STUDIES ON SOME ASPECTS OF MOLECULAR COMPLEXES

BHARATI BHATTACHARJEE
DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES

A THESIS
SUBMITTED IN FULFILMENT OF
THE REQUIREMENTS OF
THE DEGREE OF
DOCTOR OF PHILOSOPHY

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG 793 001
INDIA

AUGUST, 1985

Chem:

To

MY MOTHER

Phone :
Grams : NEHU

North-Eastern Hill University
Bijni Complex
Bhagyakul, Shillong-793003 (Meghalaya)

Department of...Chemistry

Dr. S. N. Bhat

I Certify that the thesis entitled, "STUDIES ON SOME ASPECTS OF MOLECULAR COMPLEXES", submitted by Miss Bharati Bhattacharjee for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by her under my supervision. She has been duly registered and the thesis presented is worthy of being considered for the award of the Ph. D. Degree. This work has not been submitted for any Degree of any other University.

Place : Shillong

Date : 5th Aug 85 – Signature of the Supervisor

Phone :
Grams : NEHU

North-Eastern Hill University
Bijni Complex
Bhagyakul, Shillong-793003 (Meghalaya)

Department of....Chemistry

July 15, 1985

This is to Certify that Miss Bharati Bhattacharjee has satisfactorily completed the following Pre-Ph. D. courses, as prescribed by this University:

1. CHEM 608 - BIO-INORGANIC CHEMISTRY
2. CHEM 660 - SOLID STATE CHEMISTRY
3. BASIC FRENCH LANGUAGE
4. SPS 602 - GERMAN LANGUAGE

HEAD

DEPARTMENT OF CHEMISTRY
NORTH-EASTERN HILL UNIVERSITY
SHILLONG 793 003

Head
Department of Chemistry
North Eastern Hill University
Shillong-793003

CONTENTS

ACKNOWLEDGEMENT

I would like to express my thanks to Dr. S. N. Bhat, Reader in Chemistry, North-Eastern Hill University, Shillong, for his unwavering enthusiasm and untiring guidance with constant encouragement throughout the course of this study.

My sincere thanks are due to the authorities of the Univeristy (NEHU), the Dean of School of Physical Sciences, and the Head of the Department of Chemistry for providing me the necessary laboratory and library facilities to carry out the research work.

It is my duty to acknowledge the help and good wishes of all the faculty members of the department of Chemistry, NEHU, for which I am extremely grateful to them.

I have the pleasure to place on record with thanks the good-will and cooperation of my fellow research scholars and friends, especially Dr. Mitra Bhattacharjee, Dr. V. P. Shedbalkar, Mr. B. L. Marwein, Mr. A. Sinha, Dr. M. N. Bhattacharjee, for their help and constant inspiration during the course of my research work.

My thanks goes also to the members of the non-teaching and technical staff of the Department of Chemistry, for recording the IR spectra and for extending full cooperation to me over all these years.

I am grateful to the Council of Scientific and Industrial Research, New Delhi, for awarding me a fellowship (1980-1983), which enabled me to carry out research work for the Ph. D. degree.

I would like to express my gratitude to Mother Anne, Principal, St. Mary's College, Shillong, for her kind permission and encouragement for the work.

My thanks are also due to Mr. O. Marbaniang for cyclostyling the entire thesis with great care.

Finally, I express my deep sense of gratitude to my beloved parents, brothers and sisters, and other relatives for giving me inspiration, encouragement and enthusiasm to pursue with my research work.

Shillong
the 9th August, 1985

Bharati Bhattacharjee
(Bharati Bhattacharjee)

CHAPTER I

INTRODUCTION

In this Chapter the general aspects of molecular complexes (including the theories) and some of the spectral and nonspectral methods which are of relevance to the studies, reported in this thesis, and of general interest have been briefly reviewed.

I. 1. ELECTRON DONOR ACCEPTOR SYSTEMS

It has been well known for many years that when molecules like aromatic hydrocarbons, amines, phenols, etc. are mixed with a large class of molecules like nitro-compounds, quinones, halogens, etc. in suitable solvents, the colour of the solutions change. When the solutions of the two such reagents are mixed, the profound change in colour clearly indicates the formation of a complex. The principal feature of the type of complex formation is the appearance of a new and intense absorption band in ultraviolet or visible region of the spectrum. Pfeiffer[1] who first classified these complexes suggested that the utilization of secondary valencies was involved in their formation.

When the molecules interact strongly, the molecules come very close to each other and the distance between the molecules will be very small; this leads to the formation of new chemical entities and the 'chemical' (valence) forces are operative in such cases. The energies of such interaction are of the order of 100-400 kJ/mole. The interaction occuring at large separation (i.e. weak interactions) are due to 'physical' (van der Waal) forces and the energies of such interactions are of the order of a few kJ/mole. This comprises of electrostatic (or coulombic) induction and dispersion energies. In between these two extremes of 'chemical' and 'physical' forces, there are forces which arise due to the interactions occuring at 'intermediate' separations. These are called 'Charge-transfer' forces.[2-5] They are cohesive in nature and are an 'admixture' of the chemical and physical forces, whose contributions depend on the molecules taking part in the interaction. They are relatively stronger than physical forces but much weaker than chemical forces. Thus they lead to the possibility of "graded" interaction between the molecules and the formation of "molecular complexes".

It is difficult to define precisely the term "molecular complex". However, according to Mulliken and Person,[5,3] "A molecular complex between two unlike molecules is an 'association' somewhat stronger than ordinary Van der Waal's interactions, of definite stoichiometry. (This definition can be extended to hydrogen bonding also). The partners are often already closed shell (saturated valence) electronic structures. In weak complexes the identities of the original molecules are preserved to a large extent.

I. 2. GENERAL FEATURES OF MOLECULAR COMPLEXES

Whenever the molecules interact to form an "associated species", there will be new absorption in electronic/infrared spectral regions or there may be any perturbation of the donor acceptor bonds. So any theory of molecular complexes (EDA systems) should explain satisfactorily the following general features of absorption spectra and energy changes associated with such complex formation.[4]

(i) Generally, a new absorption band (due to the complex) is observed in ultraviolet or visible region of the spectrum. However, the absence of such band in the ultraviolet or visible region does not necessarily mean that the complex does not exist and in such cases the changes in other physical properties (nonspectral) can be noticed.

(ii) The broad absorption band suggests the loose nature of binding in the ground state of the complex. The λ_{max} corresponds to the energy required to excite the electron from the most probable ground state to the excited state of the complex.

(iii) The charge-transfer band is generally highly intense. The molar extinction coefficient of the complex can be as high as 10^4 dm^3 mol^{-1} m^{-1}.

(iv) The enthalpies of formation of molecular complex are of the order of 5-75 kJ/mole. This indicates the weak nature of binding in the ground state of the complex.

(v) The intermolecular separation of the complex is much larger than normal ionic or co-valent bond lengths, but slightly smaller than the Van der Waals radii.

(vi) The complex formation affects the charge-distribution, in the donors and acceptors to some extent. Thus generally, the colour of iodine changes from violet to red or to brown as the ability of donor to donate electron increases. At the same time, the position of iodine absorption maximum shifts to shorter wave length (blue shift). When an iodine molecule in the complex is excited, the promoted electrons of donor passes from a bonding (or non-bonding) orbital to an antibonding orbital of iodine. The result is an increase in the size of the molecule. Therefore, due to the exchange repulsion in the complex and iodine molecule, more energy is required to promote the electrons. So, iodine absorption shifts to lower wavelength. The molar absorptivity coefficient of complexed iodine may increase or decrease.

(vii) The complex formation invariably occurs between molecules of low ionization potential and high electron affinity. It has been found that for a given acceptor ν_{max} varies directly with the ionization potential of donors having similar structures.

(viii) Generally, the donor, acceptor and complex differ in polarity.

(ix) The charge-transfer band position depends on the nature of the medium/solvent.

An evaluation of the thermodynamic parameters of EDA systems/molecular complexes, such as change in enthalpy, $-\Delta H^o$, entropy, $-\Delta S^o$ and standard free energy, $-\Delta G^o$, occuring on complex formation, provide useful evidence regarding the nature and strength of the binding of the complex. These thermodynamic parameters are determined from a knowledge of the equilibrium constants of complex formation at different temperatures.[6] In addition, one can also obtain useful information regarding the oscillator strength and the transition dipole moment of the charge transfer bands.[5]

Hydrogen bonding is an important aspect in the study of the interaction between electron donors and acceptors (i.e. proton acceptors and donors) and it is needless to emphasize the importance of this phenomenon in chemistry.[7-10] As hydrogen bonding is an attractive interaction between two molecules (or between two parts of the same molecule) which requires the presence of a hydrogen atom in the vicinity. So the general term molecular complexes/electron donor-acceptor system include hydrogen bonding (proton acceptor-donor system). Therefore general theory of molecular complexes can be extended to hydrogen bonding also.

I. 3. MULLIKEN'S THEORY OF MOLECULAR COMPLEXES

Electron transfer theory has been developed along two separate lines, namely, Mulliken's[5,11] Charge-transfer theory and Hush's[12] intervalence transfer theory. The former deals with electronic effects and is related to transitions in the uv and visible region (and is related to formation of molecular complexes) whereas the latter one deals with vibrational effects and is related to transitions in the infrared region. Mulliken's theory mainly concentrates on electronic effects (and it neglects molecular structural changes after complexation and vibrational structure in the transition is ignored), whereas Hush's theory in its use of two displaced harmonic oscillators neglects electronic effects (and neglects Franck-Condon overlap factor). So recently Ying-Nan Chiu[13] has developed a unified molecular charge-transfer theory and includes all ranges of molecular interactions. This unified theory of molecular charge-transfer reduces to Mulliken's theory of charge-transfer molecular complexes when only strong electronic effects are considered and becomes Hush's theory of intervalence of charge-transfer when the vibrational effects are more predominant. Person,[3] in his recent article has examined the general theory of intermolecular forces. The resonance structure theory of molecular complexes which has been developed by Mulliken,[5,11] has been generally accepted (for electronic transitions). We will summarize the salient aspects of Mulliken's theory of molecular complexes.

The interaction between an electron donor, D, and an electron acceptor, A, leading to the formation of a complex, DA (in the absence of any media), can be represented by the following resonance structures,

$$\underset{\mathrm{I}}{D + A} \longleftrightarrow \underset{\mathrm{II}}{(D,A)} \longleftrightarrow \underset{\mathrm{III}}{(D^{+}-A^{-})} \longleftrightarrow \underset{\mathrm{IV}}{(D^{-}-A^{+})}$$

The structure I is for molecules, when they are far apart and there is no interaction between the molecules. In structure II, the donor and acceptor are at equilibrium separation of the complex, but only 'physical forces' are operative between them and it is called 'no-bond' structure. The structures III and IV are the dative structures; in III an electron is transfered from donor to acceptor and in IV, from acceptor to to donor. In view of the electron donating and accepting tendencies of D and A, the contribution of the structure IV can be neglected.

The wave function for the ground state of complex, ψ_N, can be expressed as a linear combination of the wave functions of the 'no-bond' structure, ψ_0, and the dative structure, ψ_1, neglecting the contribution of the ionic structures, $(D^- — A^+)$

$$\psi_N = a^* \psi_0(D....A) + b\,\psi_1(D^+ — A^-) \quad ...I.1.$$

A corresponding excited state of the complex can be represented by the wave function, ψ_E,

$$\psi_E = a^* \psi_1 (D^+ — A^-) - b^* \psi_0(D,A) \quad ...I.2.$$

The difference in energy between the two states is equal to the energy of quantum at the maximum of the absorption band. The ratio b^2/a^2 in the normal state represents the proportion in which the dative and no-bond structure contribute and can vary from zero for no electron transfer to infinity for complete electron transfer. The coefficients, a^* and b^* are nearly equal to a and b. The energies of complexes, in its ground state (W_N) and excited state, W_E, can be obtained by solving Schrödinger Wave functions which are normalised. For weak interactions the ground state energy, W_N, and the excited state energy, W_E, may be obtained approximately by second order perturbation theory:

$$W_N = W_0 - \frac{(H_{01} - W_0 \cdot S_{01})^2}{(W_1 - W_0)} \quad \ldots \quad I.\ 3.$$

and

$$W_E = W_1 + \frac{(H_{01} - W_1 \cdot S_{01})^2}{(W_1 - W_0)} \quad \ldots \quad I.\ 4.$$

where,

$$W_0 = \int \psi_0 H \psi_0 d\tau$$

$$W_1 = \int \psi_1 H \psi_1 d\tau$$

$$H_{01} = \int \psi_0 H \psi_1 d\tau$$

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

The difference in energy between these two states, i.e., between W_E and W_N, is equal to the energy of the quantum at the maximum of the absorption band.

The schematic energy diagrams for spectra of molecular complexes are shown in Fig. I. 1. and Fig. I. 2. It can be seen from the figure I. 1 that

$$h\nu_{CT} = I_D - (E_A + E_C + W_0) + X_E - X_N \quad \ldots I.5.$$

$$= I_D - E_A - \Delta \quad \ldots \quad I.\ 6.$$

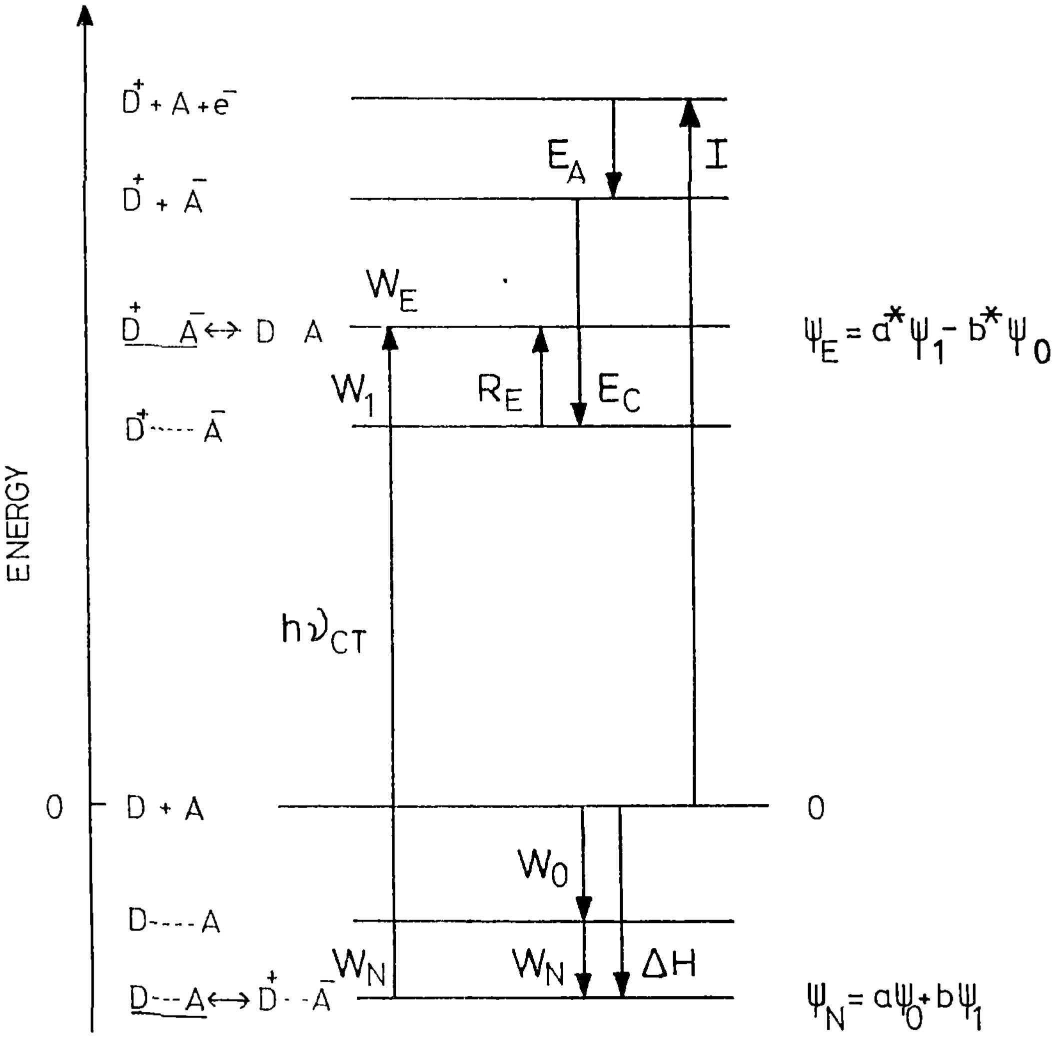

Fig. I. 1. Schematic Energy Level Diagram showing Various Contributions.

