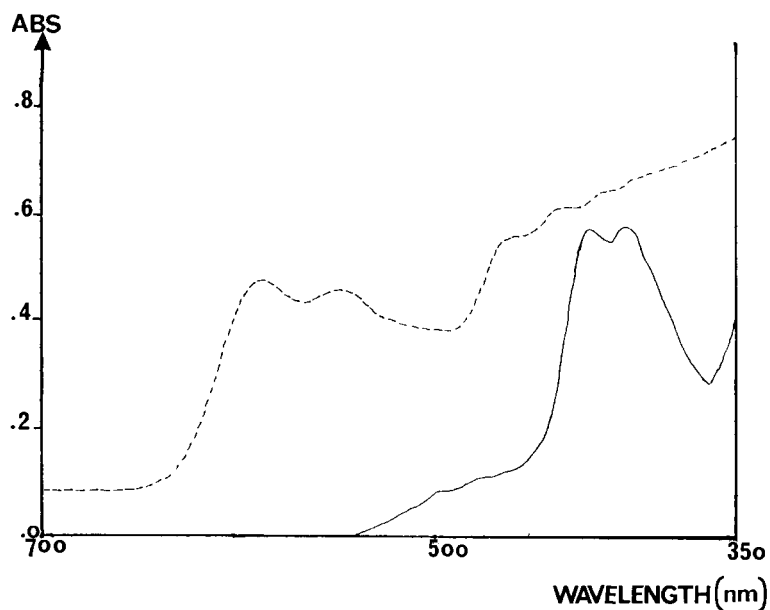


Figure 1. Visible spectra of DC 24C8 with DDQ (---) and TCNE (—) in dichloromethane.

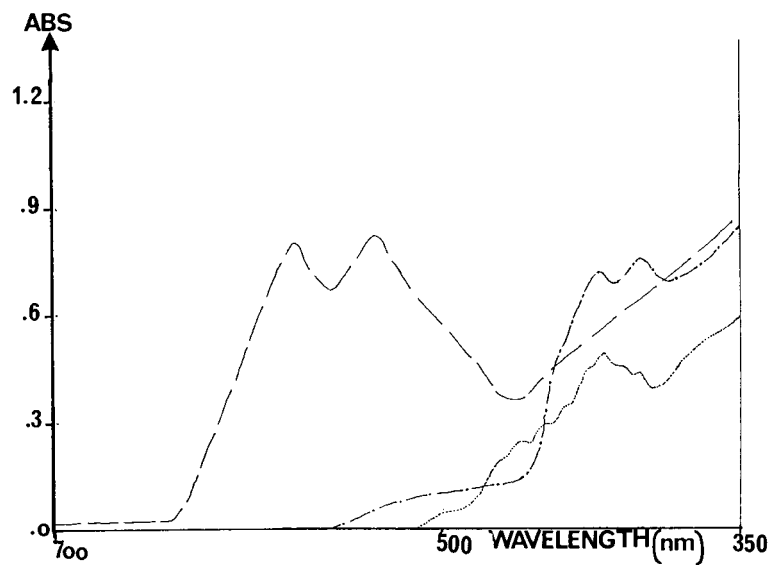


Figure 2. Visible spectra of DC 18C6 with DDQ (-----), TCNE (-.-.-) after one hour of mixing and with TCNE (.) after one day.

Table 1. Molar absorptivities and formation constants of the charge transfer complexes formed between dicyclohexano crown ethers and DDQ and TCNE in dichloromethane solution at 25 °C

Donor: Π-Acceptor	DC 18C6				DC 24C8			
	λ_{\max} (nm)	ϵ (l.mol ⁻¹ cm ⁻¹)	$K_f\epsilon$	K_f	λ_{\max} (nm)	ϵ (l.mol ⁻¹ cm ⁻¹)	$K_f\epsilon$	K_f
DDQ	540	674 ± 34	36255 ± 2175	53.77 ± 1.61	592	597 ± 30	16794 ± 1007	28.09 ± 1.40
DDQ+ NaCl	540	888 ± 53	64248 ± 3854	72.28 ± 2.17	592	1346 ± 67	90908 ± 5454	67.48 ± 3.37
DDQ+ KCl	540	1152 ± 67	174645 ± 10478	151.49 ± 4.54	592	1549 ± 93	108156 ± 6489	69.81 ± 3.49
TCNE	475	220 ± 11	1643 ± 98	7.44 ± 0.22	450	288 ± 17	798 ± 48	2.76 ± 0.16
TCNE+ NaCl	475	189 ± 10	5958 ± 357	31.46 ± 0.94	450	1127 ± 68	28376 ± 1702	25.17 ± 1.26
TCNE+ KCl	475	363 ± 21	27219 ± 1633	74.96 ± 2.25	450	96 ± 6	7152 ± 429	74.39 ± 4.46

