



Charge Transfer Complexes of Crown Ethers with Π -Acceptors. The Influence of NaCl and KCl on Their Stability

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Abstract. A spectrophotometric study was conducted on solutions of benzo-15-crown-5, dibenzo-18-crown-6 and dibenzo-24-crown-8 with the Π -acceptors, DDQ, and CHL in dichloromethane at room temperature. The stabilities of the resulting charge transfer complexes with the Π -acceptors DDQ were found to decrease in the order DB18C6>DB15C5>DB24C8 and with CHL it follows the order DB18C6>DB24C8. The addition of either NaCl or KCl affects the values of formation constants (K_c) and the order of stabilities of the charge transfer complexes. The formation constants in the absence and presence of NaCl and KCl salts were calculated and discussed.

Key words: charge-transfer complexes, crown ethers, Π -acceptors, formation constant, salt effect.

1. Introduction

Since their synthesis by Pedersen [1], crown ethers have received increasing attention [2–5] as an extractant for alkali and alkaline earth metals. Most effort has been concentrated on the ionic complexes of crown ethers. However, increasing attention has been focused on the molecular complexes of crown ethers with different acceptors.

Several published studies [6–11] reported the formation of charge transfer complexes between benzo-crown ethers with Π -acceptors such as tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and 2,3,5,6-tetrachlorobenzoquinone (CHL). However, the reported results show some discrepancy in the values of formation constants. In addition, the effect of inorganic salts on the formation constants did not receive full consideration.

It was of interest to study the spectroscopic properties of charge transfer complexes formed between benzo-15-crown-5 (B15C5), dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-18 (DB24C8) and the Π -acceptors DDQ and CHL in dichloromethane at room temperature in the absence and presence of NaCl and KCl.

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The formation constants obtained in this study are compared with those reported, and the effect of inorganic salts discussed.

2. Experimental

DDQ (Fluka) was recrystallized from benzene-chloroform mixture m.p. (213–215 °C). CHL (Aldrich) was recrystallized several times from benzene m.p. (297–298 °C). Reagent grade NaCl and KCl were used without further purification except for vacuum drying over P₂O₅ for 72 hr. Benzo-15C5, DB18C6 and DB24C8 (Merck) were used without further purification. Dichloromethane HPLC grade was used.

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 equation [12] below is used to calculate the molecular complex formation constant for $A + D \rightleftharpoons AD$.

$$\frac{[A]_0}{\text{Abs.}} = \frac{1}{K_c \cdot b\epsilon} \cdot \frac{1}{[D]_0} + \frac{1}{b\epsilon},$$

where $[A]_0$ is the initial concentration of acceptor, $[D]_0$ is the concentration of donor, Abs. is the absorbance of solution and b is the cell thickness. The reported K_c values are the average of four to five results obtained from different experiments.

3. Results and Discussion

The existence of new bands in the visible region of the electronic spectra of a mixture of benzo-crown ether and Π -acceptor in dichloromethane is taken as an indication of the formation of a charge transfer complex since neither the Π -acceptor alone nor the crown ether absorbs in this region [6]. Figures 2 and 3 show the spectra of dichloromethane solutions of DDQ and CHL and mixtures of DDQ and CHL with benzo-crown ethers.

In order to calculate the formation constants and to determine the stoichiometric ratio of the charge transfer complexes, the Benesi–Hildebrand equation was used and representative plots are shown in Figures 4 and 5. The linear plots indicate a stoichiometry of 1:1 acceptor to crown which is in agreement with reported literature [7, 9, 11].

Table I shows the K_c values, the molar absorptivities and the absorption maxima of the complexes. It is obvious that the K_c values and ϵ for a given benzo crown increase with the increase of the electron affinity of the Π -acceptor from CHL to DDQ. These observations agree with the previously reported results [13, 14].

