C H A P T E R - I

ASSOCIATION COMPLEXES : A SHORT REVIEW

1.1 Association Complexes

Interactions between molecules occur with varying degrees of intensity. At one extreme are the non-specific interactions due to vander Waals forces, including classical electrostatic and quantum-mechanical London dispersion forces of attraction and "exchange" or "Steric" forces of repulsion. At the other extreme are strong interactions leading to chemical reactions in which interacting molecules lose their identities and form new species.

Between these extremes lies the class of moleculer or association complexes. In such complexes, formed by specific interaction of two or more molecules, the moleculer partners still preserve their identities to a large extent. The interaction is primarily due to electron exchange, one partner acting as the electron donor and the other as electron acceptor. Such moleculer or Donor-Acceptor complexes, compositions of which can be expressed by integral mole ratios of the components, are in many instances so unstable that they cannot be isolated in pure state at ordinary temperatures but exist only in solutions in equilibrium with their components. In certain cases, however, the resulting products are characterised as solids, the compositions of which can be represented as simple moleculer ratios, usually 1:1 of the component parts. They can of course be detected readily because of differences in their physical properties and spectroscopic characteristics from those of the pure components. The rates of formation in solution, are generally, so rapid that Kinetic studies can seldom be made.

1.2 Types of molecules participating in molecular complex formation.

Electron donors and acceptors can be classified in various ways. The scheme adopted by Mulliken[1] is described here. Donors and Acceptors are broadly classified into increvalent and sacrificial types, the former meaning that the donor or acceptor action makes new bonds possible without affecting the bonding situations in the donor or acceptor and the latter meaning that the internal bonding is weakened thus decreasing vibrational frequencies with consequent increase in bond lengths. Individual donor or acceptor is designated by a term describing briefly the nature of the donating or accepting orbital. Thus R_3N is classified as an n - donor since its donor MO is mostly a lone-pair AO (n means non-bonding); benzene is a $b\pi$ donor, since its donor MO is a bonding π MO; BCl_3 is v acceptor, since its acceptor MO is approximately a vacant valence shell boron AO; trinitro benzene is an $a\pi$ acceptor, since its acceptor MO is an antibonding π orbital; I_2 is an $a\sigma$ acceptor. Major classes of donors and acceptors, classified by this scheme, are given in Table 1.1 and 1.2 respectively.

Table - 1.1

Major Classes of Electron Donors

Structure type		Nature of donor action.	Examples
Symbol	Site of donor action.		
n ($n\sigma$ or $n\pi$)	Valence shell lone pair[1]	Increvalent	Amines, Ethers, Halides etc.
b^2	σ-bonding electrons	Sacrificial	Aliphatic hydrocarbons; Small Cyclic hydrocarbons.
b	π-bonding electrons	Sacrificial	Aromatic and unsaturated hydrocarbons - mono and Polycyclic.
R ($R\sigma$ or $R\pi$)	Valence electron.	Depends on Partner	Atoms and radicals e.g. Na, C_2H_5; odd anions, e.g. Ar^- etc.

1) not always strictly lone.

2) Very weak donors ; unimportant type.

Table - 1.2

Major Classes of Electron Acceptors.

Structure Type		Nature of donor action	Examples
Symbol	Receiving orbital		
v ($v\sigma$ or $v\pi$)	Vacant valence shell AO[1]	Increvalent	BCl_3, Ag^+ etc.
$a\sigma$	σ antibonding electrons	Sacrificial	I_2, HQ, hydrogen halides, halo-substituted Paraffins, Pseudo-halogens etc.
$a\pi$	π antibonding MO	Sacrificial	Aromatic and Unsaturated compounds and especially derivatives such as trinitrobenzene, Tetracyanoethylene, chloranil which contains strongly electrophillic substituents.[2]
Q	Valence shell orbital	Depends on Partner	Atoms and radicals e.g. Cl, OH; odd cations like Ar^+

1) not always strictly vacant.

2) some more novel π-acceptors are given by Foster.[5]

Radical donors (R) and acceptors (Q) usually have an odd number of electrons, while classical (n or v) and most non-classical ($b\pi$, $b\sigma$ or $a\pi$, $a\sigma$) donors or acceptors most often have an even number.

Many molecules can function simultaneously as donors and acceptors in complexes stabilized by two way charge-transfer. It is also possible that a molecule may be capable of functioning in different ways at different loci. Thus H_2O can act as a strong n - donor as also as an aσ acceptor through one of the O - H bonds in H-bonding with an n-donor. Pyridine may act as n-donor through the nitrogen lone pair and also as a weak bπ donor through the aromatic ring acting as a whole. Pyridine may also act as an aσ-acceptor. Self-complexes of benzene possibly involve such amphoteric character.[2] It has been suggested that polycyclic aromatic hydrocarbons which act as good donors should also be good acceptors.[3,4] It is also important to realise that all donor or acceptor action, even if it is strongly localised, still involves to some extent the whole molecule. For example, when an n-donor begins to donate electrons from an atom largely localised on one atom, electronic charge flows into that atom by intramolecular 'inductive' action from the attached atoms to compensate for the loss. Mulliken has also presented a classification of different molecular complexes by giving the symbol for the donor and for the acceptor. Thus the $R_3N.BCl_3$ complex is classified as an n.v complex. Typical 1:1 Donor - Acceptor complexes are shown in Table - 1.3.

Table - 1.3

Typical 1:1 Donor - Acceptor Complexes

D/A	v	aσ	aπ	Q
n	$R_3N.BX_3$;	Very numerous ;	$I^-.C_6H_5N^+-CH_3$	$He.He^+$
	$I^-.Li^+$;	$R_3N.I_2$; $Me_2O.HCl$, $Q^-.DH^+$. $I^-.I_2$;	$I^-.TNB$	$Cl^-.Cl$
	$F^-.BF_3$	$F^-.HF$.		
bσ	existence of complexes doubtful.	Very weak complexes, if any; some contact complexes e.g. Heptane. I_2	Complexes not known	Not important
bπ	Ar.$AlCl_3$, etc.	$C_6H_6.I_2$;	C_6H_6.TCNE ;	Reaction intermediates, e.g. $C_6H_6.I$;
		$C_6H_6.HCl$;	C_6H_6.TNB etc.	ionized dimers Ar_2^+
		$C_6H_7^+.BF_4^-$	Very numerous	
R	$TCNE^-.Na^+$	Unknown	$(TCNE)_2^-$	Stable molecules e.g. CH_3Cl.

Abbreviations: Ar, aromatic molecule; R, alkyl radical; X, halogen atom; HQ, Bronsted acid; TNB, trinitrobenzene; TCNE, Tetra Cyanoethylene.

Not included in Table - 1.3 are the hydrogen-bonded complexes which are a group by themselves. Generally, Donor - Acceptor interactions, where the donor is an n - donor as well as a π -donor, and the acceptor is a hydrogen containing molecule like hydrogen halides, hydroxylic compounds, haloforms or halocalkanes, take place not through normal donor to acceptor charge-transfer processes but through formation of hydrogen-bond between the donor and acceptor. Actually the term 'Hydrogen donor' may be more appropriate than 'acceptor' for the description of several molecules participating in such complex formation. Infra red and NMR spectroscopic studies have been used for characterisation of such interactions. Thus, by means of infrared studies of their interactions with strong proton acceptors like Pyridine - d_5 and dimethyl sulphoxide - d_6, it was established[92] that a variety of substances containing at least one hydrogen-bonded to carbon can act as hydrogen donors. Pentachloro cyclopropane, Pentachloro ethane, Br_2CHCN, $CHBr_3$, CHI_3 and many other compounds gave larger C - H shifts than $CHCl_3$, an accepted and well-studied proton donor. The order of halogen spectral shifts was $CHBr_3 > CHI_3 > CHCl_3$; CHF_3 gave inconclusive results. $X-CH_2-Y$ compounds (X, Y = Cl, Br, I, CN) and cis - and trans - 1,2 - dichloroethylene also behaved as proton donors. The proton donating capacity of a C - H group, as manifested in the infrared spectral shifts which result on complex formation, was found to decrease with changes in hybridization of carbon in the order $C(sp) - H > C(sp^2) - H > C(sp^3) - H$. Hydrogen-bonding propensities of haloforms were also studied by NMR techniques[93] and thermodynamic constants for their association with

tetrahydrofuran were evaluated. Hydrogen-bonding with some contributions from n $\rightarrow \sigma^*$ charge-transfer absorption was suggested for complexes of several haloalkanes and haloforms with the n - donors di - n - octyl ether and di - n - octyl thioether from gas-liquid chromatography studies.[27] Association constant was found to increase on replacing a Cl atom by Br in haloforms and dihalomethanes. This was interpreted to indicate that although the acidity of the hydrogen was reduced through such replacement, the increased charge - transfer more than compensates for the diminished hydrogen - bonding. Phenols were found to interact with many nitrogen or oxygen - containing bases in CCl_4.[94]

