PART II
CHAPTER VI

CHARGE TRANSFER COMPLEXES BETWEEN CHLORANIL AND 1,10-PHENANTHROPOLY OR 2,2'-BIPYRIDINE IN DIFFERENT ORGANIC SOLVENTS AT 298 K.
CHARGE TRANSFER COMPLEXES BETWEEN CHLORANIL AND 1,10-PHENANTHROLINE OR 2,2'-BIPYRIDINE IN DIFFERENT ORGANIC SOLVENTS AT 298 K.

INTRODUCTION:
Interaction between electron donors and electron acceptors to form complexes is well known. P. Feiffer\(^1\) first showed that certain aromatic hydrocarbons and their derivatives combine with a wide variety of organic and inorganic compounds to form molecular complexes having certain characteristic features. These are:

a) The molecular complexes (usually coloured) are formed very rapidly and in simple molecular ratios.

b) The distances separating the donor and acceptor molecules in crystalline addition complexes are usually much greater than those corresponding to covalent bonds.

c) The stability of the molecular complexes is related to both ionization potential of the donor and the electron affinity of the acceptor.

The resulting complexes usually show a characteristic absorption spectrum due to intermolecular charge-transfer transition of an electron from the molecule of high charge density (donor) to the molecule with low charge density (acceptor) and are usually termed as charge transfer complexes.
Any electron-rich species can serve as a donor substance. They are classified as n-donors (like amines, alcohols, ethers, sulphoxides etc.) when a non-bonding electron is transferred or \( \pi \)-donors such as aromatic hydrocarbons, alkanes etc (where the electron available for donation is located).\(^{3,4}\)

The acceptor molecules are varied in nature and these include the Lewis acids (\( BX_3 \), \( AlX_3 \), \( SnX_4 \), \( I_2 \)), aromatic hydrocarbons containing electron-withdrawing groups such as \(-NO_2\) or \( X \) (halogen). Condensed polycyclic hydrocarbons may act both as donors and acceptors. Naturally, substances that form complexes with the solvent molecules will readily dissolve in those solvents.

A successful quantum mechanical treatment for the formation of charge-transfer complexes was put forward by Mulliken.\(^5\) In terms of Mulliken treatment, the interaction of the no bond ground state \( \Psi_0(DA) \) and the polar excited state \( \Psi_1(D^+A^-) \) was considered to produce a stabilized ground state having a wave function \( \Psi_N \) given by the expression

\[
\Psi_N = a \Psi_0(DA) + b \Psi_1(D^+A^-)
\]

and an excited state (charge transfer state) having a wave function

\[
\Psi_E = a^* \Psi_1(D^+A^-) - b^* \Psi_0(DA)
\]

\( \Psi_0 \) and \( \Psi_1 \) are the wave functions of the no-bond and ionic structures corresponding to states in which \( D \) and \( A \) are held
together by classical Vander-Zaals forces and in which an electron has been transferred from the electron donor Do to the electron acceptor A.

Since the wave functions are normalized, we have

$$\int \psi_*^* \psi_0 \, d\tau = a^2 + b^2 + 2ab \cdot S_{01} = 1$$

Where $S_{01} = \int \psi_0 \psi_1 \, d\tau$.

For weak complexes, $S_{01}$ is small and $a^2 \gg b^2$. $b^2$ represents the weight of the dative structure or fraction of the electron transferred from D to A in the ground state and $a^2 + b^2 \approx 1$.

Similarly,

$$\Psi_E^* \Psi_E \, d\tau = a^*^2 + b^*^2 - 2a^*b^* S_{01} = 1$$

The charge transfer band of the complex was considered by Mulliken to be associated with the electron transition $\Psi_E \leftarrow \Psi_N$ and since $a^*^2 \gg b^*^2$, the transition is essentially a transfer of an electron from D to A. This theory may also be used to predict a moderately high intensity for the transition $E \leftarrow N$ in accord with the values of $\varepsilon_C$, the molecular extinction coefficient. The CT transition thus involves a ground and excited state with very different dipole moments which suggests that solvent polarity effects should be marked on the position of the CT absorption band.
SOLVENT EFFECT ON THE CHARGE TRANSFER SPECTRA:

The solvent effects on the charge-transfer spectra can be understood from the following considerations.

i) Spectral shifts between vapour and solution:

The transition energies $\hbar \Sigma_{CT}$ in vapour and solution phases may be related by the cycle

$$
\begin{align*}
DA(g) & \xrightarrow{\hbar \Sigma_{CT}(g)} D^+ - A^- (g) \\
\Delta X_{DA(Solv)} & \downarrow \\
DA(Soln.) & \xrightarrow{\Delta X} D^+ - A^- (Soln.)
\end{align*}
$$

