CHAPTER II

WEAK INTERACTIONS

AROMATIC HYDROCARBONS – QUINONE SYSTEM

The experimental aspects of the study on weak interaction between the donor and acceptor in equilibrium in solution for the Aromatic hydrocarbons–CMBQ system are given here.

EXPERIMENTAL

The spectrophotometry study of the charge-transfer complex equilibrium taken up here consists of taking the absorption spectra of the donor and the acceptor separately dissolved in a suitable solvent and also those of solutions containing both of them in certain determined ratios over a wavelength range. Significant changes in the spectra are
looked for like the appearances of a new absorption band, an increase in intensity of absorption in a region or changes in the original absorption bands of the donor or acceptor. From a study of these changes as a function of concentration of these two components, the values of the formation constant $K$ and the molar absorption coefficient $\epsilon$ of the complex are sought to be determined.

In this study the acceptor chosen is the quinone CMBQ which is 2,5 dichloro 3,6 dimethoxy 1,4 benzoquinone. The donors are the aromatic hydrocarbons.
1) hexamethylbenzene 2) fluorene 3) napthalene 4) durene and 5) acenaphthene.

The materials used, the preparation of solutions and the method in spectral measurement are given below.

**MATERIALS**

2.5 - Dichloro 3-6-Dimethoxy 1,4 -Benzoquinone (CMBQ)

This was prepared by the method adopted by Vertor and Roger (85) as described below.

A solution of 9.2 g of sodium in 200 ml of methanol was added slowly to a suspension of 24.6 g of chloranil in 50 ml of methanol with constant shaking while the temperature of the mixture was kept at room temperature by means of an ice bath. The resulting mixture was slightly warmed. The orange, coloured dichloro dimethoxy quinone separated out when
cooled. It was filtered and washed with ice cold water. The quinone was then recrystallised twice from methanol m.p. 118°C.

**Hexamethylbenzene**

Cambrian chemicals, 'U.K. sample was recrystallised from alcohol.

**Fluorene**

Fluka sample was used as such.

**Naphthalene**

Sisco chem pure sample was used.

**Durene**

B.D.H. sample was used.

**Acenaphthene**

obtained from Ferak, Berlin (West Germany) was recrystallised from alcohol.

**Carbontetrachloride**

B.D.H. laboratory grade sample VMS washed repeatedly with dilute sodium hydroxide solution and water, dried over freshly fused calcium chloride and distilled through fractionating column, the middle fraction distilling at 76.5°C was collected. Complete absence of carbon disulphide was confirmed by the absence of any absorption at 320 nm.
Preparation of solutions

The solvent used was carbontetrachloride. Two primary solutions were made up gravimetrically one containing the donor as solute and the other having the acceptor. From these two solutions, a secondary set was prepared volumetrically such that the acceptor concentration alone was invariant in the mixture while the donor concentration was varied over a range.

The weights were determined on a single pan AE 240 Mettler balance with a reading accuracy of 0.05 mg. The volumetric glassware were corning A-grade within the A-certificate tolerance limit prescribed by British and Indian standards.

Spectrophotometric measurements

The optical densities of the solution were measured using UV-240 Shimadzu UV-visible recording spectrophotometer. The same 10 mm matched pair of fused silica cells were used in all measurements, the reference being in the same reference cell with the same side facing the photocell all the time. The teflon stoppered silica cells were placed in a thermostatable block in the instrument's cell compartment through which water from a precision constant temperature bath(+0.1°C) was circulated. The cells were allowed to equilibrate to the block temperature until constant optical density readings were assured. Usually
twenty minutes was a sufficient time for equilibration. All O.D. values were corrected for cell blanks by keeping the pure solvent in both cells' and ensuring the baseline at: zero before commencing the work.

The choice of concentration of the components is governed by several factors like the limited solubility of the compounds, the interfering absorption due to the individual components at the crucial wavelengths, and the likely strength of the complex for which a reasonable guess can be had from analogous studies. The condition that the concentration of donor far exceeds that of the acceptor is maintained in all these cases $D \gg A$. Further Person's criterion (86) for weak complexes as expanded by La Brtdde and Tamres (87) that the condition $0.1K < \left( \frac{[U]}{[A]} \right)_{\alpha}$ should prevail has been adopted.

Method of calculation

It is the absorption of the mixture at any wavelength minus the sum of the absorption due to the two components that is to be determined for a series of donor concentrations. In some cases some amount of absorption due to the donor becomes unavoidable. Arithmetical correction for the absorption due to donor and acceptor at the measuring wavelength is done from a knowledge of their molar absorptivity and concentration taken. The observed optical density is then taken to be due to the complex alone. This
is given in the tables and figures as (0.D.diff). A notable feature in this study here is that the acceptor CMBQ has a significant absorption band at 410 nm. This serious handicap has to be mot. The most widely used method using Bonosi-Hildobrand equation could not be used as such. So the appropriate form of another equation which takes into account the absorption of the acceptor molecule should be used.

Let us assume the system to be ideal in which a 1:1 complex AD is formed from the donor D and acceptor A as

\[ A + D \rightleftharpoons AD \] \hspace{1cm} (1)

Assuming activity coefficients of unity the equilibrium constant for the complex formation \( K^{AD} \) is

\[ K^{AD} = \frac{[AD]}{[A][D]} = \frac{[AD]}{([A]_0 - [AD]) ([D]_0 - [AD])} \] \hspace{1cm} (2)

Where \([A]_0\) and \([D]_0\) indicate the total, that is the free plus the complexed concentration of A and D in moles per litre respectively. This equation can be rearranged as

\[ \frac{1}{[AD]} = \frac{1}{K^{AD}} - \frac{1}{[A]_0 [D]_0} + \frac{1}{[D]_0} + \frac{1}{[A]_0} - \frac{[AD]}{[D]_0} \] \hspace{1cm} (3)

If an arithmetical correction for any absorption for the donor molecule in the region has been made, then we can safely assume that the optical absorption measured is due to the complex AD and free acceptor A, then for a 10 mm path length, cell, the absorption \( A_{10} \) is
\[ \Lambda_T = \zeta^{AD} [AD] + \zeta^{A} [A] \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4) \]

Where \( t'' \) ' is the molar absorption constant \( M_l \) com p. ox. AM at the wavelength of measurement and similarly \( \zeta \) is the molar absorption constant of acceptor at wavelength \( \lambda \).

From the above, two equations, it can be shown that:

\[ \frac{1}{\Lambda_T - \Lambda_q} = \frac{1}{K^{AD} (\zeta^{AD} - \zeta^{A}) [D]_0} + \frac{1}{\{A\}_0} \]

\[ \frac{1}{\{A\}_0} = \frac{1}{(\zeta^{AD} - \zeta^{A})} \]

\[ \frac{1}{\{D\}_0} = \frac{1}{(\zeta^{AD} - \zeta^{A})} \]

\[ \frac{1}{\{A\}_0} = \frac{1}{(\zeta^{AD} - \zeta^{A})} \]

\[ \frac{1}{\{AD\}} = \frac{1}{(\zeta^{AD} - \zeta^{A})} \{A\}_0 \]

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Where \( \Lambda_q \) is the absorbance clue to the acceptor; concentration \( \{A\}_0 \). We have the mixture solution in nuclei a. way that \( [D]_0 >> \{A\}_0 \) and therefore \( \lambda \) and \( fA' \) are sufficiently small, the second and fourth term on the right hand side of equation (5) may be neglected so that equation (5) becomes:

\[ \frac{1}{\Lambda_T - \Lambda_q} = \frac{1}{K^{AD} (\zeta^{AD} - \zeta^{A}) [D]_0} + \frac{1}{\{A\}_0} \]

\[ \frac{1}{\{A\}_0} = \frac{1}{(\zeta^{AD} - \zeta^{A})} \]

\[ \frac{1}{\{D\}_0} = \frac{1}{(\zeta^{AD} - \zeta^{A})} \]

\[ \frac{1}{\{A\}_0} = \frac{1}{(\zeta^{AD} - \zeta^{A})} \]

\[ \frac{1}{\{AD\}} = \frac{1}{(\zeta^{AD} - \zeta^{A})} \]

Here \( \Lambda_T - \Lambda_q \) is the same as (O.U) difference given in the tables and figures because the correction for donor absorption bias has been made. This is the modified form of Ketelaar's equation (88).
For a series of solutions in which \([D]_0 \neq \{A\}_0\) and \([A]_0\) is kept constant, a plot of \(\lambda - \lambda_d\) should be linear. The slope of the line is \([D]_0\) 1 
\((\epsilon^{AD} - \epsilon^A) K^{AD}[A]_0^{-1}\) and the intercept of the line, with the ordinate is equal to \((\epsilon^{AD} - \epsilon^A) [A]_0) -1\). From this operation and intercept we get the value of: \(K^{AD}(\epsilon^{AD} - \epsilon^A)\) and \((\epsilon^{AD} - \epsilon^A)\) which may be designated as \(K\epsilon'\) and \(\epsilon'\). By correcting for the molar absorbance of the acceptor \(\epsilon^A\), the true value for \(K\epsilon\) and \(\epsilon\) for the complex AD can be obtained.