There is also an abundance of evidence that aromatic and aliphatic π-donors may co-ordinate with hydroxyl bearing substances. The fact that phenol is less self-associated in benzene than in CCl_4 is indicative in this regard as is the fact that the fundamental and harmonics of the - OH stretching vibration appear at lower frequencies in benzene than in CCl_4.[95] The magnitude of the shift in the O - D band of CH_3OD as the solvent was changed from CCl_4 to a variety of aromatic solvents was used to give relative strengths of the various aromatic donors.[96] Interaction of water through H - bonding with π-electrons of aromatic molecules had been suggested.[97] Interactions of benzene and toluene with chloroform were shown to be through hydrogen-bonding.[65,78] Huggins et al[105] used NMR studies to establish hydrogen-bonded complexes of $CHCl_3$. Similar complexes of $CHCl_3$ with benzene, toluene mesitylene, acetonitrile and dimethyl sulfoxide were also studied[106] by NMR techniques. Benzene was shown to form π-bonds with the hydrogen atom of the CHF_2 group in $C_6H_5O\ CHF_2$, p - O_2N.

$C_6H_4.CHF_2$ and F_2 CH.CF_2. CH_2OH from NMR studies.

The presence of charge-transfer absorption along with hydrogen bond formation has been stressed by many workers from theoretical[112-118,123] as well as experimental[119-122] aspects. Determination of stability constants and dipole moments of the organic base [Tetrahydrofuran, $(C_2H_5)_3N$, C_6H_6]—halo-form complexes indicated that[124] charge-transfer as well as H - bond interactions were responsible for complexation. A competitive presence of charge - transfer and H-bond interactions were suggested in association compleses between C_pH_{4-p} X - base [p=1,2; X=Cl, Br, I; base = $(C_2H_5)_3N$, THF, $(C_4H_9)_2O$, Tetrahydropyran] which were studied by dielectric polarisation[125], Vibrational spectra, N.M.R. and microcalorimetry.

As shown in Table - 1.3, unsubstituted saturated hydrocarbons e.g., paraffins do not have any noticeable tendency to form moleculer complexes (except for contact interactions which do not lead to formation of chemically stable complex) because of the absence of suitable donor or acceptor orbitals. However, halo-substituted hydrocarbons often act as partners in molecular complexes. For example, CCl_4 and other halomethanes which have long been considered inert solvents are now known to form a number of molecular complexes. CCl_4 was found to capture slow moving electrons.[98] Charge-transfer complexes of CCl_4 with π-donors like ferrocene,[99] triethylamine[100], benzene, mesitylene, hexamethyl benzene[101,102] and with iodide ions[103] (n - donor) have been characterised. Complexes of CCl_4 with p-xylene[25] and other alkyl substituted benzenes[62] were however found to have no CT absorption band

and were characterised as weak complexes bound by physical forces. Interactions of CCl_4 with N,N - dimethyl aniline and N,N,N',N' -tetramethyl - p-phenylene diamine in n - hexane was reported[104] with association constants of 0.06 litre/mole and 0.13 litre/mole respectively. The results were interpreted in terms of weak charge - transfer interactions.

A number of recent physical studies show the possibilities of existence of molecular complexes of saturated systems like n - paraffins. Complex formation between n - paraffins and aqueous urea solutions was indicated[109] from measurements of surface activity of aliphatic and cyclic organosulphur compounds. Alphatic and Cyclic organosulphur compounds were found to exert inhibiting effect on such complex formation and this effect was related to surface activity of the sulphur compounds.

Charge-transfer absorption frequency and ^{13}C - NMR spectra of cyclopropane derivatives and epoxides were studied.[110] It was found that dichloro cyclopropane withdraws electrons from an aromatic ring inductively and the epoxide groups act through hyperconjugative and inductive action.

Molar excess enthalpy measurements have also been used to study associations of saturated and unsaturated hydrocarbons.[111] Thus, binary mixtures of n-hexane or CCl_4 + 1-hexyne, +3-n-hexyne and for n-heptane or CCl_4 +1-n-heptyne were studied in a continuous titration calorimeter over the whole composition range. The influence of the position of the triple bond on the π-π and π -n interactions was discussed.

However, no electronic spectral evidences showing

participation of n-paraffins in complex formation has so far been reported.

1.3 Nature of bonding in Molecular or Association Complexes.

Although it was recognised that only weak interactions are present in electron donor - acceptor type of association complexes, the exact nature of bonding had been a subject of extensive and controversial discussions. The fact that interactions, though often weak, take place between chemically saturated molecules was a matter of great confusion. Pfeiffer[6] suggested that bonding occurred through the saturation of "residual valencies" in the component molecules. At that time Chemistry was in an early stage because the basic laws of light absorption was not well-founded. Beneth and Willis[7], in discussing complexes of aromatic substances with nitro compounds took the opposite view and proposed that covalent bonds were established between the donors and acceptors. They adhered to the idea that colour formation implied compound formation. However, the instantaneous attainment of equilibrium in solution is incompatible with the concept of covalent bonding. X-ray diffraction studies have also clearly established that the distances between the solid complex components[8] far exceed normal covalent bond lengths. Briegleb[9,10] suggested that the aromatic hydrocarbon-nitro compound adducts were the result of electrostatic attraction between the localised dipoles of the nitro group and the induced dipoles in the hydrocarbons. Briegleb and Schachowskoy[11] emphasised that their interpretation was in terms of localised dipoles so that a molecule like 1,3,5-trinitrobenzene, while having an overall zero dipole moment, is nevertheless an effective polarizing

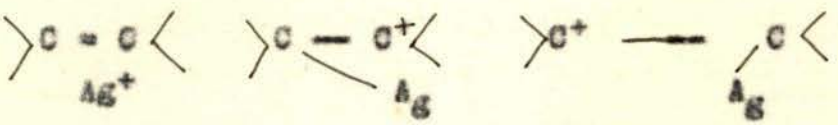
component in the complex. However, the colourations accompanying molecular association is inexplicable in terms of dipole-induced dipole type interaction.

Gibson and Loeffler[12] suggested that there might be sufficient transfer of charge in collisions of suitably oriented molecules of the two species. The intensification of colour of solutions of aromatic amines in nitro-aromatics when the hydrostatic pressure was increased and the loss of colour when such solutions were frozen, were used as evidence in support of such collisional complexes. The term 'Contact Charge-Transfer' has recently been applied in describing collisional electronic exchanges of this kind.[13]

Weiss[14] emphasised the electron donor-acceptor nature of the component molecules but held the view that the complexes were essentially ionic - a result of complete electron transfer. In support of this view, the greater strength of binding than that provided by dipole interaction or dispersion forces, very fast rate of formation of the complexes, colour of the complex arising from electronic transitions of the two free radical ions making up the complex, electrical conductivity etc. were cited. But the low enthalpy changes ($\sim$ 4 K Cal/Mole or less), high equilibrium constants, low electrical conductivities and insolubilities in and/or decomposition by water as observed in majority of the molecular complexes point to the opposite. There may, of course, be some predominately ionic complexes but they are exceptional. The majority of complexes are now generally accepted to have only a small degree of ionic character in the ground state. Despite the obvious conflict of theory and fact,

Weiss had brought his theory quite close to the correct answer as understood now.