Where $\Delta X_{Solv}$ includes all solvation contributions to the stabilization of the complex in ground and excited states. Thus,

$$
\hbar \Sigma_{CT}(g) = \hbar \Sigma_{CT(Soln)} - \Delta X_{D^+ - A^- (Soln)} - X_{DA(Solv)}
$$

Thus, if solvent stabilization of the excited state is greater than that for the ground state, a solvent shift to lower energies of the CT band on moving from vapour to solution is expected. However, since the transition from the ground state involves Franck-Condon excited state and not the equilibrium excited state, the above cycle is not accessible to calculations as will be apparent from the diagram.
The difference between Frank-Condon and equilibrium states will depend on the change in electron distribution on excitation.

**ii) Solute-Solvent interactions:**

The important types of interaction contributing to the $\Delta X(\text{Solv})$ terms above are (a) Dipolar interactions e.g., dipole-dipole, dipole-induced dipole interaction. (b) Dispersive interactions due to the so-called vanderWaals forces. (c) Short-range specific interaction like hydrogen bonding, charge-transfer interaction etc.

These interactions cause a number of electrical and optical properties of the solute to change.

However, quantitative calculations of these interactions and their correlations are yet to be achieved.

The object of the present investigation is to examine (i) the possibility of charge transfer complex formation between chloranil and azo-aromatics like 2,2'-bipyridine and 1,10-phenanthroline.
and (ii) whether the variation of solvent polarity brings about a change in the spectral and thermodynamic parameters of these charge-transfer complexes.

Though the formation of CT complexes of chloranil with phenanthroline and biphenyl are known, but CT complexes of chloranil with aza-aromatics like 1,10-phenanthroline and 2,2'-bipyridine are not reported.

Experimental: 1,10-Phenanthroline (Phen) and 2,2'-bipyridine (bipy) [G. R. E. Merck] and chloranil(A.R., B.D.H.) were used without further purification. The solvents (benzene, toluene, O-xylene, mesitylene, dichloromethane, chloroform, carbon tetrachloride) were generally of spectroscopic quality (Sisco, India). These solvents were also purified in the way described in the literature.6

Chloranil, phen and bipy all absorb strongly in the u.v.region. The absorption maxima for chloranil, phen and bipy in the u.v. region are

286 nm band for chloranil.

228 nm and 264 nm bands for phen.

233 nm and 281 nm bands for bipy.

The complex formation between chloranil and phen or bipy is characterised by the changes in absorbance values as well as
the changes in absorption maxima in the u.v. and u.v-visible region. However, since all the species absorb strongly in this region, the actual determination of the stability of the complexes is difficult. Therefore, we prefer to use the absorption of chloranil in the region of 370 - 400 nm where phen or bipy show no absorption. The complex formation between D and A are characterised by slight shift of the absorption maximum of chloranil towards the longer wave length. The complex formation is also characterised by the change in the absorbance values of chloranil.

The composition of the complexes formed between chloranil and phen or bipy have been determined in several cases by Job's method of continuous variation. The absorbance values of equimolar concentrations of chloranil and phen or bipy mixed in the ratio 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2 and 9:1 and the corresponding blank solutions (containing chloranil only) were measured at different $\lambda_{\text{max}}$ of the respective solvents as follows.

<table>
<thead>
<tr>
<th>Organic Solvent</th>
<th>$\lambda_{\text{max}}(\text{nm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Benzene</td>
<td>336</td>
</tr>
<tr>
<td>2) Toluene</td>
<td>360</td>
</tr>
<tr>
<td>3) O-Xylene</td>
<td>388</td>
</tr>
<tr>
<td>4) Mesitylene</td>
<td>416</td>
</tr>
<tr>
<td>5) Dichloromethane</td>
<td>377</td>
</tr>
<tr>
<td>6) Chloroform</td>
<td>374</td>
</tr>
<tr>
<td>7) Carbon tetrachloride</td>
<td>370</td>
</tr>
</tbody>
</table>
The difference in the absorbance values \( \overline{D} \) against composition shows that the complex formation is in the ratio 1:1. Typical data are presented in Table VI.1 and Fig. VI.1.

However, the slight variations are also noted in some cases. The reasons may be that chloranil itself forms charge-transfer complexes with the solvents leading to a change in the effective concentration of chloranil so that some anomaly may creep in the determination of the composition of the complex.

For the determination of equilibrium constant \( K_{AD} \), the absorptivity of mixtures containing donor and acceptor molecules in different proportions in the particular solvent were measured. The absorptivity of suitable blanks containing chloranil only were also measured.

