CHAPTER I

INTRODUCTION
It has been made abundantly clear from the study of many physico-chemical phenomena that molecular interactions play a very important role. They are responsible for the very existence of the liquid state and are particularly important in the chemistry of solutions. These interactions can be recognised between varieties of chemical species, such as ions, ion pairs, complexes etc. and influence the physico-chemical behaviour of molecules very strongly. In addition to dispersion, dipole-dipole, dipole-induced dipole and such like van der Waals forces, there can be certain specific molecular interactions in solution, such as hydrogen bonding and charge-transfer interactions.

Among these specific molecular interactions, charge-transfer interaction is our immediate interest. It has received a great deal of attention in recent years, and secured the Nobel Prize for its chief proponent, Robert S. Mulliken, who, it is generally recognised, made the first attempt at an explanation of charge-transfer absorption in 1950. This has in fact, become the cornerstone for virtually all subsequent work in the field. His work was prompted by the report of Benesi and Hildebrand that solutions containing an aromatic hydrocarbon and iodine had an electronic absorption band, not present in either component alone. A more detailed examination by Mulliken led to the valence bond treatment of complex formation between electron donors and
electron acceptors and provided the major stimulus for the subsequent development in this field.

The ground state of the complex formed between an electron donor $D$ and an electron acceptor $A$ was represented in a general way by Mulliken by a wave function $\psi_N$:

$$\psi_N = a\psi_0 (A,D) + b\psi_1 (A^- - D^+)$$

where $\psi_0 (A,D)$ is called a "no-bond" function and $\psi_1$ corresponds to a dative structure in which an electron has been transferred from the donor to the acceptor molecule. It is assumed that in most interactions, $a \gg b$. The valence bond treatment requires that there shall be a second state represented by $\psi_E (AD)$ given by:

$$\psi_E (AD) = a^* \psi_1 (A^- - D^+) - b^* \psi_0 (A,D)$$

where $a \sim a^*$ and $b \sim b^*$. The charge-transfer transition then corresponds to the characteristic electronic absorption $\psi_E \leftarrow \psi_N$.

In general, complexes formed between an electron donor and an electron acceptor retain the absorptions due to separate components modified to a greater or lesser extent, together with one or more absorption bands
characteristic of the complex as a whole. The realisation that the new absorption was the result of an intermolecular charge-transfer transition and not a modified transition of one or the other component was due to Brackman. The new absorption is more easily observed when the interaction is between a strong donor and a strong acceptor. The transition appears in such cases at considerably long wavelengths than the absorptions of the component molecules.

The complex may also be partially dissociated into its component species in solution, as a result of which it may be difficult to measure these absorption bands due to "local excitations" in the acceptor and donor moieties of the complex corresponding to absorption bands in the separated components.

It is regarded that in solution and in vapour phase, there is a simple equilibrium between the complex and its components:

$$A + D \rightleftharpoons AD$$

$$K_{AD}^C = \frac{C_{AD}}{C_A \cdot C_D} \quad (1.1)$$

The assumption is made implicitly in most cases, that the product of activity coefficients, $\gamma_A / (\gamma_A \gamma_D)$ is close to unity and that the expression for $K_{AD}^C$ above
is a reasonable approximation to the thermodynamic equilibrium constant. In most of the determinations of equilibrium constant, there is an implicit or explicit determination of the molar absorption coefficient of the complex.

The charge-transfer theory should strictly be applied to isolated molecules, a condition approached only in the vapour state. The spectral and thermodynamic properties of the complexes are known to be affected by the solvent, even though they are commonly regarded as "inert". This has been demonstrated even in the early experimental results of Benesi and Hildebrand and a more detailed analysis of the solvent effects has confirmed how large the influence of solvent can be. However, in view of the experimental difficulties involved in the vapour phase investigations, the more extensive studies have been made in solution. The great majority of the systems involving a diluting solvent employ sufficiently low concentrations of the various solute species so that they may be treated as dilute solutions.

In the study of the donor-acceptor equilibria, various methods have been employed to determine the position of the equilibrium. Of these, mention may be made of the following:

a) Ultraviolet and visible spectroscopy
b) Infrared spectroscopy 19-26

c) Nuclear magnetic resonance 27-29

d) Distribution 30, 31

e) Polarography 32-35

f) Direct calorimetry 36-38

g) Dielectric constant 39, 40 and so on.

