Molecular Complexes of Crown Ethers, Part 6: Complexes of Cryptand (2,2,2) and Kryptofix 5 with Some Acceptors

SALMAN R. SALMAN[1],[⋆] and JABOR K. JABOR[2]
[1]*Chemistry Department, College of Science, University of Qatar, P.O. Box 2713, Doha, Qatar*
[2]*Chemistry Department, Faculty of Science, University of Yarmouk, Irbid, Jordan*

Abstract. The UV-Visible spectra of Cryptand (2,2,2) and Kryptofix 5 as donors, and TCNE (tetracyanoethylene), DDQ (2,3-dichloro-5,6- dicyano-1,4 benzoquinone) and PA (picric acid) as acceptors were studied. Charge transfer (CT) spectra were obtained for these systems. It was found that potassium halides have little effect on the spectra. The major process was due to an electron transfer from the donor to the acceptor. This revealed itself in very high conductivity values for the CT solutions in comparison to that of the donor or the acceptor solutions. The infrared and proton NMR spectra of the complexes indicated a strong interaction between the donor and the acceptor.

Key words: UV-visible spectra, charge transfer complex, electron transfer, TCNE, DDQ.

1. Introduction

In recent years an increasing number of communications have appeared which deal with the charge transfer (CT) complexes between oxygen containing crown ethers (CE) such as 15C5, 18C6, B18C6, DB18C6 etc, and some acceptors [1–10]. There is no work concerning the charge transfer complexes between nitrogen containing CE and acceptors.

It was found that the CT complexes formed between DB18C6 and DB24C8 and DDQ [3], between DB18C6 and different acceptors [4], B15C5, B18C6, DB18C and DB24C8 with tetracyanoquinodimethane, tetracyanoethlyene (TCNE) and chloranil are weak complexes as indicated by the small values of their stability constant, Kc, or by their infrared (IR) and nuclear magnetic resonance (NMR) spectra which did not show major changes in going from the CE solution to the CT complex solution. Abolfazal and Majtaba [5] and Salman et al. [6, 7] reported that the addition of potassium halide [11] affects the complexation between the crown ether and the acceptor.

⋆ Author for correspondence.

In a previous study [11] we found that the CT complexes between DB18C6 and different acceptors are weak, but the interaction and solution conductivity of the complex increased in the presence of potassium halides.

The highest interaction between DB18C6 and the acceptors was in the presence of KF. This was explained as due to an electron transfer from the anion to the acceptor and that the crown ether plays a synergic role in this process [11].

The aim of this work is to study the charge transfer complexation between Cryptand (2,2,2) and Krytofix 5 with different acceptors, such as tetra-cyanoethylene (TCNE), 2,3-dichloro, 5,6-dicyano-1,4-benzoquinone (DDQ) and picric acid (PA).

The effect of using different halides anions with the same cation on the CT complexes of the CE, with some of the acceptors is studied. The mode of addition of CE, acceptors and the salt is varied to investigate if the different systems are interchangeable.

2. Experimental

Infrared (IR) spectra were recorded on a Pye-Unicam SP 300 instrument as potassium bromide discs. Ultraviolet-Visible spectra were recorded for the CEs and their complexes as solutions in dichloroethane, DCE, on a DMS-100 spectrophotometer.

All chemicals used in this work were of pure grade or purified before use (BDH, Fluka, and Aldrich). TCNE was recrystallized from chlorobenzene and then sublimed, m.p (198–200 °C).

DDQ was recrystallized twice from benzene, m.p (214–216 °C). Picric acid was of pure grade and was used without treatment but was kept dry using P_2O_5. In order to check the water content of PA its IR spectrum was recorded. The spectrum did not show a band corresponding to water, but it showed an intramolecular hydrogen bonded hydroxy absorption belonging to picric acid.

