

Spectrophotometric Study of the Intreaction of some Benzo, Benzyl and Phnycrown Ethers with π -Acceptor DDQ in Chloroform Solution

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ABSTRACT: *The interaction between benzo-15-crown-5 (B15C5), dibenzo-18-crown-6 (DB18C6), dibenzyl-daza-18crown-6 (DBzDA18C6), N-phenyl-aza-15-crown-5 (NPhA15C5) and dibenzopyridine-18-crown-6 (DBPy18C6) with π -acceptor 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in chloroform solution was studied spectrophotometrically. The interaction of B15C5-DDQ and DB18C6-DDQ caused the formation of 1:1 charge transfer complexes through equilibrium reaction. The interaction of others caused the formation of 1:1 complexes in an equilibrium step and the conversion of the resulting adduct to D^+DDQ^- ($D=NPhA15C5, DBPy18C6, DBzDA18C6$) in a nonequilibrium step. The formation constant of DBzDA18C6 was evaluated by computer fitting of the absorbance mole ratio data. Other stability constants were evaluated through the Hildebrand method. It was found that the stabilities vary in the order: B15C5 < DB18C6 < DBPy18C6 < NPhA15C5 < DBzDA18C6.*

All of the resulting molecular complexes were isolated in crystalline form and characterized.

KEY WORDS: *DDQ, Crown ethers, Spectrophotometry, Charge transfer complex*

INTRODUCTION

Charge transfer complexes have been applied in molecular weight determination, chromatographic separation [1], resolution of enantiomers [2] and estimation of solvent polarity [3]. But probably they're most important application originates from their unusual

conductivity property [4] and its associated technological consequences. Based on this property the use of conducting single crystals in microcircuitry of electronic devices have been widely studied, also proposals have been made for their use as components of solar cells. In

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addition the potential of superconductivity at higher temperatures makes them suitable for super computers, very powerful electromagnets and more efficient electric motors [5].

According to well defined electronic terms, charge transfer complexes have been called organic metals and have been considered as one of the most dynamic and fruitful areas of research.

One the other hand, although many investigators concentrated their research on ionic complexes of crown ethers [6-9], charge transfer complexes have almost been forgotten [10-14]. In this paper we report a spectroscopic study of charge transfer complexes between DDQ and B15C5, DB18C6, NPhA15C5, DBPy18C6 and DBzDA18C6 in chloroform solution.

EXPERIMENTAL

Reagents

Reagent grade CHCl_3 (Merck, Darmstadt, Germany) was used as received. DDQ (Merck) was used without any further purification except for vacuum drying. B15C5, DB18C6 and NPhA15C5 (Merck) were recrystallized from reagent grade n-hexane and vacuum dried. DBzDA18C6 and DBPy18C6 (both from Merck) with the highest purity available were used without any further purification except for vacuum drying. The structures of donors and DDQ are shown in Fig. 1.

Apparatus

All UV-Vis spectra were recorded on a spectrophotometer (Perkin Elmer Lambda 2) and the absorbance measurements were made with a spectrophotometer (Philips, PU875) at $25 \pm 1^\circ\text{C}$. The conductometric measurements were made with a Methrohm 660 Conductometer (Shimadzu) and the conductometric cell thermostated at 25°C . IR spectra were recorded on a Shimadzu spectrometer (Tokyo, Japan) using KBr pellets.

Computational methods

In order to evaluate the formation constants of B15C5, DB18C6, NPhA15C5 and DBPy18C6, we used Hildebrand equation [15] in the following form:

$$\frac{[A]_0}{Abs} = \frac{1}{K\epsilon} \times \frac{1}{[D]_0} + \frac{1}{\epsilon} \quad (1)$$