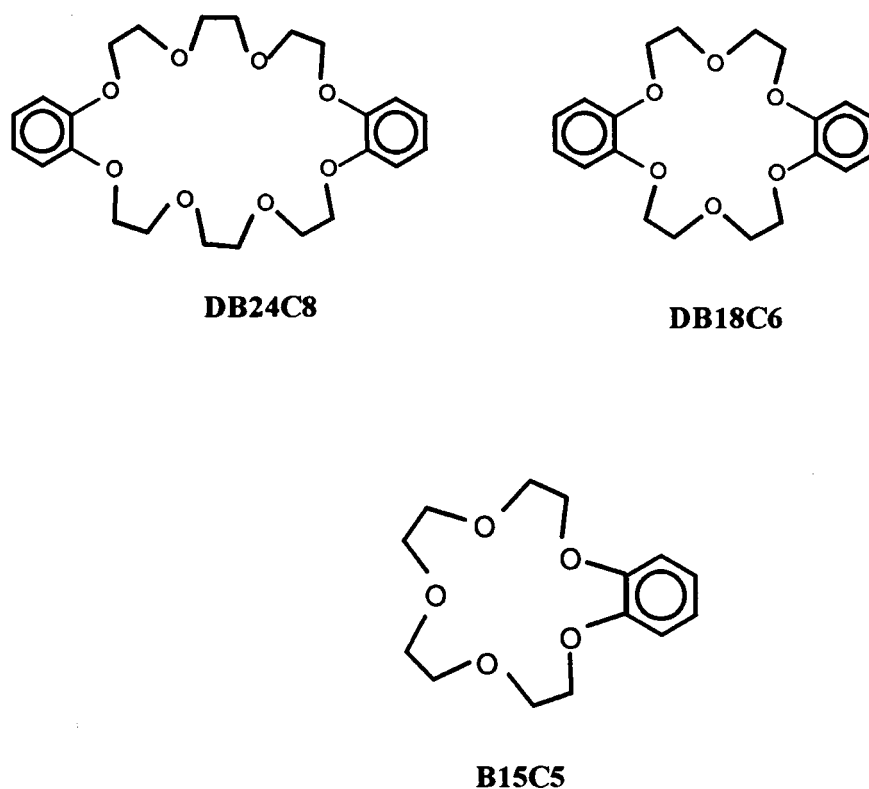


Figure 1. Structure of crown ethers used.

In addition, from Table I, it is obvious that the K_c values of the charge transfer complexes formed between DDQ and benzo crown ethers decrease in the order DB18C6 > B15C5 > DB24C8. Previous results reported by Shamsipur et al. [7] showed the order of stabilities of charge transfer complexes formed between DDQ and benzo crown ethers in the order DB18C6 > DB24C8 > B15C5. On the other hand the results reported by Krishnan et al. [11] for the system showed the stabilities of charge transfer complex decrease in the order DB24C8 > DB18C6 > B15C5.

Because of the presence of two benzo groups in the structure of DB18C6 as well as its relatively small ring size, this macrocycle has the most rigid structure among the dibenzo crowns used [15, 16]. Consequently, the Π -acceptor molecule DDQ can easily approach the plane of the benzo rings of the DB18C6 molecule to form the most stable charge transfer complex. On the other hand, the large crown ether DB24C8 is flexible enough to twist easily in solution into a proper configuration for the formation of an intramolecular charge transfer complex between the two benzo groups [17]. The existence of such intramolecular complexes in solution is expected to decrease the stability of the charge transfer complex formed between DB24C8 and DDQ.

Table I. Maximum wavelengths (λ_{\max}), molar absorptivities, and formation constants of the charge transfer complexes formed between crown ethers and the Π -acceptors DDQ and CHL in the absence and presence of NaCl and KCl in dichloromethane solution at room temperature

Donor Π -acceptor	B15C5			DB18C6			DB24C9			Ref.
	λ_{\max}	ϵ L. mol ⁻¹ cm ⁻¹	K_c L. mol ⁻¹	λ_{\max}	ϵ L. mol ⁻¹ cm ⁻¹	K_c L. mol ⁻¹	λ_{\max}	ϵ L. mol ⁻¹ cm ⁻¹	K_c L. mol ⁻¹	
DDQ	592	1657 ± 98	6.88 ± 0.34	577	591 ± 26	11.86 ± 0.71	585	1860 ± 90	5.88 ± 0.29	This work
DDQ	595	1032 ± 65	8.35 ± 0.56	585	884 ± 37	15.94 ± 0.76	590	1072 ± 60	11.65 ± 0.70	[7]
DDQ	–	2383 ± 200	2.6 ± 0.4	–	2033 ± 100	4.85 ± 0.35	–	1759 ± 110	7.50 ± 0.50	[11]
DDQ + Na ⁺	588	1810 ± 115	6.08 ± 0.30	577	1043 ± 53	6.56 ± 0.33	580	1540 ± 82	13.8 ± 0.70	This work
DDQ + K ⁺	583	1646 ± 96	24.77 ± 1.23	577	860 ± 48	8.41 ± 0.42	575	1805 ± 98	5.75 ± 0.30	This work
CHL	–	–	–	447	369 ± 21	3.06 ± 0.15	450	281 ± 13	2.90 ± 0.15	This work
CHL	500	235 ± 18	1.0	526	242 ± 16	3.6	531	307 ± 20	4.30	[9]
CHL + Na ⁺	–	–	–	443	559 ± 50	1.96 ± 0.10	446	213 ± 13	4.72 ± 0.24	This work
CHL + K ⁺	–	–	–	440	501 ± 47	2.11 ± 0.12	440	338 ± 22	2.81 ± 0.15	This work