3. Results and Discussion

3.1. CRYPTAND(2,2,2) WITH TCNE

Mixing a DCE solution of cryptand (2,2,2) with that of TCNE gives an immediate yellow color. The absorption spectrum of this solution displays two main absorption bands located at 336, 395, and 415 nm respectively (Figure 1). Neither TCNE nor cryptand (2,2,2) has any measurable absorption in this region. However, the longer wavelength band appeared as a doublet. The position and feature of this band is compared with that reported for the TCNE anion [12] formed by complexation of TCNE with the halides salts (i.e., KF, KCl, KBr, and KI) and with that previously reported for 1,1,2,3,3-pentacyanopropenide anion formed by reaction of TCNE with water traces present in the solvent in the presence of a base [13–15]. It may therefore be assumed that there was enough water in the medium to cause the basic hydrolysis of TCNE forming 1,1,2,3,3-pentacyanopropenide even
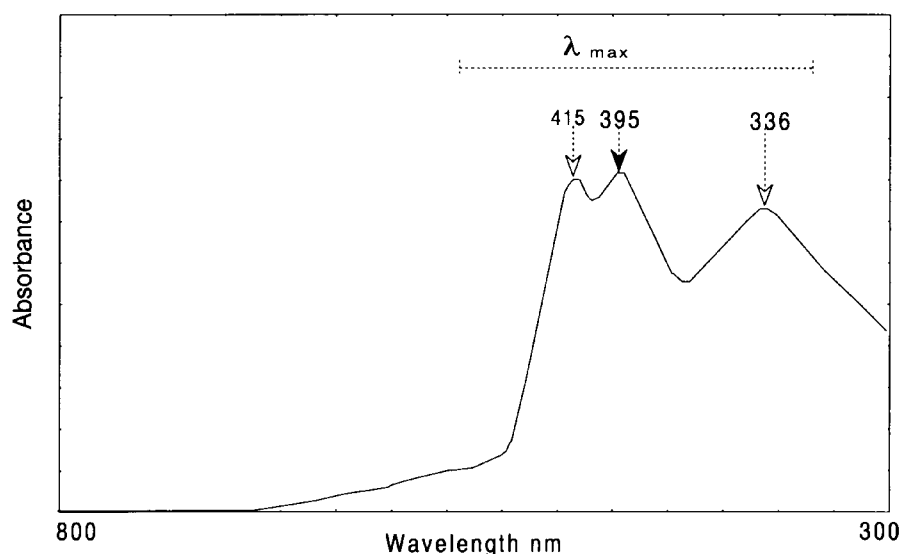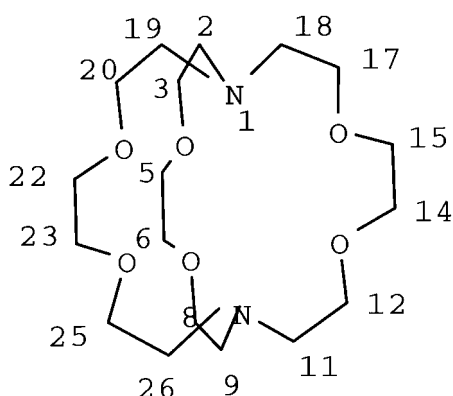
Figure 1. Absorption spectrum of cryptand (2,2,2) 0.008 M + TCNE 0.0001 M in DCE.

in a sealed vacuum system and under anhydrous condition [14]. Accordingly, the highly intense absorption band located at 336 nm could be ascribed to the formation of the intermolecular CT complex.

It is difficult to determine the stability constant of the complex formed between cryptand (2,2,2) and TCNE, because the intensity of the absorption band of the complex is time dependent. The change in the intensity of this band is so fast that it was difficult to perform a kinetic study. Six solutions of varied donor concentrations and fixed acceptor concentration were left for one day and their UV-Visible spectra were measured. It was found that in all samples the absorption band at 336 nm exhibited the same intensity, indicating that the complex formation of cryptand (2,2,2) with TCNE is complete. The conductivity measurement performed after mixing a solution of 0.001 M from each of the donor and acceptor showed that this reaction was time dependent. A rapid increase in conductivity by a factor of 100 after one hour (from $\approx 1 \times 10^{-7}$ to 2.4×10^{-5} $\mu\Omega$) was achieved. This may be due to complete transfer of an electron from the donor to the acceptor. The IR and ^{1}H-NMR spectra of a solution of this complex support this result. The IR spectrum shows a large shift in the CN stretching from 2260 cm^{-1} in TCNE to 2196 cm^{-1} upon complex formation. This may be explained by the formation of the TCNE anion radical since the addition of the electron from the N atom of the cryptand is accompanied by a decrease in the bond order and in the force constant, caused by the antibonding character of the odd electron orbital [16, 17].