In the above equation $[A]_0$ is the analytical

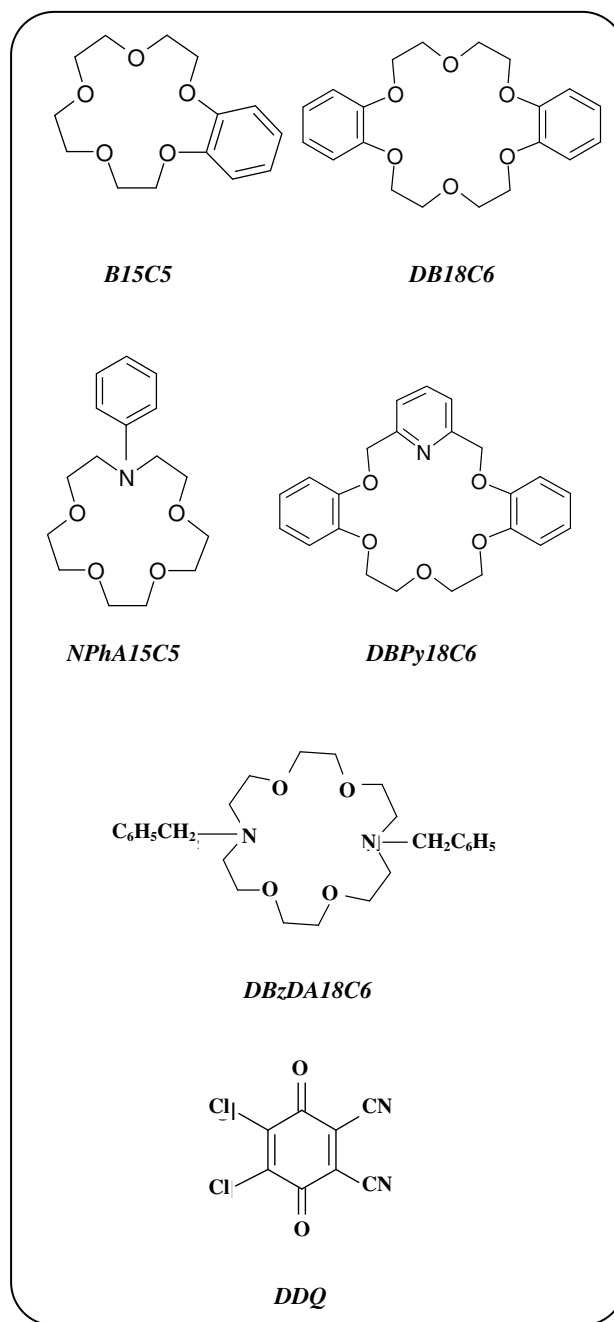


Fig. 1: Structures of donors and π -acceptor.

concentration of DDQ (as π -acceptor), $[D]_0$ is the analytical concentration of crown ethers (as donors), $K\epsilon$ is the product of formation constant and molar extinction coefficient, Abs. is the value of absorbance at 600 nm and ϵ is the molar absorptivity of the complex. The above equation is applicable in conditions that $[D]_0 \gg [A]_0$. According to the above equation a plot of $[A]_0/Abs$ vs. $1/[D]_0$ yields a straight line from which, the

value of K_f can be calculated by dividing intercept to slope.

The formation constant of DBzDA18C6-DDQ complex was evaluated from the absorbance-mole ratio data and using a non-linear least square curve fitting program "KINFIT" [16]. The program is based on the interactive adjustment of the calculated values of absorbance to the observed values by either Wentworth matrix [17] technique or Powell procedure [18]. Adjustable parameters are K_f and ϵ . The observed absorbance of charge transfer complex in chloroform solution at its λ_{\max} is given by equation (2). The mass balance equations can be written as (3) and (4) and the formation constant of the complex as (5). Substitution of equations (3) and (4) in to (5) and rearrangement yields (6).

$$A_{\text{obs}} = \epsilon b[\text{DA}] \quad (2)$$

$$C_A = [\text{A}] + [\text{DA}] \quad (3)$$

$$C_D = [\text{D}] + [\text{DA}] \quad (4)$$

$$K_f = [\text{DA}] / [\text{D}][\text{A}] \quad (5)$$

$$[\text{DA}]^2 - (K_f C_D + K_f C_A + 1)[\text{DA}] + K_f C_A C_D = 0 \quad (6)$$

The complex concentrations were calculated from Equation (6) by means of a Newton-Raphson procedure. Once the value of $[\text{DA}]$ had been obtained the concentrations of all other species involved were calculated from the corresponding mass balance equations by using the estimated K_f values at the current iteration step of the program. Refinement of the parameters were continued until the sum-of-squares of the residuals between calculated and observed absorbance values for all experimental points were minimized. The output of program "KINFIT" comprises the refined parameters, the sum of squares and the standard deviations of the data.