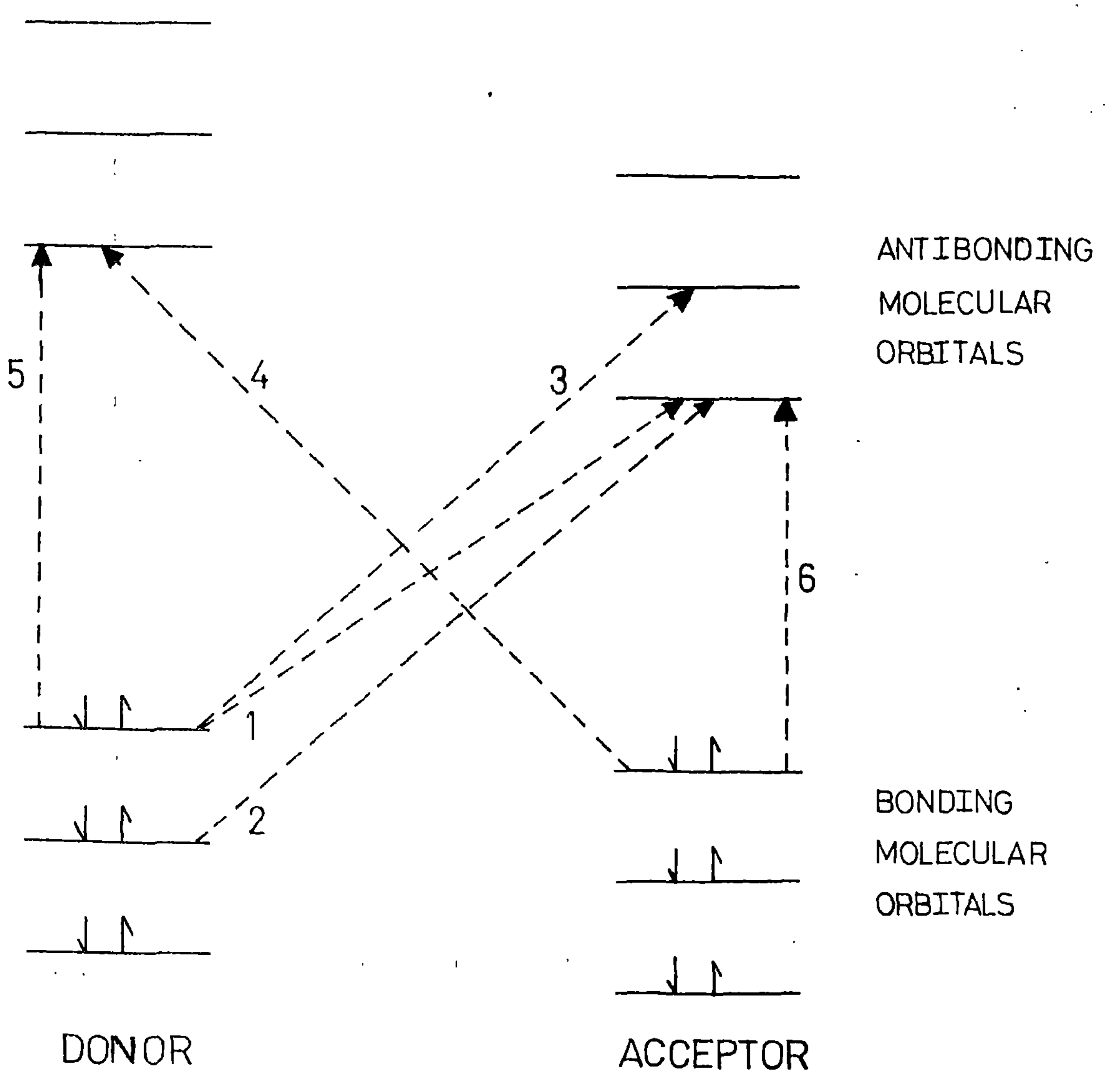

Fig. I. 2. Schematic Diagram showing Electronic Excitation:

1) Lowest Energy CT band;
2) Excitation from penultimate donor level;
3) Excitation to higher empty acceptor level;
4) Higher energy acceptor to donor CT band;
5) Intramolecular donor excitation and
6) Intramolecular acceptor excitation.

where I_D is the ionization potential of donor, E_A, is the electron affinity of the acceptor, E_C, is the Coulombic energy between $D^+—A^-$ and $D^-—A^+$, W_0 is the no-bond energy and X_E and X_N are resonance energies of the excited and ground states,

$$\Delta = E_C + W_0 - X_E + X_N$$

$$W_N = \Delta H = W_0 + X_N$$

The term, Charge-transfer absorption, thus is applicable to all absorption associated with the transitions from the normal (ground) state to the excited state of the complex.

As it can be seen from the above equation, (I.6.), Charge-transfer energy $h\nu_{CT}$, increases with the ionization potential of the donors (for a particular acceptor) having similar structure. The energy associated with the Charge-transfer transition is related to the I_D of the donor (for a particular acceptor) is given by $h\nu_{CT} = I_D - E_A - \Delta + [2\beta^2/(I_D - E_A - \Delta)]$. In the case of aromatic hydrocarbon-iodine systems, Briegleb[14] has shown that

$$h\nu_{CT} = (I_D - C_1) + \frac{C_2}{(I_D - C_1)} \quad \ldots \quad I.7.$$

where C_1 and C_2 are terms containing $(E_A - E_C + W_0)$ and $(\beta_0^2 + \beta_1^2)$ respectively, W_0 is the sum of several terms including electrostatic energy (dipole-dipole interaction etc.) and

$$\beta_0 = H_{01} - W_0 S_{01} \quad \text{and} \quad \beta_1 = H_{01} - W_1 S_{01}$$

When $h\nu_{CT}$ was plotted against I_D, Briegleb[14] found that the data could be fitted by curves of the form given by equation I.7. Although, the relation expressed by the equation (I.7) is non-linear between $h\nu_{CT}$ and I_D, the plots are only slightly curved over the observed (or practical) range of I_D. Thus, most of the data can be fitted by a linear relation of the form (for weak I_2 complexes and within the limits of experimental error).

$$h\nu_{CT} = 0.87\ I_D - 0.36 \qquad \ldots \qquad \ldots \qquad \text{I.8.}$$

Such linear relationships have slopes somewhat less than unity. The constants in the linear relation have no direct theoretical significance.

Amines do not fall in line with the $h\nu_{CT}$ vs I_D relation /̲ Eq. I.7 /̲ obeyed by weak I_2 complexes. Yada, Tanka and Nagakura[15] have derived the following equation for such strong complexes

$$(h\nu_{CT})^2 = \left[\frac{W_1 - W_0}{1 - S_{01}}\right]^2 - \left[1 + \frac{4\beta_0\beta_1}{(W_1 - W_0)^2}\right] . \text{I.9.}$$

It is now realized that linearity between $h\nu_{CT}$ and I_D is not universal rule,[15-17] since with the change of donor, the other factors such as the overlap integral vary as well.[16] A number of workers have correlated $h\nu_{CT}$ values with I_D for the interaction of a related series of donors with an acceptors and the results of such correlations are summarized by Rao, Bhat and Dwivedi.[18]

In the spectra, the band width is due to the loose coupling between the donor and acceptor components in the ground state of the complex. The loose coupling permits a continuous range of relative orientations of the two and therefore, generally causes a continuous variation in the energy of the ground state. The absorption corresponds to the transition from the most probable ground state alignment of the donor and acceptor species.

The charge-transfer absorption depends on the transition probability and transition moment. The oscillator strength, f, for an electronic transition is given by

$$\begin{aligned} f &= \frac{2.303\ mc^2}{\pi e^2 W_0} \int \epsilon_v \delta v \\ &= 4.318 \times 10^{-9} \int \epsilon_v \delta v \\ &\cong 4.32 \times 10^{-9} \epsilon_{max} \overline{\Delta\nu}_{\frac{1}{2}} \qquad \ldots \qquad \ldots \text{ I.10.} \end{aligned}$$

where $\Delta\nu_{\frac{1}{2}}$ is the width in cm^{-1} of the band between the two frequencies at which $\epsilon = (\frac{1}{2})\,\epsilon_{max}$. Here it must be noted that the accuracy of the approximation depends on the band shape.

The intensity of a charge-transfer band is proportional to the square of the transition moment, μ^2_{VN}. The oscillator strength, f; and electronic transition dipole, μ_{VN}, are related by,

$$f_{VN} = \left(\frac{8\pi^2 mc}{3b} \right) \bar{\nu} \left(\frac{\mu_{VN}^2}{c^2} \right) \quad \ldots \quad \text{I.11.}$$

$$\text{or,} \quad \mu_{VN} = 0.0958 \left[\frac{\int \epsilon \, d\bar{\nu}}{\bar{\nu}} \right]^{\frac{1}{2}}$$

$$\approx 0.0958 \left[\frac{\epsilon_{max} \cdot \Delta\bar{\nu}_{\frac{1}{2}}}{\bar{\nu}} \right]^{\frac{1}{2}} \quad \ldots \quad \text{I.12.}$$

There has been considerable discussion in literature about the role of charge-transfer to the ground state stabilities of molecular complexes (particularly in the case of weak molecular complexes). Mulliken's[5] theory has been quite successful in explaining the spectral characteristics of strong as well as weak molecular complexes. However, recent quantum chemical studies have suggested that many such complexes, especially weak complexes are formed primarily due to 'electrostatic' or 'polarization' interactions.[19-21] Umeyama et al[22] have shown that the interaction energy of a complex, comprises of five components, electrostatic, which arises from multiple interactions between the molecules D and A (which may be attractive or repulsive); polarization, which is due to induced multiple interactions and higher order coupling (and is always attractive); exchange repulsion, which is the short range repulsion due to electron distribution of A with that of D; Charge-transfer, which is due to charge-transfer from donor to acceptor (it is always attractive); and coupling energy, which accounts for higher order interactions. In addition to this, there is a contribution from correlation energy, both intra-molecular and intermolecular. A part of intermolecular correlation energy is dispersion energy, which results from instantaneous polarization of D and A. As mentioned in the beginning, Chlu[13] has developed unified molecular charge-transfer theory which includes all ranges of molecular interactions; in the limit of strong electronic effect (UV and visible region) it reduces to Mulliken's theory. It must be mentioned here, as pointed out by Person[3] that Mulliken's theory still holds good for whole range of molecular complexes; in the case of weak complexes, the no-bond structure, which comprises of above interactions, except charge transfer, is the major contribution to the overall wavefunction of the ground state of the complex ($a \gg b$), and hence to the ground state stability. So the term "molecular complex" rather than "Charge-transfer" or electrostatic complex (or Electron Donor-Acceptor Systems) seems to be reasonable to represent the systems.

After Mulliken's[5] valence bond approach for the study of molecular complexes, attempts were made to describe the donor acceptor interaction by molecular orbital method and the perturbation theory is used to describe weak interactions namely, π-π and π-σ complexes.[23-27] The stability of the complex is due to the decrease in the potential energy of the system. But this perturbation method could not be applied for strong interactions.[21] Fukui[28] used linear combination of atomic orbitals of the donor and acceptor for representing the molecular orbital of the complex. Guryanova et al[23] briefly summarized the applicability of VB and MO method for the study of interaction between molecules, and are of the opinion that both these methods are approximate and semiempirical and for describing the weak complexes, the Mulliken's VB method which is simple, is better, while the more modern MO method may be more suitable for describing complexes with stronger intermolecular bonds.

Since the intermolecular interaction is fairly weak, the original bond energies are slightly changed, leaving the absorption bands of donor and acceptor almost unchanged. In other words, the interaction energies in the ground state are small compared with the transition energies to the excited state. Each such transition may be considered as arising from the transfer of an electron from a filled orbital of the donor to an empty orbital of the acceptor. The energy of this transition is given by

$$E_{ij} = h\nu = A_j - D_i \qquad \ldots \qquad \ldots \qquad I.13.$$

where A_j and D_i are the energies of the j^{th} (lowest unoccupied orbital) and i^{th} (highest occupied) orbital. In aromatic hydrocarbons the energy of the highest occupied

M.O. in the ground state may be expressed in a simple Huckel treatment, $D_i = \alpha + \beta x_i$, where α is the coulomb integral, β is the resonance integral and x_i is the Huckel parameter for this orbital. The energy of the first transition band of the complex of such hydrocarbon donors with the given acceptor is given by,

$$h\nu_{CT} = A_j - D_i + P$$
$$= A_j - \alpha - \beta x_i + P \quad \ldots \quad \ldots \text{I.14.}$$

where P is an energy term which corresponds to a perturbation of the appropriate energy levels in the donor and acceptor. The applicability of this model was tested with tetracyanoethylene as acceptor and different aromatic hydrocarbons as donors.[6]

I. 4. CLASSIFICATION OF DONORS AND ACCEPTORS

Mulliken[5] has classified donors and acceptors of various types leading to the formation of molecular complexes of varying strengths, i.e. the energy of formation of molecular complex in the ground state (Table I.1.). At one extreme, we have the strong Lewis acid-Lewis base addition compounds, and at the other, the weak "contact pairs". The various types of donors and acceptors and the approximate energy ranges are shown in Table I.2. The π-donors-σ-

Table I. 1.

Classification of Donors and Acceptors

Number of Electrons	Function Type	Donor Type		Acceptor Type	
		Structures	Examples	Structure	Examples
Odd	Free	R	NO, C_2H_5, H	Q	X, H, OH
Even	(a) Increvalent.	n	R_3N, R_2S, R_2O, R_2CO.	v	BF_3, AlX_3, $SnCl_4$.
	(b) Sacrificial.	σ	Aliphatic hydrocarbons.	σ	X_2, CCl_4 (X = halogens)
		π	Aromatic and unsaturated hydrocarbons and those substituted with electron donating groups; intramolecular donor island groups.	π	Aromatic and unsaturated hydrocarbons with electron withdrawing groups; intramolecular acceptor island groups.

Table I. 2.

Donor Acceptor Systems and Their Energy Ranges

Type	Examples	Energy Ranges, kJ/mole
1. Contact pairs	Cyclohexane + I_2; Benzene + CCl_4	<10
2. π-σ	Benzene + I_2; Phenanthrene + I_2	5-20
3. π-π	Naphthalene + *sym*-trinitrobenzene.	5-20
4. *n*-σ	Amines + I_2; Carbonyl compounds + I_2.	15-75
5. *n*-v	Ether + BF_3; Amines + BF_3	Very strong addition compounds.

acceptor complexes and the n-donor-σ-acceptor complexes may exist as $\infty:\infty$ or as 1:1 complexes: the $\infty:\infty$ complexes are generally found in solid state and the 1:1 complexes in solution and vapor phases.

The molecular complexes formed between n-donors and σ-acceptors are very strong and there is a considerable contribution of the dative structure (D^+—A^-) to the stability of the ground state. Several attempts have been made to establish a pattern of the relationship between $h\nu_{CT}$ and μ_{DA}, the dipole moment of the charge-transfer complex in the ground state, and the heat of formation, $-\Delta H$, of the complex.[23]:

$$-\frac{\Delta H}{\mu_{DA}} = \frac{h\nu_{CT}}{er} \cdot \frac{1}{a^2(1 + \frac{a}{b} S_{01})\lbrack 1 + \frac{b^2}{a^2} + \frac{(b^*)^2}{(a^*)^2}}$$

$$= \frac{h\nu_{CT}}{erA} \cdot \ldots\ldots\ldots\ldots\ldots\ldots \quad \text{I.15.}$$

$$\text{where } A = a^2(1 + \frac{a}{b} S_{01})\lbrack 1 + \frac{b^2}{a^2} + \frac{(b^*)^2}{(a^*)^2} \quad \ldots \text{I.16}$$

From the experimental values of $-\Delta H$, μ_{DA} and $h\nu_{CT}$, equation I.10 can be used to estimate the overlap integral S_{01}. The contact molecular complexes arise out of collisions between donor and acceptor species. The enthalpies of formation of such complexes are very small. For weakly interacting systems, Ketelaar[24] assumed that $b^2 \ll a^2$ and $(b^*)^2 \ll (a^*)^2$ and derived the equation

$$\frac{\Delta H}{h\nu_{CT}} \approx \frac{b^2}{a^2} \qquad \ldots \qquad \ldots \quad I.17.$$

The magnitude b^2/a^2 is a measure of the polarity of the complex. After $-\Delta H$ and $h\nu_{CT}$ have been experimentally determined, one can use this equation to calculate b^2/a^2; this evaluation will be very approximate. In between these two extremes, the molecular complexes of varying strengths are formed depending on the particular donor and acceptor species forming the complexes. It must be mentioned here that the terms, donor and acceptor are only relative.

I. 5. METHODS USED IN THE STUDY OF MOLECULAR COMPLEXES

An important feature of weak attractive interactions (molecular complexes/hydrogen bonding) in solution is that at ordinary temperatures, only a fraction of the molecules are generally associated. At equilibrium, while a certain number of new complexes are continuously broken, due to the kinetic energy of motion of the interacting molecules. The formation of molecular complexes, hydrogen bonds may be proved and their compositions may be established from a study of the associated characteristic abrupt changes from ideal behaviour in certain physical properties. Any physical property will be suitable for such studies if it is reversible to the effects of dilution and temperature.[29] This properties include the absorption of ultra-violet or visible radiation, vapor pressure, dielectric constant, refractive index, conductometric titrations, viscosity, surface tension, etc.[23,29-34] Recently valuable information have been obtained from calorimetry,[35-37] Gas-liquid Chromatography,[29,38-40] ultracentrifugation,[41] fluorescence measurement,[42-44] solubility method,[45] constant activity method,[46] microwave spectroscopy,[47-50] double diffusion uv-method, vibrational spectroscopy,[51-55] Raman spectroscopy,[56-60] picosecond spectroscopy,[61-64] nuclear magnetic resonance,[65-71] electron spin resonance,[72,73] positron annihilation life time measurements,[74] dielectric and dipole moment measurements,[75-76] NQR spectroscopy,[77,78] chemical dynamics,[79] Mossbauer spectroscopy,[80,81] Mass spectrometry,[82-84] Overhauser effects,[85,86] optical dichroism of single crystals,[87-90] magnetic circular dichroism,[91] X-ray and neutron diffraction studies,[92-96] electrical and optical properties of solid molecular complexes,[93,97-105] magnetic properties of molecular complexes,[92,106-111] phase transition and phase diagram,[112-117] cyclic voltametry,[118-121] ultrasonic interferrometry,[122-125] differential thermal analysis.[126] The contributions of Tamres and coworkers[127-135] in understanding the nature of interactions of molecules in vapor phases and contact charge transfer complexes, Nagakura and coworkers on exciples,[136] Kuroda and others on PES/ESCA,[137-140] Matsunaga and coworkers[141] on the studies of charge transfer and proton transfer processes, Muralikrishna and coworkers[79,142-159] in using CT complexes in analytical studies, Bhowmik and coworkers[160-169] in the effect of solvents on spectra and thermodynamics of charge-transfer complexes, Plusinski and coworkers[170] on detection of charge transfer complexes in solution by the method of isosbestic points and recently photo-acoustic spectroscopy,[171] Radiotracer techniques,[172] polarographic techniques,[172a,b] stopped flow technique[168] are also being used in the study of molecular interactions. In addition, theoretical studies on molecular complexes are also being carried out.[172-180] Such studies will undoubtebly be very useful in understanding the nature of molecular interactions.