The ^{1}H-NMR spectrum of [Cryptand (2,2,2) + TCNE] was recorded in deuterated dichloromethane, CD$_2$Cl$_2$, and compared with those of the starting compounds.

Scheme 1. Structure of cryptand (2,2,2).

The ^{1}H-NMR spectrum of the methylene groups in cryptand (2,2,2) has two sets of absorption peaks, the first group absorbing at 3.63, 3.55 and 3.48 ppm corresponds to an integration of 24H. This was assigned to protons in positions 3, 5, 6, 8, 12, 14, 15, 17, 20, 22, 23 and 25 (Scheme 1) and the second group of peaks at 2.66, 2.59 and 2.52 ppm corresponds to 12H which are assigned to the protons in positions 2, 9, 11, 18, 19 and 26.

The ^{1}H-NMR spectrum of cryptand (2,2,2) shows down field changes in all proton chemical shift at positions 2, 9, 11, 18, 19 and 26 upon complex formation (3.0, 2.94 and 2.89 ppm). This may be due to a charge donation from the nitrogen atom in cryptand (2,2,2) to TCNE.

In order to study the effect of the salt on the formation and stability of CT complexes, the sequence of addition of the salt was varied such that in one system the sequence was [(Cryptand (2,2,2) + TCNE) + salt], while in the second it was [(Cryptand (2,2,2) + salt) + TCNE]. These two systems were found to be interchangeable giving the same absorption band after one day. In the first system the addition of one of the salts (i.e. KF, KCl, KBr or KI) to the complex [cryptand (2,2,2)+TCNE] results in a very slight increase in the intensity of the bands located at 395 nm and 415 nm. The band located at 336 nm was not affected by the addition of the salt. This may indicate very strong complex formation between cryptand (2,2,2) and TCNE; thus it was very difficult to follow the change in the intensity of the absorption band, which belongs to the complex and to calculate Kc from it.

In the other system, when TCNE was added to [Cryptand (2,2,2) + salt]. The band at 336 nm appeared with very low intensity before the addition of TCNE, but after the addition of TCNE, this band increased with time together with the increase in the intensity of the intense bands at 395 nm and 415 nm. The internal size of cryptand (2,2,2) is about 2.8 Å [18] and this fits nicely with the diameter of the potassium cation 2.66 Å [19] so that the CE encapsulates the cation and prevents the acceptor molecule from complexing with it, therefore the system required some time to be interchangeable.

3.2. CRYPTAND (2,2,2) WITH DDQ

Tertiary amines have low ionization potentials therefore their activity is strong enabling them to react with different acceptors to form CT complexes. DDQ has a high electron affinity so the complex formation involves electron transfer from cryptand (2,2,2) to DDQ, which results in the formation of the ion radicals, which can be observed in DCE solution by means of UV-Visible spectra, and by measuring their conductivity. The conductivity of the mixture of 0.001 M solution from each of the donor and acceptor in DCE increased about 100 times (from $\approx 1 \times 10^{-7}$ to 2.27×10^{-5} $\mu\Omega$) after one hour of mixing the donor and the acceptor. The conductivity was time dependent.

Multiple bands in the visible region (586, 540, 500, 460 and 410 nm) were observed after mixing a solution of cryptand (2,2,2) with DDQ in DCE. They are assigned to CT bands due to complex formation. Such bands were not present in the UV-Visible spectrum of the separate donor or acceptor solution in DCE. It was difficult to study the effect of the salt on the CT complex between DDQ and cryptand (2,2,2) because the same multiple bands were obtained. Therefore it is difficult to distinguish whether the donation of charge was from the anion or from the cryptand (2,2,2).