The absorbance measurements were also made for a series of solutions containing different concentrations of donor \((D)\) but with constant concentration of acceptor \((A)\), \( [D_0] >> [A_0] \). The absorbance of the suitable blank solutions were also made.

Varian 630 spectrophotometer was used for spectral measurements.

**Results:**
As in the most cases, the equilibrium between chloranil and phen or bipy have been assumed to be 1:1.
The equilibrium constant for the complex between D and A

\[ D + A \rightleftharpoons AD \] can be written as

\[ K_{AD} = \frac{[AD]}{[D][A]} = \frac{[AD]}{[D_0] [A_0]} \left( \frac{1}{[AD_0]} - \frac{1}{[AD]} \right) \]

Where \([D_0]\) and \([A_0]\) represent the total concentration of D and A respectively.

The spectrophotometric method is used most widely for the determination of \(K_{AD}\). In this method solutions of the component substances are mixed at known concentrations and the absorbance values of the mixtures are measured spectrophotometrically at suitable wavelengths against appropriate blank.

The first equation for using spectrophotometric data for the determination of stability constant \(K_{AD}^0\) and molar extinction coefficient \(\epsilon_{AD}\) of a 1:1 molecular complex was derived by Benesi and Hildebrand.7

\[ \frac{C_A^0 l}{a} = \frac{1}{K_{AD} \times \epsilon_{AD}} \cdot \frac{1}{C_D^0} + \frac{1}{\epsilon_{AD}} \]

Where \(C_A^0\) and \(C_D^0\) are concentrations of the acceptor and donor respectively in the mixture before complexation, \(l\) is the optical path length of the cell used, \(a\) is the optical density of the mixture and \(\epsilon_{AD}\) is the absorptivity of the complex at the
wavelength of measurement. The equation is based on the following assumptions:

a) Only the complex absorbs at the wavelength of measurement

b) \( C_D^0 \gg C_A^0 \)

Kettler modified this equation for cases where acceptor also absorbs at the wavelength of measurement to the form:

\[
\frac{1}{\varepsilon_a - \varepsilon_A} = \frac{1}{(\varepsilon_AD - \varepsilon_A)^{K_{AD}}} \cdot \frac{1}{C_D^0} + \frac{\varepsilon_AD - \varepsilon_A}{d}
\]

Where \( \varepsilon_a = \text{apparent extinction co-efficient of the mixture} \)

\[
\frac{d}{C_A^0 L}
\]

In applying only of the equations, the wavelength is so chosen that the donor does not absorb significantly and the donor solution at concentration \( C_D^0 \) is used as blank. \( \varepsilon_A \), the molar absorptivity of the acceptor at the wavelength used for measurement, is either known or measured separately. The plot of \( C_A^0 L/d \) or \( \frac{1}{\varepsilon_a - \varepsilon_A} \) against \( \frac{1}{C_D^0} \) should be linear, the slope and intercept giving the value of \( K_{AD} \) and \( \varepsilon_AD \).

The objections against the equations are:

i) Evaluation of \( K_{AD} \) requires the value of \( \varepsilon_AD \) by extrapolation of the line to \( C_D^0 \rightarrow \infty \).
Rearrangement of the Benesi - Hildebrand (BH) equation to

\[ \frac{C_A^0}{d} \cdot \frac{C_D^0}{d} = \frac{C_D^0}{D_{DA}} \cdot \frac{1}{K_{AD} \cdot \varepsilon_{AD}} \]

(Scott equation) \(^9\)

and

\[ \frac{d}{C_D^0} = -K_{AD} \cdot d + K_{AD} \cdot \varepsilon_{AD} \cdot C_A^0 \]

(Fester et al.) \(^10\)

eliminates some of these difficulties.

ii) According to Mulliken and Person\(^4\), the condition \(C_D^0 \gg C_A^0\) effectively changes the nature of the solvent. They showed theoretically that in the BH equation although \(K_{AD} \cdot \varepsilon_{AD}\) can be correct, the individual values \(K_{AD}\) and \(\varepsilon_{AD}\) may be seriously in error.

iii) The BH equation and the variants, there of are derived on the basis of the assumption that \(C_D^0 - C_{AD}^0 \approx C_D^0\) in the expression for \(K_{AD}\) may introduce error ranging from 30% - 70%, depending on the value of \(K_{AD}\) - the error increasing with increase in \(K_{AD}\).

iv) Drago and Rose\(^11\) pointed out that under the condition \(C_D^0 \gg C_A^0\), the solution to the final equation depends in the sets of experimental data.

