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Mulliken’s Theory in Charge-Transfer Complexation

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Abstract - **The nature of the attraction in a charge-transfer complex is not a stable chemical bond and is much weaker than covalent forces, rather it is better characterized as a weak electron resonance. As a result, the excitation energy of this resonance occurs very frequently in the visible region of the electro-magnetic spectrum. This produces the usually intense colors characteristic for these complexes. The optical absorption bands are often referred to as charge-transfer bands, or CT bands. Therefore optical spectroscopy is a powerful technique to characterize charge-transfer bands. The CT- complexes extend from hydrogen bonding to proton transfer reactions including solvent polarity scales based on them. These complexes are becoming increasingly important in all fields of human endeavour from physics and chemistry and biology to medicines. Currently there is an opinion among some scientists that these complexes are involved somewhere or the other on the reaction profile of all chemical reactions. They are, therefore, a special case of molecular association and have been most widely investigated. Charge transfer complexes are of immense importance in material science and they play a significant role in drug design and bioelectrochemical processes.**

Keywords: Acceptor, Biochemical, Electron, Energy, Molecules, Solvent, Transfer

Charge-transfer complexation is important phenomenon in biochemical and bioelectrochemical energy transfer processes. Charge-transfer phenomenon was introduction first by Mulliken and widely discussed by Foster to define a new type of adducts. Mulliken defines a molecular complex between two molecules as an association somewhat stronger than ordinary. Van der Waal’s association of definite stoichiometry (1:1 for most cases). The parteners are very often already have closed- shell (Saturated Valence) electronic structure. In loose complexes the identities of the original molecules are to a large extent preserved.

The tendency to form complexes occurs when one partener is an electron acceptor and the other is an electron donor. We abbreviate the term donor-acceptor complex to include all such associations and use D for an electron donor and A for electron acceptor. Most studies of complexes thus far have been made in solution, in solvent that are as inert as possible. It may, therefore, be assumed that the London dispersion interactions which are important between D and A in the vapour state, are very approximately cancelled by losses of solute-solvent dispersion force attractions when complex is formed from free donor and acceptor in solution. Roughly, one donor-solvent plus one acceptor- solvent contact is replaced by one donor-acceptor and one solvent-solvent contact. The theory of donor-acceptor complexes and their spectra as presented by Mulliken is a vapour-state theory, except for the omission of the London dispersion attraction terms. This theory after small correction for solvation energies, is essentially valid for solutions in inert solvents. The few studies that have been made in vapour-state complexes are in agreement with this theory but they show some puzzling features.

The new bond formed according to Benesi and Hildebrand is in the ultra-violet region for a solution of benzene and iodine dissolved in n-heptane. Similar bonds also occur in the visible region for many other complexes.

This demonstrates that a solution of tetracyanoethylene (TCNE) in methylene dichloride may be added to a series of aromatic hydrocarbons dissolved in methylene dichloride, benzene gives a yellow solution, xylene an orange, durene a deep red and hexamethyl benzene a deep purple and a green colour was obtained on interaction of colourless solution of the TCNE acceptor and purple solution of porphyrins in dichloromethane or carbon tetrachloride describing a charge transfer complexe (CTC) formation and also when tetracyanoethylene solution was added to the solution of 2,6- diaminopyridine (2,6-DAPY), strong change in colour was observed and associated with the appearance of new absorption band in region where neither donor nor acceptor have any absorption . The π-electron molecules, ethylene and benzene can act either as weak donors or weak acceptors. Other things being equal, donorability

increases with decreasing ionization potential (I_D); the acceptor ability with increasing electron affinity(E_A).

Among aromatic hydrocarbons I_D decreases and E_A increases with increasing size; graphite with $I_D = E_A$ is the extreme example and is in fact be both a good acceptor and a good donor. Starting with any unsaturated or aromatic hydrocarbon, either its donor or its acceptor capability can be strengthened by the introduction of suitablesubstituentgroups.Theweakdonorpropertiesofbenzenearefortifiedby adding more and more electron-releasing methyl groups. The two kinds of molecular complexes discussed above provide examples of n.v. (strong) and π-π* (weak) complexes. The common types of donors and acceptors are listed in Table1.