Figure 2 shows the multiple intermolecular CT bands. It is generally considered that these arise either from excitation of electrons in more than one level in the donor, e.g. from the highest and filled levels or from transition to more than one vacant level in the acceptor or both. Thus the energy differences in the transition from the cryptand (2,2,2) F^-, Cl^-, Br^-, and I^- to the DDQ are effectively independent of the strength of the donor. This suggests that this is a measure of the energies of the highest vacant levels in DDQ. It is interesting to note that the multiple bands have different intensities relative to each other depending on the donor and the shape of the complex formed. Simple valence-bond theory predicts that for a given acceptor the intensity of the absorption should increase with increasing interaction between the donor and the acceptor.

3.3. CRYPTAND (2,2,2) WITH PICRIC ACID

Picric acid forms a wide range of complexes with different acceptors [20]. A few studies have been performed on CT between CE and picric acid [8] but none on the CT between picric acid and cryptand (2,2,2). Therefore this system was examined in this work.

A strong new absorption band at 376 nm was observed after mixing a DCE solution of cryptand (2,2,2) with picric acid (Figure 3). This band may be attributed to CT or hydrogen transfer from the phenolic proton in picric acid to the nitrogen atom in the structure of cryptand (2,2,2).

The ^{1}H-NMR spectrum of cryptand (2,2,2) with picric acid was recorded in CD_2Cl_2 and compared with those of the cryptand (2,2,2) and picric acid separately. The comparison shows the following.
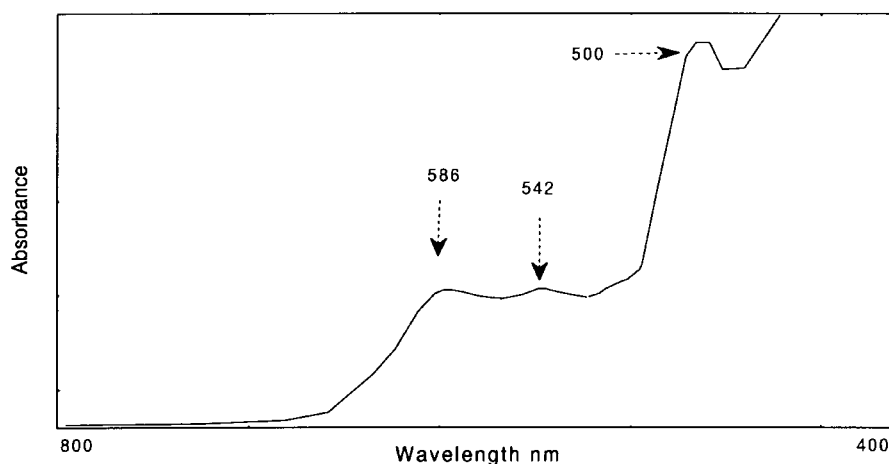
Figure 2. Absorption spectrum of [Cryptand (2,2,2) 0.008 M + TCNE 0.0001 M] in DCE.
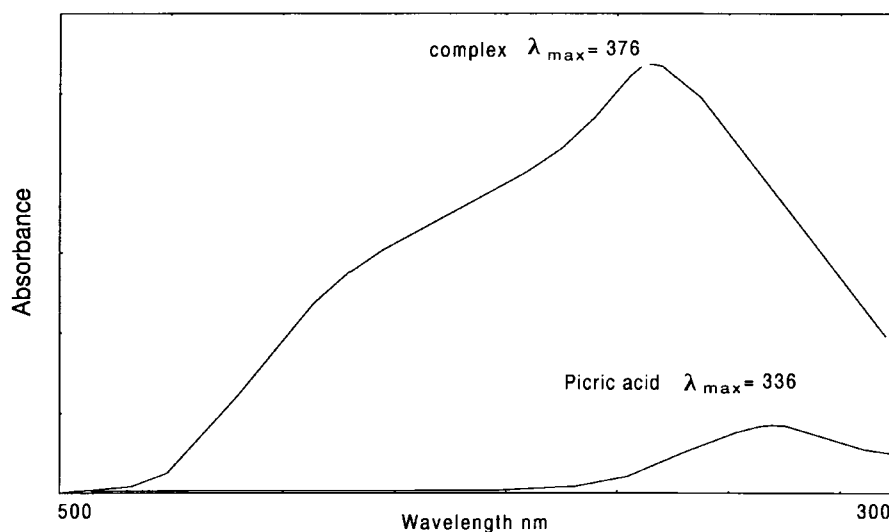

Figure 3. Absorption spectrum of [cryptand (2,2,2) 0.008 M + Picric acid 0.0001 M] in DCE.