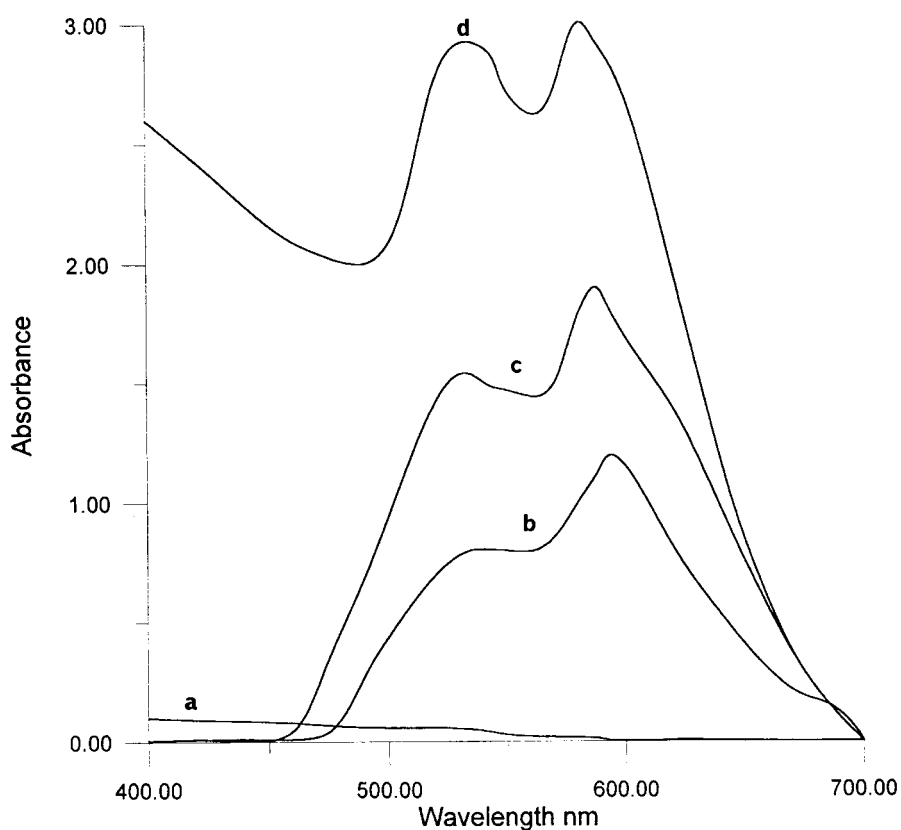


Figure 2. (a) Visible spectra of DDQ; (b) DDQ + B15C5; (c) DDQ + B15C5 + NaCl and (d) DDQ + B15C5 + KCl.

From Table I, it is clear that the stabilities of charge transfer complexes formed between CHL and the crown ethers follow the order DB18C6 > DB24C8. However, we were not able to investigate the formation of a charge transfer complex between CHL and B15C5. Derwish et al. [9] reported a K_c value of 1 for the complex CHL-B15C5 indicating a very weak interaction between B15C5 and CHL. The order of stability of CHL complexes can be explained as in the case of DDQ complexes. In addition our value of K_c for DB24C8-CHL is less than that reported by Derwish et al. [9]. Moreover, the order of stabilities of CHL-crown complexes obtained by Derwish is in reverse order to the DDQ-crown complexes.