Generally, the molecular complexes cannot be isolated in pure state, but exist in solution in equilibrium with pure components. So it is not surprising that molecular complexes have been studied most extensively in solutions, though many recent studies have been done in vapor phases as well.[181] Although, the interaction of an electron donor D, with an acceptor, A, may give rise to more than one species of complex in solution, most of the methods used for evaluating the association constant assumes that a single complex species with a definite stoichiometry is formed. Thus, for equilibrium,

$$\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{DA} \quad \ldots \qquad \ldots\ \mathrm{I.18.}$$

a thermodynamic equilibrium constant, K, is obtained:

$$K = \frac{[\mathrm{DA}]}{[\mathrm{D}][\mathrm{A}]}$$

$$= \frac{[\mathrm{DA}]}{([\mathrm{D}]_0 - [\mathrm{DA}])([\mathrm{A}]_0 - [\mathrm{DA}])} \quad ..\mathrm{I.19.}$$

where $[\mathrm{D}]$, $[\mathrm{A}]$ and $[\mathrm{DA}]$ represent the equilibrium concentration of donor, acceptor and complex and $[\mathrm{D}]_0$ and $[\mathrm{A}]_0$ are the initial concentrations of donor and acceptor, respectively. It is generally assumed that as the solutions are very dilute, the activity coefficients of the species DA, D and A are unity.[182-184] When the concentration of donor is very much in excess of that of acceptor ($\mathrm{D} \gg \mathrm{A}$), (or vice versa) then $([\mathrm{D}]_0 - [\mathrm{AD}])$ can be replaced by $[\mathrm{D}]_0$ in the above equation. Expressing the concentration of the complex in terms of experimentally measureable absorbance ($[\mathrm{DA}] = \mathrm{O.D.}/\epsilon.\mathrm{l.}$) the above equation (I.19) can be rewritten as,

$$\frac{[\mathrm{A}]_0 . l}{\mathrm{O.D.}} = \frac{1}{K.\epsilon} . \frac{1}{[\mathrm{D}]_0} + \frac{1}{\epsilon} \quad \ldots\ \mathrm{I.20.}$$

This is the original Benesi-Hildebrand equation.[182] Eventhough, the Benesi-Hildebrand equation can be used to obtain the equilibrium constant, one has to use modified equations for obtaining the correct values. These modified and new equations and summarized by Rao et al[18] as well as by Foster[32a] in recent reviews.

Recently, it has been felt that the data obtained by optical spectroscopy on molecular complexes should be supplemented by non-spectral methods.[185] The arguments in favour of above ideas are :-

(i) In using spectral methods to study complex formation, it is necessary to infer two parameters from a set of measurements at various concentrations, the equilibrium constant of complex formation, K, and the molar extinction coefficient, ϵ , of a spectral band. Although the product $K.\epsilon$ can be determined from spectral measurements restricted to the dilute solution region, the resolution of the product $K.\epsilon$ into separate values of K and ϵ , requires spectral measurements extending into concentration ranges in which a sizable fraction of the least concentrated solute (usually the acceptor) is in the complexed form.[186-188] Thus, in studies of complexes for which K is considerably less than 1 M^{-1}, it is necessary to use solute concentration well in excess of 1M. At such concentration levels, the medium remains hardly equivalent to pure solvent; in fact, it may be expected that both the spectral and the thermodynamic properties of the solute species are significantly different from those of infinite dilution.[189] Attempts have been made to account for the effects of sizable concentrations of dissolved solutes on specific and non-specific interactions of the solvent with donor, acceptor and complex molecules.[190-191] In addition, there may be higher order (n:m) complexes at higher donor/acceptor concentrations.[192-193]

(ii) The interpretation of the spectra of donor, acceptor and complex may be complicated by the presence of numerous orientation isomers, of the 1:1 complex or contact charge-transfer complexes and the calculated value of ϵ is the weighted average of extinction coefficients of various orientation isomers.[194] So, doubts have been raised on the validity of optically determined values of K and ϵ (from $K\epsilon$), particularly in the case of weak molecular complexes.[195]

In developing and testing theories of molecular interactions, it is essential that we must have accurate values of K and ϵ for weak complexes too, for which the conventional spectral method alone cannot yield reliable results. It is believed that it will be fruitful to employ several non-spectral methods (such as solubility, vapor pressure, refractive index, dielectric constant and dipole moment,[196-200] viscosity measurement,[201] surface tension,[33,34] colligative property,[202,203] conductivity, etc.). These methods are probably capable of giving reliable values of K for complexes even in solutions that are so dilute that only a small fraction of either of the donor or the acceptor molecules are in complexed form.[204] Thus, if spectral and non-spectral methods are employed conjunctively, accurate information can be obtained about both the spectra and energetics of molecular complexes. In addition, it is to be noted that the same technique can not be used under all conditions. Although it is mentioned in the literature that the stoichiometry of the complex can be determined by the continuous change method[205] or by the molar ratio method,[206] these methods using the measurements of physical properties like uv-vis radiation absorption etc. are not much helpful when either, the interaction between the molecules is so weak that there is only slight perturbation in the spectra of the interacting molecules, or when complex formed dissociates to give ions in polar media.[207] Under such circumstances, one can determine the stoichiometry of such ionizable complexes either by making use of any convenient non-spectral method or by measuring the electrical conductivities of the solutions in a suitable media.

This thesis embodies the results of studies on molecular complexes/hydrogen bonding by using the above mentioned less familiar methods — conductometry, viscometry, in addition to the usual [illegible] infrared spectroscopy.

I. 6. OUTER AND INNER COMPLEXES

When the donor and acceptor molecules interact to form a complex, the ground state of the complex which depends largely on the coulombic interaction between the components is influenced markedly by the dielectric constant of the medium. In some n-donor-σ-acceptor complexes, the new bonds which are formed are loosened due to environmental assistance and transform to the 'dissociative' inner complex, due to the rupture of the bond. In the presence of non-ionizing solvents, the two ions formed by the rupture of the σ bond will be together (ion pair); while in an ionizing solvent they are separated out. Mulliken[5,11,208] has compared the "dissociative" and "associative" donor acceptor interactions/ reactions in detail. The 'associative' mode helps to form the 'outer complex' while the dissociative mode to "inner complex". In the presence of a strong environmental conditions, the activation energy for the transformation of the outer to inner complex decreases. If the environmental influence is sufficiently strong, the inner complex may be the stable form. The kinetic study of transformation of outer complex to inner complex helps in understanding the nature of interaction and the effect of environmental influence on the transformation.[209-217]

I. 7. CONDUCTOMETRIC TITRATION

If the interaction between the donor and acceptor is very strong, then a high dielectric media will facilitate the transformation of the 'outer complex' into the 'inner complex' by loosening the new bonds which are formed[218]; such donor and acceptor species are ionic. Gutmann and co-workers[219] had demonstrated that conductometry/conductometric titration can be used to study the formation of such complexes. In addition to this, the stoichiometry of such ionizable complex can be determined conductometrically. (ref. 220-226).

I.8. VISCOMETRIC STUDIES ON MOLECULAR COMPLEXES AND HYDROGEN BONDING

When molecules interact to form complexes the physical properties of the new species formed will be different (however small it may be) from those of the reacting molecules. So in principle one can study the "interaction" between the molecules by noting the change in any of the properties, e.g. viscosity of the systems under different conditions. The viscosities of the "binary" and "ternary" systems will be different from those of calculated (i.e. using additivity rules) values and the deviation is an indication of interaction between the molecules. It has been pointed out that viscometric method can be used to obtain the equilibrium constant of complex-hydrogen bonding directly.[227-242]

I. 9. INFRARED SPECTRA OF SOLID MOLECULAR COMPLEXES

The increase in bond lengths which result when donor-acceptor interaction takes place are generally accompanied by corresponding decrease in vibration frequencies of the components.[253] These changes (and appearance of new bands as well) and other changes which are characteristic of symmetry losses leading to vibrations which are forbidden in free donors and acceptors, generally apparent in the infrared spectra of the adducts.

The interaction of donor with acceptor results either in perturbation of the vibrational frequencies (if the interaction is weak) or accompanied by pronounced changes in infrared spectra. So the "shift" of the donor/acceptor band frequency is a measure of the strength of interaction. Yarwood and co-workers[254] have carried out systematic and exhaustive investigations on measurement and interpretation of vibrational spectra of molecular complexes. Similarly Haque and co-workers,[255] Wood et al,[256] Devlin et al[257] made significant contribution in understanding the nature of interaction between molecules by vibrational spectroscopy.

The Charge-transfer complexes are of interest and are being studied in all branches of chemistry. Tamres[258] had listed the general areas of recent research (experimental) on charge-transfer complexes:

1. Vapor phase charge-transfer complexes.
2. Solvent effects on charge-transfer complexes.
3. Pressure effects on charge-transfer complexes.
4. Contact charge-transfer complexes.
5. Excited state properties of charge-transfer complexes.
6. Electrical, optical and magnetic properties of charge-transfer complexes.
7. Structure of solid charge-transfer complexes.
8. PES/ESCA studies of molecular complexes.
9. Polarised absorption spectral studies of single crystals.
10. Charge-transfer complexes of polymers.
11. Optically active charge-transfer complexes.
12. Charge-transfer complexes of biological interest involving carcinogenic compounds, drug receptors.
13. Charge-transfer complexes in analysis, chromatographic separation, catalysis.

14. Charge-transfer complexes involving donors with multiple sites, species which behave either as donors or acceptors.
15. Charge-transfer complexation for estimating electron affinity of acceptors.
16. Reaction intermediates involving CT complexes.
17. Organometallic charge-transfer complexes.

Care has been taken to give proper credit for the work of other authors in the literature. The author would like to apologize for any omission which may have occurred by oversight or error in judgement.

REFERENCES

1. P. Pfeiffer, "Organische Molekulverbindugen", 2nd ed., Ferdinand Enke, Stuttgart, 1927.
2. J. O. Hirshfieder, Ed., "Advances in Chemical Physics", Vol. 12, "Intermolecular Forces", Interscience Publishers, New York, 1967.
3. "Spectroscopy and Structure of Molecular Complexes", Ed. by J. Yarwood, Plenum Press, London, 1973.
4. C. N. R. Rao, "Ultraviolet and Visible Spectroscopy, Chemical Applications", 2nd ed., Butterworths, London, 1967.
5. R. S. Mulliken and W. B. Person, "Molecular Complexes", Lecture Note Reprints" John Wiley and Sons, New York, 1969 and the papers therein.
6. R. Foster, "Organic Charge-Transfer Complexes", Academic Press, London, 1969.
7. G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman and Co., San' Francisco, 1960.
8. A. S. N. Murthy and C. N. R. Rao, Appl. Spectroscopy Rev., **2**, 69 (1968).
9. S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding", Van Nostrand Reinhold Co., New York, 1971.
10. J. L. Wood in "Spectroscopy and Structure of Molecular Complexes", Ed. by J. Yarwood, Plenum Press, London, 1973.

11. a) R. S. Mulliken, J. Am. Chem. Soc., 74, 811 (1952).
    b) R. S. Mulliken, J. Phys. Chem., 56, 801 (1952).
12. N. S. Hush, Prog. Inorg. Chem., 8, 391 (1967).
13. Ying-Nan Chiu, J. Phys. Chem., 81, 992 (1976).
14. G. Briegleb, "Elektronen-Donator-Acceptor Komplexes", Springer Verlag, Berlin, 1961.
15. H. Yada, S. Tanaka and S. Nagakura, Bull. Chem. Soc. Japan, 33, 1660 (1960).
16. S. H. Hastings, L. J. Franklin, J. S. Schiller and F. A. Matson, J. Am. Chem. Soc., 75, 2900 (1953).
17. N. Mataga and T. Kuboza, "Molecular Interactions and Electronic Spectra", Marcel Dekker, INC., 1970, Chap. VI.
18. C. N. R. Rao, S. N. Bhat and P. C. Dwivedi, Appl. Spectros. Revs., 5, 1 (1972).
19. R. S. Mulliken and W. B. Person, Ann. Revs. Phys. Chem., 13, 107 (1962).
20. M. W. Hanna and J. L. Lippert in "Molecular Complexes", Ed. R. Foster, Elek Science, London, 1973.
21. K. Merokuma, Accounts of Chemical Res., 10, 294 (1977).
22. H. Umeyama, K. Morokuma and S. Yamabe, J. Am. Chem. Soc., 99, 330 (1977).
23. E. N. Guryanova, I. P. Gol'dshtein and I. P. Romni, "Donor-Acceptor Bond", Translated by R. Konder, John Wiley and Sons., New York, 1975

24. J. A. A. Ketelaar, J. Phys. Radium, Paris, 15, 197(1954).

25. J. N. Murrel, J. Am. Chem. Soc., 81, 5037 (1957).

26. M. J. S. Dewar and A. R. Leptey, J. Am. Chem. Soc., 83, 4560 (1961).

27. M. J. S. Dewar and H. Rogers, J. Am. Chem. Soc., 84, 395 (1962).

28. K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, Bull. Chem. Soc. Japan, 34, 1076 (1961); 35, 33 (1962).

29. M. A. Slifkin, "Charge-transfer Interactions of Biomolecules", Academic Press, London, 1971.

30. L. J. Andrews, Chem. Revs., 54, 713 (1954).

31. J. Rose, "Molecular Complexes", Pergamon Press, Oxford, 1967.

32. a) "Molecular Complexes, Vol II", Ed. by R. Foster, Elek. Science, London, 1974, Chap. III.

    b) J. Grundnes, S. D. Christian and V. Cheam, Acta Chem. Scand., 24, 1836 (1970).

    c) J. Grundnes, S. D. Christian, V. Cheam and S. B. Farnham, J. Am. Chem. Soc., 93, 20 (1971).

    d) E. Grunwald and J. F. Haley Jr., J. Phys. Chem., 72, 1944 (1968).

33. B. A. Akhverdiev, S. A. Binanda, B. M. Mirzoev and Sh. Kh. Khalilov, Izc. Vyssh. Uctiebn. Zaved. Neft. Gaz., 26, 43 (1983); CA, 99: 11806n.

34. A. Juarez, A. T. O. Donnel and M. Katz, An. Aroc. Quim. Argent., 71, 287 (1983); CA, 99: 219129b.

35. a) B. Nelonder, Acta Chem. Scand., 20, 2289 (1966).
b) W. G. Herndon, J. Feuer and R. E. Mitchell, Chem. Commn., 435 (1971).

36. Z. Pawlak, L. M. Mukherjee and R. G. Bates, J. Chem. Thermodyn., 14, 1041 (1982).

37. M. L. Lakhanpal and R. Rarashar, Ind. J. Chem.22A,48(1983).

38. J. J. Bruno, D. E. Mortire, M. W. P. Harbison, A. Nikolic and C. F. Hammer, J. Phys. Chem., 87, 2403 (1983).

39. M. A. Slifkin and S. H. Liu, J. Chromatogr., 269, 103 (1983); CA, 99: 190902k.

40. R. J. Laub and C. A. Wellington in "Molecular Association", Vol. 2. Ed. by R. Foster, Academic Press, London, 1979.

41. P. J. Trotter and D. A. Yphantis, J. Phys. Chem., 74, 1399 (1970).

42. a) P. J. McCantion., J. Am. Chem. Soc., 85, 2021 (1963).
b) M. Goutermann and P. E. Stevensen, J. Chem. Phys., 37, 2266 (1962).

43. K. Ulbrych and J. Siodmak, Zesz. Nauk. Akad. Raln. Tech. Olsztynie. Technol Zywn., 55 (1982); CA, 99: 5923g.

44. J. Fuenfschilling, M. Samoc and D. F. Williams, Chem. Phys. Lett., 96, 157 (1983).

45. T. Higuchi and K. A. Conner, in "Advances in Analytical Chemistry and Instrumentation", Vol. 4., Ed. by C. N. Reilley, Interscience, New York, 1965.

46. J. D. Childs, S. D. Christian, J. Grundness and S. R.Roach, Acta Chem. Scand., 25, 1679 (1971).

47. E.J. Goodwin and A.C. Legon., Chem. Phys., 87, 81 (1984).

48. A. Horn, K. M. Marstokk, H. Moellendal and H. Priebe, Acta Chem. Scand., Ser., A37, 679 (1983); CA,100: 120193v.

49. V. S. Deogaonkar, C. S. Adgaonkar and S. N. Jajoo, Ind. J. Pure Appl. Phys., 20, 617 (1982).

50. A. C. Legon and D. J. Millen, Faraday Diss. Chem. Soc., 73, 71 (1982); CA, 98: 134506b.

51. "Spectroscopy and Structure of Molecular Complexes", Ed. by J. Yarwood, Plenum Press, London, 1973, Chap. IIIto IV.

52. C. T. Lin, C. A. Caetano and T. D. Z. Atvars, Chem. Phys. Lett., 100, 169 (1983).

53. S. Matsuzaki, T. Moriyama, M. Onomichi and K. Toyoda, Bull. Chem. Soc. Japan., 56, 369 (1983).

54. A. Kiviner and M. Ovaslea, J. Phys. Chem.,82, 3809 (1983).

55. a) S. G. W. Ginn, I. Haque and J. L. Wood, Spectrochim Acta, 24A, 1531 (1968).

b) I. Haque and J. L. Wood, Spectrochim Acta, 23A, 959, 2523 (1967).

c) M. J. Potasek and K. W. Leeson, The Review of Scientific Instrum., 52, 1301 (1981).

56. K. H. Michaelian, K. E. Rieckhoff and E. M. Voigt, J. Phys. Chem., 81, 1489 (1977).

57. W. Zinth and W. Kaiser; Spinger Ser. Solid State Sc., 49, 124 (1983); CA, 100: 93742q.

58. MI I. S. Sastry and S. Singh, J. Raman. Spectros., 15, 80 (1984); CA: 218197z, (100)

59. R. S. Catuliotti, G. Dellepiane, G. Paliani, S. Santini and R. Tubino, J. Mol. Struct., 114, 157 (1984).

60. H. Takahashi, B. P. Asthana, W. Haefner and W. Kiefer, J. Raman. Spectros., 14, 102 (1983); CA, 98: 224519n.

61. E. F. Hilinski, J. M. Masnovi, C. Amatore, J. K. Kochi and P. M. Rentzepis,, J. Am. Chem. Soc., 105, 6167 (1983).

62. E. V. Sitzimann, J. Longan and K. B. Eisenthal, Chem. Phys. Lett., 102, 446 (1983).

63. N. Ikeda, H. Miyasaka, T. Okada and N. Matage, J. Am. Chem. Soc., 105, 5206 (1983).

64. J. M. Masnovi, Chem. Phys. Lett., 106, 20 (1984).

65. a) R. Foster and E. A. Fyfe in "Progress in NMR Spectroscopy" Vol. 4, Ed. by J. W. Emsley, J. Feeney and L. H. Sutcliffe, Pergamon Press, Oxford, 1969, Chap. I.

    b) C. A. Fyfe and J. Ripmeester, Can. J. Chem. 48, 2283 (1970).

    c) D. F. R. Gilson and C. A. McDowell, Can. J. Chem. 44, 945 (1966).