Presentation of Results

The observed absorption spectra and the results of the numerical computation obtained have been organised and presented in the following manner.

The figures 1-5 give the observed absorption spectra for the donor, acceptor and the mixture with the concentrations indicated in each case. Only the spectra obtained for the highest concentration of donor is presented as a representative of all in a system, so that the significant increase in absorption can be discerned more clearly.

The absorption measurement data required for plotting the graphs for obtaining the equilibrium values \(K\) and \(\epsilon\) from the Ketelaar's equation are tabulated in Tables 1-15 one for each temperature for each donor-acceptor pair, Figs 6-20 are the
corresponding plots which were subjected to least, square analysis and the straight line drawn. The slope and intercepts of these lines are interpreted in the discussion.

In order to get the enthalpy of formation for each system, the Van't Hoff plots using the product KE values against the reciprocal of Kelvin temperatures are given in the Tables 16-20 and the corresponding figures 21-25 in keeping with the usual practice because KE values are more dependable than the often inseparable K and E values even where it is possible.

RESULTS AND DISCUSSION

The changes in the absorption spectra of the quinone acceptor CMBQ brought about by the addition of the five donors hexamethylbenzene, fluorene, naphthalene, durone and acenaphthalene are to be analysed and interpreted in terms of the present knowledge about such donor-acceptor complexes with analogous studies on other quinones like chloranil.

The most important observation from the figures and tables is that there is in all cases an increase in the intensity of absorption over the whole wavelength range studied. Next notable observation is that there is no new absorption band clearly standing apart from the general increase in intensity of the absorption band of the quinone. Thirdly there is a slight shift of the absorption band from 410 nm to 400 nm, a kind of blue shift. This change in
intensity and the shift towards 400 nm is not due to chemical interaction for its stability with time has been tested. It is only an equilibrium situation one is dealing with.

The unusual feature with this study is that the acceptor itself has a fairly good absorption in the range of wavelength where one anticipates the charge transfer absorption to be.

Chloranil has three absorption maxima(89) namely two high intensity ones due to allowed $\pi-\pi^*$ transitions at 202 nm ($\log \varepsilon = 4.0$) and 288 nm ($\log \varepsilon = 4.2$) and a low intensity $\pi-\pi^*$ forbidden transition at 370 nm ($\log \varepsilon = 2.8$). Its counterpart CMBQ taken here and deliberately chosen for its diminished acceptor capacity has the same transitions but their positions shifted. CMBQ has three absorption maxima(90). With two high intensity $\pi-\pi^*$ allowed transitions at 216 nm and 410 nm and one low intensity $\pi-\pi^*$ forbidden transition at the visible region 410 nm ($\log \varepsilon = 2.48$).

It is the "low" intensity band at 410 nm for the CMBQ that is confronting here. In all studies with chloranil, however the charge transfer band appears clearly away from the weak $\pi-\pi^*$ forbidden band firstly because this is at 370 nm more towards the ultraviolet and secondly because the compound has an increased electron affinity yielding complexes with much lower charge transfer excitation and so absorbing at longer wavelength in the visible. The
corresponding absorptions for the same donor's from available literature are (16) found to be as follows for chloranil:

- Hexamethylbenzene : 510 nm
- Fluorene : 500 nm
- Naphthalene : 430 nm
- Durene : 475 nm
- Acenaphthene : 560 nm

As two chlorines have been replaced by two methoxy groups, while the donor from chloranil to dichloro dimethoxy quinone CMBQ, the electron affinity may be expected to have moved to lower values. From the electron affinity values in ev of 1:4 benzoquinone (0.77), chloro benzoquinone (0.97) and methoxy benzoquinone (0.65) it is possible to anticipate the value of CMBQ to have come down from 1.37 of chloranil to about 0.8 in which case it is likely to behave like 1,3,5-trinitrobenzene. This nitro compound has the following absorptions for its complexes with aromatic donors (13).

- Hexamethylbenzene : 392 nm
- Naphthalene : 370 nm
- Durene : 342 nm
- Acenaphthene : 425 nm

It is possible to expect the absorption of the complexes, for the donors chosen, with CMBQ to be in the same range as above between 340-450 nm. This is exactly the place where the acceptor itself has a significant band with E-300.
The $\lambda_{\text{max}}$ for CMBQ at 410 nm is actually measured to be $332.6$. This intensity is low but enough to obscure the possible charge transfer absorption here particularly because the expected molar absorbance of the weak complex even with the best of the donors is also likely to be low.

Sometimes the presence of an absorption band for the acceptor is not such an unwelcome feature because even this can be turned to an advantage. Such has been the case with complex studies with iodine as an acceptor. Free iodine has a low intensity ($\varepsilon = 960$) absorption in the visible at 520 nm. This locally excited iodine band in the visible gets a blue shift on the addition of α or n-donors. As the concentration of the second component say benzene is increased there is a decrease in the absorption at the blue shifted iodine peak and this has been used to estimate the association constant of the complex formed (92, 93). But the redeeming aspect here is that as this band due to free iodine comes down on complexing, the new charge transfer band appears at a shorter wavelength near 300 nm with an isosbestic point at 400 nm. In fact the beginnings of the subject of charge transfer spectra had its origin only in such an investigation on the colour changes in iodine solutions.

But in the case of CMBQ as an acceptor the charge transfer band itself is likely to be submerged under the acceptor band. A decrease in the acceptor absorption due to
complexing and an increase in intensity because of complex absorption' may be occurring at nearly the same wavelength region. The emergence above or submergence below the acceptor-band should depend on the relative contribution by these two factors.

One can envisage three kinds of situations. **Case 1** When the molecular absorption constant of the acceptor is equal to the same of the complex where $\varepsilon_{AD} = \varepsilon_{CMBQ}$. In such a case the absorption decrease due to the complexing of the acceptor is exactly matched by the increase due to the new complexed species. So there will be no change in the intensity of absorption band.

**Case 2:** When $\varepsilon_{AD} < \varepsilon_{CMBQ}$. In this case as one goes on adding more donor molecules, the complex with low absorption will be replacing the acceptor with higher absorption. One should then observe a decrease in intensity an unusual prospect though.

**Case 3:** When $\varepsilon_{AD} > \varepsilon_{CMBQ}$. Here whatever part of the acceptor is complexed contributes to an increase in intensity.

On examining the spectra from figures 1 to 5 and tables 1-15 it is found that in the case of all the five donor-acceptor-pairs only an increase in the absorption band at 400 nm is observed. So it appears certain that the molar absorptivities of the complexes formed in all these cases are higher than those of CMBQ itself.
As there is no new absorption peak evident in any of the systems, the energy of the charge transfer transition cannot be estimated here, perhaps the most important of parameters looked for in any charge transfer studies. But one can get at the range in which it can lie. According to Briegleb weak complexes will show the broadest charge-transfer bands. These being further coincident with the broad band of the acceptor, only an estimate of the range is possible here. From the nature of the composite absorption, the charge transfer wavelength may be said to range from 350 nm to 450 nm, in the case of CMBQ with these five aromatic donors.