G.N. Lewis explained co-ordination compounds or dative compounds (e.g.,

$R_3N{:}BCl_3$ which can also be considered essentially as an stable molecular complex) in terms of a structure with sharing of the electron lone pair of the nitrogen atom as well as the B (Boran) atom are surrounded by a complete octet of outer-shell electrons. This sharing can be expressed in quantum language by anapproximate wave function ψ that is a combination of two resonance structure D (R_3N) and A (BCl_3):

$$\psi_N(AD) \sim a\psi_0\underset{\text{no-bond}}{(A,D)} + b\psi_0\underset{\text{dative}}{(A^{-}\text{--}D^{+})} \qquad (1)$$

The dative structure corresponds to an ionic plus a covalent bond and has been called sometimes as semipolar double bond. The interpretation of the N-B dative bond in the complex, given by equation (1), is analogous to the approximate ionic covalent resonance interpretation of the chemical bond in HCl:

$$\psi_{(HCl)} \simeq a\,\psi_0\underset{\text{ionic}}{(H^{+}, Cl^{-})} + b\psi_1\underset{\text{covalent}}{(H\text{--}Cl)} \qquad (2)$$

Table 1

Donor Type	Example	Dative Electron[a] from	Acceptor Type	Example	Dative Electron[a] goes to
n	: NR_3	Non-bonding lone pair	V	BCl_3	Vacant orbital
$b\pi$	Benzene	Bonding π-orbital	$a\pi$	TCNE	Antibonding π-orbital
			$a\sigma$	I_2,HQ[b]	Antibonding σ-orbital

a. Dative electron‖ refers to the electron transferred from donor toacceptor.

b. Molecules such as phenol, water, and other molecules that give hydrogen bonding.

In both examples b>>a.

The inclusion of the no-bond structure in equation (1) is given more importance than that of the ionic structure in equation(2).

Complexes are classified as strong or weak depending on whether the energy of formation and the equilibrium constant (K) are large or small. Relatively strong donors and/or acceptors form relatively stablecomplexes.

$$A + D \overset{K}{\rightleftharpoons} A.D.$$

Equation (1) shows that the complex is stabilized by resonance between ψ_0

and ψ_1

The forces involved being called charge-transfer (CT) forces. However, classical electrostatic forces (including induction forces) also contribute to the stability of the complexes and may even be of predominant importance for the stability of the most hydrogen bonded complexes and of the weaker of the complexes of the b.π -- a.σ and the benzene-iodine (b.π -- a.σ)type

In terms of the resonance structure description of (1) the structure of the ground state of any 1:1 complex is

$$\psi N = a\psi 0\ (A,D) + b\psi 1\ (A^{-} -- D^{+})$$

This function is normalized as follows:

$$\int\psi N\psi N d\tau = \int a^2\psi 0^2\ d\tau + \int b^2\psi 1^2 d\tau + \int 2ab\psi 0\psi 1 d\tau \qquad (3)$$

When $\psi N, \psi 0$ and $\psi 1$ are normalized, then:

$$\int\psi N^2 d\tau = 1, \int\psi 0^2\ d\tau = 1 \text{ and } \int\psi 1^2\ d\tau = 1$$

Substituting these values in equation (3) we obtain

$$a^2 + 2ab\int\psi 0\psi 1\ d\tau + b^2 = 1 \qquad (4)$$

$\int\psi_0\psi_1\ d\tau$ is the so called the overlap integral and is represented by So_1 with the integration carried over all space. If the complex is loose So_1 is small and

$$a^2 + b^2 \simeq 1 \qquad (5)$$

Here, b^2 approximately measures the weight of the dative structure or the fraction of an electron transferred from the donor to the accept or in the ground state.

The term $2abSo_1$ can easily be as large as b^2 or even larger. Half of this term can reasonably be assigned to the donor and half to the acceptor so that the fractions F_0 and F_1 in the no-band and dative structure are:

$F_0 = a^2 + abSo_1$, $F_1 = b^2 + abSo_1$ (6) In loose complexes between closed -shell donors and acceptors $b^2 << a^2$.

For benzene. I_2, I^2 is approximately 0.06 or less; for pyridine. I_2, b^2 is approximately 0.2; for trimethylamine. I_2, b^2 may be 0.4.

If the ground state structure of the complex (weak or strong) is given by ψ_N thene according to quantum theory principles, there must be an excited state ψ_E where ψ_E refers to the CT state. ψ_E is given by

$$\psi_E(AD) = a^*\psi_1(A^{-} – D^{+}) – b^*\ \psi_0(A,D) \qquad (7)$$

The coefficient a* and b* are determined by the quantum theory requirement that the excited state wave function be orthogonal to the ground state function i.e.

$\int\psi_N\psi_E\ d\tau = 0$. The excited state function ψ_E is normalized as follows:

$$\int\psi_E^2\ d\tau = a^{*2} + b^{*2} – 2a^*b^*So_1 = 1 \qquad (8)$$

This makes $a^* \simeq a$ and $b^* \simeq b$. If So_1 were zero, a=a* and b=b* would be true exactly.