1. The phenolic proton peak of picric acid at 11.8 ppm, which is related to intermolecular hydrogen bonding [21] between the phenolic proton and the adjacent nitrogen groups, disappeared upon complex formation and a new peak appeared at 5.19 ppm which may be attributed to hydrogen transfer from the phenolic proton of picric acid to the nitrogen atom in cryptand (2,2,2). This peak disappeared upon the addition of D_2O.

2. The peak at 9.2 ppm assigned to the protons in position 3 and 5 in picric acid shifts to 8.71 ppm upon complex formation. This indicates an increase in charge density of these protons. This may be explained as due to the formation of picrate anion.

3. The ^{1}H-NMR spectrum of cryptand (2,2,2) shows a large down field shift in all protons at positions 2, 9, 11, 18, 19 and 26 upon complex formation (3.05, 2.98, 2.93 ppm). This may be due to hydrogen transfers from picric acid to cryptand (2,2,2) to form the complex.

The strong peak located at 3.63 ppm did not show any shift upon complexation while the peaks at 3.55 and 3.48 ppm shifted down field (3.72 and 3.66), therefore the peak at 3.63 ppm may be assigned to the protons at positions 5, 6, 14, 15, 22 and 23 while the others peaks at 3.55 and 3.48 ppm may be assigned to the protons at positions 2, 9, 11, 18, 19 and 26.

3.4. KRYPTOFIX 5 WITH TCNE

Mixing a DCE solution of Kryptofix 5 with that of TCNE results in an immediate yellow color. The absorption spectrum of this solution displays two main absorption bands located at 395 and 415 nm respectively. Neither TCNE nor Kryptofix 5 has any measurable absorption in this region. The reason for the appearance of these bands was discussed previously. It is believed that the 395 and 415 nm bands are due to a CT from the Kryptofix 5 to TCNE because the intensity of this band varied according to the concentration of the donor. The Benesi-Hildebrand plot shows a deviation from linearity indicating different ratios for the complex formation.

Kryptofix 5 has two donor centers in the molecule, namely the lone pair of electrons on the nitrogen atom in the quinoline ring and the π system in the aromatic ring. Such a molecule may react as an n-donor (leaving an unshared electron pair of the nitrogen atom for the formation of CT bond with the acceptor molecule) or a π-donor (leaving the electrons occupying the highest π level for the formation of the intermolecular bond). In accordance with experiment evidence N-heterocyclics will be considered as donors of non-bonded (n) electrons [22].

The conductivity measurement performed after mixing a solution of 0.001 M from each of the donor and acceptor showed that this reaction was time dependent. A rapid increase in conductivity after one hour (from $\approx 1 \times 10^{-7}$ to 2.1×10^{-5} $\mu\Omega$) was observed. This may be due to complete transfer of an electron from the donor to the acceptor. The IR and NMR spectra of a solution of this complex support this result. The IR spectra show a large shift in the CN stretching from 2260 cm^{-1} in TCNE to 2196 cm^{-1} upon complex formation.