66. I. Horman and B. Dreux, Anal. Chem., 55, 1219 (1983).

67. D. Catalano, C.A. Veracini, P.L. Barili and M. Longeri, J. Chem. Soc. Perkin Trans., II, 171 (1983).

68. J. H. Clark, J. Sherwood Taylor and A. J. Goodwin, Spectrochim. Acta, 38A, 1101 (1982).

69. W. Naknishi, Y. Yamato, Y. Kusuyama, Y. Ikeda and H. Iwamura, Chem. Lett., 675 (1983).

70. W. Lamberty, H. Stamm and J. Stafe, J. Phys. Chem., 87, 1589 (1983).

71. J. A. Chudek, R. Foster and F. M. Jarrett, J. Chem. Soc. Faraday Trans, I, 79, 2729 (1983).

72. C. Sieiro, A. Sanchez and P. Prados, Spectrochim. Acta, 38A, 1329 (1982).

73. Y. Kotako and K. Kuwata, Bull. Chem. Soc. Japan, 55, 3686 (1982).

74. Y. C. Jean and H. J..Ache, J. Phys. Chem., 80, 1693(1976).

75. a) N. Kulvesky in "Molecular Associations", Vol. 7, Ed. by R. Foster, Academic Press, London, 1975.

    b) S. N. Bhat and C. N. R. Rao, J. Am. Chem. Soc., 90, 6006 (1968).

    c) A. H. Price in "Spectroscopy and Structure of Molecular Complexes", Ed. by J. Yarwood, Plenum Press, London, 1973, Chap. VII.

76. P. Krzyrztof and J. Jan, Pol. J. Chem., 56, 1459 (1982). CA, 101: 38052k.

77. a) R.A. Bennett and H.O. Hopper, J.Chem.Phys.,47,4855(1965).

    b) Y.K. Maksyutin, T.A. Babushking, Y.N. Gurganova and G. K. Semin, Theor. Chim. Acta, 14, 48 (1969).

77. c) G. A. Bowmaker and S. Hacobian,
Aust. J. Chem., 22, 2047 (1969).
d) H. G. Fleming and M. W. Hanna, J.
J. Am. Chem. Soc., 93, 5030 (1971).

78. S. V. Anferova, Zh. Fiz. Kheim, 57, 959 (1983).
CA, 99: 15282m.

79. a) U. Muralikrishna, Y. V. S. K. Seshasayi and
M. Krishnamurthy, React. Kinet. Catal. Lett., 24, 193(1984).
b) U. Muralikrishna, Y. V. S. K. Seshasayi and
M. Krishnamurthy, J. Ind. Chem. Soc., 60, 1048 (1983).
c) U. Muralikrishna and M. Krishnamurthy,
Ind. J. Chem., 21A, 1018 (1982); 22A, 512 (1983).

80. a) S. Ichiba, M. Mishina, H. Sakai and H. Negita,
Bull. Chem. Soc. HJapan, 41, 49 (1968).
b) S. Ichiba, H. Sakai, H. Negita and Y. Maeda,
J. Chem. Phys., 54, 1627 (1971); 72, 6192 (1980).
c) H. Sakai, T. Malsujama, H. Yamaoka and Y. Maeda,
Bull. Chem. Soc. Japan., 56, 1016 (1983).

81. M. Vanrossum, I. Dezzi, L. Longouche, K. C. Mishra,
A. Coker and T. P. Das, Hyperfine Interactions, 15, 475(1983).

82. a) J. E. Collin and R. Cabay, Bull. Cl. Sci. Acad. Roy.
Belg., 52, 606 (1966), CA, 67: 58307e.
b) B. E. Job and W. R. Patterson in "Some Newer Phys.
Methods", Struct. Chem. Proc. Symp. (R. Bonnet, Ed.),
United Trade Press, London, 1966; CA, 70: 52216g.

83. M. Tsuchiya and H. Kuwabara, Shitsuryo Bunseki, 30, 305 (1982); CA, 98: 188561j.

84. A. A. Tichonov, V. V. Sokolov, N. N. Grishin and A. A. Petrov, Zh. Org. Khem, 19, 1404 (1983); CA, 99: 139165v.

85. H. Goetz, H. Schulze and K. Werha, Phys. Status Solidi, 24, K95 (1967); CA, 68: 25308y.

86. M. A. Khaled and C. L. Watkins, J. Am. Chem. Soc. 105, 3363 (1983).

87. a) K. Yakushi, M. Iguchi and H. Kuroda, Bull. Chem. Soc. Japan, 52, 3180 (1979).
    b) T. Sugano, K. Yakushi and H. Kuroda, Bull. Chem. Soc. Japan, 51, 1041 (1978).

88. V. I. Permogorov, B. L. Tyaglov, Yu. A. Semiletov and Yu. P. Shvachkin, Khim. Pror. Soedin, 119 (1983); CA, 98 : 211700q.

89. M. Sheves, B. Kohne, N. Friedman and Y. Mazur, J. Am. Chem. Soc., 106, 5000 (1984).

90. A. Tajiri, N. Gonohe and M. Hatano, Ber. Bunsen Ges. Phys. Chem., 87, 684 (1983); CA, 100 : 6862n.

91. a) E. L. Kourshy, G. Adel and G. Roger, J. Chem. Soc. Faraday Trans, II, 72, 1860 (1976).
    b) R. Solaro and E. Chiellini, Chem. Commn., 580, 583 (1980).

92. a) The Scientific papers of Prof. H. Akanatu and his group, Tokyo University Press, 1971.

92. b) C. K. Prout and B. Kamener in "Molecular Complexes", Vol. I, Ed. by R. Foster, Elek, Science, London, 1973.

93. a) H. Kobyashi, Bull. Chem. Soc. Japan, 46, 2595, 2675, 2945 (1973).

b) H. Kobayashi, Y. Ohashi, F. Marumo and Y. Saito, Acta Cryst., B26, 459 (1970).

94. a) O. Hassel and K. O. Strome, Acta Chem. Scand., 12, 1178 (1958).

b) O. Hassel, C. Romming and T. Tufte, Acta Chem. Scand., 15, 967 (1961).

c) A. C. Bailey and C. K. Prout, J. Chem. Soc., 4867(1965).

d) T. Uchida, Bull. Chem. Soc. Japan, 40, 2244 (1967).

95. J. Howard, J. Tomkinson, J. Eckert, J. A. R. Goldstone and A. D. Taylor, J. Chem. Phys., 78, 3150 (1983).

96. E. Kalman, I. Serke, G. Palinkas, M. D. Zeidler, F. J. Wiesmann, H. Bertugnolli and P. Chieux, Z. Naturfors. Phys. Chem. Kosmophys. 38A, 231 (1983); CA, 98: 132693m.

97. F. Gutmann and L. E. Lyons, "Organic Semiconductors", John Wiley, New York, 1967.

98. H. Anzai, Kogyo Zairyo, 32, 88 (1984); CA, 101: 37815z.

99. O. P. Studzinskii, Yu. A. Makashev and L. S. Kozhevnikova, Zh. Obshch. Khim., 53, 480 (1983).

100. M. Z. Hoffmann, D. R. Prasad, G. Jones II and V. Malba, J. Am. Chem. Soc., 105, 6360 (1983).

101. M. Samoc and D. F. Williams, J. Chem. Phys., 78, 1924 (1983).

102. A. Deronzier and F. Ezposita, Nouv. J. Chim., 7, 15 (1983); CA, 98 : 182555p.

103. G. Wolmershauser, M. Schnauber and T. Wilhelm, J. Chem. Soc. Chem. Commun., 9, 573 (1984).

104. A. Aumuller, E. Hadicke, S. Hunig, A. Schatzle and J. V. Vonschutz, Angevo. Chem. Ind. Ed., 23, 449 (1984).

105. C. I. Siminescu, M. Grigorar and V. Barboiu, Polymer Bulletin, 9, 537 (1983).

106. a) M. Kinoshita, Bull. Chem. Soc. Japan, 35, 1137, 1609 (1962).
    b) M. Kinoshita, Y. Sato, M. Sano and A. Akamatu, Bull. Chem. Soc. Japan, 43, 2370 (1970).

107. M. Kinoshita, Bull. Chem. Soc. Japan, 37, 428 (1964).

108. Y. Sato, M. Kinoshita, M. Sano and H. Akamatu, Bull. Chem. Soc. Japan, 40, 2539 (1967).

109. M. Ohmasa, M. Kinoshita, M. Sano and H. Akamatu, Bull. Chem. Soc. Japan, 41, 1998 (1968).

110. Y. Sato, M. Kinoshita, M. Sano and H. Akamatu, Bull. Chem. Soc. Japan, 43, 2370 (1970).

111. a) H. Kuroda, M. Kobayashi, M. Kinoshita and S. Takemoto, J. Chem. Phys., 36, 457 (1962).
    b) M. Ohmasa, M. Kinoshita and H. Akamatu, Bull. Chem. Soc. Japan, 44, 391, 395 (1971).
    c) N. Iwasaki and M. Kinoshita, Chem. Phys. Lett., 86, 81 (1982).

112. A. Miniewicz, J. Sworakowski and D. F. Williams, Ferroelectrics, 55, 939 (1984).

113. S. Kagoshima and H. Anzai, J. Phys. Colloq., 1289 (1983). CA, 99 : 185597k.

114. H..R. Swamy, S. Ganguly and C. N. R. Rao, Spectrochim. Acta, 39A, 23 (1983).

115. T. Luty, R. W. Munn, J. Chem. Phys., 80, 3321 (1984).

116. S. Fukuzumi, N. Nishizawa and T. Tanaka, Chem. Lett., 1755 (1983).

117. B. M. Shukla, N. P. Singh and N. B. Singh, Molecular Crystals and Liq. Cryst., 104, 265 (1984).

118. A. Giravdeav, A. Louti, M. Gross, J. J. Andre, J. Simon, C. Ho Su and K. M. Kadish, J.Am. Chem.Soc.,105,2917(1983).

119. V. D. Parker, Acta Chem. Scand. Ser, B 38, 125 (1984). CA, 101 : 54493k.

120. G. Beggiato, G. Casalbore, G. Marconi and M. Mustragostino, Montash Chem., 114, 675 (1983);CA,100; 34058y.

121. Y. Yamaguchi, T. Nogami, H. Mikawa, I. Kumadaki and Y. Kobayashi, Bull. Chem. Soc. Jp., 56, 1907 (1983).

122. J. Nath and D. A. Prakash, J. Chem. Eng. Data, 29, 320 (1984).

123. Sh. F. Faizullaev, Opt.-Akust., Elektr. Magn. Issled. Kondons. Serd., 8 (1982); CA, 99 : 146483a.

124. T.K. Nambinaravanan and A.S. Rao, Acustica,53, 264(1983).

125. B. L. Marwein and S. N. Bhat, Acustica, 55, 0000 (1985).

126. K. A. Khaldoyanidi, Z. A. Grankina, I. I. Yakovler and N. V. Protasova, Izv. Sib. Old. Akad. Nauk, SSSR, Ser. Khim Nauk., 85 (1983); CA, 98 : 205161y.

127. M. Tamres, Mol. Complexes, 1, 49 (1973).

128. Z. Kokot and M. Tamres, Inorg. Chem., 14, 2441 (1975).

129. M. Tamres and J. Yarwood, Spectros. Struct. Mol. Complexes, 217 (1973); CA, 81 : 143524q.

130. S. N. Bhat, M. Tamres and M. S. Rahaman, J. Phys. Chem., 77, 2756 (1973).

131. M. Tamres and S. N. Bhat, J.Am.Chem.Soc., 95, 2516(1973).

132. H. Morita and M. Tamres, J.Phys. Chem., 80, 891 (1976).

133. M. Tamres and R. L. Strong, Mol. Assoc., 2, 331 (1979).

134. S. J. Lo and M. Tamres, Can. J. Chem., 61, 1933 (1983).

135. S. J. Lo and M. Tamres, Can. J. Chem., 62, 814 (1984).

136. a) T. Kobayashi and S. Nagakura, Bull. Chem. Soc. Japan, 45, 987 (1972).

b) H. Hayashi and S. Nagakura, Mol. Phys., 19, 45 (1970).

c) M. Yagi and S. Nagakura, Chem.Phys.Lett.,21, 119(1973).

d) S. Matsumoto and S. Nagakura, Mol.Phys.,26,1465(1973).

e) S. Matsumato, S. Nagakura, Y. Shimozory, H. Hayashi and J. Nakamura, Bull. Chem. Soc. Japan, 47, 604(1974).

f) Y. Achiba, K. Nomotu and K. Kimura, J. Phys. Chem., 86, 681 (1982).

137. a) I. Ichemoto, Y. Cao, M. Yamada, H. Kurada, I. Harada, H. Shirakawa and S. Ikeda, Bull. Chem. Soc. Japan, 55, 721 (1982).

b) I. Ichemoto, M. Yamada, T. Sugano and H. Kuroda, Bull. Chem. Soc. Japan, 53, 1871 (1980).

138. L. Zhao, S. Liu and D. Zher, Kexue Tongbao, 28, 28(1983).

139. S. Tomoda and K. Kimura, Chem. Phys., 74, 121 (1983).

140. D. X. Wang, J. B. Chiu, R. S. Ding and J. H. Da, Acta Chim. Sin., 42, 718 (1984).

141. Y. Matsunaga, Bull. Chem. Soc. Japan, 47, 1020, 1589 (1974); 48, 3728 (1975); 53, 3085 (1980).

142. U. Muralikrishna and K. V. Bapanaiah, Fresenius, Z. Anal. Chem., 26, 29 (1972).

143. U. Muralikrishna and K. V. Bapanaiah, Curr. Sci., 42, 460 (1973).

144. U. Muralikrishna and K. V. Bapanaiah, Ind. J. Chem., 12A, 380 (1974).

145. U. Muralikrishna, K. V. Bapanaiah and J. V. Ramanadham, Curr. Sci., 43, 706 (1974).

146. U. Maralikrishna and N. S. Rao, Curr.Sci., 44, 659(1975).

147. U. Muralikrishna, N. S. Rao and G. V. Ramanadham, Curr. Sci., 44, 534 (1975).

148. U. Muralikrishna and K. Bapanaiah, Z. Phys. Chem. (Leipzig), 256, 225 (1975); CA, 83 : 66110f.

149. U. Muralikrishna, N. S. N. Prasad and G.V. Ramanadham, Curr. Sci., 45, 276 (1976).

150. U. Muralikrishna, G. V. Ramanadham and P. Kanna Rao, Acta Cienc. Indica, 2, 344 (1976).

151. U. Muralikrishna, P. Kanna Rao and K. V. Bapanaiah, Ind. J. Chem., 14A, 368 (1976).

152. U. Muralikrishna, K. V. Bapanaiah, N. S. N. Prasad and P. Kanna Rao, Ind. J. Chem., 14A, 291 (1976).

153. U. Muralikrishna and G. V. Ramanadham, J. Ind. Chem. Soc., 53, 95 (1976).

154. U. Muralikrishna, G. V. Ramanadham and N. S. Rao, Fresenius, Z. Anal. Chem., 279, 208 (1976).

155. U. Muralikrishna and N. S. Rao, Acta Cienc. Indica, 5, 188 (1979).

156. U. Muralikrishna, T. V. Ram, R. Sayi and Y.V.S.K. Sesha, Ind. J. Chem., 18A, 372 (1979).

157. U. Muralikrishna, Y. V. S. K. Sesha, R. Sayi and T. V. Ram, J. Indian. Chem. Soc., 56, 794 (1979); 57, 343 (1980).

158. a) U. Muralikrishna, K. V. Bapanayya and P. S. R. Sarma, Ind. Chem. J., 14, 21 (1980).

b) U. Muralikrishna, M. Krishnamurthy and Y. V. S. K. Seshasayi, Ind. J. Chem., 22A, 904 (1983).

c) U. Muralikrishna and M. Krishnamurthy, Spectros. Lett., 16, 711 (1983).

159. U. Muralikrishna and M. Krishnamurthy, Spectrochim. Acta, **40A**, 65 (1984).

160. B. B. Bhowmik and P. Nandy, Spectrochim Acta, **40A**, 173 (1984).

161. B. B. Bhowmik, J. Phys. Chem., **74**, 4442 (1970).

162. B. B. Bhowmik and P. K. Srimani, Spectrochim. Acta, **29A**, 935 (1973).

163. B. B. Bhowmik and M. K. Basu, Ind. J.Chem., **11**, 257(1973).

164. B. B. Bhowmik, D. C. Mukherjee and P. K. Srimani, Ind. J. Chem., **13**, 1314 (1975).

165. M. K. Basu and B. B. Bhowmik, Ind. J. Chem., **13**, 721(1975).

166. B. B. Bhowmik and S. P. Chattopadhyay, Ind. J. Chem., **17A**, 85 (1979).

167. B. B. Bhowmik and S. P. Chattopadhyay. Spectrochim. Acta, **36A**, 543 (1980); **37A**, 5, 135 (1981).

168. B. B. Bhowmik, D. Roy and P. Nandy, Ind. J. Chem., **23A**, 157 (1984).

169. B. B. Bhowmik and T. K. Paul, Spectrochim. Acta, **40A**, 601 (1984).

170. A. Plucinski and L. Skellski, Pol. J. Chem., **55**, 1423 (1981); CA, **98** : 197523a.

171. H. E. Eaton, Jr. and J. D. Strum, Spectroscopy Lett., **15**, 275 (1982).

172. a) S. P. Mishra and R. A. Singh,
J. Chem. Soc. Faraday Trans. I, 78, 1967 (1982).
b) R. Nakata, S. Okazaki and T. Fujinaga,
Electronalytical Chem., 125, 413 (1981).
c) L. Ramaley and S. Gaul, Can. J. Chem., 56, 2381 (1978).
173. M. S. Sambhi and S. K. Khoo,
J. Phys. Chem., 79, 666 (1975)
174. S. Fraga, Comput. Phys. Commun., 29, 351 (1983).
175. R. R. Dogonadze, G. M. Chonishvriti and T. A. Marsagishvili,
J. Chem. Soc. Faraday Trans, 80, 355 (1984).
176. V. Brandani, Fluid Phase Equilib., 12, 87 (1983).
CA, 99 : 94580h.
177. I. Murata, Pure Appl. Chem., 55, 323, (1983).
178. A. V. Zubkov and T. V. Ivanova,
J. Solution Chem., 11, 699 (1982); CA, 98 : 133088e.
179. C. Castiglioni, M. Gussoni and G. Zerbi,
J. Chem. Phys., 80, 3916 (1984).
180. B. K. Seal, A. K. Mukherjee and D. C. Mukherjee,
Z. Phys. Chem., 265, 353 (1984).
181. M. Tamres in "Molecular Complexes", Vol. I, Ed. by
R. Foster, Elek Science, London, 1973.
182. H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc.,
71, 2703 (1949).
183. H. Gaston and L. Klasine, J. Phys. Chem., 76, 2452 (1972).