To study the effect of inorganic salts on the formation and stability of the $\Pi-\Pi^*$ intermolecular complex, the formation constants K_c of the crown ethers with DDQ and CHL were determined in the presence of NaCl and KCl and compared with those obtained in the absence of salts.

Table I shows with the presence of NaCl the stabilities of the charge transfer complexes formed between DDQ and crown ethers decrease in the order DB24C8 > DB18C6 > B15C5. However, it is important to notice that the presence

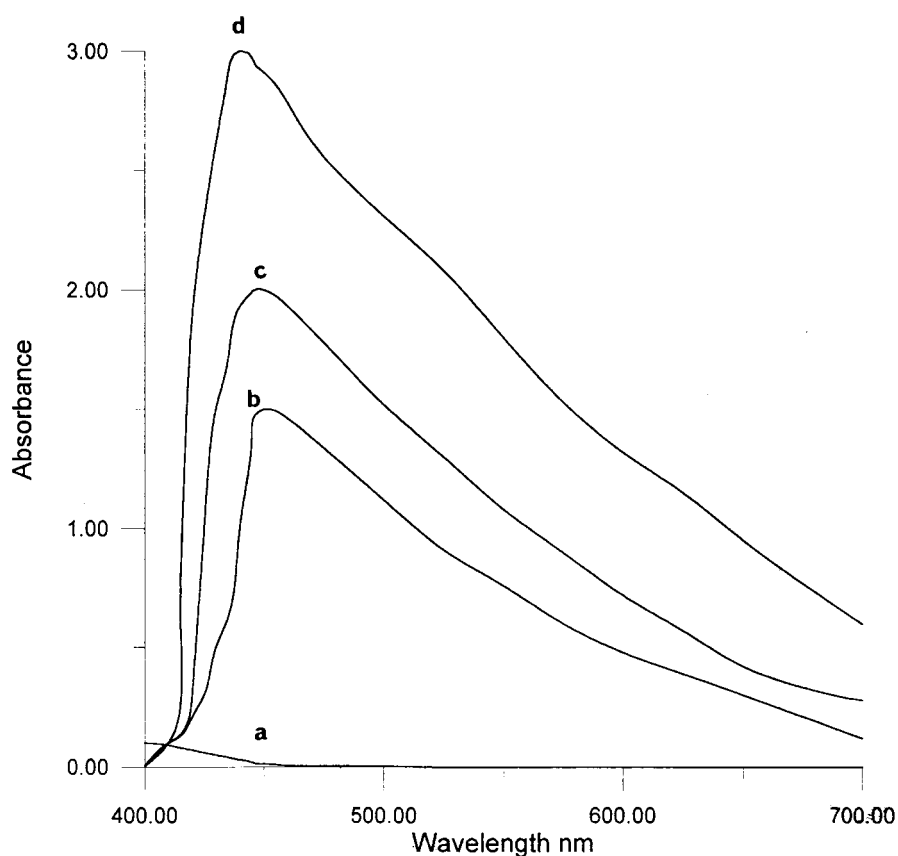


Figure 3. (a) Visible spectra of CHL; (b) CHL + DB24C8; (c) CHL + DB24C8 + NaCl and (d) CHL + DB24C8 + KCl.

of NaCl decreases the formation constants of the DB18C6-DDQ and B15C5-DDQ complexes while its presence increases dramatically the formation constant of the DB24C8-DDQ complex.

It has been reported that the metal ion Na^+ with ionic radius 1.02 \AA [15] fits into the cavity of B15C5 ($0.85\text{--}1.1 \text{ \AA}$) [16] and binds with the unshared pairs of electrons on the oxygen atoms. Such a suggestion would lead to a decrease of the donor ability of the crown ether and consequently a decrease of the formation constant K_c of the B15C5-DDQ complex.

The addition of NaCl to the DB18C6 solution will cause Na^+ to complex with the crown. Since the metal ion radius 1.02 \AA approximately matches the cavity of DB18C6, ($1.3\text{--}1.6 \text{ \AA}$) [19] and binds with the unshared pairs of electrons on the oxygen atoms, such a suggestion is expected to lead in our case to a decrease in the donor ability of the crown ether and consequently a decrease in the formation constant K_c and the absorption band maxima of the crown ether-DDQ complex.