A different approach was made by Brackman.[15] He proposed the term 'complex resonance' to describe the interaction as a resonance hybrid of a no-bonded structure and a structure in which a bond is established. Brackman, however, did not suggest that the second of the two Canonical structures had involved single electron transfer between the components. Pauling[16] made a formulation, similar to Brackman, regarding the olefin-silver ion complex.



Benesi and Hildebrand[17], in 1949, reported that solutions of iodine in aromatic hydrocarbons had an electronic absorption not present in either component alone. They recognised this band as characteristic of the complex as a whole and obtained the formation constant as also ϵ max (Peak molar absorptivity) by measuring the absorption as a function of the concentrations of the hydrocarbon solvent and iodine. Since K proved to be small, the interaction was termed 'weak'. However ϵ max is very large, about 1.5×10^4 for $C_6H_6.I_2$ complex.

Mulliken[1,18] provided a quantum-mechanical explanation for the stability of such complexes, the strong absorption band and the dipole moment of the complex. His work has provided explanation for many previous observations and was the main stimulus to the extensive developments which have taken place in this field since 1952.

Mulliken's valence - bond (resonance) descriptions explains weak interactions between an electron donor (D) and an electron acceptor (A) in terms of the ground state wave function Ψ_N which is the lowest-energy solution of the Schroedinger wave equations for all the electrons in the complex. Assuming an 1:1 complex:

$$\Psi_N \quad (D.A) = a\,\Psi_0(D,A) + b\,\Psi_1(D^+ - A^-) \quad \text{.....(1.1)}$$

no-bond dative

Here D and A are in their totally symmetric ground states and have been assumed to be even-electron systems but the same, with appropriate modification, would be true for odd-even or odd-odd donor-acceptor interactions. The no-bond wave function $\Psi_0(D,A)$ corresponds to that structure in the complex (DA) in which binding results from such 'physical' forces as dipole-dipole and dipole-induced dipole interactions, London dispersion forces and H - bonding. The dative wave-function Ψ_1 corresponds to a structure in which one electron from an MO in D has been transferred into a previously unoccupied MO of A and a bond between the odd electrons available on D^+ and A^- has been formed. This wave function represents the extra stability of the complex, its dipole - moment, changes in geometry, a new U.V. or visible absorption band and other noticeable effects. The mixing of the no-bond and dative structures imparts resonance stabilizations to the complex.

The idea embodied in eqn. (1.1) explains a variety of molecular complexes, even the 'classical' complexes of the Lewis type: $R_3N.BX_3$ (other types, like $C_6H_6.I_2$ complex, may then be called non-classical while complexes like $R_3N.I_2$ having classical

donor but non-classical acceptor may be called semi-classical).

The eqn. may be generalised to include the following particulars:

(1) The electron provided by D does not necessarily have to come from a lone pair AO but can be an electron from an MO involved in the bonding within D.

(2) The vacant orbital on A does not have to be a vacant AO, but can be an anti-bonding MO.

(3) The transfer of the electron from D to A does not have to be complete but can occur fractionally to any extent from zero to one.

(4) The stabilization of the complex is not due simply to an increased weighting of the dative bond in the structure of the complex, but is a quantum-mechanical resonance stabilization, even in classical complexes, and especially in weak complexes.

The description of the ground state in eqn. (1:1) implies the existence of an excited state using the same Ψ_0 and Ψ_1. This excited state is given by the wave function Ψ_V :

$$\Psi_V \approx a\,\Psi_1\,(D^+ - A^-) - b^*\,\Psi_0\,(D,A) \qquad .....(1.2)$$

Here a, b are determined by the requirements that Ψ_V be normalised and othogonal to Ψ_N. As a first approximation, $a^* \approx a$, $b^* \approx b$. The V state described by eqn. (1.2) is called a charge-transfer (CT) state. This state is often lower in energy than any of the locally excited states of the complex

(excited states primarily of D and A separately, but somewhat modified because of the interaction of D and A in the complex). The complex has in general a strong absorption band (allowed transition) called the charge-transfer band (CT band) corresponding to this $V \longleftarrow N$ transitions at longer wavelengths than any of the band due to transitions to the locally excited states. The charge-transfer transition energy should be a function both of the ionization potential of the donor and the electron affinity of the acceptor. Qualitative evidence of the dependence of the transition energy on the donor ionization potential is to be found in the fact that the intense UV. absorption peaks for iodine complexes shift to longer wavelengths as the donors are changed from benzene ($\lambda_{max} \approx 290$ nm) to toluene ($\lambda_{max} \approx 300$ nm) to mesitylene ($\lambda_{max} \approx 330$ nm).

For weak donor-acceptor complexes, simple perturbation theory gives the following expression for the energy of the C.T. band:[18]

$$E_{CT} = h\nu_{CT} = I^D - E^A + (G_0 - G_1) + (X_1 + X_0) \quad \ldots \quad (1.3)$$

where I^D and E^A, are the donor I.P. and acceptor E.A. respectively. X_0 is the ground state resonance energy of interaction between the states $\Psi_0(D, A)$ and $\Psi_1(D^+ - A^-)$ while X_1 is that for the excited state. G_0 is the energy of the "no bond" interaction and G_1 is the interaction of D^+ and A^- in the excited state. X_0 and X_1 are given by:

$$X_0 = \frac{(H_{01} - S_{01}W_0)^2}{W_1 - W_0} \quad \ldots\ldots \quad (1.4)$$

$$X_1 = \frac{(H_{01} - S_{01}W_1)^2}{W_1 - W_0} \quad \ldots\ldots \quad (1.5)$$

where W_1 and W_0 are the energies of the dative structure and the 'no bond' structure in eqn. (1.1) ;

$H_{01} = \int \psi_0 H \psi_1 d\tau$, H being the exact Hamiltonian for the entire set of nuclei and electrons; the overlap integral $S_{01} = \int \psi_0 \psi_1 d\tau$.

If $\beta_0 = (H_{01} - S_{01} W_0)$ and $\beta_1 = (H_{01} - S_{01} W_1)$,

we have

$$E_{CT} = h\nu_{CT} = I^D - (E^A + G_1 - G_0) + \frac{\beta_0^2 + \beta_1^2}{I^D - (E^A + G_1 + G_0)} \quad \ldots (1.6)$$

This equation is only applicable to interactions which are sufficiently weak. For strong complexes like $R_3N \rightarrow BF_3$ type, in which the binding energy is fairly high, the variation method has been suggested for calculating the resonance energies.[19] The resulting expression is:

$$E_{CT} = h\nu_{CT} = \frac{(W_1 - W_0)}{(1 - S_{01}^2)} \left[1 + \frac{4 \beta_0 \beta_1}{(W_1 - W_0)^2} \right] \quad \ldots (1.7)$$

Many examples showing the usefulness of these expressions for E_{CT} have been reviewed by Foster[20] and Andrews & Keefer.[21]

The expression given by eqn. (1.6) can be approximated as $E_{CT} = I^D - E^A - C$ where C represents all coulombic interactions. It is this coulomb contributions to the CT energy which is usually the most difficult to estimate since the dimensions of the complex are often unknown. This is particularly so for weak complexes which exist in solution only. Their binding energies are usually small so that in solution many different configurations of the complex may exist in equilibrium with one

another. The CT energy will differ for each configuration and the net result will be a broad absorption band without any vibrational fine structure.