Procedure

In order to obtain absorption spectra of DDQ in the presence of varying concentrations of crown ethers, several 5 ml portions of $\sim 10^{-4}$ M of DDQ was transferred to volumetric flask. The spectra were recorded once immediately after addition of appropriate amounts of crown ethers and once after 24 hours. Formation

constants were simply obtained from absorbance measurements of 5.1×10^{-4} M (5 mL) of DDQ and different concentrations of crown ethers and the results were fitted to either Equation (1) or (6). Conductivity measurements were made in 10 mL solutions that were previously placed in a conductometric cell and thermostated at 25°C. Solid complexes were isolated from the solutions containing stoichiometric amounts of DDQ and macrocycles in chloroform followed by solvent vaporization. The solids were used to obtain the IR spectra and melting points.

RESULTS AND DISCUSSION

Absorption spectra of 4.58×10^{-4} M DDQ in the presence of increasing quantities of DB18C6 are shown in Fig. 2. The existence of an isosbestic point at 375 nm is indicative of an equilibrium reaction [19]. Also the appearance of a new band at 500-700 nm region can certainly be assigned to a charge-transfer absorption band. A similar band was observed in our previous investigation of charge-transfer adducts between a series of benzocrown ethers and DDQ in dichloromethane solution [20]. It was attributed to a $\pi \rightarrow \pi^*$ transition.

Because of similarity the spectra of B15C5-DDQ mixtures are not shown. However according to the above discussion the interaction of B15C5 and DDQ also results in the formation of charge-transfer adduct through an equilibrium reaction.

UV-Vis spectra of 2.51 , 1.85 and 5.71×10^{-4} M DDQ in the presence of different quantities of NPhA15C5, DBPy18C6 and DBzDA18C6 are shown in Figs 3-5 respectively. The spectra were recorded just after mixing the reagents. The existence of isosbestic points beside the appearance of new bands in 400-600 nm, are indicative of the formation of charge transfer complexes through equilibrium reactions. The similarity of bands indicates that in all systems, the charge transfer transitions are of the same kind. Comparison of the spectra of DB18C6-DDQ mixtures (Fig. 2) with other spectra (Figs. 3-5) clearly shows that charge transfer bands are not identical. The difference can be attributed to the existence of the nitrogen atom in the structures of DBPy18C6, NPhA15C5 and DBzDA18C6. In fact substitution of one oxygen by nitrogen atom causes the conversion of $\pi \rightarrow \pi^*$ to $n \rightarrow \pi$ transition. Such difference results in different spectra. Since DDQ does not have any interaction with

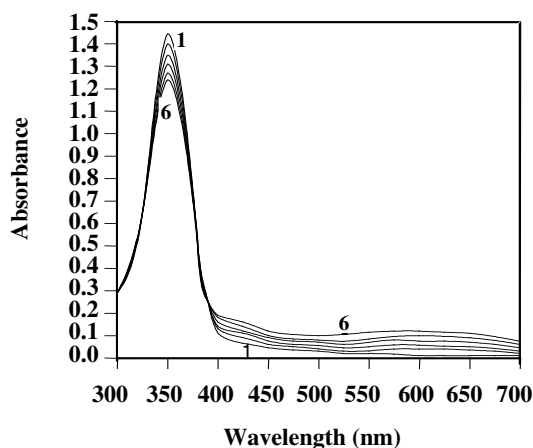


Fig. 2: Absorption spectra of 4.58×10^{-4} M DDQ in the presence of increasing quantities of DB18C6, just after mixing the reagents. The DB18C6: DDQ mole ratios are: 1, 0.00; 2, 5.71; 3, 9.92; 4, 16.63; 5, 21.02; 6, 27.14