An equation free from these objections has been derived by Rose and Drago\(^12\)
The method is laborious and iterative and wide scatter in the values of and We, have, however, adopted a slightly different but an iterative method which impose no restriction regarding the concentrations of D and A.

\[ K_{AD} = \frac{C_A^0 C_D^0 (\varepsilon_{AD} - \varepsilon_A)}{d - d_A^0} - (C_A^0 + C_D^0) + \frac{d - d_A^0}{\varepsilon_{AD} - \varepsilon_A} \]

where \( d_A^0 = C_A^0 \varepsilon_A \).

The method is laborious and iterative and wide scatter in the values of \( K_{AD} \) and \( \varepsilon_{AD} \).

We, have, however, adopted a slightly different but an iterative method which impose no restriction regarding the concentrations of D and A.

The equilibrium is written as

\[ \text{A + D} \xrightarrow{\text{Accepto Donor Complex}} \]

Let \( C_1 \) and \( C_2 \) be the initial concentrations of acceptor and donor respectively. Let \( \chi \) be the complex formed at equilibrium.

Now, we have,

\[ d_1 = \varepsilon_1 C_1 \] (for chloranil)

\[ d_2 = \varepsilon_1 (C_1 - \chi) \] + \( \varepsilon_2 \chi \) (chloranil complex)

where \( \varepsilon_1 \) and \( \varepsilon_2 \) be the extinction coefficients of chloranil and the complex respectively.

Thus, \( d_2 - d_1 = (\varepsilon_2 - \varepsilon_1) \chi \).

or \( d_1 - d_2 = (\varepsilon_2 - \varepsilon_1) \chi \)

or, \( \chi = \frac{d_2 - d_1}{(\varepsilon_2 - \varepsilon_1)} \)

Now, \( K = \frac{x}{(C_1 - x)(C_2 - x)} = \frac{d_2 - d_1}{(\varepsilon_2 - \varepsilon_1)(C_1 - x)(C_2 - x)} \) ( \( K = K_{AD} \) )
or, \( c_1 - x = \frac{d_2^2 - d_1^2}{(\varepsilon_2 - \varepsilon_1) l (c_2 - x) K} \)

or, \( \frac{c_1}{d_2 - d_1} = \frac{x}{d_2 - d_1} - \frac{1}{(\varepsilon_2 - \varepsilon_1)(c_2 - x)} \cdot \frac{1}{l} \cdot \frac{1}{k} \)

Assuming \( x \) to be small, we plot \( \frac{c_1}{d_2 - d_1} \) against \( \frac{1}{c_2} \) from which initial values \( \frac{1}{\varepsilon_2 - \varepsilon_1} \) and \( K \) are determined. Now, from the approximate values of \( x \) (calculated), we get the refined values of \( \frac{1}{\varepsilon_2 - \varepsilon_1} \) and \( K \). The iteration is repeated till constant values of \( \frac{1}{\varepsilon_2 - \varepsilon_1} \) and \( K \) are obtained. Usually 3-4 iterations are sufficient to get the actual values.

Some typical sets of data are presented in Table VI.2. Though there may be some differences in \( \varepsilon_2 \) values but \( K \) values are found to be almost constant from different sets of measurements.

The equilibrium constants and the extinction coefficient values of the complexes formed between chloranil and phenanthroline or bipyridine at the wavelengths of measurement, in different solvents are presented in Table VI.3.

It is to be noted that the variations in the concentrations of phenanthroline, is less compared to that of bipyridine due to
solubility limitations of phenanthroline in these solvents.

Discussion:
The spectral transitions of chloranil in different solvents are very much dependent on solvents and the transitions are regarded to be charge transfer complexes.

The charge-transfer complexes are known to be strongly solvent dependent but quantitative interpretation of the solvent effect on the charge-transfer spectra is few. However, the sensitivity of the energy in the intermolecular charge-transfer of pyridinium iodides to changes in the nature of the solvent, has been utilised by Kosower\textsuperscript{13} to determine solvent polarity or ionising properties of solvents in terms of 'Z'-value scale of solvent polarity. The Z-value of a given solvent is the energy of the intermolecular charge-transfer band in \textit{kcal mole}^{-1} of 1-ethyl-4-carbomethoxy pyridinium iodide.

\[
\text{COOCH}_3
\]

When dissolved in that solvent. This is a result of the degree of solvation of the ground state of the complex which is effectively an ion-pair.