One further characteristic of the charge-transfer bands is their wavelength sensitivity to the solvent polarity. This is because the excited state is highly polar relative to the ground state. This has been confirmed by Kosower for alkyl Pyridinium Iodide complexes [90] and by several other workers.

According to eqn. (1.1), a whole range of molecular complexes starting from $a \approx 1$, $b \approx 0$ to $a \approx 0$, $b \approx 1$ are possible, the former extreme refers to the case where the charge-transfer state does not make any significant contribution to the ground state, while the latter refers to cases where the ground state is ionic. In between these extremes lies the cases characterised by the presence of charge-transfer absorption which are commonly termed as the charge-transfer complexes. Mulliken's classification of such complexes in terms of the orbitals used by the donor and the acceptor given in table 1.3 illustrates this point.

Not all complexes which may be classified according to Table 1.3 are necessarily of charge-transfer type. Bentley and Dewar [22] as also Dewar and Thompson [23] have shown that some π-molecular complexes formed by p-toluene sulphonic esters with Polynuclear aromatic hydrocarbons as donors do not show any CT absorption. They considered such complexes as vander walls aggregates i.e. physical forces were the only mode of binding. Similar conclusions have been drawn from recent considerations of the measured dipoles of so-called charge-transfer complexes. [24]

In the solid 1:1 complexes CCl_4 . p-xylene, CBr_4 . p-xylene and Br_2 . C_6H_6, measurement of halogen pure quadrupole frequencies of the complexes[25] and the halogen containing compounds (CCl_4, CBr_4 , Br_2) together with information from X-ray structure determinations, it was concluded that little, if any, charge-transfer exists in the ground state of these complexes. Evidences for inter molecular associations in binary mixtures of 1,2 - dichloroethane with benzene, toluene, p-xylene have been obtained from ultrasonic and thermodynamic studies.[26] These weak complexes of dichloroethane with the aromatic molecules are shown to be neither of the charge-transfer type nor have any hydrogen bonding, the association being through dipole-induced dipole interactions.

Haloalkanes like dichloromethane, Bromochloromethane, dibromoethane, haloforms, as also CCl_4, $CBrCl_3$, CBr_4 have been found to behave as acceptors in complexing with donors like di-n-ortyl ether and di-n-octyl thioether.[27] It was concluded that the major contributions towards the binding forces in such complexes are predominantly dipole-dipole and/or dipole-induced dipole interactions.

Patrick and Prosser[28] reported the formation of complexes between hexafluorobenzene and various aromatic hydrocarbons, for example, a 1:1 solid complex by mixing benzene with hexafluorobenzene. Swinton et al. made a careful study of the phase diagrams,[29] excess volumes of mixing[30] and dipole moments[30] of various binary hexafluorobenzene aromatic hydrocarbon systems. Evidence for charge-transfer interaction in most cases is not

overwhelming.[30] Thus, the measured dipole moments of hexafluorobenzene, a well known π-acceptor in various aromatic solvents are unusually low for charge-transfer complexes though complexation is indicated by 19_F NMR measurements.[31] The very small shift of 19_F resonance suggests a very small degree of charge-transfer in such complexes. Charge-transfer absorption, however, occurs in mixtures of hexafluorobenzene with various n-donors.[32,33] Beaumont and Davis[32] also confirmed absence of any charge-transfer absorption band between π-donors like benzene and polycyclic aromatic hydrocarbons and hexafluorobenzene. They concluded that principal stabilization energy was due to classical and weak hydrogen bonding forces, with very little contribution from charge-transfer interaction.

In view of these it should be borne in mind that many of the weak association complexes may derive their stability from factors other than charge-transfer interaction.

However, it must also be noted that even in truly charge-transfer complexes, the identification of the charge-transfer band is often made difficult by many factors. It is particularly difficult where the components have strong local excitations which tend to mask the charge-transfer band of the complex. The extra absorption characteristic of the complex as a whole (CT absorption) is however, more easily observed than those resulting from 'local excitations' in strong complexes resulting from interaction between a strong donor and a strong acceptor. In such cases, the transition usually appears as a separate band at considerably longer wavelengths than the absorptions of the component molecules. In general, it may be said that only rarely is

the C.T. band not overlapped by other bands and due to very poor resolution of the CT band, calculation of the oscillator strength is often difficult. The molar absorptivity is then taken as a measure of intensity of the absorption band.

1.4 Contact charge-transfer spectra:

The application of Benesi-Hildebrand equation[17] to determine K and ϵ_{DA} of donor-acceptor systems, in some situations, leads to apparantly surprising result : K = 0 with $\epsilon_{DA} = \infty$. An explanation for this behaviour resulted in the prediction[13] of "contact" charge-transfer pairs in which charge-transfer takes place through random encounters of component molecules without any specific interaction.

The classic example of contact charge-transfer spectra is that of I_2 or Br_2 dissolved in n-heptane[86] where a new band appears in a solvent which has so little donor strength that there is no evidence of complex formation. The band for I_2 in n-heptane has been identified[13,14] with a shoulder at 225 nm on the strong local absorption band of I_2 with peak at 180 nm. Corresponding bands of I_2 in other aliphatic hydrocarbons (in some cases with distinct peak instead of just a shoulder) appear to correlate with ionization potential of the hydrocarbon, as expected for contact CT bands.[86] Evans had shown earlier[85] that O_2 dissolved in n-heptene or in stronger donor solvents shows the same kind of behaviour — a new absorption band around 200 nm. Association constant for the interaction, as in the I_2-n-heptane case, is Zero. For this reason, n-heptane and other aliphatic hydrocarbons must be made free from O_2 before using them as

inert solvents in study of CT bands in this region. Evans also showed[87] that dissolved NO also yielded contact CT spectra; $C(NO_2)_4$, SO_2 and trinitrobenzene also act as "contact" acceptors.[87]

The intensities of the contact CT bands are much greater than normally should be expected considering the weakness of the interaction of the components in the ground states. Orgel and Mulliken[13] considered the problem theoretically. They had shown that there are two contributions to the transition moment — one is related to the ground state stabilization through b in eqn. (1.1) and the other is the moment of the transition density between the state $\Psi_0(D,A)$ and the orthogonal state $\Psi_1(D^+ - A^-) - S_{01}\Psi_0(D,A)$. They showed that the transition moment may be non-negligible even when b = 0 in eqn. (1.1) and attributed the contact CT band to this effect.[88,89] On the other hand, Murrell suggested that the major part of the contact CT absorption may result through mixing of the charge-transfer excited state with nearby excited states of the donor or acceptor to which strong transition occurs in the free component. The extent of mixing of the two states depends not only on the Hamiltonian matrix element between them but also on the difference in energy. Since $(D^+ - A^-)$ will usually be closer in energy to (D^*,A) and (D,A^*) (the first excited states) than to the ground state (D,A), this will favour the introduction of donor and acceptor excited-state character in the charge-transfer state. Combining both the energy and overlap considerations it has to be concluded that the CT state will almost certainly take on more donor-excited-state character than ground state character, and it may have more acceptor-excited-state character also, depending on the balance between overlap and energy considerations.

With weak complexes like the C_6H_6 . I_2 complex, there will certainly be different configurations of the complex present in the solution. Some of these configurations will be better described as contacts. Orgel and Mulliken[13] presented an interesting and reasonable argument to support the conclusion that approximately one-fourth of the charge-transfer band intensity for C_6H_6 —I_2 interaction in CCl_4 is attributable to absorption by a complex and the remaining three-fourth results from contact absorption. Evidence has also been presented that in solutions of I_2 and Polynucleur aromatic hydrocarbons in CCl_4 in which the halogen concentration is very high, the characteristic U.V. absorption should be attributed mainly to CT absorption.

1.5 Experimental Methods for the Study of Donor - Acceptor Association Complexes.

A number of different experimental methods have been used in investigating equilibrium between Donor-Acceptor complexes and their components. Some of the more important techniques are briefly discussed below.