Even in cases where there is maxima in an inconvenient region equilibrium constants for the complex formation can be determined by working at wavelengths away from the maxima near the descending tail portion of a band. Even in case of general increase in absorption without a maximum this is possible. Keet' er and Andrews (94), and Foster and Ilmmick (95) have done so in their work. Therefore using the modified Benesi-Hildebrand equation with all its usual assumptions and with a knowledge of its limitations (13), the attempt to determine the $K_C$ values has been done here with the data gathered here—in tables 1-15 by measuring the changes in intensity at the slightly shifted peak wavelength 400nm.

Equilibrium Constant for Hexamethybanzene - CMBQ system

Taking up the results on this system, it is seen that
for a series of solutions in which \([D]_0 \gg [A]_0\), the plot of 
\[ \frac{1}{(O.D.)} \text{jjff} \] against \[ \frac{1}{[D]_0} \] gives a linear plot. (O.D) Qjiff is the extra absorption after correcting for any contribution by the donor and acceptor. The slope of the line gives the value \( \{K(\varepsilon^{AD} - \varepsilon^A) \cdot [A]_0\}^{-1} \) from which \( K \cdot \varepsilon^{AD} \), the value for the complex is obtained. The intercept of the line with the ordinate gives \( \{((\varepsilon^{AD} - \varepsilon^A) \cdot [A]_0)\}^{-1} \). From this can be obtained the value of \( \varepsilon^{AD} \). The suitable correction for the molar absorbance of the acceptor \( \varepsilon^A \) at the measured wavelength namely 400 nm has to be made. From these two values the factors \( K^{AD} \) and \( \varepsilon^{AD} \) for the complex can be derived. \( K \) and \( \varepsilon \) are not determinable independently by this optical spectroscopic method. The value of \( K \varepsilon \), as obtained for this complex is 44.3 \( l^2 \text{mol}^{-2} \text{cm}^{-1} \)

A look at the plots in Fig 6 shows that the plot has a finite intercept with the ordinate. Using this the derived value for \( \varepsilon \) as obtained is 113.54 \( l \text{mol}^{-1} \text{cm}^{-1} \) and after correction for the acceptor absorption becomes 445.5. The equilibrium constant \( K \) is derived as 1.00. The experimental data when analysed by the method of least square, curve fitting gives the values with their attendant errors. The final values at 27°C are.

\[
K \varepsilon = 443 \pm 214 \ l^2 \text{mol}^{-2} \text{cm}^{-1}
\]
\[
\varepsilon = 445 \pm 215 \ l \text{mol}^{-1} \text{cm}^{-1}
\]
\[
K = 1.00 \pm 0.48 \ l \text{mol}^{-1}
\]
Such lax-ge values of errors are not uncommon for very weak complexes. It shows that when one has to deal with much weaker complexes with other donors whose ionisation potentials are much lower than hexamethylbenzene, one enters into an area with abnormal possibilities. It is possible to bunch together all the other four donors and try to analyse the results obtained for them.

**Results with other donors:**

The spectral Figures 2-5 also show that there is only an enhanced absorption in each case. In all these the acceptor absorption is unavoidable because of the very weak nature of the complex. Considerable amount of acceptor has to be taken in order to find significant changes in the spectra. Slight shift of the band from 410 to 400 nm is also seen in these spectra. The choice of donor concentration is also governed by the need to get observable increase in absorption. Anyway suitable correction for this is made while finding the extra absorption due to the complex.

When the tables 5-15 and the linear plots in figures 9-20 are examined a remarkable new observation is that the slope is positive but the intercept in all the cases becomes
This abnormal finding has to be carefully interpreted. Before doing so, a comparison of the non-controversial product $K\varepsilon'$ values may be made. These values are given below. Values for hexamethylbenzene is also included for the sake of completeness.

<table>
<thead>
<tr>
<th>Donor</th>
<th>$K\varepsilon'$ $\pm$</th>
<th>$l^2$ mol$^{-2}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethylbenzene</td>
<td>443 $\pm$ 214</td>
<td></td>
</tr>
<tr>
<td>Fluorene</td>
<td>149 $\pm$ 54</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>26.8 $\pm$ 4.8</td>
<td></td>
</tr>
<tr>
<td>Durene</td>
<td>57.8 $\pm$ 50.1</td>
<td></td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>145 $\pm$ 74</td>
<td></td>
</tr>
</tbody>
</table>

Values at 27°C for the wavelength 400 nm.
According to theory the charge transfer intensity as indicated by $\epsilon$ values is alone a measure of the charge transfer interaction whereas $K$, the equilibrium constant relates to the stability due to classical electrostatic forces along with a small measure due to charge transfer contribution in the ground state. Only in the case of very strong complexes where the binding strength is predominantly due to charge transfer resonance, can the values of $K$ and $\epsilon$ go together in the same direction. However, it is possible that $KE$ is a reasonable measure of the relative strengths of the complexes if donors of a similar nature are taken with the same acceptor and compared.

The donors are all aromatic hydrocarbons and are known to act as $\pi$-donors towards acceptors like chloranil. So the relative values of $KE$ have a significance as indicative of relative strengths of electron donor acceptor interaction of these donors towards CMBQ.

Complexes of CMBQ with hexamethylbenzene, acenaphthene and fluorene taken together are found to be comparatively stronger of these weak complexes while naphthalene and durene complexes are very weak. By and large this is a reflection of the ionisation potential values of these donors. Acenaphthene has an $I_D$ value about 7.66 ev while hexamethylbenzene and fluorene are variously quoted in the
range 7.8 to 8.1 eV. Naphthalene and durene have higher \( I_D \) values in the range 8.1-8.3 eV. In these complexes charge transfer is shown to be of some importance in determining the differences in binding energies.

This is evidence enough to show that CMBQ is a \( \pi' \)-acceptor like chloranil towards aromatic \( \pi' \)-donors but with a very much diminished electron accepting role.

The enthalpy of formation should be a better measure than the association constant for the stabilisation energy in the ground state of the complex. As separation of \( K \) and \( f \) is riddled with problems, use of values at different temperatures is generally recommended for obtaining All** from van't Hoff plots of the variation of In \( k \epsilon \) against \( T^{-1} \) where \( T \) is the absolute temperature. The results obtained of such a study at three temperatures are given in the tables 20-22 and the plots are shown in figures 21-23. The obtained values are given below.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Enthalpy change (-\Delta H^0) of the complex with CMBQ in kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethylbenzene</td>
<td>11.7 ± 4.6</td>
</tr>
<tr>
<td>Fluorene</td>
<td>2.8 ± 2.1</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>15.9 ± 2.9</td>
</tr>
<tr>
<td>Durene</td>
<td>10.9 ± 9.6</td>
</tr>
<tr>
<td>acenaphthene</td>
<td>27.6 ± 14.2</td>
</tr>
</tbody>
</table>
For the sake of comparison the corresponding values available from published literature for chloranil is found as follows (16).

<table>
<thead>
<tr>
<th>Donor</th>
<th>$\Delta H^\circ$ for complex with chloranil $\text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethylbenzene</td>
<td>22.2</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>46.9</td>
</tr>
<tr>
<td>Durene</td>
<td>19.1</td>
</tr>
</tbody>
</table>

On comparison the values of $\Delta H^\circ$ for CMBQ seem to be very reasonable in keeping with its much reduced acceptor ability. However it should be pointed out that the $\Delta H^\circ$ values obtained for this set of donors do not show any tendency for a trend with the ionisation potential $i^*$ of the donors. The low value for fluorene seems odd and the reason for this is unclear, Hanna and Lippert (10) while analysing a large number of data find only a wide scatter in relating $i^*$ or $\text{HV}_{-p}$ with $\Delta H^\circ$ values and it appears that in some cases any tendency found is fortuitous. As both electrostatic and induction forces contribute to the stability along with charge transfer, it is difficult to clearly say when and where one or the other predominates. The case with strong complexes is different and there is regular correlation as the charge transfer is the dominant contributor for stability. With weak complexes like in the case of CMBQ it is
enough consolation that the expected order of magnitude values for $K\zeta$ obtained as compared to chloranil.