Dimroth and Reichhardt's\textsuperscript{14} Z-values are based on the solvent sensitivity of light absorption (an intramolecular) charge-transfer transition of a pyridinium phenol betain and hence may be applied to those solvent effects for which the Z-values are applicable.
It is seen that chloranil also shows charge transfer interactions with solvent molecules (Table VI-3) and the variations of charge-transfer energy can be similarly utilized to characterize the solvent molecules. However, no strict correlation of E values of chloranil in different solvents with $E_T$ or $Z$ are possible. It is likely that this type of correlation is not possible with a single parameter as the CT obviously implies the charge-density rearrangement due to charge-transfer and polarizability effects resulting from the interaction between an electron donor and an electron acceptor.

According to Gutmann$^{15}$, the structure of a molecule is not rigid but rather adaptable to environment. The structural variability of a given molecule in different solvents is reflected in its chemical variability. Differences in spectroscopic properties of a molecule in different molecular environments are related to the differences in electronic and spatial rearrangements.

According to Gutmann$^{15}$ $Z$-values do not represent effectively the donor properties of a solvent. Nearly identical $Z$-values are assigned to solvents of vastly different donor properties but similar acceptor properties. He believes that the $Z$-values
bear a close relationship to the acceptor properties of a solvent rather than representing a general measure of the polarity or of the ionising properties of the solvent.

Similar arguments also hold good for $E_T$. However, clear correlation of the $Z$ or $E_T$ values with acceptor properties are also not apparent.

In case of chloranil, a well-known acceptor, the charge-transfer energy should represent donor character of the solvents. However, no such correlation is possible as solvation means not only stabilisation of the ground state and excited state properties but also different types of chemical interactions depending on the nature of the solvents.

The stability constants of these complexes are fairly high if we compare the values usually obtained in case of charge-transfer complexes. The stability constants are dependent on the solvent properties. The $K_{AD}$ values in aliphatic solvents are almost the same except in dichloromethane. However, the $K_{AD}$ values differ considerably in aromatics solvents where the values are very close. The lower values in aromatic solvents may be due to interaction of solvents with the acceptor molecule. The closeness of values in one class of solvents appear reasonable in view of similar solvent characteristics.
However, proper correlation of the solvent effects are hardly possible in view of lack of data in the gaseous phase. Moreover, in dilute solutions, solvents show donor properties in competition with the solute donor molecules. Naturally, it may have profound influence on $K_D$ values. Interactions like hydrogen-bonding (as in CHCl$_3$ or CH$_2$Cl$_2$ etc.) are also of importance. However, correlation of stability constant of the complexes with physical properties like dipole moment ($\mu$), refractive index ($\eta$), dielectric permittivity ($\varepsilon$), density ($\rho$) and polarizability ($\alpha$) was not observed. It has been generally observed that the poorest ionizing solvents give rise to the highest values of $K_C^{AD}$ (C$_4$H$_6$ > CHCl$_3$ > CH$_2$Cl$_2$)\(^3\) but the observation is not found to be true in the present case.

It is expected that the association constants of the C-T complexes are very much dependent on the donor and acceptor moieties. The fairly large values of $K_C^{AD}$ suggests considerable overlap. It is to be noted both phen and bipy show predominantly $\pi \rightarrow \pi^*$ transitions and $\pi \rightarrow \pi^*$ transitions may be overshadowed by $\pi \rightarrow \pi^*$ transitions\(^16\) whereas chloranil shows both $\pi \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions.

The stability constant values for chloranil bipyridine complexes are higher than the corresponding chloranil-phenanthroline
complexes. It is difficult to suggest a possible explanation. The reasons may be that phen is characterised by resonance stabilization and coplanarity compared to bipy, as a result greater ground state stabilization of phen + chloranil complexes compared to bipy + chloranil complexes are expected and these lead greater $K_{AD}$ values for bipy + chloranil complexes.

Moreover, bipy is present as trans configuration in these solvents. Therefore, the trans bipy provides statistically twice the number of sites for interaction compared to phen in which the orientation of two rings within the molecule naturally screens one side of each ring from the approach of the acceptor molecule similar to those observed in case of cis and trans stilbene.³

Difference in stability may also result from the changed geometry of the molecules due to twisting of bipyridine. The dipole-moment of cis-bipy and phen are 0.91 D and 4.11 D respectively.

We have not tried to correlate the $K_{AD}$ values to the various measures of the electron donating abilities of the electron-donor.