I. Ultraviolet and Visible Spectrophotometry:

In situations where interacting D (electron donor) and A (electron acceptor) species show not only absorptions of D and A, sometimes noticeably modified, but also a new band or bands due to intermolecular charge-transfer transitions in the complex DA, the intensity of this new band may be used to determine the equilibrium constant.

One of the most frequently used methods for determining the equilibrium constant from the Spectrophotometric data is based on the use of the well known Benesi-Hildeband equation[17] (eqn.1.8) for 1:1 complexes

$$\frac{[A]_i}{d} = \frac{1}{\epsilon_{DA}} + \frac{1}{K.\epsilon_{DA}} \cdot \frac{1}{[D]_i} \quad \ldots\ldots\ldots (1.8)$$

where $[A]_i$ and $[D]_i$ are the initial concentrations of the acceptor and donor respectively, d is the optical density of the solution, K is the equilibrium constant of the interaction:

$$D + A \rightleftharpoons DA \quad \ldots\ldots\ldots\ldots (1.9)$$

and ϵ_{DA} is the molar extinction co-efficient of the complex. The assumptions made in deriving this equation are that only the complex absorbs at the region of measurement, Beer's law is obeyed, the cell path length is 1 cm. and that $[D]_i \gg [A]_i$. Plots of $[A]_i/d$ against $1/[D]_i$ gives straight lines with slope of $1/K\epsilon_{DA}$ and intercept of $1/\epsilon_{DA}$. K and ϵ_{DA} may thus be calculated. For using this equation, the donor concentration is made much greater than that of the acceptor. Donor solution in the same concentration is used as blank and measurements are made on solutions of widely varying $[D]$ and $[A]$. The constancy of K values under such conditions confirms presence of a single 1:1 species in solution.

Many variants of the Benesi-Hildebrand equation has been used by other workers.[35,36,37] Ketelaar et al.[38] devised the following relationship for determination of association constants when the acceptor molecule has some absorption at the wavelength of

measurement:

$$\frac{1}{\epsilon_a - \epsilon_A} = \frac{1}{K[D]J_1 (\epsilon_{DA} - \epsilon_A)} + \frac{1}{\epsilon_{DA} - \epsilon_A} \quad \ldots (1.10)$$

where ϵ_a and ϵ_A are the apparent and actual molar absorptivities of the acceptor (A) at the wavelength of measurement. It was assumed that $[D]J_1 \gg [A]J_1$. Straight lines are obtained by plotting $1/\epsilon_a - \epsilon_A$ against $1/[D]J_1$ whose slope and intercept gives K and ϵ_{DA}. This equation reduces to the Benesi-Hilderband eqn. when ϵ_A is negligible compared to ϵ_{DA} or ϵ_a. The Ketelaar eqn. is thus a more general form. This eqn. has also been used in many different forms by different investigators.

Other attempts have also been made to use Spectrophotometry in the study of donor-acceptor complexes. Thus the Rose-Drago equation[39] is applicable when both D and A have significant absorptions at the wavelength of measurement and when no conditions are made regarding values of $[D]J_1$ and $[A]J_1$

II. <u>Infrared Spectrophotometry</u>:

Donor-Acceptor interaction leads to change in bond lengths of the components with consequent changes in vibration frequency. These changes and others which are characteristic of symmetry losses leading to vibrations forbidden in free donors and acceptors, are generally apparent in the infrared spectra of the complexes.

Thus shifts in ν H - Cl result when hydrogen

halides interact with alkyl benzenes.[40] The >H - Cl values are linearly dependent on the ionization potentials of the donors in keeping with the assumption that decreases in frequencies are qualitative measures of the relative strengths of interactions. >H - Cl in CCl_4 solutions of C_6H_6, $C_6H_5 \cdot CH_3$, 1,3 - $C_6H_4(CH_3)_2$, 1,3,5 - $C_6H_3(CH_3)_3$ are respectively 2765 Cm^{-1}, 2735 Cm^{-1}, 2733 Cm^{-1}, 2718 Cm^{-1}.

Interaction of aromatic hydrocarbons with halogen is accompanied by an enhancement of the intensity of aromatic I.R. absorption bands. The 850 and 992 Cm^{-1} peaks of benzene are enhanced both by Br_2 and I_2. These intensity changes are presumed to result because of changes in symmetric ring breathing modes.[41] Related increases in symmetric methyl stretching modes are reported to accompany iodine - polymethylbenzene interaction.[41]

The interactions of halogens and ICN with nitrogen containing compounds are accompanied by pronounced changes in I.R. spectra.[42] The absorption bands around 1000 Cm^{-1} found in the spectra of pyridine and subetituted pyridines entirely disappear when halogen complexes are formed and are replaced by strong new bands at some what higher frequencies.

Many other examples are given elsewhere in this chapter.

Analytical determinations are based on measurements made on a band occuring in the spectrum of one or other component and in the spectrum of the complex. There must be a sufficient difference in intensity of absorption by these two

species at some wavelength. If the extinction co-efficient for a transition in the donor is ϵ_λ^D and that in the complex is ϵ_λ^{DA}, then for a pathlength of 1 Cm of solution:

$$\frac{A}{1} = \epsilon_\lambda^D \left([D]_i - [DA] \right) + \epsilon_\lambda^{DA} [DA] \quad \ldots \quad (1.11)$$

where A is the absorbance of 1 Cm of solution and $[D]_i$ is the initial concentration of the donor.

As an alternative, an expression involving integrated band intensities may be used. The equilibrium constant may be evaluated from measurements of a series of solutions in which $[A] \gg [D]$ by employing the following expression[43] (of the type described by Ketelaar et al.):[38]

$$\frac{[A]_i [D]_i}{(A - A_0)} = \frac{1}{1(\epsilon_\lambda^{DA} - \epsilon_\lambda^D)} + \frac{[A]_i}{1(\epsilon_\lambda^{DA} - \epsilon_\lambda^D)} \quad \ldots\ldots\ldots (1.12)$$

where A_0 is the absorbance of 1 Cm of solution and $[D]_i$ is the initial concentration of the donor.

Intermolecular interactions in the systems CH_3CN-

C_5H_5N, CH_3CN - $(CH_3)_2SO$ and CH_3CN - CH_3CHO have been studied by I.R. spectra using the shift of -CN stretching vibration band at 2254 Cm^{-1} which depends on CH_3CN concentration. The spectral shifts suggest hydrogen bonding (2 Cm^{-1} shift) between - CN gr. and H - atoms in Pyridine, hybridization of electron clouds of interacting N and O atoms in CH_3CN-$(CH_3)_2$ SO system (5 Cm^{-1} shift). No shift was found in CH_3CN - CH_3CHO system.[74]

Far infrared studies of the crystals separated from mixtures of benzene have confirmed the existence of 2:1 CCl_4-C_6H_6 molecular complex and 2:1 and 1:1 $CHCl_3$ - C_6H_6 complexes.[78]

The composition and structures of $CHCl_3$ with π and n-donors have been determined from their I.R. and Raman band intensities.[79]

Infrared studies have also been utilised to demonstrate the complexation of trinitromethane and 1:1 dinitroethane with dioxane, tetrahydrofuran, $(C_2H_5)_2O$ and $CH_3O\ CH_2\ CH_2\ OCH_3$.

The use of infrared spectrophotometry in the study of association constants has been reviewed by Keefer and Andrews.[21]

Estimates of association constants may also be obtained from intensities of Raman lines. This method, however, appears to have been applied only to complexes of inorganic Lewis acids.[44,45]

III. Nuclear Magnetic Resonance Spectroscopy:

When the molecular environment of a nucleus undergoes rapid reversible change, the position of the magnetic resonance absorption of the nucleus will represent a time-averaged

resultant of its behaviour in the different environment. The measured chemical shifts of such a nucleus is $\delta = \sum P_i \delta_i$ where P_i is the population of the nucleus in the i^{th} environment relative to the total populations of the nucleus (i.e. $\sum P_i = 1$), and δ_i is the chemical shift the nucleus would have if it were purely in the i^{th} environment.