It was pointed out earlier in this discussion that the anomalous values of negative intercepts found in all cases except in hexamethyIbenzene deserve a separate treatment. Looking at the Figs 6-20 giving the plots of $1/(O.D)|_{t\to\infty}$ versus $1/(O.D)_{\infty}$ it is found that in all cases the slope of the line is positive but only the extrapolated value of the intercept at the ordinate is negative, meaning thereby that the $K\zeta$ values as obtained are positive but the $\zeta$ values of the complex become negative.

It is known that in very weak complexes the intercept representing $1/\zeta$ tends to become very small, this would mean that $\zeta$ tends to reach infinity, in such cases the line may be almost passing through the origin meaning that as $K\to0$, $\zeta\to\infty$. The association constant may reach a value of zero. This phenomenon was explained by Orgel and Mulliken by invoking the concept of contact charge transfer by which it is possible to have charge transfer spectra even for random collisional contact pairs without a finite value for association constant. But to expect a negative value for molar absorption coefficient, has no place in this concept. As the $K\zeta$ value is positive and finite as noted from the figures, it also means that the association constant is negative.
Surely negative values for equilibrium constants should be an artifact of the method employed for arranging at the values. A closer look reveals that the basic' assumption of assuming the same theoretical construct or it in a J ly proposed for vapour phase interaction of donor-acceptor pairs to be applicable as such to interaction in solution phase has to be reexamined and modified. The effect of solvent seems to hold the key for unravelling this anomalous situation of negative K values and therefore of negative value.

The idea of specific solvation effect is not new. Carter, Murrell and Rosch (96) have proposed that in a 1:1 complex formation between a donor and an acceptor, the species actually involved should be considered as solvated, Thus,

\[ A_{n}S_{n} + D_{m}S_{m} \rightleftharpoons A^D_{p}D_{p} + qS \]

where S represents a molecule of the solvent, n, m and p the number of solvent molecules solvating A, D and AD respectively, and where \( q(=n+m-p) \) molecules of solvents are extruded from between A and D when the solvated complex is formed. In experimental determinations where the condition \([D]_{o}>>[A]_{o}\) is used, if an evaluation of an experimental association constant \( K_{exp} \) is made based on the assumption that only unsolvated species are involved, the true association constant \( K^* \) will be related to the observed
Experimental value $K_{\text{exp}}$ thus

\[
\frac{C_{\text{exp}}}{K_{\text{exp}}} = \frac{C^*}{K_{\text{exp}}}
\]

Where $[S]_0$ is the concentration of the solvent when $[D]_0 = 0$

and

\[
C_{\text{exp}} = \frac{C^*}{K_{\text{exp}}}
\]

For sufficiently weak interactions between $D$ and $A$ in solvintR of high solvating power, the theory predicts that $K_{\text{exp}}$ could become negative when

\[
\frac{q(m+1)}{[S]_0} > K^*
\]

Incidentally it may be noted that the product $K_{\text{exp}} E_{\text{exp}}$ becomes equal to $K^* C^*$. It is thus clear that where there is a specific solvent effect in which there is a competition between donor and the solvent for an acceptor or between the acceptor and the solvent for a donor, the possibility of obtaining a negative $K$ value exists in theory.

A dramatic demonstration of the truth of this prediction is this notable observation in this investigation on the weak acceptor action involving CMBQ and aromatic donors in Carbontetrachloride. With the relatively stronger complexes with chloranil this would have gone unnoticed.
It is relevant to point out here that the negative values of \( \xi \) arising out of the possibility that \( \xi_{\text{AD}} \) of the complex has a molar absorptivity lower than that of the acceptor \( (\xi_{\text{AD}} < \xi_{\text{A}}) \) has been ruled out by arguments given earlier. The clue lies only in the solvent effect.

Competition between the acceptor CMBy find carbon tetrachloride used here as solvent seems to be the major factor. Ordinarily this solvent is considered inert and number one solvent for studies on charge transfer spectra of organic complexes. The irony is that even for studying the competition between dimethylacetamide and benzene as donors for complexing with iodine as a common acceptor, this seemingly innocuous solvent carbon tetrachloride has been (97) taken as a standard for comparison. That carbon tetrachloride can behave as a weak electron acceptor was first brought to light by the work of Stevenson and Coppinger (98) who proposed contact charge transfer for this solvent with aliphatic amines, about which more will be said in the next part of this thesis. Its electron affinity is quoted (91) to be around 0.6 ev. Therefore it can be a likely candidate for competing with another weak acceptor CMBQ for complexing with the aromatic donors chosen here. Prausnitz and coworkers (99) and later Kellawi and Rosseinsky (100) have found an association constant of 0.64 \( \pm \) 0.12 and 0.55 \( \pm \) 0.16 respectively for complexing carbon tetrachloride with
hexamethylbenzene. Subsequently Bhat, Bhaskar and Rao (101) reported a higher value of 0.85 for the same and a \( -A \Delta H^\circ \) value of 3.0 kcal mol\(^{-1}\) (12.5 kJ mol\(^{-1}\)). It is therefore possible that all the values determined in the solvent for hexamethylbenzene have to be corrected. Trotter and Iamia (102) propose two competing equilibria such as

\[
A + D \rightleftharpoons AD \\
A + S \rightleftharpoons AS
\]

for such situations and conclude that the true \( K'' \) value is given by

\[
K^* = K^{obs}(1 + K^{AS}[S]_0)
\]

where \( [S]_0^{-1} \) is the molar volume of the pure solvent. For carbon tetrachloride \( [S]_0^{-1} = 0.097 \) l.mol\(^{-1}\). Using this value the relation becomes

\[
K^* = K^{obs}[1 + (0.55 \times 10.3)]
\]

\[ K^* = 6.66 K^{obs} \]

The most conservatively low value of 0.55 is used for \( K^{AS} \).

The observed value of \( K \) has therefore to be scaled up. In the context here the corrected \( K \) value for hexamethylbenzene complex with CMBQ turns out to be \( 6.66 + 3.21 \) l.mol\(^{-1}\).

This correction becomes significant only in the case of very weak acceptors since the concentration of the solvent is large, relative to either \( [D]_0 \) or \( [A]_0 \). When a stronger acceptor like chloranil is taken it is possible that the amount of firm complexes with this is overwhelmingly large as
compared to contact pairs with carbon tetrachloride.

Taking the case of donors weaker than hexamethylbenzene the role of contact pair interaction between the donor and the solvent is likely to become more important. Any intensity increase on addition of the donor to CMBQ is likely to have a major contribution from such contact pairs. Fluorene, naphthalene, durene andacenaphthene seem to fall in this category.

Murrel (103) explains that the donor excited state $D'$ may interact with the excited state $\Psi_{E}$ of the complex, thus modifying it to $\Psi_{E}'$. Therefore

$$\Psi_{E}' = a^* \Psi_{1} (A^{-}, D^{+}) - b^* \Psi_{0} (A, D) + c^* \Psi_{2} (A, D^{+})$$

The charge-transfer band due to the transition $\Psi_{D} \rightarrow \Psi_{D}^{*}$ will now involve some borrowing of intensity from the donor transition $\Psi_{D} \rightarrow \Psi_{D}^{*}$. The amount of borrowing will depend upon the overlap $S_{AD^{*}}$ between $\Psi_{D}^{*}$ and the vacant acceptor orbital.

With these weak donors in this work one appears to be in the twilight zone between weak, but firm complexes and very weak contact pairs. Only in the case of hexamethylbenzene at least a value of $K$ about 1.00 could be found; in the case of other four weaker donors, the contribution to intensity enhancement appears to be more due to contact pairs with CMBQ as well as with the solvent molecules. Milton Tamres (104) is
of the view that spectrophotometric study does not really distinguish between very weak, complexes and contacts. Seemingly, such distinction according to him is more a question of semantics.