However, further works with different acceptor molecules are needed before we try better correlation.
<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Concentration of Acceptor $\times 10^4$</th>
<th>Concentration of Donor $\times 10^4$</th>
<th>Complex Absorbance (588 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>2.7</td>
<td>0.544</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>2.4</td>
<td>0.492</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>2.1</td>
<td>0.455</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>1.8</td>
<td>0.372</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>1.5</td>
<td>0.305</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
<td>1.2</td>
<td>0.241</td>
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<td>7</td>
<td>0.7</td>
<td>0.9</td>
<td>0.184</td>
</tr>
<tr>
<td>8</td>
<td>0.8</td>
<td>0.6</td>
<td>0.125</td>
</tr>
<tr>
<td>9</td>
<td>0.9</td>
<td>0.3</td>
<td>0.066</td>
</tr>
</tbody>
</table>

**Table VI.1. Presentation of Typical Data for Job's Method of Continuous Variation**

- **Acceptors**: Chloranil, 1,10-Phenanthroline
- **Donors**: 0-Xylene
- **Solvent**: O-ylene

Composition of complex:

- Chloranil: Concentration $\times 10^4$
- 1,10-Phenanthroline: Concentration $\times 10^4$
- 0-Xylene: Concentration $\times 10^4$

Absorbance at 588 nm for various serial numbers of the complex.
Table VI.2. Complex formation and Determination of Equilibrium Constant, $K_{AD}$ between Chloranil and 1,10-Phenanthroline/2,2-Bipyridine at 298°K

(i) Acceptor : Chloranil
Donor : 1,10-Phenanthroline
Solvent : Toluene

(A) Jobs Method of Continuous Variation

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Ratio of mixture (ml)</th>
<th>Concentration of Acceptor $M \times 10^4$ ($C_1$)</th>
<th>Absorbance at 360 nm (d$_1$)</th>
<th>$\frac{C_1}{d_1-d_2} \times 10^3$</th>
<th>Concentration of Donor $M \times 10^4$ ($C_2$)</th>
<th>Equilibrium Constant $K_{AD}$ (Graphically)</th>
<th>Average $K_{AD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.0:1.0</td>
<td>1.35</td>
<td>0.274</td>
<td>16.90</td>
<td>1.00</td>
<td>227.30</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8.0:2.0</td>
<td>1.20</td>
<td>0.244</td>
<td>6.67</td>
<td>2.00</td>
<td>227.30</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7.0:3.0</td>
<td>1.05</td>
<td>0.213</td>
<td>17.50</td>
<td>3.00</td>
<td>227.90</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.0:4.0</td>
<td>0.90</td>
<td>0.183</td>
<td>18.00</td>
<td>4.00</td>
<td>226.10</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5.0:5.0</td>
<td>0.75</td>
<td>0.151</td>
<td>18.75</td>
<td>5.00</td>
<td>228.30</td>
<td>227.82</td>
</tr>
<tr>
<td>6</td>
<td>4.0:6.0</td>
<td>0.60</td>
<td>0.121</td>
<td>20.00</td>
<td>6.00</td>
<td>226.60</td>
<td></td>
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<tr>
<td>7</td>
<td>3.0:7.0</td>
<td>0.45</td>
<td>0.089</td>
<td>11.25</td>
<td>7.00</td>
<td>227.90</td>
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<tr>
<td>8</td>
<td>2.0:8.0</td>
<td>0.30</td>
<td>0.039</td>
<td>7.50</td>
<td>8.00</td>
<td>223.20</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.0:9.0</td>
<td>0.15</td>
<td>0.030</td>
<td>15.00</td>
<td>9.00</td>
<td>229.80</td>
<td></td>
</tr>
</tbody>
</table>
Table VI.2 (Contd.)