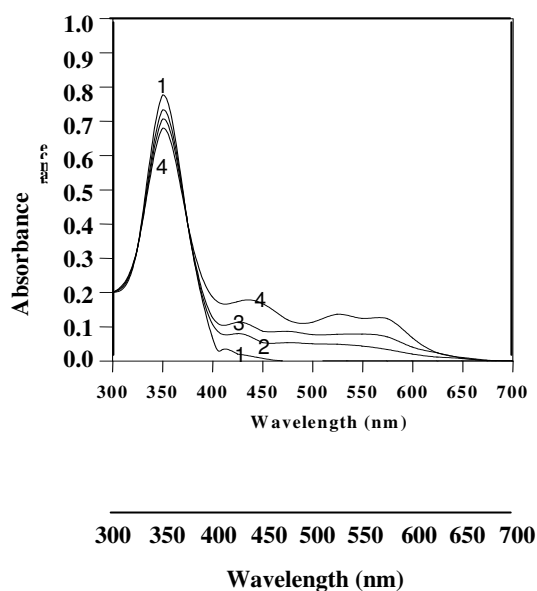


Fig. 3: Absorption spectra of 2.51×10^{-4} M DDQ in the presence of increasing quantities of NPhA15C5, just after mixing the reagents. The NPhA15C5: DDQ mole ratios are: 1, 0.00; 2, 6.54; 3, 12.74; 4, 18.93.

oxygen atoms [21], the observed difference can not be assigned to oxygen's.

The Hildebrand plots for B15C5, DB18C6, DBPy18C6 and NPhA15C5 are shown in Fig. 6. The linear plot of Hildebrand equation indicates that the stoichiometry of the resulting charge transfer complexes is 1:1. Also the absorbance vs. DBzDA18C6/DDQ mole ratio plot (Fig. 7) confirms the 1:1 stoichiometry of

DBzDA18C6-DDQ charge-transfer complex [22]. The resulting curve fitting of absorbance-mole ratio data is shown in Fig. 8. The good agreement between the observed and the calculated absorbance further supports the 1:1 stoichiometry. (Eqn. 5).

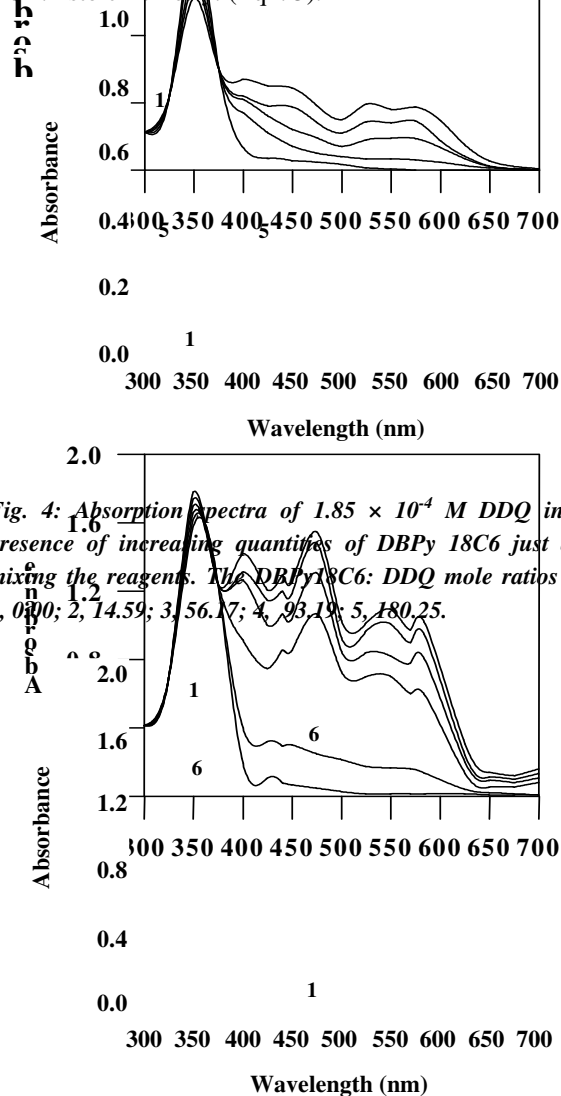


Fig. 4: Absorption spectra of 1.85×10^{-4} M DDQ in the presence of increasing quantities of DBPy18C6 just after mixing the reagents. The DBPy18C6: DDQ mole ratios are: 1, 0.00; 2, 14.59; 3, 56.17; 4, 93.19; 5, 180.25.