The ^{1}H-NMR of Kryptofix 5 was recorded in CD$_2$Cl$_2$ and compared with those of the starting compounds

The ^{1}H-NMR peak of the protons of the methylene groups of Kryptofix 5 shifted to high field (from 3.91–4.03 to 3.75–3.87, and from 4.26–4.38 to 4.32–4.43 ppm) upon complexation. This may be due to the conformation adapted by CE in solution upon complex formation, and this causes the methylene protons to be exposed to the ring current of the aromatic ring of the CE (Scheme 2). The aromatic protons in positions a, b, c and d shifted down field upon complex formation, from 7.48–6.99
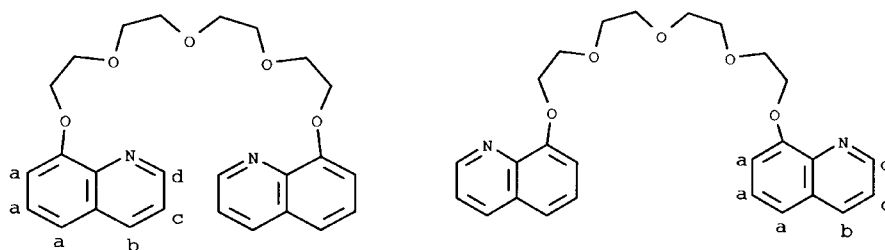
Scheme 2. Structure of Kryptofix 5.

to 7.72–7.39 ppm for the protons in position a overlap with the protons in position c. The protons in position b shifted from 8.07–8.19 to 8.45–8.6 ppm. The proton in position d was very slightly shifted down field (from 8.92 to 8.95 ppm) upon complexation while that at position b shifted to low field to a larger extent. A CT from the nitrogen atom in the aromatic ring to the acceptor cannot explain by itself this unusual result. On the other hand the resonance effect in position b may be larger than that in position d.

3.5. KRYPTOFIX 5 WITH DDQ

A mixed DCE solution of Kryptofix 5 and DDQ exhibits immediately a red color due to the formation of a CT complex. The absorption spectrum of this solution displays multiple absorption bands in the visible region (586, 540, 500 and 460). These are assigned to CT bands due to complex formation as Kryptofix 5 and DDQ did not show any measurable absorption in this region when they were taken separately. The conductivity measurement performed after mixing a 0.001 M solution of each of the donor and acceptor showed that this reaction was time dependent. A rapid increase in conductivity after one hour (from $\approx 1 \times 10^{-7}$ to 19.6×10^{-5} $\mu\Omega$, was observed. This may be due to complete transfer of an electron from the donor to the acceptor.

3.6. KRYPTOFIX 5 WITH PICRIC ACID

A strong new absorption band at 376 nm was observed after mixing a DCE solution of Kryptofix 5 with picric acid. This band may be attributed to CT or hydrogen transfer from the phenolic proton in picric acid to the nitrogen atom in the structure of Kryptofix 5.

   The ^{1}H-NMR spectrum of Kryptofix 5 with picric acid was recorded in CD_2Cl_2 and compared with those of Kryptofix 5 and picric acid separately. The comparison shows the following.

 1. The phenolic proton peak of picric acid at 11.8 ppm, which is related to intramolecular hydrogen bonding [21] between the phenolic proton and the adjacent nitrogen groups, disappeared upon complex formation and a new

peak appeared at 3 ppm which may be attributed to hydrogen transfer from the phenolic proton of picric acid to the nitrogen atom in Kryptofix 5 which was proved by disappearance of this peak upon the addition of D_2O.

2. The proton peak at 9.2 ppm, which is assigned to protons in positions 3 and 5 in picric acid, shifted down field upon complex formation to 8.81 ppm. This may be explained as due to the formation of the picrate anion.

3. The ^{1}H-NMR peak of the methylene group protons of Kryptofix 5 shifted to high field (from 3.91–4.03 to 3.75–3.87, and from 4.26—4.38 to 4.32–4.43 ppm) upon complexation. This may be due to the conformation adopted by CE in solution upon complex formation, and this causes the methylene protons to be exposed to the ring current of the aromatic ring of the CE (Scheme 2). The aromatic protons in position a, b, c and d shifted down field upon complex formation, from 7.48–6.99 to 7.9–7.67 ppm for the protons in position a overlap with protons in position c. The protons in position b shifted from 8.07–8.19 to 8.65–8.7 ppm. The proton in position d shifted slightly down field (from 8.92 to 9.1 ppm) upon complexation while that at position b shifted to low field by a larger extent. A CT from the nitrogen atom in the aromatic ring to the acceptor cannot by itself explain this unusual result. On the other hand the resonance effect in position b may be larger than that in position d.