184. J. H. Hildebrand, J. M. Prausnitz and R. L. Scott, "Regular and Related Solutions", Von Nostrand Reinhold Co., New York, 1970.

185. a) J. D. Childs, S. D. Christian and J. Grundness, J. Am. Chem. Soc., 94, 5657 (1972).

b) R. Foster, B. Dodson, A. S. Bright, M. I. Foreman and J. Gorton, J. Chem. Soc., B, 1283 (1971).

186. W. B. Person, J. Am. Chem. Soc., 87, 167 (1965).

187. R. A. Labudde and M. Tamres, J. Phys. Chem., 74, 4009(1970).

188. D. A. Deronleau, J. Am. Chem. Soc., 91, 4044 (1969).

189. S. D. Christian and E. E. Tucker, J. Phys. Chem., 74, 214 (1970).

190. S. Carter, J. N. Muerrel and E. J. Rosch, J. Chem. Soc., 2048 (1965).

191. R. S. Drago, T. F. Bolles and R. J. Niedzielski, J. Am. Chem. Soc., 88, 2717 (1966).

192. R. J. Bailey, J. A. Chudek and R. Foster, J. Chem. Soc. Perkin Trans., II, 1591 (1976).

193. Ref. No. 185.

194. L. E. Orgel and R. S. Mulliken, J. Am. Chem. Soc., 79, 4839 (1957).

195. M. Tamres and S.N. Bhat, J. Phys. Chem., 75, 1057 (1971).

196. P. Huyskens, P. Mahillon and F. Kapuku, J. Mol. Liq., 25, 13 (1983).

197. C. Castiglioni, M. Gussoni and G. Zerti,
J. Mol. Struct., 115, 319 (1984).

198. M. Chattopadhyay, A. Kumar and R. Basu,
J. Ind. Chem. Soc., 61, 312 (1984).

199. A. Wojtowiez, M. Jerzy and S. Balanicka, CA, 101:22891x;
Bull. Pol. Acad. Sci. Chem., 31, 63 (1983).

200. V. Shanmugasundaram and R. Mohan,
J. Ind. Chem. Soc., 60, 298 (1983).

201. I. C. Wei and R. L. Rowley,
J. Chem. Eng. Data, 29, 336 (1984).

202. A. A. Bugaevskii and V. I. Drupova,
Zh. Fiz. Khim., 57, 1280 (1983); CA, 99 : 11808q.

203. B. A. Zhubanov, G. I. Baiko and S. K. Kudaikulova,
Izc. Akad. Nauk. Kaz. SSR. Ser. Khim. 20 (1983);
CA, 99 : 139241s.

204. S. D. Christian, A. A. Taha and B. N. Gash,
Quart. Rev. Chem. Soc., 24, 20 (1970).

205. P. Job, Annals. Chim., 9, 113 (1928).

206. J. H. Joe and A. L. Jones,
Ind. Eng. Chem. Alalyt. Edn., 16, 111 (1944).

207. F. Gutmann and M. Keyzer,
Electrochim. Acta, 11, 555, 1163 (1963).

208. C. Reid and R.S. Mulliken, J. Am.Chem.Soc., 76, 3869(1954).

209. S. R. Palit, J. Ind. Chem. Soc., 53, 1238 (1976).

210. S. N. Bhat and C.N.R. Rao, J.Am.Chem.Soc., 88,3216(1966).

211. R. A. Zingaro, C. A. Vandewerf and J. Kleinbers,
J. Am. Chem. Soc., 73, 88 (1951).

212. S.B. Shah and A.S.N. Murthy, J.Phys.Chem., 79, 322 (1975).

213. R. M. Bixon and G. Gileadi, J. Phys.Chem.,84, 715 (1980).

214. H. Cheung and M. Tamres, J. Phys. Chem., 81, 1367 (1977).

215. H. Hayakawa and S. Namakura,
Bull. Chem. Soc. Japan, 50, 556 (1977).

216. R. H. Stokes, J. Am. Chem. Soc., 76, 1988 (1954).

217. F. G. K. Baulke, R. Bertran and K. Case,
J. Electroanal. Chem., Interfacial Electro. Chem.,
32, 247 (1971).

218. a) Ref. No. 210.
b) C. N. R. Rao, S. N. Bhat and P. C. Dwivedi,
Appl. Spectros. Rev., 5, 1 (1972).

219. F. Gutmann and M. Keyzer,
Electrochim. Acta, 11, 555, 1163 (1963).

220. a) J. Kleinberg, E. Cotton, J. Sattizahn and
C. A. Vanderwerf, J. Am. Chem Soc., 75, 442 (1953).
b) L. F. Audrieth and E. J. Birr,
J. Am. Chem. Soc., 55, 668 (1933).

221. a) A. E. Beezer, M. Orban and J. V. Tyrrel,
Acta Chem. Acad. Sci. Hung., 99, 415 (1974).

222. J.J.Tonder and A. Borghese, Electrochim. Acta,22, 129(1977).

223. R. D. Srivastava, V. M. Mishra, and P. N. Tripathi,
Electrochimica Acta, 27, 863 (1982).

224. A. K. Trofimchukao, E. Ya. Groenbein,
Zh. Obsch. Khim., 41, 34 (1971); CA, 74 : 146998f.

225. H. Gasten and L. Klasini, J.Phys.Chem., 76, 2452 (1972).

226. M. V. Ramanmurthy and P. V. S. S. Prabhu,
Electrochim. Acta, 27, 481 (1982).

227. J. R. Geoates, R. J. Sullivan and J. B. Ott,
J. Phys. Chem., 63, 589 (1959).

228. C. V. Chaturvedi and S. Prakash, Acusitca, 27, 248 (1972).

229. N. Prasad, O. Prakash, S. Singh and S. Prakash,
Ultrasonics, 16, 77 (1978).

230. M. Karvo and A. Nissema, Finn. Chem. Lett., 132 (1979).

231. M. M. Chaudhury, V. A. Hendric, C. Abbott and
M. Michael, J. Chem. Eng. Data, 25, 254 (1980).

232. T. S. Nguyen, U. V. Dang, H. H. Tran, B. B. Nguyen,
T. H. Trann and N. T. Pham, Tap. Chi. Hoa. Hoc.,
18, 25 (1980); CA; 94 : 53697e.

233. M. Carvo, J. Chem. Thermodyn., 12, 635 (1980).

234. K. Masanao, Bull. Chem. Soc. Jpn., 53, 1937 (1980).

235. M. Karvo, A. Nissema and T. Kaivamo,
Finn. Chem. Lett., 7-8, 137 (1983).

236. M. R. Nayer and K. D. Nayer,
J. Ind. Chem. Soc., 29, 250 (1952).

237. H. A. Heintz and D. N. Hume, J. Phys. Chem., 61, 462(1957).

238. T. Kaivamo, A. Nissema and M. Karvo,
Finn. Chem. Lett., 7-8, 141 (1983).

239. J. Singh, H. D. Pflug and G. C. Benzoo,
J. Phys. Chem., 72, 1939 (1968).

240. I. Nagata and T. Ohta, J. Chem.Eng. Data, 28, 256 (1983).

241. H. M. N. Irving and J. S. Smith,
J. Inorg. Nucl. Chem., 31, 159 (1969).

242. R. A. Singh, S. P. Mishra and S. N. Bhat,
Proc. Ind. Acad. Sci. (Chem. Sci.), 89, 139 (1979).

243. R. A. Singh and S. N. Bhat, Can. J. Chem., 59, 1212 (1981).

244. a) R. A. Singh and S. N. Bhat,
Bull. Chem. Soc. Jpn., 55, 1623 (1982).
b) V. P. Shedbalkar and S. N. Bhat, J. Mol.
Bull. Chem. Soc. Jpn., 57, 852 (1984);
J. Mol. Liquids, 31, 0000 (1985); also, ref. 125.

245. R. Gopal, S. Agarwal and D. K. Agarwal,
J. Ind. Chem. Soc., 55, 501 (1978).

246. H. M. N. Irving and J. S. Smith,
J. Inorg. Nucl. Chem., 31, 3163 (1969).

247. R. P. Shukla and B. P. Bhatnagar,
J. Phys. Chem., 60, 809 (1956).

248. A. N. Campbell and F. M. Kartzmark,
J. Chem. Thermodyn., 5, 163 (1973).

249. W. I. Chien, R. L. Rowley,
J. Chem. Eng. Data, 29, 336 (1984).

250. M. Palma and J. P. Morel, Can. J. Chem., 59, 3248(1981).

251. M. Dizechi and E. Marschall,
J. Chem. Eng. Data, 27, 358(1982).

252. P. Skubla, Colect. Czech. Chem. Commun., 46, 329 (1981).

253. Spectroscopy and Structure of Molecular Complexes,
Ed. by. J. Yarwood, Plenum Press, London, 1973 and
the references therein.

254. a) J. Yarwood and W. P. Person,
J. Am. Chem. Soc. 90, 594 (1968).
b) J. Yarwood, Trans. Farad. Soc. 65, 934 (1969).

255. a) I. Haque and J. L. Wood,
J. Phys. Chem., 72, 2438 (1965); also, ref. 55(b).
b) I. Haque, N. N. Dass and T. Bora,
Ind. J. Chem., 12, 70 (1974).

256. a) S. G. Ginn and J. L. Wood,
Trans. Farad. Soc., 62, 777 (1966).
b) S. G. Ginn, I. Haque and J. L. Wood,
Spectrochim. Acta, 24A, 1531 (1968).

257. J.P. Devlin, J. Phys. Chem., 86, 3064 (1982)
J.P. Devlin, and J. E. Bertic,
J. Chem. Phys., 78, 6340 (1983).
B. Hall and J. P. Devlin,
J. Phys. Chem., 71, 465 (1967).

258. M. Tamres, J. Chem. Edn., 45, 221 (1968).

CHAPTER II

KINETICS OF TRANSFORMATION OF OUTER CHARGE TRANSFER COMPLEXES TO INNER COMPLEXES*

II. 1. INTRODUCTION

The interaction of electron donor 'D' and acceptor 'A' leads to the formation of new molecular species, 'Molecular Complexes' or 'Charge-transfer Complexes'. Mulliken[1] pointed out that a donor acceptor pair can form either the associative "outer complex" or the dissociative "inner complex" depending on the distance of approach between the donor and the acceptor and the relative magnitude of the no-bond or dative wave functions. It was also suggested that the formation of the inner complex from

---

* A paper based on this work has appeared in the Journal of the Indian Chemical Society, 60, 842 (1983).

the outer complex should be strongly dependent on environmental conditions, i.e. the probability of charge-transfer in solution increases with increasing permittivity, ϵ, of the medium. If the environmental influence is sufficiently high, the inner complex may become the stable form of the donor-acceptor pair and with little or no environmental influence the outer complex may represent the stable form.[2] Thus, for a given donor-acceptor pair under a particular set of environmental conditions, one usually observes either an inner complex or an outer complex; the outer complex once formed can transform to the inner complex under favourable conditions. One of the early evidences for the transformation of outer complex to inner complex was the increase in electrical conductance of iodine in pyridine (with time) which was explained on the basis of the equilibrium involving the outer and inner complexes;[3]

$$C_5H_5N + I_2 \rightleftharpoons C_5H_5N.I_2$$

$$C_5H_5N.I_2 \rightleftharpoons (C_5H_5NI)^+ + I^-$$

Outer Complex Inner Complex

An examination of the literature shows that in many donor-acceptor systems with halogen acceptors, the formation of trihalide ion is often noticed, which can only result through the formation of inner complexes from the initial outer complexes.[2,4-28] Typical of such systems are dimethylsulphoxide-iodine, acetonitrile-iodine. It is surprising that even though one can obtain information about the stabilities of the complexes by noting the electrical conductivity of the solution with time (whenever a reaction occurs with a change in the number or kind of ions present so that the electrical conductivity changes, measurement of the resistance/conductance offers a convenient and accurate means of following the course of the reaction), hardly any attempts have been made in this direction. In view of the limited information available in the literature (on the kinetics of transformation of outer molecular complexes into inner complexes) we have investigated the transformation of a few outer complexes between *n*-donors (methanol, ethanol, water and acetonitrile) with iodine (σ-acceptor) with particular reference to the factors affecting the formation of inner complexes.

II. 2. MATERIALS AND METHODS

Methanol, ethanol, acetonitrile and iodine were purified by following the standard procedures, the details of which are given below.[29]

Methyl alcohol (SD's B.N. 031/11/24021) and *Ethyl alcohol* (drum sample) were refluxed over quicklime (which was pre-heated in a Muffel furnace at 500 °C for 5 to 6 hr) and were distilled; care was taken to avoid moisture. These were finally treated with Mg/I_2 cake to obtain absolute methyl alcohol [b.p. 62 °C/662 mm; lit. 64 °C/760mm] and ethyl alcohol [b.p. 76 °C/660 mm; lit. 78 °C/760 mm)]

Acetonitrile (IDPL B. No. 09400182) was refluxed over phosphorus pentoxide for 4-5 hours, distilled and collected in stoppered bottles, [b.p. 79 °C/661 mm; lit. 80°C/760mm]

Iodine (Sarabhai M. Chemicals B. No. 9GP9192) was resublimed thrice from a mixture of 10 g of iodine with 4 g of potassium iodide. The m.p. of iodine was found to be 111 °C (lit 113.5 °C).

Conductivity water was used as such.

A known amout of iodine was dissolved in required amount of solvent (alcohols, water or acetonitrile) which has already been kept in a thermostated jacketed bath (at the required temperature) and the electrical conductivities were noted at 25, 30, and 35 °C (± 0.1 °C). The concentrations of iodine in the solutions were also determined by titrating the iodine solutions with standard sodium thiosulphate solutions and the concentrations of iodine determined by both the methods agreed well (with experimental error limit of ± 0.0001 M); this indicates that iodine has not formed any new compound with the donor, but is attached loosely (reversibly) to the donor /‾Our attempts to determine the electrical conductance of the complexes ($ROH.I^{+}.I^{-}$) in less polar solvent like CH_2Cl_2,etc. were not successful due to very low conductivities of the solutions_7.

As the transformation of outer complex into inner complex occurs with a change (increase) in the number of ions present, the electrical conductivity increases with time and the measurement of electrical conductivity offers a convenient (assuming the conductivity and concentration have a simple relationship at high dielectric constant) means of following the course of the process. The time dependence of electrical conductance of the solutions at 25, 30 and 35 °C were measured by using Elico Conductivity Bridge (Model CM - 82) during the first half an hour. The temperature of the solution was maintained constant (±0.1°C) using a thermostat. The velocity constant for the transformation of outer charge-transfer complex to inner complex was calculated using the first order rate constant

$$k = \frac{1}{t} \ln \frac{a}{a - x} \qquad \ldots \quad \ldots \; II.1.$$

where k = the rate constant; t = time ; a = initial concentration of the reactant ; x = change in concentration of reactant in time t.

The conductivity of any solution depends on (i) the number of charge carriers, (ii) charge on the charge carriers, and (iii) the mobility of the charge carriers. In the present case as the charge on the charge carriers and mobility of the charge carriers (as long as the dielectric constant of the medium, charge on the charge carriers and temperature of the system are constant) are not affected the electrical conductivity of the solution mainly depends on the concentration of the charge-carriers, i.e. ions, which in turn, depend on the concentration of the products; the increase in conductivity of the solution (with time) is a measure of the increase in concentration of the product. So one can calculate the rate constant by measuring the increase in conductance with time and using the equation,

$$k = \frac{2.303}{t} \log \frac{\sigma_{\infty} - \sigma_{0}}{\sigma_{\infty} - \sigma_{t}} \qquad \ldots \quad \ldots \text{ II.2.}$$

where σ_0, σ_∞ and σ_t are the conductivities at 0, ∞ and t time respectively. The rate constants were evaluated by subjecting the experimental data to least square treatment. The energy of activation, E_a, for the transformation was calculated from the Arrhenius equation ($\log k = - E_a/2.303RT + \log A$) (i.e. by plotting log K against 1/T). The uncertainity in the value of E_a was generally ± 400 J/mole. Entropy of activation was determined by using

Eyring equation, from absolute rate theory[30-32]

$$k = \frac{KT}{h} . e^{\Delta S^{\#}/R} . e^{-\Delta H^{\#}/RT} .$$

where, k = rate constant; K = Boltzman's constant,

h = Plank's constant; $\Delta S^{\#}$ = Entropy of Activation;

$\Delta H^{\#}$= Enthalpy of Activation; R = Molar Gas Constant;

T = Temperature in Absolute Unit.

II. 3. RESULTS AND DISCUSSION

Ethyl and Methyl alcohols form 1:1 outer charge-transfer complexes with iodine and their charge transfer bands appear ~225 and 220 nm respectively.[33] The equilibrium constants of formation of these complexes in n-Heptane at 25 °C were 0.95 and 0.65 dm^3 Mol^{-1} while the enthalpy values were 13.398 kJ mol^{-1} and 12.55 kJ mol^{-1} respectively.[12,34] Water-iodine on the other hand does not show any charge-transfer band above 220 nm. Bhowmik and Chattopadhyay[35] have reported that they could detect a band at 202.5 nm for water-iodine system. These observations go in parallel with ionization potentials of the donors. The ionization potentials of EtOH, MeOH and H_2O are 10.49, 10.84 and 12.61 eV respectively.[36] The equilibrium constant for iodine-water system at 25 °C is very low 0.0420[13] M; 1.4×10^{-3} M^{-1}).[37] These results show that the stability of iodine-ROH systems vary in the order Ethanol-Iodine$>$ Methanol-Iodine$>$ Water-Iodine.