In the simple case of an equilibrium between a 1:1 complex DA and its components D and A, in which the forward and back reactions are very fast, the measured chemical shift of a nucleus in, for example, the acceptor moiety is $\delta = P_A \delta_A + P_{DA} \delta_{DA}$, where P_A is the fraction of A uncomplexed and P_{DA} is the fraction of complexed acceptor molecules, Since $(P_A + P_{DA}) = 1$, this eqn. may be written as:

$$\delta = P_{DA} (\delta_{DA} - \delta_A) + \delta_A \quad \ldots\ldots\ldots (1.13)$$

A plot of P_{DA} Vs. δ should be linear. This requires the insertion of K_{DA} as a variable parameter which is adjusted until the values of P_{DA} obtained from it vary linearly with the corresponding values of δ .[46]

Although qualitative and quantitative evidence for complex formation may be obtained from chemical shift changes, the results will not in themselves distinguish the so-called charge-transfer complexes from others having no charge-transfer contribution. It is impossible to make a clear demarcation between such complexes and some other types of complex, for example, those involving dipole-induced dipole or H-bonding forces. Thus 'Aromatic solvent - induced shifts' (A.S.I.S.) have often been used to suggest formation of association complexes

for example, of carbonyl compounds and ethers with aromatic solvents.[47,48] But there is little evidence of significant charge -transfer component in these complexes.

However, many examples are also known for complexes where N.M.R. studies have confirmed their charge-transfer nature. This requires that a significant fraction of the donor or acceptor nucleus being measured is in the complexed state.

Some recent examples on the use of NMR Spectroscopy in identification of association complexes are described below.

Complex formation between 1,3,5 - trinitrobenzene and aliphatic amines in DMSO has been examined by NMR, electrical conductance measurement[107] and UV - visible spectroscopy. Evidence for interaction could be obtained only with primary and secondary amines and NH_3 but not with tertiary amines.

Interactions of N,N - dimethyl formamide with benzene, toluene, toluene - d_3 and halobenzene derivatives were studied from the chemical shifts of the CH_3 - Protons of DMF by the method of ideally associated mixture.[72] Association constants and free enthalpies of mixing were calculated.

N.M.R. data established that in the interaction between $CHCl_3$ and $C_6H_5NH_2$, co-ordination occurs far more extensively at the π -electron system of the aromatic ring than at the nitrogen atom of aniline.[73]

Molecular association was detected between CH_3CN and CCl_4 by reaction field contribution to the Proton magnetic shielding.[75]

N.M.R. study of C_{3-6} -cycloalkanes and corresponding saturated heterocycles showed intermolecular interactions in the $-CH_2$ groups of the Cycloalkanes, in the α-CH_2 groups of the heterocyclic compounds.[76] Association of acetone with $CHBr_3$, $CHCl_3$, CH_2Cl_2, Br CH_2 CH_2 Br, Cl CH_2 CH_2 Cl, Br_2 CH $CHBr_2$ and Cl_2 CH CH Cl_2 has also been studied by NMR and equilibrium constants as well as heats and entropies have been calculated.[77]

IV. Distribution Methods:

In some cases it is convenient to measure the distribution of one component, usually the donor, between a liquid phase in which only that component is appreciably soluble and a liquid phase which contains both donor and acceptor and all of the complex. Complex formation between Ag^+ ion acceptor with various unsaturated hydrocarbon donors in aqueous solution was studied[49] by measuring the solubility of the donor in aq. $AgNO_3$ solutions of constant ionic strength.

An interesting variant of this method is the measurement of association constant for complex formation between a volatile and non-volatile reactant in a volatile solvent by measuring the partitioning between the liquid and the vapour phase.[50] The experiment involves the determination of the ratio of two volatile components in the vapour over the ternary mixture, which is compared with that over the binary mixture in which the non-volatile component is omitted. The method appears to have been applied only to hydrogen-bonded systems.

V. Polarography:

The reversible one-electron reduction of organic acceptor molecules in aprotic solvents is modified when an electron donor is added to the system and the first wave of the acceptor shifts to more negative potentials.[51] This shift ($\Delta E_{1/2}$) is related to the association constants. Holm et al.[52] obtained association constants for a series of Polymethylbenzene - 7,7,8,8 - tetracyanoquinodimethane complexes in chloroform solution.

There is, however, some uncertainity about the results obtained by Polarographic methods. But even then this constitutes a reasonable approach to the determination of equilibrium constants of association complexes when other methods may not be easily applied.

VI. Dielectric constant measurements:

Estimates of association constant for hydrogen-bonded complexes have been obtained from measurement of the dielectric constants of solution of one solute in a solvent in various constant mixtures of the second solute and solvent.[53,54] The method is applicable to systems where the complex formation is accompanied by appreciable change in dipole moments.

Intermolecular interactions in ferrocene solutions were investigated by following the difference between experimental and additive dielectric constant values. Solvents studied included benzene, Cyclohexane and hexane at the temp. range -80° to 20°C. Most effective intermolecular interactions were

observed in the Ferrocene-Benzene solutions.[60] The increase in dipole moment of dioxane in C_6H_6 as compared to more fully inert solvents was shown to be due to both the displacement of the chair-boat equilibrium toward the boat form in C_6H_6 as well as to the formation of a polar π-complex between C_6H_6 and dioxane.[66] Association constants were obtained for mixtures of Pyridine, aniline, 2- and 3-amino-pyridines with phenol and 2,3-dihydroxy-napthalene in benzene. The interactions in these systems occur through hydrogen bonding.[82]

VII. Other methods:

Maxima or minima frequently are observed in plots of physical properties versus compositions of donor and acceptor mixtures. Stoichiometry of the adducts formed can be deduced from locations of these maxima or minima. Freezing point Vs. composition diagrams are commonly used as bases for establishing the formula of complexes. Less commonly employed are procedures in which heats of mixing,[55] viscosities[56] and surface tensions[57,58] are determined as a function of component composition. Generally these procedures are not adaptable to the evaluation of association constants, although a method for calculating such constants from the results of surface tension measurements has been suggested.[58] A procedure for the evaluation of enthalpies of interaction which is based on the results of cryoscopic measurements has also been developed.[59] Physical methods of determination of association constants have been reviewed by Andrews.[61]

Determination of thermodynamic properties have often been used to study association complexes. Thus enthalpies of mixing were determined to show complex formation between CCl_4

and alkyl substituted benzenes.[62] Molar volume, dielectric constant and viscosity measurements have shown (1:1) molecular association between N,N - dimethyl aniline and bromobenzene.[63] Heats and entropies of solution of CH_2Cl_2, $CHCl_3$, CCl_4, $(CH_3)_2CO$, CH_3CN and N,N dimethyl formamide in 2,4 - dinitrobenzene showed formation of stable intermolecular bonds.[64] Complexation between $CHCl_3$ and C_6H_6, $C_6H_5.CH_3$ has been demonstrated by determination of excess enthalpies of the binary mixtures.[65] Chemical contribution to excess enthalpy was calculated and the difference between the calorimetric and calculated excess enthalpies has been attributed to physical (non-complexing) contributions. Association constants for interaction of donor hydrocarbons like benzene, toluene, xylene, mesitylene with the acceptor 1,2,4 -trichlorobenzene have been obtained from measurement of the excess volumes of mixing and the values are found to correlate with the ionization potentials of the hydrocarbons.[81]

A structural and thermodynamic study of the association of halomethanes with Pyridines or benzenes in or without cyclohexane by dielectric polarization, I.R. and micro-calorimetry[83] indicate charge-transfer (due to the halogen of halomethanes) as well as hydrogen-bonding interactions. Nigam et al.[84] observed interactions in benzene aniline mixtures.