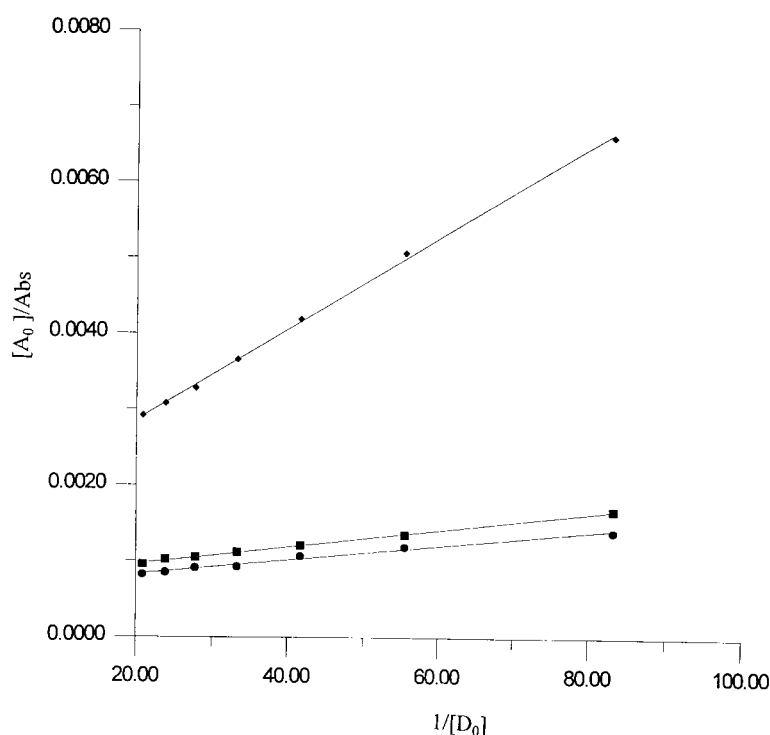


Figure 3. Benesi-Hildebrand plots for DC24C8 with \blacklozenge DDQ; \blacksquare DDQ + NaCl; \bullet DDQ + KCl.

The charge-transfer complex formation of the benzo-crown ethers was explained as due to the interaction of the π -electrons of the donor phenyl group in the crown ether and the electron-deficient acceptor. The phenyl group in this case acts as an electron withdrawing group which pulls the electrons from oxygen atoms of the crown ether. In the case of DC18C6 and DC24C8, it is believed that an electrostatic interaction between the electrons of the oxygen ethers occurs with the π -electron acceptor. In addition the basic cyclohexyl group, which is an electron donating group will assist in pumping electrons towards oxygen. As a consequence the formation of the charge transfer complex is favoured.

Sample Benesi-Hildebrand plots are shown in Figures 3 and 4 which indicates a ratio of 1 : 1 donor to acceptor. Table I shows the K_f values obtained for the complexes, the molar absorptivities (ϵ) and the absorption maxima. It is interesting to note that both K_f and ϵ for a given crown increase with the increase of the electron affinity of the π -acceptors from TCNE to DDQ. These observations agree well with previously reported results [6, 7]. From Table I, it is obvious that the stabilities of the charge transfer complexes between both TCNE and DDQ with the crown ethers decrease in the order DC18C6 > DC24C8. Both crown ethers exist in different isomers and have a certain degree of flexibility. However, DC18C6 has a smaller size than DC24C8; as a result it is expected to be less flexible than DC24C8,