(ii) Acceptor : Chloranil
Donor : 2,2'-Bipyridine
Solvent : Chloroform

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Ratio of Mixture (ml)</th>
<th>Concentration of Acceptor : Donor (M x 10^3)</th>
<th>Absorbance at 374 nm (C)</th>
<th>Concentration of Mixture (M x 10^3)</th>
<th>Equilibrium Constant K_{AD} (Graphically)</th>
<th>Average K_{AD}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.0 : 1.0</td>
<td>1.80</td>
<td>0.481</td>
<td>163.64</td>
<td>0.20</td>
<td>174.24</td>
</tr>
<tr>
<td>2</td>
<td>8.0 : 2.0</td>
<td>1.60</td>
<td>0.429</td>
<td>152.40</td>
<td>0.40</td>
<td>185.20</td>
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<td>3</td>
<td>7.0 : 3.0</td>
<td>1.40</td>
<td>0.371</td>
<td>153.80</td>
<td>0.60</td>
<td>177.08</td>
</tr>
<tr>
<td>4</td>
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<td>1.20</td>
<td>0.320</td>
<td>68.57</td>
<td>0.80</td>
<td>175.90</td>
</tr>
<tr>
<td>5</td>
<td>5.0 : 5.0</td>
<td>1.00</td>
<td>0.268</td>
<td>61.73</td>
<td>1.00</td>
<td>172.04</td>
</tr>
<tr>
<td>6</td>
<td>4.0 : 6.0</td>
<td>0.80</td>
<td>0.214</td>
<td>53.33</td>
<td>1.20</td>
<td>174.70</td>
</tr>
<tr>
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<td>3.0 : 7.0</td>
<td>0.60</td>
<td>0.162</td>
<td>50.00</td>
<td>1.40</td>
<td>180.55</td>
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<tr>
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<td>2.0 : 8.0</td>
<td>0.40</td>
<td>0.106</td>
<td>66.67</td>
<td>1.60</td>
<td>176.70</td>
</tr>
<tr>
<td>9</td>
<td>1.0 : 9.0</td>
<td>0.20</td>
<td>0.057</td>
<td>40.00</td>
<td>1.80</td>
<td>172.40</td>
</tr>
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</table>
Table VI.2 (Contd.)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Ratio of mixture (ml)</th>
<th>Concentration of Acceptor: Donor</th>
<th>Absorbance at 336 nm ($C_1/d_1$)</th>
<th>$C_1/d_1 - d_2$</th>
<th>$1/C_2$</th>
<th>$1/(C_2 - x_2)$</th>
<th>$1/(C_2 - x_3)$</th>
<th>$1/(C_2 - x_4)$</th>
<th>Equilibrium Constant $K_{AD}$</th>
<th>Average $K_{AD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0 : 1.0</td>
<td>4.50</td>
<td>1.029</td>
<td>64.30</td>
<td>2.00</td>
<td>3.30</td>
<td>10.30</td>
<td>35.70</td>
<td>10.95</td>
<td>33.30</td>
</tr>
<tr>
<td>2</td>
<td>5.0 : 2.0</td>
<td>4.00</td>
<td>0.913</td>
<td>16.70</td>
<td>5.00</td>
<td>7.80</td>
<td>5.90</td>
<td>5.70</td>
<td>5.60</td>
<td>6.00</td>
</tr>
<tr>
<td>3</td>
<td>7.0 : 3.0</td>
<td>3.50</td>
<td>0.799</td>
<td>7.14</td>
<td>3.33</td>
<td>6.50</td>
<td>4.20</td>
<td>4.00</td>
<td>3.20</td>
<td>4.30</td>
</tr>
<tr>
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<td>6.0 : 4.0</td>
<td>3.00</td>
<td>0.672</td>
<td>3.60</td>
<td>5.00</td>
<td>2.50</td>
<td>6.60</td>
<td>5.90</td>
<td>5.70</td>
<td>5.60</td>
</tr>
<tr>
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<td>5.0 : 5.0</td>
<td>2.50</td>
<td>0.568</td>
<td>3.13</td>
<td>2.00</td>
<td>3.30</td>
<td>2.50</td>
<td>2.40</td>
<td>2.94</td>
<td>228.57</td>
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<tr>
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<td>4.0 : 6.0</td>
<td>2.00</td>
<td>0.449</td>
<td>2.00</td>
<td>1.67</td>
<td>3.37</td>
<td>2.10</td>
<td>2.00</td>
<td>2.50</td>
<td>227.80</td>
</tr>
<tr>
<td>7</td>
<td>3.0 : 7.0</td>
<td>1.50</td>
<td>0.355</td>
<td>1.15</td>
<td>1.43</td>
<td>3.30</td>
<td>1.87</td>
<td>1.80</td>
<td>2.30</td>
<td>229.79</td>
</tr>
<tr>
<td>8</td>
<td>2.0 : 8.0</td>
<td>1.00</td>
<td>0.229</td>
<td>0.78</td>
<td>1.25</td>
<td>2.40</td>
<td>1.60</td>
<td>1.50</td>
<td>1.90</td>
<td>231.80</td>
</tr>
<tr>
<td>9</td>
<td>1.0 : 9.0</td>
<td>0.50</td>
<td>0.108</td>
<td>0.33</td>
<td>1.11</td>
<td>2.30</td>
<td>1.40</td>
<td>1.34</td>
<td>1.70</td>
<td>231.29</td>
</tr>
</tbody>
</table>
Table VI.2A. Equilibrium Constants, free energy changes and extinction coefficient values of Donor-Acceptor Complexes in different solvents at 298°K