Fig. 5: Absorption spectra. of 5.71×10^{-4} M DDQ in the presence of increasing quantities of DBzDA18C6, Just after mixing the reagents. The DBzDA18C6: DDQ mole ratios are: 1, 0.00; 2, 0.16; 3, 0.41; 4, 0.63; 5, 0.85; 6, 1.26.

The formation constants and molar absorptivities obtained by the Hildebrand and curve fitting methods are given in Table 1. As it can be seen the stability of the charge-transfer complexes vary in the order: B15C5 < DB18C6 < DBPy18C6 < NPhA15C5 < DBzDA18C6. Because of the presence of two benzo groups in the

structure of DB18C6 (Fig. 1) and its rigid structure, the π -acceptor can easily approach to the plane of its benzo rings to form a more stable complex relative to B15C5. The higher stability of DB18C6 has also been observed in

our previous work in dichloromethane solution [20]. As it was mentioned previously in DBPy18C6, NPhA15C5 and DBzDA18C6 the donation take place via nitrogen

Table 1: The values of K_f and molar absorption coefficient for different donor-acceptor complexes. The data have been obtained from Hildebrand plot and curve fitting program.

Donor	ϵ	K or log K
B15C5	107±55	^a 13±2 (K)
DB18C6	1303±84	^a 21±2 (K)
DBPyA18C6	1490±33	^b 51±1 (K)
NPhA15C5	1483±48	^b 76±4 (K)
DBzDA18C6	1495±77	^b 5.11±0.15 (K)

a) Obtained at 600 nm.

b) Obtained at 525 nm.

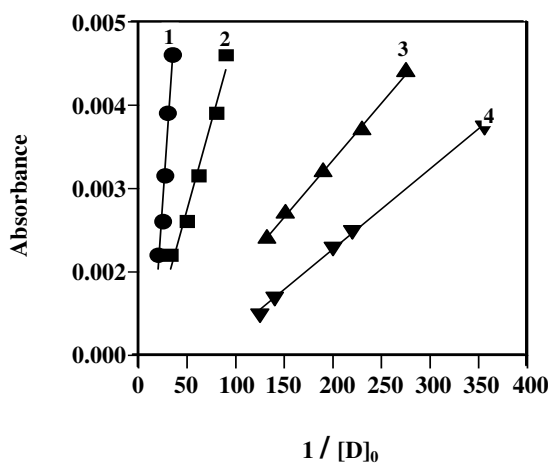


Fig. 6: Hildebrand plots for different donor-acceptor systems in chloroform solution obtained at 25°C: 1, B15C5; 2, DB18C6; 3, NPhA15C5 and 4, DBPy18C6.

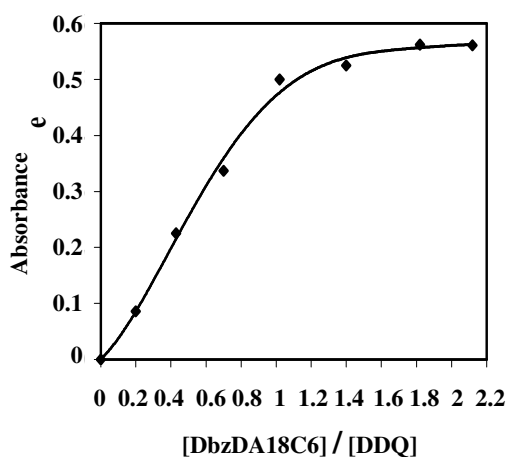


Fig. 7: \log of absorbance vs. DBzDA18C6/DDQ mole ratio obtained at 25°C and 525 nm.

atom. Because of better donation property of nitrogen relative to benzene ring [23], the stability of DBPy18C6