4. Conclusions

The addition of cryptand (2,2,2) to one of the acceptors in DCE solution results in a strong CT complex formation which can be detect by UV-Visible, NMR, conductivity and IR techniques. It is safely concluded that the CT due to the presence of the nitrogen atom in the structure of CE may involve electron transfer from a n-bonding orbital of the donor to the one of the anti-bonding orbitals of DDQ or TCNE to form the anion radical. IR measurements for the complexes between cryptand (2,2,2) and Kryptofix 5 with TCNE show the extent of complexation between donors and acceptor. Therefore the ν_{CN} shift for this group in cryptand (2,2,2)-TCNE and Kryptofix 5-TCNE is very large revealing the strong interaction between the donor and the acceptor.

^{1}H-NMR spectroscopy was useful in the study of complexation between cryptand (2,2,2) and Kryptofix 5 with TCNE. It is shown that for the system Kryptofix 5-TCNE the CT is from the nitrogen and the aromatic ring to the antibonding orbital of TCNE and this causes the protons of the aromatic ring to shift to low field upon complexation.

As for the calculation of Kc this work indicated that the usual method used to monitor the change in the intensity of the CT band cannot be used because the interaction between the donor and the acceptor is so strong that the whole process takes a very short time compared to the time needed to run a UV-Visible spectrum. There is a need to follow a new procedure which will enable us to follow the change in the UV-Visible band and thus to calculate Kc.

References

1. E. Shchori and J. Jaquar-Grodzinski: *Isr. J. Chem.* **10**, 953 (1972).
2. H.P. Hopkins, D.V. Jahagirdar and J. J. Windler: *J. Phys. Chem.* **82**, 1254 (1978).
3. R. Malin and V. Krishnan: *J. Phys. Chem.* **84**, 551 (1980).
4. A.M. Nour El-din: *Spectrochim Acta* **42A**, 637 (1986).
5. A. Semnani and M. Shamsipur: *Spectrochim Acta* **49A**, 411 (1993).
6. G.A.W. Derwish, S.R. Salman and S. Al-Marsoumi: *J. Incl. Phenom.* **20**, 123 (1995).
7. S.R. Salman, G.A.W. Derwish and S. Al-Marsoumi: *J.Incl. Phenom.* **23**, 175 (1995).
8. S.R. Salman, G.A.W. Derwish, S Al-Marsoumi: *J. Incl. Phenom.* **25**, 295 (1996).
9. Y. Jayathirtha and V. Krishnan: *Natl. Acad. Sci. Lett.* **1**, 365 (1978).
10. R. Malin and V. Krishnan: *J. Chim. Phys. Chim. Biol.* **78**, 503 (1981).
11. S.R. Salman and J.K. Jabor: *J. Incl. Phenom.* **33**, 5–16 (1999).
12. J.A.A. De Boer, and D.N. Reinhoudt: *J. Chem. Soc. Perkin Trans 2*, 377 (1986).
13. W.J. Middleton, E.L. Little, D.D. Coffman and V.A. Engelhardt: *J. Am. Chem. Soc.* **80**, 2295 (1958).
14. H.J. Shine and R.D. Goodin: *J. Org. Chem.* **35**, 949 (1970).
15. J. Badard: *J. Chem. Phys.* **66**, 221 (1969).
16. J.J. Hinkel: *J. Phys. Chem.* **58**, 325 (1973).
17. Y. Iida: *Bull. Chem. Soc. Jpn.* **46**, 423 (1973).
18. J.M. Lehn and J.P. Sauvage: *Chem. Commun.* 440 (1971).
19. G. Briegleb, W. Liptay and R. Fick: *Z. Electrochem.* **66**, 859 (1959).
20. R. Foster: 'Organic Charge Transfer Complexes', Academic Press (1969).
21. R.M. Silverstein, G.C. Basller and T.C. Morrill: *Spectrometric Identification of Organic Compounds*, Fourth Edition, John Wiley and Sons, (1981).