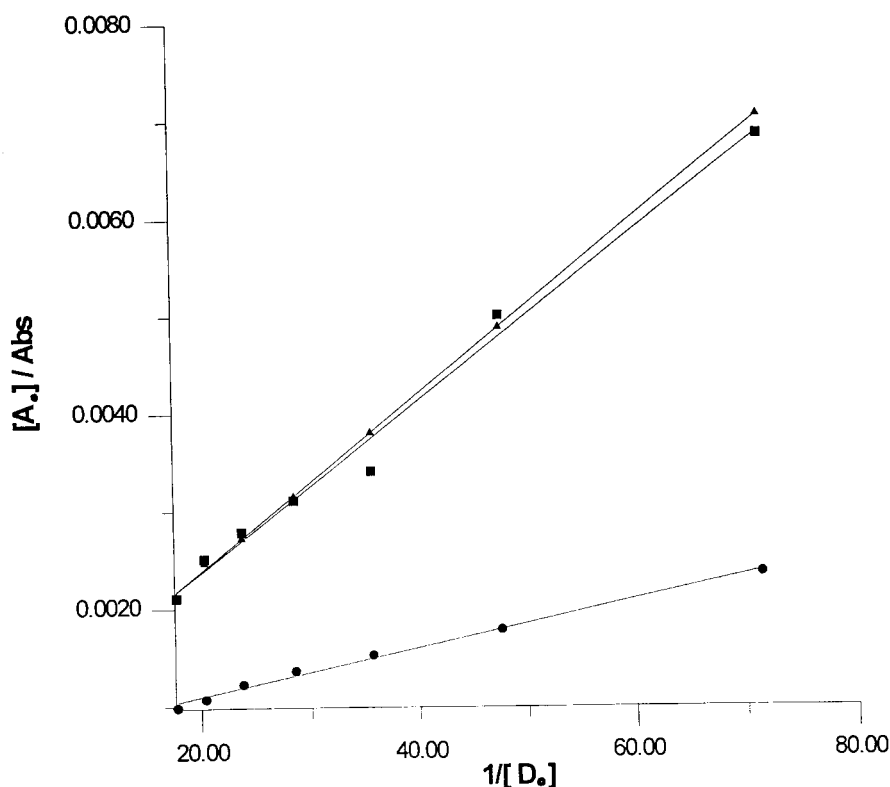


Figure 4. Benesi-Hildebrand plots for B15C5 with ● DDQ; ▲ DDQ + NaCl; ■ DDQ + KCl.

On the other hand, the addition of NaCl to the DB24C8-DDQ complex increases its stability. Since the cavity of the flexible DB24C8 (4.5–5 Å) [19] is much larger than the radius of Na⁺, it is possible for such a crown to complex with two Na⁺ ions. Such a case will lead to a more rigid system and phenyl groups will flatten out which facilitates the approach of DDQ to the phenyl groups enhancing the stability of the charge transfer complex. It has been reported that the Na⁺ cation can form complexes with DB24C8 with a ratio of 1 : 1 and 2 : 1 Na⁺ to crown [20]. The addition of NaCl to the crown ethers-CHL system show the same trend as with DDQ and the same above arguments are valid.

The effect of KCl on the stabilities of crown ethers-DDQ complexes was also investigated. As shown in Table 1, the stabilities of the charge-transfer complexes of DDQ decrease in the order B15C5 > DB18C6 > DB24C8. It is worth mentioning that in the presence of KCl, the formation constant of B15C5-DDQ increases, while it decreases with DB18C6 and almost has no effect on the K_c of the DB24C8-DDQ complex.

Since the potassium ion with an ionic radius of 1.38 Å [18] fits nicely inside the cavity of DB18C6 with a radius of 1.3–1.6 Å [19] the cation is bound with the unshared electron pairs on the oxygen atoms [21]. Such a situation is expected