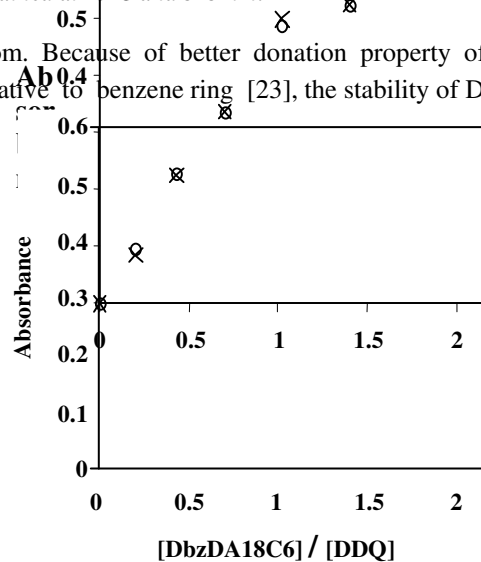
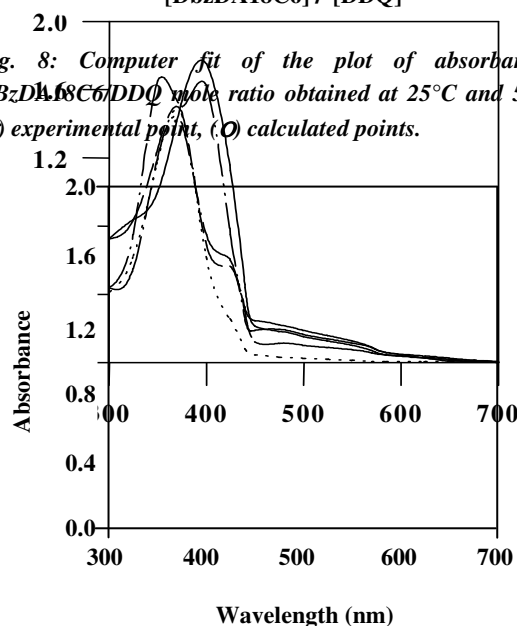


Fig. 8: Computer fit of the plot of absorbance vs. DBzDA18C6/DDQ mole ratio obtained at 25°C and 525 nm. (x) experimental point, (o) calculated points.



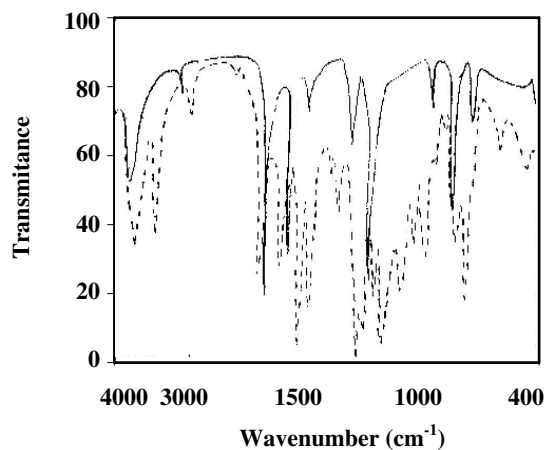


Fig. 10: IR Spectra of DDQ (-) and DDQ - DB18C6 complex (...).

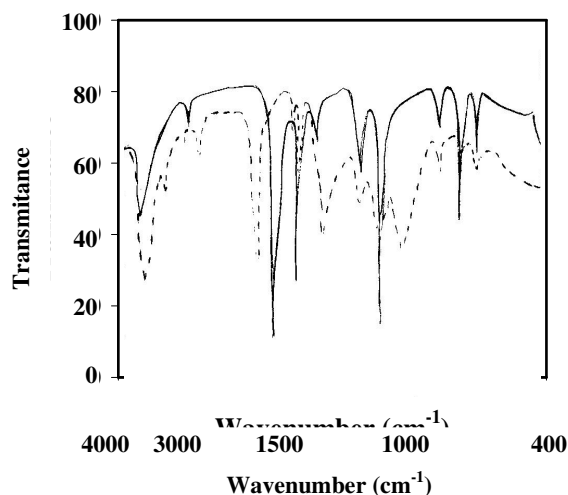


Fig. 11: IR Spectra of DDQ (-) and DDQ - DBzDA18C6.

is higher than DB18C6. The order of stability of azacrownethers is in parallel with the basicity of nitrogen atom. In fact in DBPy18C6 the high electron withdrawing property of pyridine [21] weakens the basicity of nitrogen atom. However in NPhA15C5 the nitrogen located out of the benzene ring and more basicity is observed. Finally in DBzDA18C6, the phenyl groups have the farthest distance and the highest basicity is observed.