Tse and Tamres[33] have reported that the iodine complexes of ethanol and methanol are quite stable in nonpolar solvents like cyclohexane; similarly, iodine complex of DMSO is quite stable in non-polar solvents.[38] As these complexes are quite stable in non-polar solvents the electrical conductivities of these complexes in cyclohexane were very low ($\sim 10^{-12}$ Mho cm^{-1}) and there was no appreciable change in the conductivity with time. When iodine was directly dissolved in methanol (dielectric constant 32.5), ethanol (dielectric constant 24.3), water (dielectric constant 78.5) and acetonitrile (dielectric constant 36.7) the initial electrical conductivities were 0.208×10^{-4}, 0.201×10^{-4}, 1.180×10^{-4} and 3.120×10^{-4} mho cm^{-1} at 25 °C for 0.05 M iodine (except in iodine-water where the concentration of iodine was 0.00125 M) in the respective solvents, and the conductivities increased with time and reached a maximum value in about 24 hours (Table II. 1.). However, for the sake of brevity the variation of electrical conductivities with time, concentration, temperature of iodine-MeOH, iodine-EtOH, iodine-H_2O and iodine-acetonitrile for the first half an hour are given in Tables II.1.—II.IV. It is reported in the literature that the intensities of

Table II. 1.

Variation of Electrical Conductance of Iodine Complexes of Methanol, Ethanol, Water and Acetonitrile, with **Time**

Temp. : 25 °C: Conc. ≙ 0.05 M

Time Minutes	Conductance x 10^4 Mho			
	$MeOH-I_2$	$EtOH-I_2$	H_2O-I_2*	CH_3CN-I_2
0	0.208	0.201	1.180	3.12
1	0.218	0.216	1.191	3.38
2	0.222	0.227	1.205	3.70
3	0.233	0.229	1.209	3.98
4	0.238	0.234	1.212	4.29
5	0.238	0.236	1.215	4.62
10	0.290	0.248	1.227	5.97
15	0.333	0.264	1.232	6.70
20	0.385	0.265	1.235	7.80
25	0.444	0.272	1.238	8.70
30	0.480	0.279	1.241	8.90
⋮	⋮	⋮	⋮	⋮
∞	2.174	0.763	1.302	37.20

* Concentration of Iodine in Water is 0.00125 M.

Error Limit = ± 0.001.

Table II. 2a.

Variation of Electrical Conductance of Iodine Complexes of Methanol with Time at Different Concentrations

Temp. : 25 °C

Time, Minutes	Conductance x 10^4 Mho		
	0.05 M	0.025 M	0.01 M
0	0.208	0.196	0.157
1	0.218	0.208	0.164
2	0.222	0.217	0.169
3	0.233	0.222	0.175
4	0.238	0.227	0.179
5	0.238	0.227	0.182
10	0.290	0.244	0.200
15	0.333	0.250	0.212
20	0.385	0.333	0.222
25	0.444	0.357	0.232
30	0.480	0.377	0.244
⋮	⋮	⋮	⋮
∞	2.174	1.49	0.667

Error Limit = ± 0.001.

Table II. 2b

Variation of Electrical Conductance of Iodine Complexes of Ethanol with Time at Different Concentrations

Temp. : 25 °C

Time, Minutes	Conductance x 10^4 Mho		
	0.01 M	0.025 M	0.05 M
0	0.105	0.130	0.201
1	0.111	0.147	0.216
2	0.176	0.159	0.227
3	0.122	0.167	0.229
4	0.125	0.170	0.234
5	0.126	0.172	0.236
10	0.136	0.183	0.248
15	0.141	0.193	0.264
20	0.150	0.201	0.265
25	0.154	0.210	0.272
30	0.157	0.214	0.279
⋮	⋮	⋮	⋮
∞	0.405	0.508	0.763

Error Limit = ± 0.001.

Table II. 2c

Variation of Electrical Conductance of Iodine Complexes of Acetonitrile with Time at Different Concentrations.

Temp. = 25 °C

Time, Minutes	Conductance x 10^4 Mho		
	0.01 M	0.025 M	0.05 M
0	1.18	1.97	3.12
1	1.28	2.14	3.38
2	1.36	2.18	3.70
3	1.37	2.27	3.98
4	1.43	2.37	4.29
5	1.47	2.61	4.62
10	1.59	2.96	5.97
15	1.68	3.28	6.70
20	1.89	3.67	7.80
25	1.99	3.99	8.70
30	2.06	4.26	8.90
⋮	⋮	⋮	⋮
∞	11.70	23.6	37.20

Error Limit = ± 0.001.

Table II. 3a

Variation of Electrical Conductance of Iodine Complexes of Methanol with Time at Different Temperatures

Conc. = 0.05 M

Time, Minutes	Conductance x 10^4 Mho		
	25 °C	30 °C	35 °C
0	0.208	0.333	0.435
1	0.218	0.364	0.488
2	0.222	0.377	0.526
3	0.233	0.392	0.625
4	0.238	0.400	0.667
5	0.238	0.400	0.714
10	0.290	0.417	0.769
15	0.333	0.435	0.909
20	0.385	0.476	1.00
25	0.444	0.500	1.020
30	0.480	0.526	1.064
⋮	⋮	⋮	⋮
∞	2.174	2.50	2.77

Error Limit = ± 0.001.

Table II. 3b

Variation of Electrical Conductance of Iodine Complexes of Ethanol with Time at Different Temperatures

Conc. = 0.05 M

Time, Minutes	Conductance x 10^4 Mho		
	25 °C	30 °C	35 °C
0	0.201	0.301	0.315
1	0.216	0.309	0.347
2	0.227	0.348	0.358
3	0.229	0.350	0.366
4	0.234	0.360	0.375
5	0.236	0.362	0.380
10	0.248	0.391	0.420
15	0.264	0.405	0.439
20	0.265	0.409	0.461
25	0.272	0.413	0.481
30	0.279	0.422	0.488
⋮	⋮	⋮	⋮
∞	0.763	1.23	1.90

Error Limit = ± 0.001.

Table II. 3c

Variation of Electrical Conductance of Iodine Complexes of Acetonitrile with Time at Different Temperatures.

Conc. = 0.05 M

Time, Minutes	Conductance x 10^4 Mho		
	25 °C	30 °C	35 °C
0	3.12	3.37	4.08
1	3.38	3.94	4.59
2	3.70	3.99	4.98
3	3.98	4.48	5.35
4	4.29	5.38	5.92
5	4.62	5.97	6.28
10	5.97	8.10	8.17
15	6.70	9.12	10.20
20	7.80	10.90	11.10
25	8.70	12.0	12.80
30	8.90	12.80	13.20
⋮	⋮	⋮	⋮
∞	37.20	39.70	43.80

Error Limit = ± 0.001.

Table II. 3d

Variation of Electrical Conductance of Iodine Complexes of Water with Time at Different Temperatures

Conc. = 0.00125 M

Time, Minutes	Conductance x 10^4 Mho		
	25 °C	30 °C	35 °C
0	1.180	1.435	1.764
1	1.191	1.449	1.931
2	1.205	1.477	2.092
3	1.209	1.479	2.174
4	1.212	1.481	2.242
5	1.215	1.488	2.398
10	1.227	1.511	2.688
15	1.232	1.520	2.874
20	1.235	1.524	3.049
25	1.238	1.534	3.145
30	1.241	1.541	3.257
⋮	⋮	⋮	⋮
∞	1.302	1.667	4.587

Error Limit = ± 0.001.

charge-transfer bands of MeOH-I_2, EtOH-I_2, acetonitrile-I_2 and H_2O-I_2 decreases with increase in time and accompanying the decrease in the intensity of the charge-transfer band, progressive intensification of the triiodide ion absorption (at 297 and 363 nm) is noticed.[1] So it is felt that the time dependence of the electrical conductivity (i.e. increase in conductivity with time) is due to the transformation of the initially formed outer charge-transfer complex followed by the very fast reaction of the inner complex with iodine to form the triiodide ion.

$$\underset{}{R.OH + I_2} \rightleftharpoons \underset{\text{(Outer Complex)}}{ROH.I_2} \xrightarrow{\text{slow}} \underset{\text{(Inner Complex)}}{(ROHI^+)I^-}$$

$$(ROHI^+)I^- + I_2 \overset{\text{fast}}{\rightleftharpoons} (ROHI)^+ + I_3^-.$$

($R = CH_3$, C_2H_5, H or $ROH = CH_3CN$).

The kinetics of transformation of the outer complexes of iodine, namely $CH_3OH.I_2$, $C_2H_5OH.I_2$, $H_2O.I_2$, $CH_3CN.I_2$ to the inner complexes were studied employing the time dependence of the electrical conductivities of the solutions. Since the formation of the triiodide ion from the inner complex is likely to be a fast step, the rate determining step will be the transformation of the outer complex to inner complex. The reactions are of pseudo first order (Fig. II. 1) and the rate constants are quite large. (It

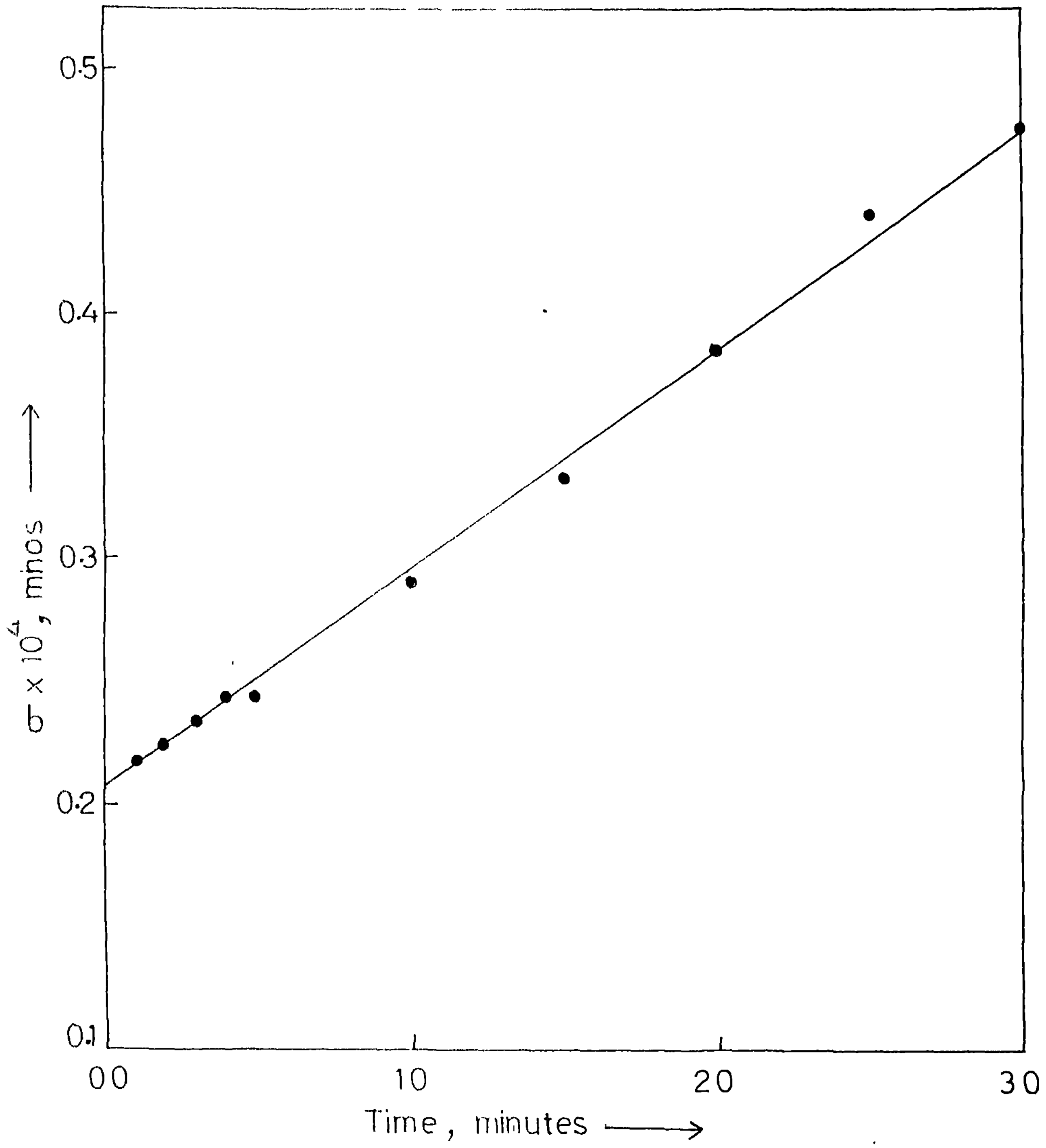

Fig. II. 1. Variation in the Electrical Conductivity of MeOH-I_2 with Time
Conc. of I_2 = 0.05 M; Temp. = 25 °C.

appears that in these cases, the driving force is the solvation of ions formed). The rate data are summarised in Table II. 4 and II. 5 along with the values of activation energies and entropies of activation (the enthalpy values are included for comparison). It can be seen from the data (Table II. 4) that the velocity constant for the transformation of outer complex to inner complex increases with concentration of the reactants/complexes (which is expected). The transformation of the outer complex of $C_2H_5OH.I_2$ to the inner complex is much slower and is associated with higher activation energy than the transformation of $CH_3OH.I_2$. In all these systems, the activation energy for the transformation of the outer complex to inner complex is small. The activation energy decreases with the increase in dielectric constant of the medium. It is interesting to note that the enthalpy value for the formation of the outer complex is also much lower in the latter case. In the case of $C_2H_5OH.I_2$, where the enthalpy ($-\Delta H^0$) value is higher, the transformation would be expected to be much slower than $CH_3OH.I_2$. Water, on the other hand, seems to form a less stable outer complex (very low $-\Delta H^0$) with iodine which can be visualized due to high I.P. of water (12.61 eV). The low $-\Delta H^0$ value facilitates the easier transformation of outer complex to inner complex.[1]

Table II. 4

The Velocity Constants for the Transformation of Outer Charge-Transfer Complexes into Inner Complexes at Different Concentrations

Temp. = 25 °C

System	Average K#, $Min^{-1} \times 10^3$			
	Concentration (M)			
	0.05	0.025	0.01	0.00125
$MeOH-I_2$	5.73	5.04	4.62	-
$EtOH-I_2$	3.17	2.38	1.68	-
$Water-I_2$	-	-	-	13.4
$Acetonitrile-I_2$	4.23	3.12	1.77	-

Error limit in the value of K = ± 0.002.

Table II. 5

The Velocity Constant, Entropy of Activation, Activation Energy for the Transformation of Outer Charge-Transfer Complexes into Inner Complexes (Concentration of Iodine = 0.05 M)

System	Average K^a Min^{-1} x 10^3			Average Entropy of Activation $-\Delta S^b$, $JK^{-1}M^{-1}$	Activation Energy, E_a^c, J/mole x 10^3	$-\Delta H^o_,$ d kJ/mole
	25 °C	30 °C	35 °C			
Methanol-Iodine	5.73	8.32	15.8	75.7	73.4	12.55 (7.94)^e
Ethanol-Iodine	3.17	4.89	6.30	152.3	52.3	13.39 (8.78)^e
Water-Iodine**	13.40	14.50	20.10	212.7	30.4	7.80^f
Acetonitrile-Iodine	4.23	5.78	7.78	162.2	48.5	7.95

** Concentration of Iodine in Water = 0.00125 M.

a) Error limit in the value of K = ± 0.002

b) Error limit in the value of ΔS = ± 3 J K^{-1} M^{-1}.

c) Error limit in the value of E_a = ± 400 J $K^{-1}M^{-1}$.

d) Appl. Spectros. Revs., 5, 1)(1972).

e) J. Chem. Phys., 26, 1192 (1957).

f) Indian J. Chem., 17A, 85 (1979).

On the basis of these findings it is possible to propose a potential energy diagram of the type shown in Fig. II. 2 for the formation of outer complex (- ΔH) as well as the energy activation, E_a, for the transformation of outer to inner complex. A stable outer complex (associated with greater charge-transfer in the ground state as well as a higher value of - ΔH) shows a larger E_a for the transformation of outer charge-transfer complex. The velocity constant for the transformation of outer complex of water-iodine (in water) to inner is 13.4×10^{-3} min^{-1} at 25 ^{o}C (conc. = 1.25×10^{-3} M) indicating that the transformation is quite fast. This can be easily visualized in terms of high polarity of the medium. Similar cases have been reported in the literature for triphenyl phosphine-iodine, etc. in highly polar solvents.[39-41]

Acetonitrile forms an outer complex with iodine and the velocity constant and the activation energy for the transformation of outer to inner complexes are given in Table II. 5. Eventhough the interactions involved are $\underline{n}$-σ type, it is not possible to compare the data with those of $ROH.I_2$ systems as ROH (R = CH_3, C_2H_5, H) is inter-molecularly hydrogen bonded systems.[34]

The **entropy** of activation is large and negative in all the systems that we have studied. The negative $\Delta S^{\neq}$

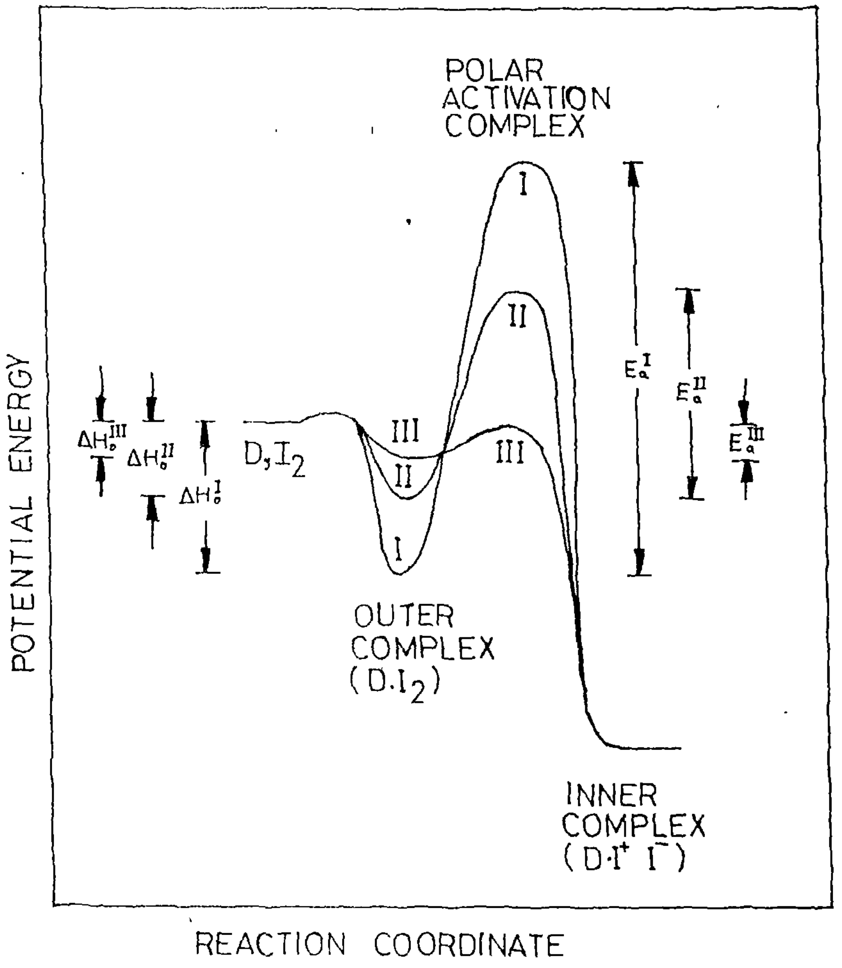

Fig. II. 2. Potential energy diagram for the formation of outer and inner complexes between donors (D) and iodine. Three cases (I, II and III) are shown with progressively decreasing - H^o of formation of the outer complex and E_a. Case III is for a system which may not form the outer complex, but directly gives the inner complex, while case I is for a system which forms a stable outer complex and may not form the inner complex with ease. Case II is an intermediate case. Dielectric constant of the medium or substituent effects affect E_a appreciably. For the sake of simplicity the energy of the inner complex is shown to be the same for all the cases.

values are indeed what one would expect in reactions involving ionization of neutral molecules.[30,31] Since the transformation of the outer to the inner complex involves ionization, it is likely that the activated complex is also similar to an ion pair, and will therefore be stabilized by solvation to a greater extent than the outer complex (initial state).[42] The negative entropy indicates that the activated complex is less probable (and the reaction should be slower than normal) and the probability factor P is very low.[30] In the present case, methanol, ethanol and water already exist in a partially frozen state due to strong intermolecular forces - hydrogen bonding. So we are not in a position to comment on the reverse trend of activation energies when these solvents are used. The loss in entropy in an ionization includes, the change in entropy of the complex (molecules) which ionizes and the change in entropy of the solvent molecules which surround the ions.