If the donor, the acceptor or the complex is an ion, the formation constant may be evaluated by the use of appropriate electrochemical cells.[67,68] The choice of solvent used in this procedure is limited to water or other substances of relatively high dielectric constant.

A conductometric method has been used in determining

equilibrium constants for formation of -complexes, such as, Ar H_2^+ + F^-, in solutions of Polymethylbenzenes in HF.[69] Electrical conductivity study was used to establish ionic association in a medium of aliphatic alcohols and their binary mixtures with aromatic hydrocarbons.[70]

Ultrasonic studies have sometimes been used to establish molecular association. Kiyohara et al. established complex formation between 1,2 - dichloro ethane and benzene, toluene, xylene, p-xylene.[26] Ultrasonic velocity and compressibility of the mixtures aniline - CCl_4, N,N-dimethyl aniline - CCl_4, Pyridine - CCl_4 or quinoline-CCl_4 were found to exhibit a non-linear behaviour due to molecular association and this was confirmed by N.M.R. studies.[71]

REFERENCES :

1. R.S. Mulliken : J. Phys. Chem., 56, 801 (1952).
2. R.E. Schuler : J. Chem. Phys., 21, 765 (1953).
3. B. Pullman & A.Pullman : Nature, Lond. 199, 467 (1963).
4. P.R. Hammond & R.H. Knipe: J. Am. Chem. Soc., 89, 6063 (1967).
5. R. Foster : Organic charge-transfer complexes, Chapter I, (Academic Press, London & New York, 1969).
6. P. Pfeiffer : Organische Molekulverbindungen, 2nd Edition, Ferdinand Enke, Stuttgart, Germany, 1927.
7. G.M. Benett & G. H. Willis : J. Chem. Soc., 256 (1929).
8. H. M. Powell & G.Huse : J. Chem. Soc., 435 (1943).
9. G. Briegleb, : Z. Physik. Chem., B16, 249 (1932)
10. G. Briegleb : Zwis Chem. molekulare Krafte, Germany, 1949.

11. G. Briegleb & T. Schachowskoy : Z.Phys. Chem. B19,255 (1932).

12. R. E. Gibson & O.E.Loeffler : J. Am. Chem. Soc. 62, 1324 (1940)

13. L. E. Orgel & R.S. Mulliken : J. Am. Chem. Soc. 79, 4839 (1957).

14. J. Weiss : J. Chem. Soc., 245 (1942); 462 (1943)

15. W. Brackman : Rec. Trav. Chim. 68 147 (1949).

16. L. Pauling : Proc. Natn. Acad. Sci., USA, 25, 581 (1939).

17. H.A. Benesi & J.H.Hildebrand : J. Am. Chem. Soc. 71, 2703 (1949).

18. R. S. Mulliken : J.Am. Chem. Soc. 74, 811 (1952).

19. H. Yada, J. Tanaka & S. Nagakura : Bull. Chem. Soc. Japan, 33, 1660 (1960).

20. R. Foster : Organic Charge-Transfer Complexes, Academic Press, London & New York, 1969.

21. L. J. Andrews & R.M.Keefer : Moleculer Complexes in Organic Chemistry, Holden-Day, Inc., London, 1964.

22. M.D. Bentley & M.J.S. Dewar : Tetrahedron Letters, 5043 (1967).

23. M.J.S. Dewar & C.C. Thompson Jr: Tetrahedron Suppl. 7, 97 (1966)

24. R.J.W.Le Fevre, D.V. Radford, G.L.D. Ritchie & P.J. Stiles : Chem. Commun. 1221 (1967).

25. H. O. Hooper : J. Chem. Phys., 41, 599 (1964).

26. O. Kiyohara & K.Arakawa : Bull. Chem. Soc. Japan, 43 (10), 3037 (1970).

27. J.P.Sheriden, D.E.Martire & Y.B. Tewari : J.Am. Chem. Soc., 94(10), 3294 (1972).

28. C.R. Patrick and G.S.Prosser : Nature, London, 187, 1021 (1960).

29. W.A. Duncan & P.L.Swinton : Trans. Faraday. Soc., 62, 1082 (1966).

30. R. Foster & C.A. Fyfe : Chem. Commun. 642 (1965).

31. T. G. Beaumont & K.M.C. Davis : J.Chem. Soc. (B), 1131 (1967).

32. P. R. Hammond : J. Chem. Soc. (A), 145 (1968).

33. R.S. Mulliken : Rec. Trav. Chim., 75, 845 (1965).

34. R. L. Scott : Proc. Int. Conf. on Co-ordination compounds, Amsterdam (1955), P. 265.

35. R. Foster, D.L.Hammick & A.A. Wardley : J.Chem. Soc., 3817 (1953).

36. G. Cilent & D.L. Sanioto : Z. Phys. Chem., 223, 333(1963).

37. J.A.A. Ketelaar, C.Van de Stolpe, A. Goudsmit and W.DZcubas : Rec. Trav. Chim., 71, 1104 (1952).

38. N. J. Rose & R.S.Drago : J.Am. Chem. Soc., 81, 6138, 6141 (1959).

39. D.Cook : J. Chem. Phys., 25, 788 (1956).

40. E.E. Ferguson & I.Y. Chang : J. Chem. Phys., 34, 628 (1961).

41. W.B. Person, R.E.Humphrey, W.A. Deskin & A.I. Popav : J.Am. Chem. Soc., 80, 2049 (1958).

42. J. Laurensan, P. Pineau & J. Lascombe : J. Chim. Phys., 63, 635 (1966).

43. G. Michel & G. Duyckaerts : Spectrochim. Acta, 21,279(1965)

44. G. Leclere & G. Duyckaerts : Spectrochim. Acta, 22,403(1966).

45. C.J. Creswell & A.L.Allred : J. Phys. Chem., 66, 1469(1962).

46. P. Laszlo : "Progress in Nuclear Magnetic Resonance Spectroscopy", Vol.3, eds. J.W. Emsley, J.Feeney & L.H.Sutcliffe, Pergamon,Oxford & New York (1969), Chapter 6.

47. J. Ronayne & D.H. Williams : J.Chem. Soc. (B), 540 (1967) and references therein.

48. L.J. Andrews & R.M.Keefer : J. Am. Chem. Soc., 72, 3113 (1950).

49. R.L. Denyer et al. : J. Chem. Soc., 3889 (1955).

50. H.M.N.H. Irving : in "Advances in Polarography," Vol.I., ed. I.S.Longmuir, Pergamon (1960) P.42.

51. R.D. Holm et al. : J.Phys. Chem., 71, 3960 (1967).

52. A.V. Few & J.W.Smith : J.Chem. Soc., 2781 (1949).

53. R.J. Bishop & L.E. Sutton : J.Chem. Soc., 6100 (1964).

54. M. Tamres : J.Am. Chem. Soc., 74, 3365 (1952).

55. M.I. Usanovich & E. Pichugina : Zhur. Obschei Khim., 26, 2130 (1956) [Chemical Abstracts, 26: 5614d (1956)].

56. E.Ferroni & G.Gabriello : J. Phys. Chem. 60, 1258 (1956).

57. N. Cagnoli : Ann. Chim. (Rome), 48, 839, 1122 (1958).

58. P.A.D. Maine : Can. J.Chem., 38, 1635 (1960).

59. S.I. Nazarkin & B.S. Ksenofontov : ISV. Vyssh. Ucheb. Zaved. 14(7), 159 (1971). [(Chemical Abstracts, 75:144451 (1971)].

60. L.J. Andrews : Chem. Rev., 54, 713 (1954).

61. A. Ahmed : J.Chem. Soc., Faraday Trans., 1, 69(3), 540 (1973).

62. M.Grodowski & T.Labowski : Zest. Nauk. Wydz. Mat., Fiz. Chem. Univ. Gdanski Chem., 1, 131 (1971). [Chemical Abstract, 78: 110312, (1973)].