The most extensively used method is the one involving the ultraviolet and visible spectrophotometric technique. The first quantitative study involving donor-acceptor equilibrium was made by Benesi and Hildebrand, when they examined the molecular complex formed between iodine and benzene spectrophotometrically. They assumed that it was an ideal system, in which a 1:1 complex was formed. For such a system, they deduced the relationship:

\[ \frac{c_A^0}{d} = \frac{1}{K_C \cdot \lambda^{AD}} \cdot \frac{1}{C_D} + \frac{1}{\lambda^{AD}} \]  

(1.2)

Where \( c_A^0 \) and \( c_D^0 \) are initial molar concentrations of the acceptor and donor, \( K_C^{AD} \) and \( \lambda^{AD} \) are the formation constant and molar absorption coefficient of the complex \( AD \) respectively and 'd' the measured absorbance for a 1 cm cell. In deriving equation (1.2), the assumption has been made that \( c_D^0 \gg c_A^0 \) in all the measurements and that the absorption was due entirely to the complex. The above equation is the
Benesi-Hildebrand equation (B-H equation). It is apparent that a plot of \( \frac{c_A^0}{d} \) vs \( \frac{1}{c_D^0} \) should be linear with a slope of \((K_C^{AD} \cdot \xi_A^{AD})^{-1}\) and an intercept of \((\xi_A^{AD})^{-1}\) from which the value of \(K_C^{AD}\) may be evaluated.

However, the inadequacy of this equation has been pointed out by Scott\(^41\) Nagakura\(^42\) and Rose and Drago\(^43\). The extrapolation towards more concentrated solutions is not only highly undesirable but the linearity is not found to be a good test for the absence of termolecular complexes.\(^44\)

An important modification of the B-H equation is due to Scott\(^41\). He pointed out the undesirability of the extrapolation towards concentrated solutions and suggested a rearrangement of the B-H equation which involves an extrapolation towards more dilute solutions in determining the values of \(K_C^{AD}\) and \(\xi_A^{AD}\). The Scott modification is given as follows:

\[
\frac{c_A^0 \cdot c_D^0}{d} = \frac{c_A^0}{\xi_A^{AD}} + \frac{1}{K_C^{AD} \cdot \xi_A^{AD}} \tag{1.3}
\]

A linear plot results when \(c_A^0 \cdot c_D^0/d\) is plotted vs \(c_D^0\), whose slope gives the value of \((\xi_A^{AD})^{-1}\), while the intercept gives \((K_C^{AD} \cdot \xi_A^{AD})^{-1}\).

Modifications have also been suggested by Moriguchi and Kaneniwa\(^45\) and Foster, Hammick and Wardley\(^46\), all of
which apply to systems, where the absorption is due only to the complex.

Reasoning that if \( C_D^\circ \gg C_A^\circ \), any decrease in \( C_D^\circ \) through complex formation may be ignored or a sufficient compensation for any small absorption effected by having a solution of donor of concentration \( C_D^\circ \) in the reference beam of the spectrophotometer. Ketelaar and his co-workers devised a relationship for systems where \( \lambda \) has a significant absorption at the wavelength of measurement. Their equation is given in the form

\[
\frac{1}{\xi_{\lambda}^a - \xi_{\lambda}^A} = \frac{1}{K_C (\xi_{\lambda}^{AD} - \xi_{\lambda}^A)} \cdot \frac{1}{\xi_{\lambda}^C} + \frac{1}{\xi_{\lambda}^{AD} - \xi_{\lambda}^A} \tag{1.4}
\]

where

\[
\xi_{\lambda}^a = \frac{d'}{C_A^\circ} \quad \text{and} \quad d' = \xi_{\lambda}^{AD} C_{AD} + \xi_{\lambda}^A C_A
\]

\[
= \xi_{\lambda}^{AD} C_{AD} + \xi_{\lambda}^A (C_A^\circ - C_{AD})
\]

Equation (1.4) may be expressed in a form similar to the Scott equation (1.3) as follows:

\[
\frac{C_D^\circ}{(\xi_{\lambda}^a - \xi_{\lambda}^A)} = \frac{C_D^\circ}{(\xi_{\lambda}^{AD} - \xi_{\lambda}^A)} + \frac{1}{K_C (\xi_{\lambda}^{AD} - \xi_{\lambda}^A)} \tag{1.5}
\]