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Solvents</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Acceptors: Chloranil</th>
<th>Donor: 1,10-Phenanthroline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_{AD}$</td>
<td>$\Delta G^0$ in KJ</td>
<td>$k_{AD}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Extinction Coefficient of complex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Benzene</td>
<td>2174.71</td>
<td>100.00</td>
<td>-11.41</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>1971.64</td>
<td>100.16</td>
<td>-11.42</td>
</tr>
<tr>
<td>3</td>
<td>O-Amylene</td>
<td>4793.74</td>
<td>103.12</td>
<td>-11.49</td>
</tr>
<tr>
<td>4</td>
<td>Mesitylene</td>
<td>1779.45</td>
<td>101.98</td>
<td>-11.46</td>
</tr>
<tr>
<td>5</td>
<td>Dichloro- methane</td>
<td>624.43</td>
<td>272.20</td>
<td>-13.89</td>
</tr>
<tr>
<td>6</td>
<td>Chloroform</td>
<td>169.17</td>
<td>176.53</td>
<td>-12.82</td>
</tr>
<tr>
<td>7</td>
<td>Carbon tetrachloride</td>
<td>237.21</td>
<td>198.10</td>
<td>-15.11</td>
</tr>
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</table>
Table VI.3. Charge Transfer interactions of Chloranil with different Solvent Molecules and Variations of Charge-Transfer Energy and other Properties of the Solvent Mixtures

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Solvents</th>
<th>$2 \times 10^{-14}$ sec.</th>
<th>$E$ (Kcals/mole) (based on chloranil)</th>
<th>$E_T$</th>
<th>$Z$</th>
<th>DN</th>
<th>AN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMF</td>
<td>10.96</td>
<td>104.55</td>
<td>43.8</td>
<td>68.5</td>
<td>26.6</td>
<td>16.0</td>
</tr>
<tr>
<td>2</td>
<td>Ether</td>
<td>10.39</td>
<td>99.05</td>
<td>34.5</td>
<td>-</td>
<td>19.2</td>
<td>3.9</td>
</tr>
<tr>
<td>3</td>
<td>DMSO</td>
<td>10.31</td>
<td>98.36</td>
<td>45.0</td>
<td>71.1</td>
<td>29.8</td>
<td>19.3</td>
</tr>
<tr>
<td>4</td>
<td>C$_2$H$_5$OH</td>
<td>10.31</td>
<td>98.36</td>
<td>51.9</td>
<td>79.6</td>
<td>20.0</td>
<td>37.1</td>
</tr>
<tr>
<td>5</td>
<td>CH$_2$COOC$_2$H$_5$</td>
<td>10.28</td>
<td>98.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>C$_6$H$_5$Cl</td>
<td>10.21</td>
<td>97.34</td>
<td>37.5</td>
<td>58.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>NCCH$_2$COOC$_2$H$_5$</td>
<td>10.21</td>
<td>97.34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>CH$_2$OH</td>
<td>10.14</td>
<td>96.67</td>
<td>55.5</td>
<td>83.6</td>
<td>19.0</td>
<td>41.3</td>
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<tr>
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<td>C$_6$H$_5$</td>
<td>8.81</td>
<td>84.01</td>
<td>34.5</td>
<td>-</td>
<td>0.1</td>
<td>8.2</td>
</tr>
<tr>
<td>10</td>
<td>C$_6$H$_5$CH$_3$</td>
<td>8.22</td>
<td>78.41</td>
<td>33.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>CCl$_4$</td>
<td>8.00</td>
<td>76.29</td>
<td>32.5</td>
<td>-</td>
<td>-</td>
<td>8.6</td>
</tr>
<tr>
<td>12</td>
<td>CH$_2$ON</td>
<td>8.00</td>
<td>76.29</td>
<td>46.0</td>
<td>71.3</td>
<td>14.1</td>
<td>19.3</td>
</tr>
<tr>
<td>13</td>
<td>CHCl$_3$</td>
<td>7.91</td>
<td>75.48</td>
<td>39.1</td>
<td>63.2</td>
<td>-</td>
<td>23.1</td>
</tr>
<tr>
<td>14</td>
<td>CH$_2$Cl$_2$</td>
<td>7.85</td>
<td>74.88</td>
<td>41.1</td>
<td>64.2</td>
<td>-</td>
<td>20.4</td>
</tr>
<tr>
<td>15</td>
<td>C$_6$H$_4$(CH$_3$)$_2$</td>
<td>7.63</td>
<td>72.75</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>C$_6$H$_4$(CH$_3$)$_3$</td>
<td>7.12</td>
<td>67.86</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$E_T$ = Energy Value (Dimroth et al.)
Z = Kosower's Z-Value
DN = Donor Number
AN = Acceptor Number
Acceptor - Chloranil
Donor - 1:10 Phenanthroline
Solvent - O-Xylene

Fig II 1 Composition curve.
Fig. VII.2: Determination of equilibrium constant of Donor-Acceptor Molecular complex in organic solvent at 298°K.
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