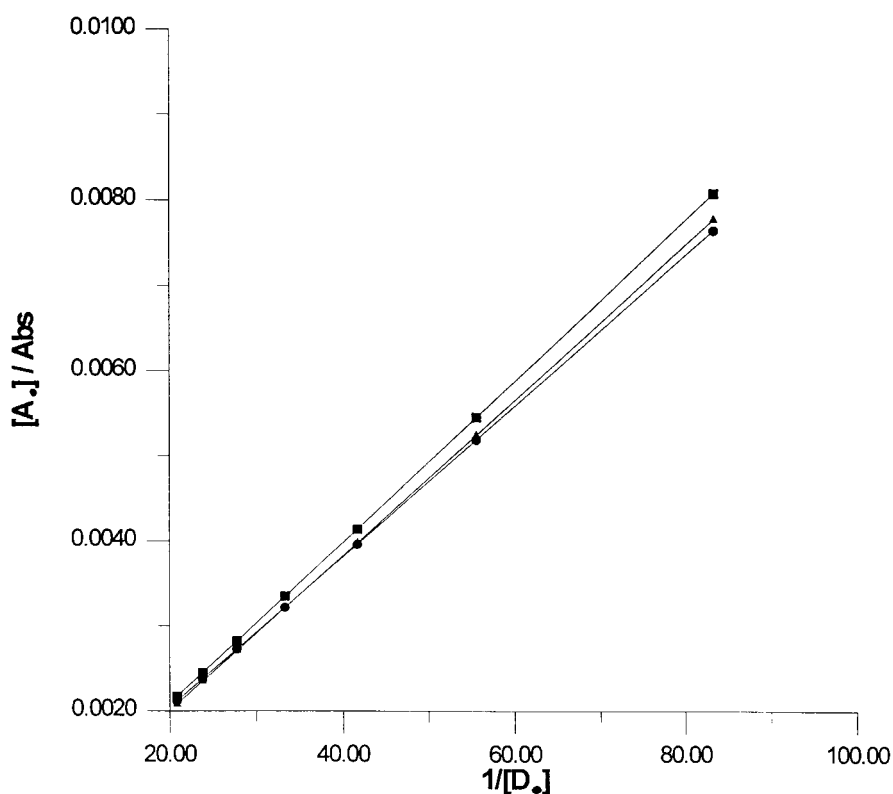


Figure 5. Benesi-Hildebrand plots for DB24C8 with ● CHL; ▲ CHL + NaCl; ■ CHL + KCl.

to lead to a decrease in the donating ability of the crown ether and consequently decrease the stability of the DB18C6-DDQ complex. On the other hand, the cavity of B15C5 (0.85–1.1 Å) [19] is too small for the K^+ ion and therefore, this crown ether can form a 2:1 crown to cation sandwich complex. The formation of such a sandwich complex will cause the benzo groups to flatten out [22, 23], which therefore, facilitates the formation of a charge transfer complex between B15C5 and DDQ. The very small effect of KCl on the formation constant of DB24C8-DDQ can be explained as follows: while the complexation of K^+ (ionic radius 1.38 Å) with DB24C8 (4.5–5.0 Å) decreases the donor ability of the crown thus decreasing the stability of the DB24C8-DDQ complex, it will lead to a more rigid system which decreases the intramolecular charge transfer between the two phenyl groups. This latter effect will increase the stability of the DB24C8-DDQ complex and tends to cancel the effect due to K^+ complexation with the crown ether. As a result a very small effect of addition of KCl on the K_c value of the DB24C8-DDQ complex is observed.

For comparison purposes of the effect of addition of KCl on the formation constants for the charge transfer complexes formed between TCNE and crown

Table II. The formation constants of the charge transfer complexes formed between crown ethers and TCNE in the absence and presence of KCl in dichloromethane solution

Donor	B15C5	DB18C6	DB24C8	
Π -acceptor	K_c	K_c	K_c	Ref.
TCNE	2.30 ± 0.16	3.97 ± 0.35	2.74 ± 0.12	[7]
TCNE + KCl	3.66 ± 0.07	1.80 ± 0.20	3.64 ± 0.12	[7]

ethers are shown in Table II. It can be seen in Tables I and II, that except for the DB24C8 case, our results agree with the reported trend regarding the effect of KCl on the formation constants. However, while the addition of KCl increases the formation constant of TCNE-DB24C8 from 2.79 to 3.67, our results show a very small decrease of the value of the formation constant of the DDQ-DB24C8 complex.

The effect of the addition of KCl on the formation constants of the charge transfer complexes formed between crown ethers and CHL were also investigated. As shown in Table I, while the addition of KCl increases the K_c of the DB18C6-CHL complex, it decreases the formation constant of the DB24C8-CHL complex. This is in accordance with the crown-DDQ systems and the same arguments are valid.

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