For loose molecular complexes the ground state is mostly no-bond state that is,

$a^2 >> b^2$. According to the orthogonality requirements the excited state is mostly dative i.e. $a^{*2} >> b^{*2}$. The excitation of an electron from ψ_N to ψ_E essentially amounts to the transfer of an electron from D to A. The theory further shows that spectroscopic absorption from ψ_N to ψ_E should occur with generally high intensity.

Complexes have been studied mostly in solution but some studies have been made in solids and in the case of (non-bonded vacant orbital) n.v. compounds and also recently of a few complexes of weaker types in the vapour state. Complexes in solids even with 1:1 stoichiometry do not always occur in the form of pairwise units. Studies in the vapour state are difficult because K is small and interference of overlapping spectra of the uncomplexed components is often severe. These difficulties are also found for solution studies but they are less troublesome because K is larger.

The complete absorption spectrum of a complex consists of absorption due to the following:

(1) Locally excited states (states of A or of D, more or less but usually not greatly modified in thecomplex).

(2) CT States [(ψ_E, as in eqn. (7) and other CT states involving excited dative structures, for example $\psi(D^{+*} – A^{-}), \psi(D^{+} – A^{-*})$.

Fig. 1.1 shows the change that occurs in the spectrum of iodine when it is dissolved in n-heptane and then when ethanol is added (Ethanol is transparent upto 220 nm). Iodine is well known for its electron-accepting properties, which may be deduced from molecular orbital consideration. It has been used in the past as a model acceptor to investigate the electron-donating properties of organic molecules and during the past few decades the charge-transfer complexation of iodine with a wide variety of drugs molecule has been the subject of extensive research.

The maxima of the $C_2H_5OH.I_2$ CT band is marked in the Fig. (1.1), and the position of the shifted visible absorption band of I_2 in the complex (a transition to a locally excited state) is also indicated. The contact CT band appears as a long wavelength shoulder on the ultraviolet iodine band when I_2 is dissolved in heptane. It is felt by some authors that the importance of CT forces in stabilizing the ground state of such complexes has been exaggerated.

1.3. Multiple Charge-transfer Spectra

We can see from Table 2 that the intensity of CT spectra of the iodine-benzene complex is very large and that both the K value and the value of –ΔH increases

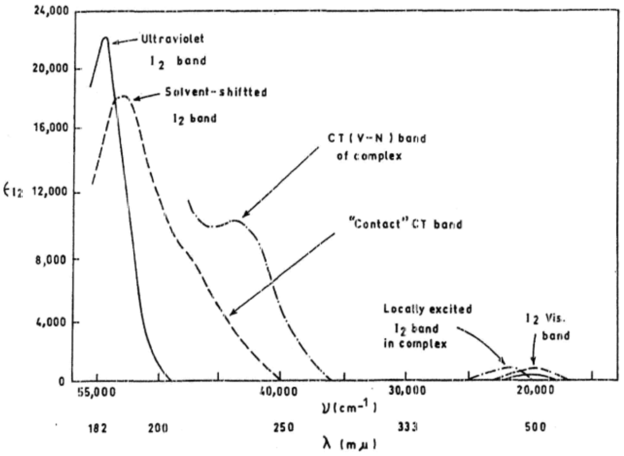

Fig. 1.1. The apparent molar absorptivity of I_2 vapour and of I_2 and EtOH. I_2 in n-heptane,

Here (A) is for I_2 vapour; (B) for I_2 in n-heptane, and (C) for I_2 in n-heptane with 3.4 M ethyl alcohol.

Table2

Spectroscopic and thermodynamic data of ionic complexes with some aromaic hydrocarbons

Donor	**K_C (Temp.)**	**∈CT (λmax CT)**	**ΔH (Solv)**
	(Solve)	**(Solve)**	**K cal mole^{-1}**
Benzene	0.15 (25^{0}C)^{a}	16.400 (292 mμ)	-1.3 (Hexane)^{b}
	CCl_4	(CCl_4)^{a}	(CCl_4)^{C}
Naphthalene	0.25 (25^{0}C)^{a}	7.150 (360 mμ)	-1.8 (Hexane)^{b}
	CCl_4	(hexane)^{b}	
Phenantherene	0.45 (23^{0}C)^{d}	7,100 (364 mμ)	--
	CCl_4	(CCl_4)^{d}	
Anthracene	3.0 (23^{0}C)^{d}	~550 at 430 mμ	-1.61 (CCl_4)^{d}
	CH_2Cl_2, CCl_4	(430 mμ) (CCl_4)^{d}	

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