For a more general case, where the donor and acceptor have significant absorption at the wavelength of measurement
and for which no special conditions regarding the initial concentrations of donor and acceptor need be applied, Rose and Drago have developed an equation in the following form:

$$\frac{1}{K_{AC}^{AD}} = \frac{d'}{\xi'_\lambda} = (c_A^0 + c_D^0) + \frac{c_A^0 c_D^0}{d'} \xi'_\lambda$$  \hspace{1cm} (1.5)

where

$$d' = d - d_A - d_D$$ and $$\xi'_\lambda = \xi_{AC}^{AD} - \xi_{A}^{D} - \xi_{D}^{A}$$

For the application of this equation to experimental data in order to obtain $\xi_{AC}^{AD}$ and $K_{AC}^{AD}$, it is suggested that the $\xi_{AC}^{AD}$ values are selected at random and the values of $(K_{AC}^{AD})^{-1}$ calculated for each set of experimental data. The $(K_{AC}^{AD})^{-1}$ values that are calculated for each assumed value of $\xi_{AC}^{AD}$ are plotted as functions of $\xi_{AC}^{AD}$, whereby a number of straight lines with differing slopes are obtained. Ideally, these straight lines should intersect at a single point, from which the correct values of $K_{AC}^{AD}$ and $\xi_{AC}^{AD}$ may be determined. In practice, these lines intersect in a certain finite area which is the inverse measure of the accuracy of the data. It is possible that from the several values of $K_{AC}^{AD}$, corresponding to several points of intersection, an average value of $K_{AC}^{AD}$ may be obtained. This method, while it is laborious, is capable of giving highly reliable values of the equilibrium constant, as well as an estimate of the error in the determination.
A modification of the above equation, which avoids the laborious methods involved, has been employed by Jayadevappa and Nagendrappa in their investigation of the 1:1 equilibria of p-benzoquinone and 1,4-naphthoquinone with N-methylaniline and N,N-dimethylaniline in various solvent systems. The equation (1.6) may be modified by dividing throughout by $\xi'_{\lambda}$ to get:

$$\frac{1}{K_{C}^{AD} \xi'_{\lambda}} = \frac{d}{\xi'^{2}_{\lambda}} - \frac{(C_{A}^{0} + C_{D}^{0})}{\xi'_{\lambda}} + \frac{C_{A}^{0}C_{D}^{0}}{d'} \quad (1.7)$$

If one takes into account the magnitude of the terms on the right hand side of the equation (1.7), the first term may be neglected and a rearrangement of the equation gives:

$$\frac{C_{A}^{0}C_{D}^{0}}{d'} = \frac{1}{K_{C}^{AD} \xi'_{\lambda}} + \frac{(C_{A}^{0} + C_{D}^{0})}{\xi'_{\lambda}} \quad (1.8)$$

A plot of $C_{A}^{0}C_{D}^{0}/d'$ vs $(C_{A}^{0} + C_{D}^{0})$ would then be expected to give a slope of $(\xi'_{\lambda})^{-1}$ and an intercept of $(K_{C}^{AD} \xi'_{\lambda})^{-1}$. The linearity of such a plot can be considered to be a test of 1:1 stoichiometry.

While in literature, most of the studies of equilibrium constants correspond to systems of 1:1 stoichiometry, not much attention has been paid to the consideration of
termolecular complexes, and a few attempts have been made to
treat them on the basis of 2:1 stoichiometry. \(^{44,49-52}\)

An attempt has been made to obtain equations capable of
giving linear graphical plots for systems of 2:1 (donor : acceptor) stoichiometry under the simplifying assumption that
the \(AD_2\) complex is the only one of significance at the wave-
length of measurement by Jayadevappa and Nagendrappa. \(^{48}\)

For an equilibrium of the kind,

\[
A + 2D \rightleftharpoons AD_2
\]

\[
k_{c}^{AD_2} = \frac{C_{AD_2}^{2}}{C_{A}C_{D}^{2}}
\]

(1.9)

The equation derived by them has the form:

\[
\frac{C_{A}^{o}C_{D}^{o}}{d} = \frac{1}{k_{c}^{AD_2} \xi_{\lambda}^{AD_2}} + \frac{(C_{D}^{o} + 4C_{A}^{o})C_{D}^{o}}{\xi_{\lambda}^{AD_2}}
\]

(1.10)