From the above study it appears that the rate determining step in the formation of triiodide ion is probably the transformation of the outer complex and it follows the first order rate law and the ease with which the transformation proceeds depends on the relative magnitude of enthalpy of formation of the outer charge transfer complexes. It is possible that in some cases, the inner complex may be the more stable form, particularly in solvents favouring solvation of the inner complex or its ions.

REFERENCES

1. a) R. S. Mulliken, J. Phys. Chem., 56, 801 (1952).
   b) R. S. Mulliken and W. B. Person, "Molecular Complexes" — A Lecture and note volume, Wiley Interscience, New York, 1969.
2. S. N. Bhat and C. N. R. Rao, J. Am. Chem. Soc., 88, 3216 (1966).
3. R. S. Mulliken and C. Reid, J.Am. Chem.Soc., 76, 3869(1954).
4. A. I. Popov and W. A. Deskin, J. Am. Chem. Soc., 80, 2976 (1958).
5. F. G. K. Baucke, R. Bertram, and K. Cruse, J. Electroanal. Chem. Interfacial Electrochem., 32, 247 (1971).
6. D. Wobschall and D. A. Norton, J. Am. Chem. Soc., 87, 3559 (1965).
7. G. Beggiato, G. Casalbore, G. Marconi, M. Mastragostino, Montasch Chem., 114, 675 (1983); CA, 100 : 340584.
8. R. A. Zingaro, C. A. Vanderwerf and J. Kleinberg, J. Am. Chem. Soc., 73, 88 (1951).
9. L. S. Lilich and . E. Presnikova, Serkhim. Nauk., 12, 3 (1953); CA, 49 : 5939 (1955).
10. M. S. Sambhi and S. K. Khoo, J. Phys. Chem., 79, 666(1975).
11. M.D. Alan and W.J. Robin, J. Chem. Phys., 75, 993 (1979).

12. P. Hyskens, N. Felix, A. Janssens, F. Vonden Brieck and F. Kapuk, J. Phys. Chem., 84, 1387 (1980.
13. D. de Maine, J. Chem. Phys., 26, 1192 (1957).
14. R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc., 75, 3561 (1953).
15. C. R. Das and A.N. Bose, Bull.Chem.Soc.Jpn.,46, 818(1973).
16. J. Larry, M. Bennett, W. Farl and W. B. Person, J. Am. Chem. Soc., 91, 6915 (1969).
17. S. B. Shah and A. S. N. Murthy, J. Phys. Chem., 79, 322 (1975).
18. W. B. Person, W. C. Golton and A. I. Popov, J. Am. Chem. Soc., 85, 891 (1963).
19. N. Kulevsky and G.K. Liu, J. Phys. Chem., 74, 751 (1970).
20. J. B. Ainscough and E. F. Caldin, J. Chem. Soc., 2528, 2540, 2546 (1956).
21. U. Muralikrishna and N. Someswara Rao, J. Ind. Chem. Soc., 57, 524 (1980).
22. Z. B. Alfassi and P. M. Golden, J. Phys. Chem., 76, 3314 (1972).
23. L. F. Audrieth and E. I. Birr, J. Am. Chem. Soc., 55, 668 (1933).
24. S. Fukuzumi and J. K. Kochi, J. Phys. Chem.,84, 617(1980).
25. A. W. D. Ghazi and Z. M. Kassir, Bull. Coll. Sci., 9, 31 (1966).

26. P. C. Dwivedi, A. K. Banga and R. Agarwal, Electrochim. Acta, 27, 169 (1982).

27. M. Yamamoto, T. Sano, S. Harada and T. Yasunaga, Bull. Chem. Soc. Japan, 55, 3702 (1982).

28. T. Samo, M. Yamamoto, H. Hori and T. Yasunaga, Bull. Chem. Soc. Jpn., 57, 678 (1984).

29. a) S. M. Brandon, M. Tamres and S. Searles, Jr., J. Am. Chem. Soc., 82, 2129 (1960).

    b) A. Weissberger, Ed., "Techniques of Chemistry", Vol. II, "Organic Solvents", Wiley Interscience, New York, 1970.

    c) "A Text Book of Practical Organic Chemistry" by A. I. Vogel, 4th Ed., 1978.

30. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd ed., Wiley International Edition, New York, 1961.

31. K. J. Laidler, "Chemical Kinetics", 3rd ed., Tata McGraw Hill Publishing Co. Ltd., New Delhi, 1976.

32. S. W. Benson, "The Foundation of Chemical Kinetics", McGraw Hill Book Company, New York, 1960.

33. H. C. Tse and M. Tamres, J. Phys. Chem., 81, 1367 (1977).

34. H. C. Tse and M. Tamres, J. Phys. Chem., 81, 1376 (1977).

35. B. B. Bhowmik and S. P. Chattopadhyay, Ind. J. Chem., 17A, 85 (1979).

36. Hand Book of Chemistry and Physics, 58th Ed.,(1977-1978).

37. J. D. Burger and H. A. Liebhafsky,
Anal. Chem., 45, 600 (1973).

38. P. Klaeboe, Acta Chem. Scand., 18, 18 (1964);
CA, 60 : 15305 (1964).

39. K. R. Bhaskar, S. N. Bhat, S. Sing and C. N. R. Rao,
J. Inorg. Nucl. Chem., 28, 1915 (1966).

40. R. Sahai, P. C. Pande and V. Singh,
Ind. J. Chem., 18A, 217 (1979).

41. R. Sahai and V. Singh, Ind. J. Chem., 19A, 1003 (1980).

42. W. F. K. Wynne-Jones and H. Eyring,
J. Chem. Phys., 3, 492 (1935).

CHAPTER III

CONDUCTOMETRIC STUDY OF CHARGE TRANSFER COMPLEXES*

III. 1. INTRODUCTION

The interaction of electron donor 'D' and electron acceptor 'A', leads to the formation of new molecular species : Molecular Complexes or Charge-transfer complexes. Mulliken[1] pointed out that a donor-acceptor pair can form either the associative "outer complex" or the dissociative "inner complex" depending on the distance of approach between the donor and the acceptor and the relative magnitude of the no bond or dative wave functions. It was also suggested that if the environmental influence is sufficiently high, the inner complex may become the stable form of the donor-acceptor pair, and with little or no environmental influence the outer complex may represent the

---

* A paper based on this work has been communicated for publication in Electrochimica Acta.

stable form.[2] When the interaction between the donor and acceptor is very strong and the dielectric constant of the medium is high, the complex may dissociate into ions giving rise to appreciable ionic conductivity, according to the general scheme,[1-4]

$$D + A \rightleftharpoons DA$$

$$DA \rightleftharpoons D^{+}A^{-} \rightleftharpoons D^{+} + A^{-} \quad \ldots III.1.$$

(Outer Complex) (Inner Complex)

The formation of inner (charge-transfer) complex can be followed by measuring the changes in the electrical conductivities of the solutions, of say, the donor in an inert (or nearly inert) solvent of sufficiently high permittivity, upon addition of a solution of acceptor in the same solvent or vice versa.[4-21]

For determining the equilibrium constant and the other thermodynamic parameters, either by Benesi-Hildebrand[22] or the modified forms of Benesi-Hildebrand,[17,23,24] one must know the stoichiometry of the complex. The usual method — Job's[25] Continuous Variation procedure, is of limited application when the outer complex is transformed into inner complex, due to, say environmental cooperation, leaving behind only a small amount of neutral complex in solution. Under such circumstances one may be able to obtain the stoichiometry of the complex in highly polar media by measuring the electrical conductivities of the solutions by following the procedure suggested by Gutmann and Keyzer.[6] So, we have made an attempt in this direction to obtain information on the nature of interaction between the donor and acceptor, the stoichiometry of the complex in polar media, the effect of concentration, temperature and dielectric constant of the medium on the electrical conductivities of the complexes in solutions. For this purpose, the electron donors chosen are acetone, methyl ethyl ketone, iso-butyl methyl ketone, dimethyl sulphoxide, triphenylphosphine, triphenylarsine, triphenylstibene, methanol, ethanol, n-propanol (all n-donors) and the electron acceptor chosen is iodine (σ-acceptor). The solvents used are acetonitrile and mixtures of acetonitrile and carbontetrachloride.

III. 2. MATERIALS AND METHODS

III. 2(i) Materials:

The electron donors, namely acetone, methyl ethyl ketone, iso-butyl methyl ketone, dimethylsulphoxide, triphenyl phosphine, triphenyl arsine, triphenyl stibene, methanol, ethanol and n-propanol and the electron acceptor iodine were purified following the standard procedures.[26]

Acetone (Sarabhai M. Chemicals, B.N. 1H8 11052) was refluxed with successive small quantities of potassium permanganate until the violet colour persists. It was then dried with anhydrous potassium carbonate, filtered from the desiccant and distilled. Precautions were taken to exclude moisture. B.P. 52.5 $^{\circ}$C/662 mm (lit. 56.2/760 mm).

Methyl Ethyl Ketone (BDH, B.N. L326/20.3610) and iso-Butyl Methyl Ketone (BDH, B.N.L353/10-2612) were dried with anhydrous calcium sulphate, filtered and distilled. The boiling points of methyl ethyl ketone was 77 $^{\circ}$C/662 mm (lit. 79.5 $^{\circ}$C/760 mm), whereas that of iso-butyl methyl ketone was found to be 107 $^{\circ}$C/661 mm (lit. 110 $^{\circ}$C/760 mm).

Dimethyl sulphoxide (SD's B.N. 28089/9840) was kept over calcium sulphate overnight, refluxed over KOH and distilled and collected over molecular sieves of 5A (B.P. 187 $^{\circ}$C/662 mm; lit. 189 $^{\circ}$C/760 mm).

Triphenyl phosphine (Aldrich, USA), Triphenyl arsine (Aldrich, USA) and Triphenyl stibene (Aldrich, USA) were used as such.

Methyl alcohol, Ethyl alcohol, n-propyl alcohol were purified by following the procedures given in Chapter II.

The procedure for purifying Iodine is described in Chapter II.

Acetonitrile was purified following the procedure given in Chapter II.

One litre of Carbon tetrachloride (BDH, B.N. L084/974602) was treated with potassium hydroxide, dissolved in an equal weight of water and 100 ml of rectified spirit and the mixture vigorously shaken for 30 minutes. After washing with water, the process was repeated with half the quantity of potassium hydroxide. The alcohol was then removed by shaking several times with water, followed by shaking well with small portions of concentrated sulphuric acid until there was no further colouration. Carbon tetrachloride was then dried overnight over anhydrous calcium chloride and distilled. B.P. 74 °C/662 mm (lit. 76 °C/760 mm).

III. 2(ii). Method:

The stock solutions (0.1 M) of electron donors were prepared in acetonitrile and acetonitrile-CCl_4 mixtures of various compositions for obtaining media of different dielectric constants. For obtaining the stoichiometry of the complex formed, the conductivities of the solutions containing different amounts of donors and acceptors (keeping the total volume constant) were measured at constant temperature. In conductometric titration, a known volume (of known concentration) of either the donor or the acceptor solution was taken in the conductivity cell which was thermostated and the acceptor or the donor solution (in the same solvent) was added from burette; the solution was stirred after each addition and a constant time interval (~5 min) was permitted to elapse between the addition of titrant and the bridge adjustment. The electrical conductivity of donor solutions, acceptor solutions (of different strengths) and their mixed solutions were measured at 25, 30, 35 and 40 °C (± 0.1 °C) in different dielectric media. (For obtaining media of different dielectric constant, appropriate amounts of acetonitrile and carbontetrachloride were mixed). Philips PR 9500 conductivity bridge was used for measuring the electrical conductivities of the solutions. The cell constant was 1.5.

Acetonitrile, which is used as solvent, has low conductivity and the conductivity of the solution appears to be mainly ionic. The stoichiometry of the complex may be deduced from the conductivity peak by slightly modifying the procedure which was originally suggested by Gutmann and Keyzer[6].

The total net conductivity, σ, of a given system of non-interacting charge carriers is given by,

$$\sigma = e \sum [n_i z_i \mu_i] \quad \ldots \quad \ldots \quad \text{III.2.}$$

where i is the different species of charge-carriers present, n_i is the concentration of each species having a valence Z_i (i.e. the number of electronic charge carried), μ_i is the mobility of the species and the summation has to be extended over all the i species of charge carriers.

If there is only a negligible interaction between the different carrier species, so that each moves as if the other were absent (i.e. the law of independent migration holds good), the addition of a solution of conductivity σ_A to another solution of conductivity, σ_D, gives rise to conductivity σ given by,

$$\begin{aligned} \sigma &= \sigma_D + \sigma_A \\ &= Ze\,[\,C_D(\mu_D + C_A\mu_A)\,] \qquad \ldots \text{ III.3.} \end{aligned}$$

where C_D and C_A are the concentration of the solutes D and A respectively, and the μ's refer to the mobilities of the carriers contributed by the D and A solution. We shall assume that $Z = 1$ for all the carriers, concentration will be used instead of activities and the conductivity of the solvent (or medium) will be neglected.

In a titration, where the volume changes upon addition of titrant, donor and acceptor, are supplied to the system in concentrations, C_D^o and C_A^o, respectively, so that

$$\left.\begin{aligned} C_D^{\,o} &= D_o C_o^{\,D}/(A_o + D_o) \\ C_A^{\,o} &= A_o C_o^{\,A}/(A_o + D_o) \end{aligned}\right\} \quad \ldots\ldots \quad \text{III. 4}$$

where D_o and A_o refer to the volumes of stock solutions of D and A, with concentrations, $C_o^{\,D}$ and $C_o^{\,A}$, respectively, which have been supplied to the system, e.g., from a burette.

If there is no interaction between donor and acceptor (neglecting the solute-solvent interactions), then $C_D = C_D^{\,o}$ and $C_A = C_A^{\,o}$. Since the conductivities are additive, it follows that, δ, in the absence of interaction should be linearly related to the concentration of the titrant (Fig. III. 1).

Considering now, a case where charge-transfer does occur, resulting first in the formation of a complex, DA, followed by its dissociation into ions D^+ and A^- (i.e. transformation of outer charge-transfer complex into inner complex) and thus giving rise to excess conductivity (above any due to the solvent and stock solutions themselves). Let, the concentration of the complex DA be given by C_{DA} and the concentrations of D^+ and A^- be $C_D^{\,+}$ and $C_A^{\,-}$ respectively. C_D and C_A refer to the concentration of unreacted donor and acceptor, i.e., $(C_D^{\,o} - C_{DA})$ and $(C_A^{\,O} - C_{DA})$.