Fig. 9: Absorption spectra of 5.71×10^{-4} M DDQ in chloroform in the presence of increasing quantities of DBzDA18C6. The spectra were recorded 24 hours after making the solutions. The DBzDA18C6: DDQ mole ratios are: 1,0.00; 2,0.16; 3,0.41; 4, 0.63 ; 5, 0.85.

Absorption spectra of 5.71×10^{-4} M DDQ in the presence of different quantities of DBzDA18C6 are shown in Fig. 9. The spectra are recorded 24 hours of after preparing the solutions. Comparison of the recent spectra with the spectra which have been recorded just after making the solutions (Fig. 5) indicates: 1)

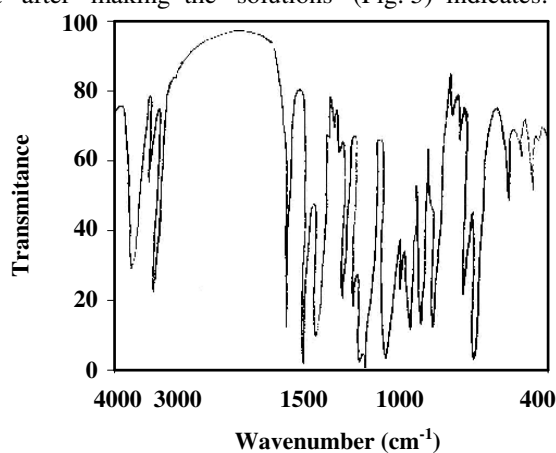


Fig. 12: IR Spectrum of DB18C6.

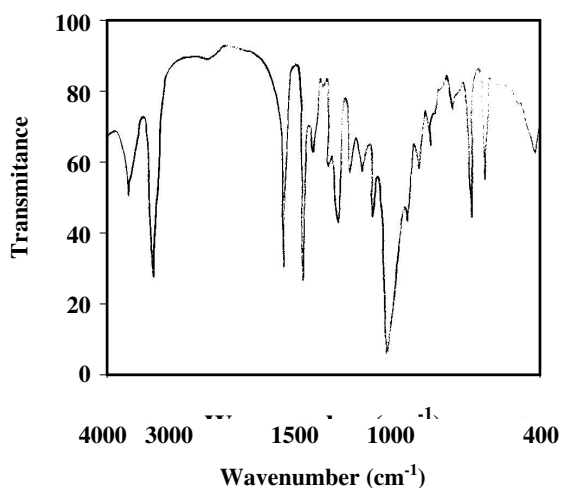


Fig. 13: IR Spectrum of NPhA15C5

the break up of the isosbestic point, 2) disappearance of the bands in 400-600 nm region and 3) appearance of a new band at 390 nm. Similar behavior was observed for

NPhA15C5 and DBPy18C6, but the corresponding spectra are not shown. These observations indicate that the charge transfer complex, has been converted to another adduct via a nonequilibrium reaction. The conversion of DDQ to DDQ⁻ has been observed frequently and many investigators applied it in oxidation observation of gradual increase in conductance of D-DDQ mixtures.

As after 24 hours there was no variation in the spectra of B15C5-DDQ and DB18C6-DDQ mixtures. So it can be concluded that in both systems the corresponding adducts are sufficiently stable.

The IR spectra of all charge transfer complexes in the crystalline form were obtained in KBr pellets. Sample spectra are shown in Figs. 10-13. As it can be seen:

1) The methylene stretching of the ethoxy groups of crown ethers coupled with the ring vibration (2980-2810) do not show any considerable shift when these ligands form charge-transfer complexes with DDQ. This can be ascribed to negligible contribution of ethoxy groups of crown ethers in the interaction with acceptors.

2) The CO and CN peaks of DDQ shift to higher and lower frequencies respectively, the shift upon complexation is indicative of higher charge density of the carbonyl and lower charge density on the cyano groups [29].

3) The C-N stretching band shows considerable shift to lower frequencies indicating the direct involvement of nitrogen atom in complexation.

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