A plot of \(C_{A}^{o}C_{D}^{o}/d\) vs \((C_{D}^{o} + 4C_{A}^{o})C_{D}^{o}\) would then be
expected to give a straight line with a slope \((\xi_{\lambda}^{AD_2})^{-1}\) and
an intercept, \((k_{c}^{AD_2}, \xi_{\lambda}^{AD_2})^{-1}\) from which \(k_{c}^{AD_2}\) and \(\xi_{\lambda}^{AD_2}\)
may be determined. Satisfactory linear plots were obtained
by Jayadevappa and Nagendrappa \(^{18}\) for systems of \(p\)-benzoquinone
and 1,4-naphthoquinone with N-methyl and N,N-dimethylanilines in a number of solvents in the concentration ranges employed, indicating predominantly 2:1 equilibria.

In the general case, however, the above assumption cannot be expected to hold when termolecular complexes are present and one has to recognise simultaneous equilibria of the kind:

\[
A + D \rightleftharpoons AD; \quad K_{AD}^C = \frac{C_{AD}}{C_A \cdot C_D} \tag{1.11}
\]

\[
AD + D \rightleftharpoons AD_2; \quad K_{AD_2}^C = \frac{C_{AD_2}}{C_{AD} \cdot C_D} \tag{1.12}
\]

Under the circumstances, no simple linear relationships are possible. If one considers, for simplicity, that \(C_D^0 \gg C_A^0\), one may obtain an equation of the form:\(^53\)

\[
d = \frac{\xi_{AD}^\lambda \cdot K_{C}^{AD} \cdot C_A^0 \cdot C_D^0 + \xi_{AD_2}^\lambda \cdot K_{C}^{AD_2} \cdot C_A^0 \cdot C_D^2}{1 + K_{C}^{AD} \cdot C_D^0 + K_{C}^{AD_2} \cdot C_D^2} \tag{1.13}
\]

containing the four unknown parameters, \(K_{C}^{AD}\), \(K_{C}^{AD_2}\), \(\xi_{AD}^\lambda\) and \(\xi_{AD_2}^\lambda\). Equation (1.13) may also be expressed in a form similar to the Scott's equation (1.3) as follows:
\[
\frac{c_A^0 c_D^0}{d} = \frac{(1 + K_{CD}^{AD2} c_D^0)}{(1 + \frac{K_{AD}^{AD2} c_D^0}{\epsilon_{AD}^{AD}})} \cdot \frac{c_D^0}{\epsilon_{AD}^{AD}} + \frac{1}{(1 + \frac{K_{CD}^{AD2} c_D^0}{\epsilon_{AD}^{AD}})}
\]

(1.14)

If the appropriate Scott functions are plotted on the assumption that only one complex with a 1:1 stoichiometry is present, whereas, in fact significant quantities of a complex with a different stoichiometry are also present, then the apparent association constant values which are dependent on the concentration \( c_D^0 \) will be obtained. The apparent association constant and molar absorptivity on the assumption of 1:1 stoichiometry may then be increased or decreased by contribution from termolecular complexes. The presence of the terms \( \epsilon_{AD}^{AD} \) and \( \epsilon_{AD}^{AD2} \) in equation (1.14) also implies that the apparent \( K_{CD}^{AD} \) values are wavelength dependent. This has actually been observed in some systems.44,51,55-59

Further, it has also been shown58 that the absorption spectra for the naphthalene-tetracyanoethylene system in carbon tetrachloride and in chloroform can be simulated closely, using synthetic data, by assuming the presence of termolecular complexes. Quantitative determinations of the formation constants and the molar absorptivities in such
cases are rather few and involve non-graphical trial and error computer methods involving some iteration processes.\textsuperscript{59-61}

There are some nonlinear methods using the general least-squares adjustment that have also, recently been used.\textsuperscript{62,63}

Each of these methods have different degrees of reliability and several of them also show disagreements between the results obtained from the optical and n.m.r. data.\textsuperscript{61,64}

We have in this work, investigated several equilibria involving many new acceptors in order to determine the nature of the complexes formed, their stoichiometry, their spectral characteristics and the thermodynamics of their formation. Some of the systems investigated fall into the well-recognised class of 1:1 complexes while others show the presence of termolecular complexes. There are also systems, that exhibit time-dependent optical absorption, whose kinetics have been studied by spectrophotometric methods. From the information obtained from the above studies, it is possible, also, to determine the substituent effects on the optical characteristics as well as thermodynamic properties of the complexes.