Mixing of the charge transfer state and the ground state for the donor acceptor pair is the case of ordinary charge-transfer spectra for firm complexes. This contributes to the intensity of the spectrum. But the mixing of the charge transfer state with the excited state of the donor \( \xi^* \) or acceptor \( A^* \) would be the contributor for contact pair intensity.

In the case of Naphthalene-CMBQ complex (fig 3) the spectra could be taken without any need for correction due to donor absorption. An examination of the gradual increase in the intensity of added absorption wavelengthwise shows clearly an exponential increase in intensity while going from 500 nm to 350 nm. This is of the nature of a contact pair interaction as exemplified in the vapour phase spectra of iodine vapour and saturated hydrocarbons like n-hexameth (105). Such an enhancement is also shown in solutions by Julien and Person (10G). There is only an extended tail and the absorption rises rapidly at lower wavelengths without reaching a maxima. Similar is the case seen here in the Naphthalene-CMBQ system in carbon tetrachloride.
Finally the slight blue shift of the acceptor band at 410 nm towards 400 nm appears to get an explanation here. An overlapping of the broad band of CMBQ with a maximum at 410 nm with the ascending absorption due to the contact pair raising towards 350 nm would produce this slight shift of the band towards the ultraviolet.
FIG: 1

Optical Absorption Curves

Temp: 27°C

CMBQ - Hexamethylbenzene System

D - Donor --------------- 2.668 x 10^1 M
A - Acceptor ------------ 12.500 x 10^-3 M
M - Mixture ------D---- 2.668 x 10^1 M
                     A---- 12.500 x 10^-3 M
FIG : 2

Optical Absorption Curves
Temp : 27°C
CMBQ - Fluorene System

D - Donor \quad 4.396 \times 10^{-1} \text{ M}
A - Acceptor \quad 15.595 \times 10^{-1} \text{ M}
M - Mixture \quad D \quad 4.396 \times 10^{-1} \text{ M}
\quad A \quad 15.595 \times 10^{-4} \text{ M}
Optical Absorption Curves

Temp: 27°C
CMBQ - Naphthalene System

D-Donor : ----- 6.939 x 10^{-1} M
A-Acceptor : ----- 23.882 x 10^{-1} M
M-Mixture : D----- 6.939 x 10^{-1} M
A----- 23.882 x 10^{-1} M
FIG: 4

Optical Absorption Curves  Temp : 27°C

CMBQ - Durene System

D - Donor  ------  4.179 x 10⁻¹ M
A - Acceptor  -----  6.802 x 10⁻³ M
M - Mixture  ----  D  4.179 x 10⁻¹ M
                  A  6.802 x 10⁻³ M
FIG. 5
Optical Absorption Curves
Temp: 27°C

CMBQ - Aceanphthene System

D - Donor ----------- 3.115 x 10⁻¹ M
A - Acceptor ------ 12.294 x 10⁻⁴ M
M - Mixture ------ D --- 3.115 x 10⁻¹ M
A---12.294 x 10⁻⁴ M
TABLE 1

**CMBO - HEXAMETHYLDENZENE SYSTEM**

wavelength = 400 nm  
Temp = 27°C  

\[ [A] = 12.5 \times 10^{-4} \text{M} \]

<table>
<thead>
<tr>
<th>NO.</th>
<th>([D] \times 10^{-3}) M</th>
<th>([D]^{-1}) M^{-1}</th>
<th>O.D. diff</th>
<th>((O.D.\text{ diff})^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.668</td>
<td>3.748</td>
<td>0.074</td>
<td>13.519</td>
</tr>
<tr>
<td>2</td>
<td>2.490</td>
<td>4.016</td>
<td>0.070</td>
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</tr>
<tr>
<td>3</td>
<td>2.312</td>
<td>4.325</td>
<td>0.066</td>
<td>15.152</td>
</tr>
<tr>
<td>4</td>
<td>2.135</td>
<td>4.684</td>
<td>0.064</td>
<td>15.625</td>
</tr>
<tr>
<td>5</td>
<td>1.957</td>
<td>5.110</td>
<td>0.061</td>
<td>16.363</td>
</tr>
<tr>
<td>6</td>
<td>1.779</td>
<td>5.621</td>
<td>0.059</td>
<td>16.942</td>
</tr>
</tbody>
</table>

Fig: 6  
Plot \((O.D.\text{ diff})^{-1}\) vs \([D]^{-1}\)

\[
\begin{align*}
\kappa \varepsilon' &= 443.28 \pm 213.55 \\
\varepsilon' &= 113.53 \pm 54.52 \\
\varepsilon' &= (\varepsilon_{400} - \varepsilon_{A})
\end{align*}
\]
**TABLE 2**

**CBQ - HEXAMETHYLBENZENE SYSTEM**

wavelength = 400 nm  \[\text{Temp} = 35^\circ\text{C}\]

\[[\Lambda] = 12.5 \times 10^{-4}\text{M}\]

<table>
<thead>
<tr>
<th>NO.</th>
<th>([D]\times10^2\text{ M}^{-1})</th>
<th>([D]\text{-1}\text{ M}^{-1})</th>
<th>O.D.(\text{diff})</th>
<th>((\text{O.D.(\text{diff}))^{-1}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.668 (\times 10^2)</td>
<td>3.748 (\times 10^2)</td>
<td>0.069</td>
<td>14.493</td>
</tr>
<tr>
<td>2</td>
<td>2.490 (\times 10^2)</td>
<td>4.016 (\times 10^2)</td>
<td>0.066</td>
<td>15.152</td>
</tr>
<tr>
<td>3</td>
<td>2.312 (\times 10^2)</td>
<td>4.325 (\times 10^2)</td>
<td>0.063</td>
<td>15.873</td>
</tr>
<tr>
<td>4</td>
<td>2.135 (\times 10^2)</td>
<td>4.684 (\times 10^2)</td>
<td>0.061</td>
<td>16.591</td>
</tr>
<tr>
<td>5</td>
<td>1.957 (\times 10^2)</td>
<td>5.110 (\times 10^2)</td>
<td>0.059</td>
<td>16.948</td>
</tr>
<tr>
<td>6</td>
<td>1.779 (\times 10^2)</td>
<td>5.621 (\times 10^2)</td>
<td>0.055</td>
<td>18.182</td>
</tr>
</tbody>
</table>

**Fig. 7**

\[\text{Plot(}\text{O.D.\(\text{diff}\))^{-1} vs [D]^{-1}}\]

\[K \varepsilon' = 413.18 \pm 200.20\]

\[\varepsilon' = 110.15 \pm 49.90\]

\[\varepsilon' = (\varepsilon'_{\text{AD}} - \varepsilon'_{\text{A}})\]
**TABLE 3**

**CMDO - HEXAMETHYLBENZENE SYSTEM**

Wavelength = 400 nm  
Temp = 40°C

\( [A] = 12.5 \times 10^{-4} \text{M} \)

<table>
<thead>
<tr>
<th>NO.</th>
<th>( [D] \times 10^1 ) M</th>
<th>( [D]^{-1} ) M^{-1}</th>
<th>O.D. diff</th>
<th>((O.D.\ diff)^{-1})</th>
</tr>
</thead>
<tbody>
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<td>1</td>
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<td>4.016</td>
<td>0.061</td>
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<tr>
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<td>4.325</td>
<td>0.058</td>
<td>17.244</td>
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<td>4.684</td>
<td>0.055</td>
<td>18.432</td>
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<td>1.957</td>
<td>5.110</td>
<td>0.054</td>
<td>18.862</td>
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<tr>
<td>6</td>
<td>1.779</td>
<td>5.621</td>
<td>0.051</td>
<td>19.608</td>
</tr>
</tbody>
</table>

Fig 8:  
Plot \((O.D.\ diff)^{-1}\) vs \([D]^{-1}\)

\[
K \epsilon' = 360.81 \pm 178.20 \\
\epsilon' = 197.4 \pm 53.40 \\
\epsilon' = (\epsilon^{A0} - \epsilon^B)
\]
TABLE 4