63. N.G.Fedorov & S.N. Pershin : Zh. Fiz. Khim., 48(4), 1051 (1974) (Russ). [Chemical Abstracts, 81:24861 m, (1974)].

64. P.P. Rastogi & R.R.Misra : Indian J.Chem., Section A., 14A(7), 521 (1976).

65. J.Harwic et al. : C.R.Hebd. Seances Acad. Sci., Ser. C., 284(21), 869(1977) (Fr). [Chemical Abstracts, 87: 101828c, (1977)].

66. F.J.C. Rossotti & H. Rossotti : The determination of Stability constants, McGrew - Hill Book Co., New York, 1961.

67. S. Cabani & E.Scrocco : J.Inorg. and Nuclear Chem., 8, 332 (1958).

68. M.Kilpatrick & F.E. Luborsky : J.Am. Chem. Soc., 75, 577 (1953).

69. G.L.Starobinets et al. : Vestn. Kharkov. Un-ta,139, 41(1976) [Chemical Abstracts 87:5244 p, (1977)].

70. S.C.Adgaonkar et al. : Acoust. Lett., 1,11 (1977).

71. G. Rudakoff et al. : Z.Chem. 12(1), 37 (1972) [Chemical Abstracts, 76: 126213j, (1972)].

72. Soon Ng : Spectrochim Acta, Part A, 28(2), 321 (1972).

73. B.N. Narziev, D.Makhkambaev, N.V. Berestova, Dokl : Akad. Nauk Tadzh. SSR, 15(2), 24 (1972). [Chemical Abstracts, 77:40857f, (1972)]

74. W.T. Raymes, M.A.Raza : Molec. Phys., 24(6), 1241 (1972).

75. J. Le Brumant, M.Selim, G.Martin : C.R. Acad. Sci., Ser. B. 276(8), 311 (1973) [Chemical Abstracts, 78:135128d, (1973)]

76. B.A. Geller, L.K.Skrunts : Teor. EKsp. Khim., 9(4), 556 (1973). [Chemical Abstracts, 79:145758, (1973)].

77. G.W.Chantry, H.A.Geffie & H.N.Mirza : Spectrochim. Acta., 23A, 2749 (1967).

78. R. Mierzecki : Advn. Mol. Relaxation Processes, 5(1-3), 123 (1973).

79. M.Yu. Golub et al. : Izv. Akad. Nauk. SSSR.Ser. Khim. (3), 527 (1976). [Chemical Abstracts, 85: 5014, (1976)].

80. S. Agarwal : J. Solution Chem., 7(10), 795 (1978).

81. M.I. Baraton, I.Krishan J. Gerbier : Adv. Mol. Relaxation Processes, 13(3), 275, (1978).

82. C. Geron, M. Gomel : J. Chim. Phys. Phys.-Chim. Biol., 76(4), 411 (1979). [Chemical Abstracts, 91: 157043t (1969)].

83. K.R.Nigam et al. : Can. J. Chem., 57(17), 2211 (1977).

84. D.F. Evans : J.Chem. Soc., 345 (1953).

85. D.F. Evans : J. Chem. Phys., 23, 1424, 1426 1429 (1955).

86. D. F. Evans : J. Chem. Soc., 3885 (1957b).

87. J. N. Murrell : J. Am. Chem. Soc., 81, 5037 (1959).

88. J. N. Murrell : Quart. Rev. (London), 15, 191 (1961).

89. E. M. Kosower, W.D. Closson, H.L.Goering & J.C. Gross : J. Am. Chem. Soc., 83, 2013 (1961).

90. M. Chowdhury & S. Basu : J. Chem. Phys., 32, 1450 (1960).

91. A. Allerhand and P.Von. R. Schleyer : J. Am. Chem. Soc., 85, 1715 (1963).

92. C.J. Creswell and A.L. Allred : J. Am. Chem. Soc., 85, 1723 (1963)

93. M. D. Joesten and R.S. Drago : J. Am. Chem. Soc., 84, 3817 (1962).

94. L. H. Jones and R.M. Badger : J. Am. Chem. Soc., 73, 3132 (1951).

95. M. Tamres : J. Am. Chem. Soc., 74, 3375 (1952).

96. R. L. Bohon and W.F. Claussen : J. Am. Chem. Soc., 73, 1571 (1951).

97. Buchelnikova : Zhur. Eksp. Theoret. Fiz., 34, 519 (1958). [Chemical Abstracts, 52: 9779b (1958)].

98. Brand and Snedden : Trans. Faraday Soc., 53, 894 (1957).

99. D.P. Stevenson and G.M. Coppinger : J. Am. Chem. Soc., 84, 149 (1962).

100. R. Anderson and J.M. Prausnitz : J. Chem. Phys, 39, 1225 (1963) and 40, 3443 (1964).

101. R.F. Weimer and J.M. Prausnitz : J. Chem. Phys. 42, 3643 (1965).

102. M. J. Balndmer, T.E. Gough & M.C.R. Symons : Trans. Faraday Soc., 62, 301 (1966).

103. K.M.C. Davis and M.F. Farmer : J. Chem. Soc. (B), 28 (1967).

104. C.M.Huggins, G.C. Pimental & J.N. Schoolery : J. Chem. Phys. 23, 1244 (1955).

105. Lin Wei-Chuwan and Tsay shyr-jin : J.Phys. Chem. 74,1037 (1970).

106. M.R. Crampton & V.Gold : J. Chem. Soc.(B), 23, (1967).

107. L. V. Semenov, A. Gaile, V.A. Proskuryakov & V.I. Zakharov : Zh. Fiz. Khim., 48(4), 995 (1974). [Chemical Abstracts, 81:24889v, (1974)].

108. A. M. Syrkin, B.V.Klimenok : Khim. Seraorg. Soedin, Soderzhashchi Khesya Neft. Neftepred., 9, 139 (1972). [Chemical Abstract, 80:70134x (1974)].

109. K. Shudo and T. Okamoto : Tetrahedron, 22(44), 1717 (1977).

110. W. Woycicki, P.Rhensius : J. Chem. Thermodyn., 11(2), 153 (1979).

111. K. Nukasawa, J. Tanaka & S. Nagakura : J. Phys. Soc., Japan 8, 792 (1953).

112. H. Tsubomura : Bull, Chem. Soc., Japan, 27, 445 (1954).

113. C.A., Coulson : Research 10, 149 (1957).

114. F.B. Von Duijneveldt & J.N. Murrell : J.Chem. Phys., 46, 1759 (1967).

115. P.A. Kollman & L.C. Allen : Chem. Rev., 92, 283 (1972).

116. H. Umeyama & K.Morokuma : J. Am. Chem. Soc., 99, 1316 (1977).

117. S. Bratoz : Advances in Quantum Chemistry, Vol. 3, ed. P. Lowdin, Academic Press, New York, 1967, P. 209.

118. H. Tsubomura : J. Chem. Phys., 23, 2130 (1955).

119. H. Tsubomura : J.Chem. Phys., 24, 927 (1956).

120. H. Ratajczak & W.J.Orville - Thomas : J. Chem. Phys., 58, 911 (1973).

121. H.Ratajczak, W.J.Orville & C.N.R. Rao : Chem. Phys., 17, 197 (1976).

122. H. S. Mulliken & W.B. Person : Molecular complexes, Wiley - interscience, New York, 1969.

123. M.L. Kande, C.Geron & M. Gomel : Int. Symp. Specific Interact. Mol. Ions, [Proc.], 3rd, 1, 296 (1976). [Chemical Abstracts, 88: 10450x (1978)].

124. C. Geron & M. Gomel : .. Chim. Phys. Phys.-Chim. Biol., 75(2), 241 (1978). [Chemical Abstracts, 89: 23570 (1978)]