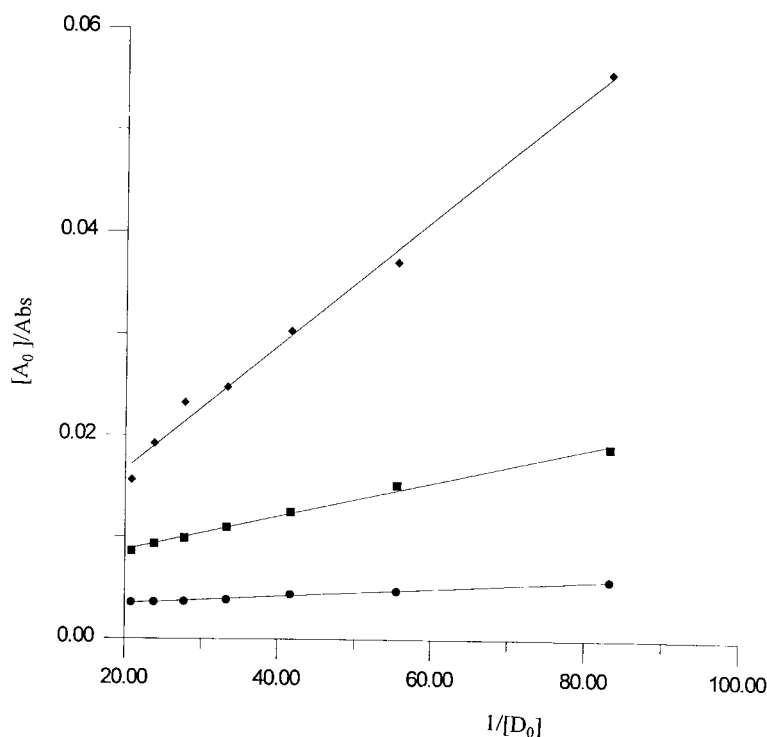


Figure 4. Benesi-Hildebrand plots for DC18C6 with \blacklozenge TCNE; \blacksquare TCNE + NaCl \bullet TCNE + KCl.

consequently, the Π -acceptor molecules probably can easily approach the oxygen atoms of the DC18C6 to form the most stable complex. The same trend for the same reasoning was observed with the benzo-crown ethers. The stabilities of the charge transfer complexes between TCNE and DDQ and the donating ligands decrease in the order DB18C6 > DB24C8 = DB30C10 [7].

The addition of either KCl and NaCl increased the stability dramatically and the effect of KCl is more pronounced. It is well known that large crown ethers with a considerably large flexibility and enough oxygen atoms in their macrocyclic ring are able to twist around a cation of proper size to form a rigid "wrap around" complex in solution. This rigidity makes more oxygens available for the formation of a charge transfer complex with the Π -acceptors.

It is well known that a potassium ion with an ionic radius of 1.38 Å [12] fits better into the cavity of DC18C6 and DC24C8 than the Na⁺ ion with an ionic radius 1.02 Å [12]. For this reason, it is expected that the K⁺-crown complex is the more stable complex and as the rigidity increases, it causes the crown ether to flatten out which in turn facilitates the formation of charge transfer complexes between crown ethers and the Π -acceptors.

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References

1. C.H. Pedersen: *J. Am. Chem. Soc.* **89**, 7017 (1967).
2. C.J. Pedersen and H.K. Frensdorff: *Angew. Chem.* **11**, 16 (1972).
3. R.M. Izzat, J.S. Bradshaw, S.A. Nielsen, J. Lamb, and J.J. Christensen: *Chem. Rev.* **85**, 271 (1985).
4. R.M. Izzat, J.S. Bradshaw and J.J. Christensen: *Chem. Rev.* **91**, 1721 (1990).
5. I.M. Kolthoff and M.K. Chantooni: *Anal. Chem.* **52**, 1039 (1980).
6. A.M. Nour El-din: *Spectrochim. Acta* **42A**, 637 (1986).
7. A. Semnani and M. Shamsipur: *Spectrochim. Acta* **49A**, 411 (1993).
8. S.R. Salman and S.M. Al-Marsoumi: *Spectrochim. Acta* **49A**, 435 (1993).
9. G.A.W. Derwish, S.R. Salman, and S.M. Al-Marsoumi: *J. Incl. Phenom.* **20**, 123 (1995).
10. S.R. Salman, G.A.W. Derwish, and S.M. Al-Marsoumi: *J. Incl. Phenom.* **25**, 295 (1996).
11. H.A. Benesi and J.H. Hildebrand: *J. Am. Chem. Soc.* **71**, 2703 (1949).
12. H.F. Frensdorff: *J. Am. Chem. Soc.* **93**, 600 (1971).