CMBO – FLUORENE SYSTEM

wavelength = 400 nm

\[ \text{Temp} = 27^\circ\text{C} \]

\[ [A] = 15.595 \times 10^{-4} \text{M} \]

<table>
<thead>
<tr>
<th>NO.</th>
<th>([D] \times 10^{-4} \text{ M}^{-1})</th>
<th>([D]^{-1} \text{ M}^{-1})</th>
<th>O.D. diff</th>
<th>((\text{O.D. diff})^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.396</td>
<td>2.275</td>
<td>0.164</td>
<td>6.098</td>
</tr>
<tr>
<td>2</td>
<td>4.058</td>
<td>2.464</td>
<td>0.139</td>
<td>7.194</td>
</tr>
<tr>
<td>3</td>
<td>3.720</td>
<td>2.688</td>
<td>0.120</td>
<td>8.333</td>
</tr>
<tr>
<td>4</td>
<td>3.382</td>
<td>2.957</td>
<td>0.101</td>
<td>9.901</td>
</tr>
<tr>
<td>5</td>
<td>3.044</td>
<td>3.285</td>
<td>0.092</td>
<td>10.870</td>
</tr>
<tr>
<td>6</td>
<td>2.705</td>
<td>3.697</td>
<td>0.082</td>
<td>12.198</td>
</tr>
</tbody>
</table>

Fig.9

Plot \((\text{O.D. diff})^{-1}\) vs \([D]^{-1}\)

\[
K \epsilon' = 149.30 \pm 54.50
\]

\[
\epsilon' = -192.39 \pm 70.20
\]

\[
\epsilon' = (\epsilon_{\text{AB}} - \epsilon_A)
\]
TABLE 5
CHEQ - FLUORENE SYSTEM

wavelength = 400 nm
Temp = 35°C

\([A] = 15.595 \times 10^{-4} \text{M}\)

<table>
<thead>
<tr>
<th>NO.</th>
<th>([D]\times 10^{-3} \text{M})</th>
<th>([D]^{-1} \text{M}^{-1})</th>
<th>O.D. diff</th>
<th>((\text{O.D. diff})^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.396</td>
<td>2.275</td>
<td>0.141</td>
<td>7.092</td>
</tr>
<tr>
<td>2</td>
<td>4.058</td>
<td>2.464</td>
<td>0.123</td>
<td>8.130</td>
</tr>
<tr>
<td>3</td>
<td>3.720</td>
<td>2.688</td>
<td>0.109</td>
<td>9.174</td>
</tr>
<tr>
<td>4</td>
<td>3.382</td>
<td>2.957</td>
<td>0.098</td>
<td>10.204</td>
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<tr>
<td>5</td>
<td>3.044</td>
<td>3.285</td>
<td>0.083</td>
<td>12.042</td>
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<td>6</td>
<td>2.705</td>
<td>3.697</td>
<td>0.070</td>
<td>13.158</td>
</tr>
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</table>

Fig: 10
Plot \((\text{O.D. diff})^{-1}\) vs \([D]^{-1}\)

\[K C' = 140.38 \pm 51.29\]
\[C' = -247.39 \pm 89.25\]
\[C' = (C'_{AB} - C'_{A})\]
### Table 6
**CMDO - Fluorene System**

wavelength = 400 nm  
Temp = 40°C  
\([A] = 15.595 \times 10^{-4} M\)

<table>
<thead>
<tr>
<th>NO.</th>
<th>[D] x 10^(-3) M</th>
<th>[D]^{-1} M^{-1}</th>
<th>O.D. diff</th>
<th>(O.D. diff)^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.396</td>
<td>2.275</td>
<td>0.125</td>
<td>8.090</td>
</tr>
<tr>
<td>2</td>
<td>4.058</td>
<td>2.464</td>
<td>0.115</td>
<td>8.696</td>
</tr>
<tr>
<td>3</td>
<td>3.720</td>
<td>2.683</td>
<td>0.102</td>
<td>9.804</td>
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<tr>
<td>4</td>
<td>3.382</td>
<td>2.957</td>
<td>0.092</td>
<td>10.870</td>
</tr>
<tr>
<td>5</td>
<td>3.044</td>
<td>3.285</td>
<td>0.078</td>
<td>12.821</td>
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<tr>
<td>6</td>
<td>2.705</td>
<td>3.697</td>
<td>0.063</td>
<td>14.706</td>
</tr>
</tbody>
</table>

**Fig. 11**  
Plot (O.D. diff)^{-1} vs [D]^{-1}

\[ K \epsilon' = 133.23 \pm 48.09 \]
\[ \epsilon' = -208.21 \pm 73.80 \]
\[ \epsilon' = (\epsilon^{AD} - \epsilon^{A}) \]
TABLE 7
CHBQ - NAPHTHALENE SYSTEM

wavelength = 400 nm
Temp = 27°C

\[ [A] = 23.882 \times 10^{-4} \text{M} \]

<table>
<thead>
<tr>
<th>NO.</th>
<th>[D]x10 M</th>
<th>[D] M^{-1}</th>
<th>O.D. diff</th>
<th>(O.D. diff)^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.939</td>
<td>1.441</td>
<td>0.088</td>
<td>11.164</td>
</tr>
<tr>
<td>2</td>
<td>6.476</td>
<td>1.544</td>
<td>0.077</td>
<td>12.987</td>
</tr>
<tr>
<td>3</td>
<td>6.014</td>
<td>1.663</td>
<td>0.069</td>
<td>14.493</td>
</tr>
<tr>
<td>4</td>
<td>5.551</td>
<td>1.801</td>
<td>0.050</td>
<td>16.667</td>
</tr>
<tr>
<td>5</td>
<td>5.099</td>
<td>1.965</td>
<td>0.052</td>
<td>19.733</td>
</tr>
<tr>
<td>6</td>
<td>4.626</td>
<td>2.162</td>
<td>0.044</td>
<td>22.727</td>
</tr>
</tbody>
</table>

Fig: 12

Plot (O.D. diff)^{-1} vs [D]^{-1}

\[
K \epsilon' = 26.83 \pm 4.80 \\
\epsilon' = -37.16 \pm 6.50 \\
\epsilon' = (\epsilon^{A} - \epsilon^{B})
\]
**TABLE 8**

**CMBQ - NAPHTHALENE SYSTEM**

wavelength = 400 nm  
Temp = 35°C  

\[ [\lambda] = 23.682 \times 10^{-4} \text{M} \]

<table>
<thead>
<tr>
<th>NO.</th>
<th>([D] \times 10^{-3} \text{M})</th>
<th>([D])</th>
<th>O.D. diff</th>
<th>(O.D. diff)^{-1}</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>6.939</td>
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<td>0.080</td>
<td>12.500</td>
</tr>
<tr>
<td>2</td>
<td>6.476</td>
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<td>14.085</td>
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<tr>
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<td>1.663</td>
<td>0.064</td>
<td>15.609</td>
</tr>
<tr>
<td>4</td>
<td>5.551</td>
<td>1.801</td>
<td>0.054</td>
<td>18.519</td>
</tr>
<tr>
<td>5</td>
<td>5.089</td>
<td>1.965</td>
<td>0.047</td>
<td>21.277</td>
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<tr>
<td>6</td>
<td>4.626</td>
<td>2.162</td>
<td>0.040</td>
<td>25.000</td>
</tr>
</tbody>
</table>

Fig: 13  
Plot(O.D. diff)^{-1} vs \([D]\)^{-1}

\[ K \varepsilon' = 23.97 \pm 4.40 \]
\[ \varepsilon' = -32.32 \pm 5.70 \]
\[ \varepsilon' = (\varepsilon_A - \varepsilon_K) \]
**TABLE 9**

**CMQ – NAPHTHALENE SYSTEM**

wavelength = 400 nm  
Temp = 40°C  

\[ [A] = 23.882 \times 10^{-4} M \]

<table>
<thead>
<tr>
<th>NO.</th>
<th>([D] \times 10^M)</th>
<th>([D]^{-1}) M⁻¹</th>
<th>O.D. diff</th>
<th>((O.D. \text{diff})^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.939</td>
<td>1.441</td>
<td>0.075</td>
<td>13.33</td>
</tr>
<tr>
<td>2</td>
<td>6.476</td>
<td>1.544</td>
<td>0.067</td>
<td>14.925</td>
</tr>
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<td>1.663</td>
<td>0.060</td>
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<td>1.801</td>
<td>0.047</td>
<td>21.277</td>
</tr>
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<td>5.089</td>
<td>1.965</td>
<td>0.041</td>
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<tr>
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<td>4.626</td>
<td>2.162</td>
<td>0.036</td>
<td>27.778</td>
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</tbody>
</table>

Fig: 14

Plot \((O.D. \text{diff})^{-1}\) vs \([D]^{-1}\)

\[
K \epsilon' = 19.99 \pm 3.80
\]
\[
\epsilon' = -24.43 \pm 4.49
\]
\[
\epsilon' = (\epsilon^A - \epsilon^D)
\]
### TABLE 10

**CHDQ - DURENE SYSTEM**

*Wavelength = 400 nm*  
*Temp = 27°C*

\[
\text{[A]} = 6.802 \times 10^{-4}\text{M}
\]

<table>
<thead>
<tr>
<th>No.</th>
<th>([D] \times 10^{-1}) M</th>
<th>([D]^{-1}) M(^{-1})</th>
<th>O.D. diff</th>
<th>(O.D. diff)(^{-1})</th>
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<td>30.304</td>
</tr>
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<td>4</td>
<td>2.985</td>
<td>3.350</td>
<td>0.017</td>
<td>58.284</td>
</tr>
<tr>
<td>5</td>
<td>2.488</td>
<td>4.108</td>
<td>0.015</td>
<td>66.259</td>
</tr>
<tr>
<td>6</td>
<td>1.791</td>
<td>5.583</td>
<td>0.009</td>
<td>111.111</td>
</tr>
</tbody>
</table>

**Fig. 15**

Plot (O.D. diff\(^{-1}\) vs [D]\(^{-1}\))

\[
\begin{align*}
K & = 57.83 \pm 50.10 \\
\epsilon' & = -42.40 \pm 33.20 \\
\epsilon' & = (\epsilon_B - \epsilon_A)
\end{align*}
\]
TABLE 11
CHDQ - DURENE SYSTEM

wavelength = 400 nm
Temp = 35°C

\[[A] = 6.802 \times 10^{-4} \text{M}\]

<table>
<thead>
<tr>
<th>NO.</th>
<th>([D] \times 10^1 \text{M})</th>
<th>([D]^{-1} \text{M}^{-1})</th>
<th>O.D. diff</th>
<th>(O.D. diff)^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.478</td>
<td>2.233</td>
<td>0.037</td>
<td>27.027</td>
</tr>
<tr>
<td>2</td>
<td>4.179</td>
<td>2.393</td>
<td>0.022</td>
<td>45.455</td>
</tr>
<tr>
<td>3</td>
<td>3.582</td>
<td>2.792</td>
<td>0.017</td>
<td>58.224</td>
</tr>
<tr>
<td>4</td>
<td>2.985</td>
<td>3.350</td>
<td>0.014</td>
<td>71.429</td>
</tr>
<tr>
<td>5</td>
<td>2.383</td>
<td>4.188</td>
<td>0.009</td>
<td>111.111</td>
</tr>
<tr>
<td>6</td>
<td>1.791</td>
<td>5.583</td>
<td>0.007</td>
<td>142.057</td>
</tr>
</tbody>
</table>

Fig: 16
Plot (O.D. diff)^{-1} vs. [D]^{-1}

\[K \varepsilon' = 45.07 \pm 40.30\]
\[\varepsilon' = -19.74 \pm 36.40\]
\[\varepsilon' = (\varepsilon_{AD} - \varepsilon_A)\]
**TABLE 12**

**CMBQ - DURENE SYSTEM**

wavelength = 400 nm  
Temp = 40°C  

\([\lambda] = 6.802 \times 10^{-4} \text{m}\)

<table>
<thead>
<tr>
<th>NO.</th>
<th>([D] \times 10^{-3} \text{M})</th>
<th>([D]^{-1} \text{M}^{-1})</th>
<th>OD.diff</th>
<th>((\text{OD.diff})^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.478</td>
<td>2.233</td>
<td>0.029</td>
<td>34.483</td>
</tr>
<tr>
<td>2</td>
<td>4.178</td>
<td>2.393</td>
<td>0.017</td>
<td>53.824</td>
</tr>
<tr>
<td>3</td>
<td>3.582</td>
<td>2.792</td>
<td>0.012</td>
<td>83.133</td>
</tr>
<tr>
<td>4</td>
<td>2.985</td>
<td>3.350</td>
<td>0.010</td>
<td>100.000</td>
</tr>
<tr>
<td>5</td>
<td>2.389</td>
<td>4.188</td>
<td>0.006</td>
<td>166.667</td>
</tr>
<tr>
<td>6</td>
<td>1.791</td>
<td>5.583</td>
<td>0.005</td>
<td>200.000</td>
</tr>
</tbody>
</table>

Fig: 17  

\[P \log (\text{OD.diff})^{-1} \text{ vs } [D]^{-1}\]

\[k \varepsilon' = 39.05 \pm 26.40\]

\[\varepsilon' = -24.39 \pm 21.40\]

\[\varepsilon' = (\varepsilon_{\lambda0} - \varepsilon_{\lambda})\]
### TABLE 13

**CHBQ - ACENAPHTHENE SYSTEM**

\[ \text{wavelength} = 400 \, \text{nm} \quad \text{Temp} = 27^\circ \text{C} \]

\[ [A] = 12.294 \times 10^{-4} \, \text{M} \]

<table>
<thead>
<tr>
<th>NO.</th>
<th>( [D] \times 10^3 )</th>
<th>( (D)^{-1} )</th>
<th>O.D. diff</th>
<th>( (\text{O.D. diff})^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.115</td>
<td>3.210</td>
<td>0.064</td>
<td>15.676</td>
</tr>
<tr>
<td>2</td>
<td>2.975</td>
<td>3.478</td>
<td>0.064</td>
<td>15.922</td>
</tr>
<tr>
<td>3</td>
<td>2.656</td>
<td>3.704</td>
<td>0.056</td>
<td>17.523</td>
</tr>
<tr>
<td>4</td>
<td>2.386</td>
<td>4.171</td>
<td>0.049</td>
<td>25.704</td>
</tr>
<tr>
<td>5</td>
<td>2.156</td>
<td>4.633</td>
<td>0.042</td>
<td>23.344</td>
</tr>
<tr>
<td>6</td>
<td>1.917</td>
<td>5.216</td>
<td>0.038</td>
<td>26.314</td>
</tr>
</tbody>
</table>

**Fig. 12**

\[ \epsilon_{\text{IC}} = 145.00 \pm 75.10 \]

\[ \epsilon_{\text{OC}} = -389.73 \pm 144.29 \]

\[ \epsilon_{\text{OC}} = (\epsilon_{\text{IC}} - \epsilon_{\text{OC}}) \]
**TABLE 14**

**CHDO - ACENAPHTHENE SYSTEM**

wavelength = 400 nm  
Temp = 35°C

\[(A) = 12.294 \times 10^{-4} \text{M}\]

<table>
<thead>
<tr>
<th>NO.</th>
<th>(D \times 10^6) M (^{-1})</th>
<th>(D^{-1}) M (^3)</th>
<th>O.D. diff</th>
<th>(O.D.\text{diff}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.115</td>
<td>3.210</td>
<td>0.054</td>
<td>18.510</td>
</tr>
<tr>
<td>2</td>
<td>2.875</td>
<td>3.478</td>
<td>0.048</td>
<td>20.933</td>
</tr>
<tr>
<td>3</td>
<td>2.636</td>
<td>3.794</td>
<td>0.038</td>
<td>26.316</td>
</tr>
<tr>
<td>4</td>
<td>2.396</td>
<td>4.174</td>
<td>0.031</td>
<td>30.392</td>
</tr>
<tr>
<td>5</td>
<td>2.156</td>
<td>4.638</td>
<td>0.031</td>
<td>32.258</td>
</tr>
<tr>
<td>6</td>
<td>1.917</td>
<td>5.216</td>
<td>0.029</td>
<td>34.483</td>
</tr>
</tbody>
</table>

Fig: 19

\[
\begin{align*}
K \xi' &= 99.32 \pm 52.40 \\
\xi' &= -128.53 \pm 67.70 \\
\xi' &= (\epsilon_A^{-1} - \epsilon_A^{-1})
\end{align*}
\]
### TABLE: 15

**CMBQ - ACENAPHTHENE SYSTEM**

wavelength = 400 nm  
Temp = 40°C  

\[ [\lambda] = 12.294 \times 10^{-4} M \]

<table>
<thead>
<tr>
<th>NO.</th>
<th>( [D] \times 10^3 ) M</th>
<th>( \lambda^{-1} ) M(^{-1})</th>
<th>O.D. diff</th>
<th>( \text{O.D. diff}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.115</td>
<td>3.210</td>
<td>0.041</td>
<td>24.390</td>
</tr>
<tr>
<td>2</td>
<td>2.875</td>
<td>3.478</td>
<td>0.036</td>
<td>27.778</td>
</tr>
<tr>
<td>3</td>
<td>2.636</td>
<td>3.794</td>
<td>0.034</td>
<td>29.412</td>
</tr>
<tr>
<td>4</td>
<td>2.396</td>
<td>4.174</td>
<td>0.029</td>
<td>34.483</td>
</tr>
<tr>
<td>5</td>
<td>2.156</td>
<td>4.638</td>
<td>0.026</td>
<td>38.462</td>
</tr>
<tr>
<td>6</td>
<td>1.917</td>
<td>5.216</td>
<td>0.024</td>
<td>41.667</td>
</tr>
</tbody>
</table>

Fig: 20  
Plot \( \text{O.D. diff}^{-1} \) vs \( [D]^{-1} \)

\[
\begin{align*}
K \varepsilon' &= 92.60 \pm 47.30 \\
\varepsilon' &= \frac{-255.42 \pm 130.40}{\lambda} \\
\varepsilon' &= ([\varepsilon] - \varepsilon')
\end{align*}
\]
**Table 16**

**VAN'T HOFF PLOT**

**CMBQ - HEXAMETHYLBENZENE SYSTEM**

<table>
<thead>
<tr>
<th>$T \theta_K$</th>
<th>$1/T \times 10^3$</th>
<th>$K \xi'$</th>
<th>$\log K \xi'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3.333</td>
<td>443.1</td>
<td>2.647</td>
</tr>
<tr>
<td>308</td>
<td>3.247</td>
<td>413.2</td>
<td>2.616</td>
</tr>
<tr>
<td>313</td>
<td>3.195</td>
<td>360.8</td>
<td>2.567</td>
</tr>
</tbody>
</table>

Fig. 21 plot ($1/T \times 10^3$) vs ($\log K \xi'$)
TABLE: 17

VAN'T HOFF PLOT

CDHQ - FLUORENE SYSTEM

<table>
<thead>
<tr>
<th>T K</th>
<th>1/T x 10^3</th>
<th>K ε'</th>
<th>log K ε'</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3.333</td>
<td>149.3</td>
<td>2.174</td>
</tr>
<tr>
<td>308</td>
<td>3.247</td>
<td>140.4</td>
<td>2.147</td>
</tr>
<tr>
<td>313</td>
<td>3.195</td>
<td>133.2</td>
<td>2.125</td>
</tr>
</tbody>
</table>

Fig. 22: plot (1/T x 10^3) vs (log K ε')
### Table 18

**VAN'T Hoff Plot**

**CMBQ - Naphthalene System**

<table>
<thead>
<tr>
<th>$T_0$</th>
<th>$1/T \times 10^3$</th>
<th>$K \xi'$</th>
<th>$\log K \xi'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3.333</td>
<td>26.8</td>
<td>1.429</td>
</tr>
<tr>
<td>308</td>
<td>3.247</td>
<td>24.0</td>
<td>1.380</td>
</tr>
<tr>
<td>313</td>
<td>3.195</td>
<td>20.0</td>
<td>1.301</td>
</tr>
</tbody>
</table>

Fig. 23: plot($1/T \times 10^3$) vs $\log K \xi'$
<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T x 10^2</th>
<th>logK</th>
<th>logf'</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3.333</td>
<td>57.8</td>
<td>1.760</td>
</tr>
<tr>
<td>308</td>
<td>3.247</td>
<td>45.1</td>
<td>1.663</td>
</tr>
<tr>
<td>313</td>
<td>3.195</td>
<td>39.4</td>
<td>1.547</td>
</tr>
</tbody>
</table>

Fig. 24: plot (1/T x 10^2) vs. log f'
### TABLE: 20

**VAN'T Hoff Plot**

**CMBQ - ACENAPHTHENE SYSTEM**

<table>
<thead>
<tr>
<th>T K</th>
<th>1/T x 10³</th>
<th>K ε'</th>
<th>log K ε'</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3.333</td>
<td>144.5</td>
<td>2.160</td>
</tr>
<tr>
<td>308</td>
<td>3.247</td>
<td>99.3</td>
<td>1.997</td>
</tr>
<tr>
<td>313</td>
<td>3.195</td>
<td>92.6</td>
<td>1.967</td>
</tr>
</tbody>
</table>

![Image](plot_1/T x 10^3 vs. log K ε')
Fig : 7  Ketelaar Plot  CMBQ-Hexamethylbenzene System

Wavelength : 400 nm  Temp. : 35 °C
Fig: 8  Ketelaar Plot  CMBQ-Hexamethylbenzene System

Wavelength: 400 nm  Temp.: 40°C
Fig: 9  Ketelaar Plot  CMBQ-Fluorene System

Wavelength: 400 nm  Temp: 27°C
Fig: 10  Ketelaar Plot  CMBQ-Fluorene System

Wavelength: 400 nm  Temp.: 35°C
Fig: 11  Ketelaar Plot  CMBQ-Fluorene System

Wavelength : 400 nm  Temp. : 40°C
Fig : 12  Ketelaar Plot  CMBQ-Naphthalene System

Wavelength : 400 nm  Temp. : 27°C
Fig: 13  Ketelaar Plot  CMBQ-Naphthalene System

Wavelength: 400 nm  Temp.: 35°C
Fig: 14  Ketelaar Plot  CMBQ-Naphthalene System

Wavelength: 400 nm  Temp.: 40°C
Fig: 15  Ketelaar Plot  CMBQ-Durene System

Wavelength: 400 nm  Temp.: 27°C
Fig: 16  Ketelaar Plot  CMBQ-Durene System

Wavelength: 400 nm   Temp.: 35°C
Fig: 17  Ketelaar Plot  CMBQ-Durene System

Wavelength: 400 nm   Temp.: 40°C
Fig: 18 Ketelaar Plot CMBQ-Acenaphthene System

Wavelength : 400 nm    Temp. : 27°C
Fig: 19  Ketelaar Plot  CMBQ-Acenaphthene System

Wavelength: 400 nm  Temp: 35°C
Fig. 20  Ketelaar Plot  CMBQ-Acenaphthene System

Wavelength : 400 nm  Temp. : 40°C
Fig. 21 van't Hoff plot  CMBQ-Hexamethylbenzene System
Fig: 22  van't Hoff plot  CMBQ-Fluorene System
Fig: 23  van't Hoff plot  CMBQ-Naphthalene System
Fig: 24  van't Hoff plot  CMBQ-Durene System
Fig : 25  van't Hoff plot  CMBQ-Acenaphthene System
Fig. 26. Exponential increase of O.D$_{diff}$ at lower wavelengths
CMBQ-Naphthalene System