For the interaction of D and A (1:1), we can write

(a) complex formation: $D + A \rightleftharpoons DA$

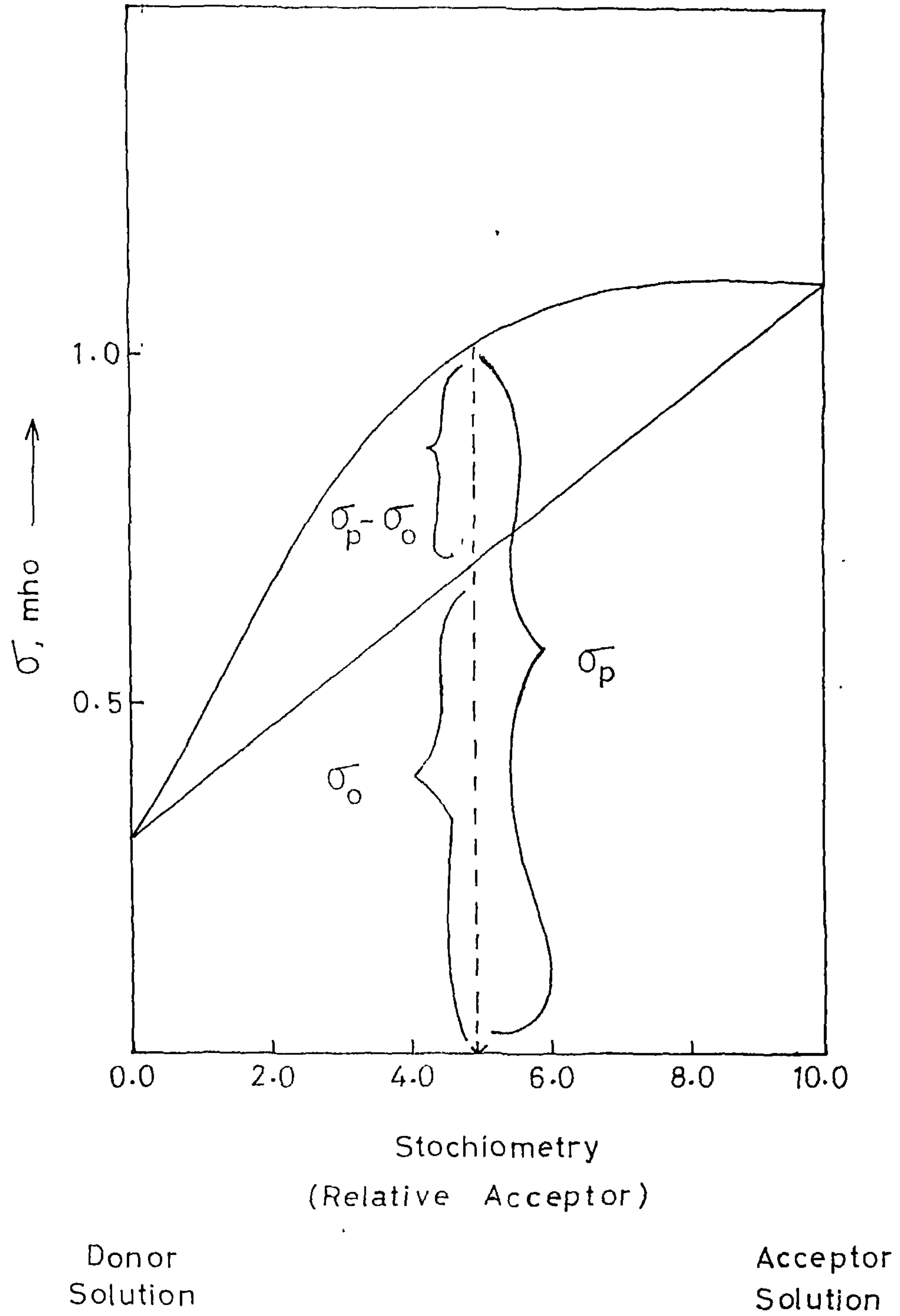

Fig. III. 1. Idealised plot for Conductometric Titration.

$$K_1 = \frac{C_{DA}}{C_D . C_A} = f(\epsilon, T) \qquad ....III.5.$$

(b) complex dissociation:

$$DA \rightleftharpoons D^+ A^- \rightleftharpoons D^+ + A^-$$

$$K_2 = \frac{C_D^+ . C_A^-}{C_{DA}} = f'(\epsilon, T...) \qquad ....III.6.$$

(c) direct transfer and recombination:

$$D^+ + A^- \rightleftharpoons D + A$$

$$K_3 = \frac{C_D . C_A}{C_D^+ . C_A^-} = f''(\epsilon, T)..) \qquad ....III.7.$$

The solution must be electrically neutral.

$$C_D^+ = C_A^- = n \qquad ....III.8.$$

The conductivity, $\sigma = en(\mu^+ + \mu^-)$

$$= \sigma_0 n \qquad ... \qquad ....III.9.$$

Now, $C_D \neq C_D^o$ and $C_A \neq C_A^o$ and the charge carriers, D^+ and A^-, are present in the solution. Assuming that the contact charge-transfer interaction is negligible, we can write,

$$\left.\begin{aligned} C_D &= C_D^o - C_{DA} - n \\ C_A &= C_A^o - C_{DA} - n \end{aligned}\right\} \qquad ....III.10.$$

From III.5 and III.6, we get,

$$\frac{C_D^+ . C_A^-}{C_D . C_A} = K_1 K_2 = K_3^{-1} \qquad ....III.11.$$

Introducing n from III.8 and comparing with III.7, we obtain,

$$\left.\begin{aligned} \frac{C_D . C_A}{n^2} &= K_3 (=K_1 K_2)^{-1} \\ C_{DA} &= \frac{n^2}{K_2} \end{aligned}\right\} \quad \ldots . \text{ III. 12.}$$

Equation III.10 becomes,

$$\left.\begin{aligned} C_D &= C_D^o - \left[\frac{n^2}{K_2} + n \right] \\ C_A &= C_A^o - \left[\frac{n^2}{K_2} + n \right] \end{aligned}\right\} \ldots . \text{ III. 13.}$$

Combining III.12 and III.13, we get,

$$\left[C_D^o - \left(\frac{n^2}{K_2} + n \right) \right] \left[C_A^o - \left(\frac{n^2}{K_2} + n \right) \right]$$
$$= n^2 K_3$$
$$= n^2 (K_1 K_2)^{-1} \quad \ldots . \text{ III. 14.}$$

The conductivity, σ, which is proportional to n, thus follows as fourth power relation to the added donor or acceptor. However, it can be seen that n, and thus σ, is a maximum for $C_D^o = C_A^o$, i.e., for 1:1 complex.

So, equating dn/dC_D^o to zero yields,

$$- C_A^o + \left(\frac{n^2}{K_2} \right) + n = 0 \ldots . \text{ III. 15.}$$

But, from III.13, $n + (n^2/K_2) = C_D^o - C_D$, and σ

will be peak if,

$$C_D^o - C_D = C_A^o \qquad \text{.... III.16.}$$

By combining III.10 and III.16,

$$n + C_{DA} = C_A^o \qquad \text{.... III.17.}$$

From III.10,

$$n + C_{DA} = C_A + n + C_{DA} \qquad \text{..III.18.}$$

So that,

$$C_A = 0; \quad C_D = 0 \quad \text{and} \quad C_D^o = C_A^o \qquad \text{..III.19.}$$

or, in terms of titrating solutions:

$$\left.\begin{aligned} D_oC_o^D &= A_oC_o^A \\ D_o/A_o &= [C_o^D/C_o^A]^{-1} \end{aligned}\right\} \qquad \text{....III.20.}$$

Thus, the stoichiometry of the complex may be deduced from the titration volumes at the end point, i.e., the conductivity peak and from the known concentrations of the stock solutions.

The above derivation assumes both the donor and the acceptor to be univalent resulting in a 1:1 complex. (The same treatment applies to other stoichiometries. The sharp conductivity peak is to be expected only for ideal cases).

The value for the conductivity peak above the base line connecting the conductivity of the donor and acceptor solutions is a measure of the excess conductivity caused by the formation and subsequent dissociation of the complex. The molar conductivity coefficient, δ_m, was calculated using the well known equation of Gutmann.[6]

$$\delta_m = \left(\frac{1}{\alpha M}\right)\left[\frac{\delta_p - \delta_o}{\delta_o}\right] \quad \text{....III.21.}$$

$$\alpha\delta_m = \left(\frac{1}{M}\right).\left[\frac{\delta_p - \delta_o}{\delta_o}\right]$$

where, α is the dissociation constant of the complex, M is the molar concentration of the titrant (either donor or acceptor) at the conductivity peak where $\delta = \delta_p \cdot \delta_o$ is linearly interpolated conductivity background read off a base line joining the conductivities of pure donor and pure acceptor solutions.

III. 3. RESULTS AND DISCUSSION

III. 3(i) IODINE COMPLEXES OF ACETONE, METHYL ETHYL KETONE, iso-BUTYL METHYL KETONE AND DIMETHYLSULPHOXIDE:

It is well known that the electrical conductivity of iodine in pyridine changes with time and this has been ascribed to dissociation of the loosely bound donor-acceptor interaction product to form N-iodo-pyridinium iodide, an inner (ionic) complex.[3] It is reported in the literature that the iodine complexes of acetone, ethyl methyl ketone are not stable, that too in highly polar solvent (The absorption of CT peaks of these complexes decrease with the increase in time). In the present case, iodine, acetone, methyl ethyl ketone, iso-butyl-methyl ketone and dimethyl sulphoxide were dissolved separately in acetonitrile and the conductivities of "pure" solutions (whereever feasible) and those of the mixed solutions were measured. For the sake of brevity the electrical conductivity data of iodine complexes of acetone, methyl ethyl ketone, iso-butyl methyl ketone and dimethyl sulphoxide at one temperature and one concentration are summarised in Table III. 1. It can be seen from the Table III. 1 and Fig. III. 2 that the electrical conductivity of iodine in acetonitrile (0.01 M) which was initially 1.25 x 10^{-4} (the low conductivity is due to few I^- formed) has increased with the addition of acetone (0.01 M, keeping the total volume/concentration constant, i.e. 5 ml of 0.01 M) and reached a maximum value of 1.54 x 10^{-4} Mho and then started decreasing with further addition of acetone. (The conductivity of the complex rises linearly, though slowly, with time. This may be due to the slow dissociation of the complex as well as due to the adsorption on the electrode). The decidedly non-linear plot in an isomolar series indicates the presence of a complex. A peak becomes evident at a

Table III. 1

The Electrical Conductivity Data of Iodine Complexes (of Isomolar Series) of Acetone, Me-Et-Ketone, iso-Bu-Me-Ketone and Dimethylsulphoxide in Acetonitrile

Temp. :: 25 °C; Conc. of Iodine Solution : 0.01 M

Conc. of Ketone/DMSO sol.: 0.01 M

Volume of donor added (ml)	Volume of Iodine soln. added (ml)	Conductivity x 10^4 Mhos*			
		Acetone-I_2	Me-Et-Ketone-I_2	iso-Bu-Me-Ketone-I_2	DMSO-I_2
0.0	5.0	1.25	1.25	1.25	1.25
0.5	4.5	1.40	1.54	1.75	1.56
1.0	4.0	1.51	1.61	1.81	1.64
1.5	3.5	1.54	1.64	1.85	1.69
2.0	3.0	1.49	1.51	1.75	1.63
2.5	2.5	1.39	1.44	1.64	1.49
3.0	2.0	1.20	1.28	1.43	1.34
3.5	1.5	1.00	1.11	1.20	1.16
4.0	1.0	0.77	0.83	0.95	0.91
4.5	0.5	0.48	0.56	0.64	0.61
5.0	0.0	0.25**	0.30**	0.40**	0.38**

* Error Limit : ± 0.01; ** Extrapolated Value.

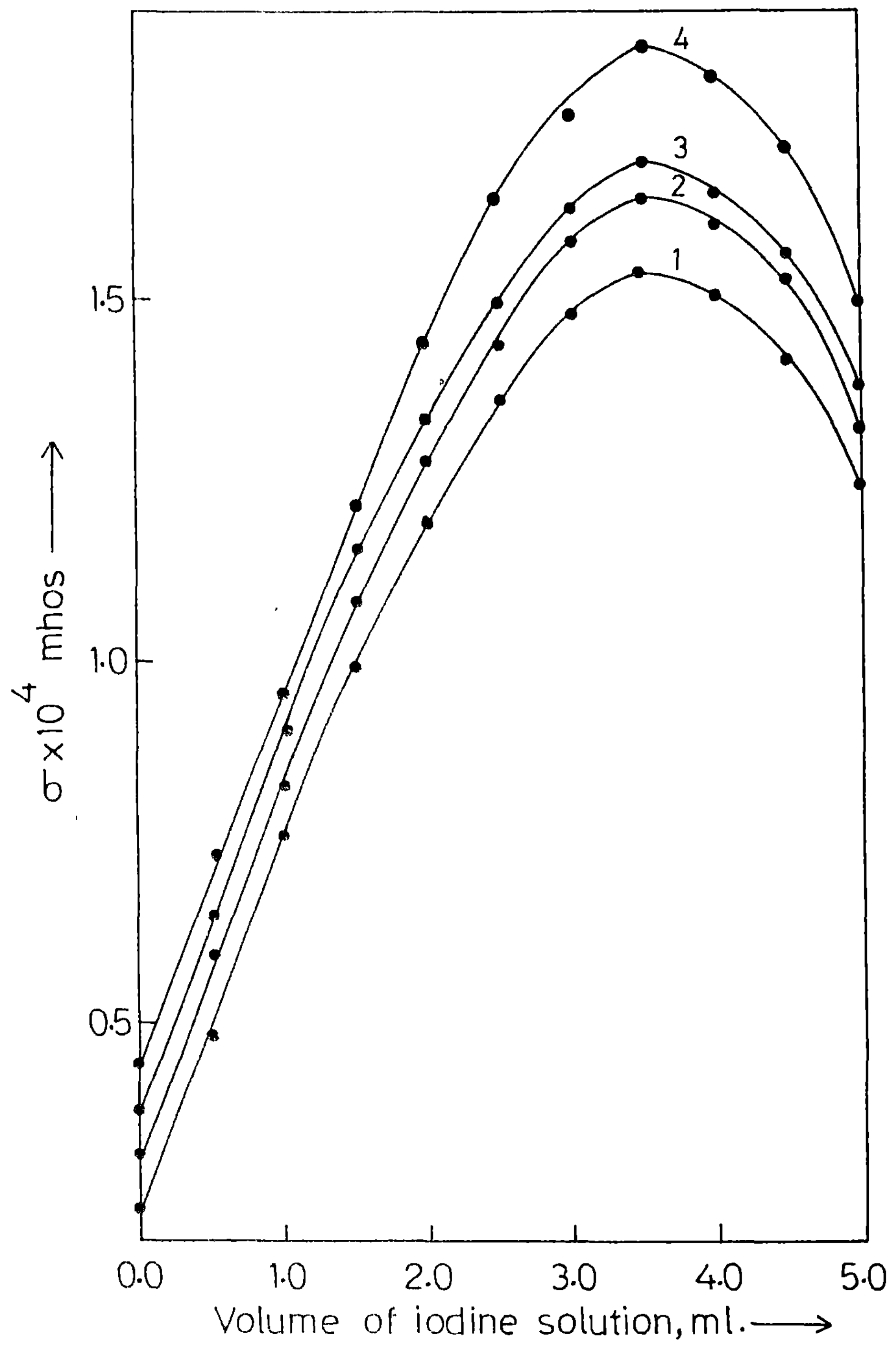

Fig. III. 2. Variation of Electrical Conductivity of Ketones/DMSO-I_2 Systems (Isomolar) at 25 °C. Conc. = 0.01 M.

Solvent :: Acetonitrile.

1. Acetone-I_2; 2. Methyl Ethyl Ketone-I_2;

3. DMSO-I_2; 4. iso-Butyl Methyl Ketone-I_2.

stoichiometry of 2:3 (D:A). (It must be noted here that due to non-ideal behaviour the conductivity peaks occur slightly off the stoichiometry).

In conductivity measurements correct choice of the solvent is also important. If its conductivity is too high, conductance changes due to complex formation may become obscured, if its permittivity is too low, the complex may fail to dissociate. If the solubility of the complex is low, the complex might precipitate which may even lead to the reduction of the number of charge carriers present in solution and cause the appearance of a conductivity minimum in the titration. If the solvent itself can function as an electron donor or acceptor, then it may compete with the reagents and actively enter into the reaction and thus may affect the stoichiometry, equilibrium constants etc. In the present case, acetonitrile and aacetonitrile-carbon tetrachloride mixtures are used as solvent. It is well known that acetonitrile itself has donor character. So it is possible that acetonitrile may compete with ketones/DMSO for forming complexes (with iodine). In addition, even the donors (ketones/DMSO) may also interact with carbon tetrachloride which is a weak electron acceptor. So in such cases one has to take into consideration all these aspects before coming to a definite conclusion about the stoichiometry of the complex. The preliminary experimental results for the determination of stoichiometry of acetone-iodine in acetonitrile and acetonitrile-carbon tetrachloride mixtures by refractometric method showed that the stoichiometry of the complex was 2:3, whereas for acetone-iodine in cyclohexane it was 1:1. (We have made an attempt to determine the stoichiometry of acetone-iodine complex in cyclohexane by conductometric titration method using Keithley 610 High Resistivity Meter ,and it was really heartening to note that the stoichiometry of the complex was found to be ≈1:1. Our further attempts to study these in detail was not successful due to the limitation of the instrument). Here it can be noted that in the case of pyridine-iodine, Gutmann and coworkers[6] have noticed (during the conductometric studies) the change in stoichiometric ratio from 1:1 to 2:3 and 1:3 when the solvent was changed from acetonitrile to carbon tetrachloride and they feel that acetonitrile is an inert solvent towards pyridine-iodine, whereas pyridine can interact with carbon tetrachloride. So we feel that our present results, i.e. the stoichiometry of ketone/DMSO-I_2 (2:3) in acetonitrile and acetonitrile-carbon tetrachloride mixtures is not contradicting the literature data (obtained by spectral method), i.e. the 1:1 stoichiometry of ketone/DMSO-Iodine in cyclohexane/heptane). In fact, as pointed out earlier, the conductometric studies can be successfully used to know the stoichiometry of such complexes which dissociate in polar media and where the concentration of undissociated species may so low that it may be difficult for spectroscopic studies.

In order to understand the effect of media on the electrical conductivities of solutions, the media dielectric constants were changed by mixing appropriate amounts of acetonitrile with CCl_4.[2] It can be seen from Table III.2 and Fig. III.3 that the dielectric constant of the media affects the electrical conductivities. As the dielectric constant of the medium is increased from 15 to 36.7 (the dielectric constant of the medium can be changed either by changing the solvent or by mixing appropriate amounts of two solvents of different dielectric constants. The latter method is better as the "nature" of interaction between solute and solvent remains the same whereas in the former it differs due to the difference in nature of solvents. So, we have varied the dielectric constant of the medium by varying the compositions of the mixtures of CH_3CN and CCl_4 to eliminate the contribution of varying degrees of solute solvent interaction), the electrical conductivity increases, probably due to the increase in the degree of dissociation of the complex (and hence increase in the number of charge carriers) and the increase in the mobilities of the charge

Table III. 2

Effect of Dielectric Constant on the Electrical Conductivity of Acetone-Iodine System at 25 °C

Solvent :: Acetonitrile + Carbon tetrachloride

Concentration of Iodine Solution ≈ 0.01 M

Concentration of Acetone Solution= 0.01 M.

Volume of Acetone Solution (ml)	Volume of Iodine Solution (ml)	Conductivity, x 10^4 Mhos*			
		$\epsilon = 36.7$	$\epsilon = 30$	$\epsilon = 25$	$\epsilon = 15$
0.0	5.0	1.25	0.52	0.24	Resistance of the solution was too high ($>10^6$ Ohm)
0.5	4.5	1.40	0.63	0.29	
1.0	4.0	1.51	0.69	0.30	
1.5	3.5	1.54	0.71	0.31	
2.0	3.0	1.49	0.69	0.29	
2.5	2.5	1.39	0.65	0.28	
3.0	2.0	1.20	0.59	0.26	
3.5	1.5	1.00	0.53	0.23	
4.00	1.00	0.77	0.42	0.18	
4.5	0.5	0.48	0.33	0.14	
5.0	0.0	0.25**	0.20**	0.09**	

* Error Limit: ± 0.01; ** Extrapolated Value.

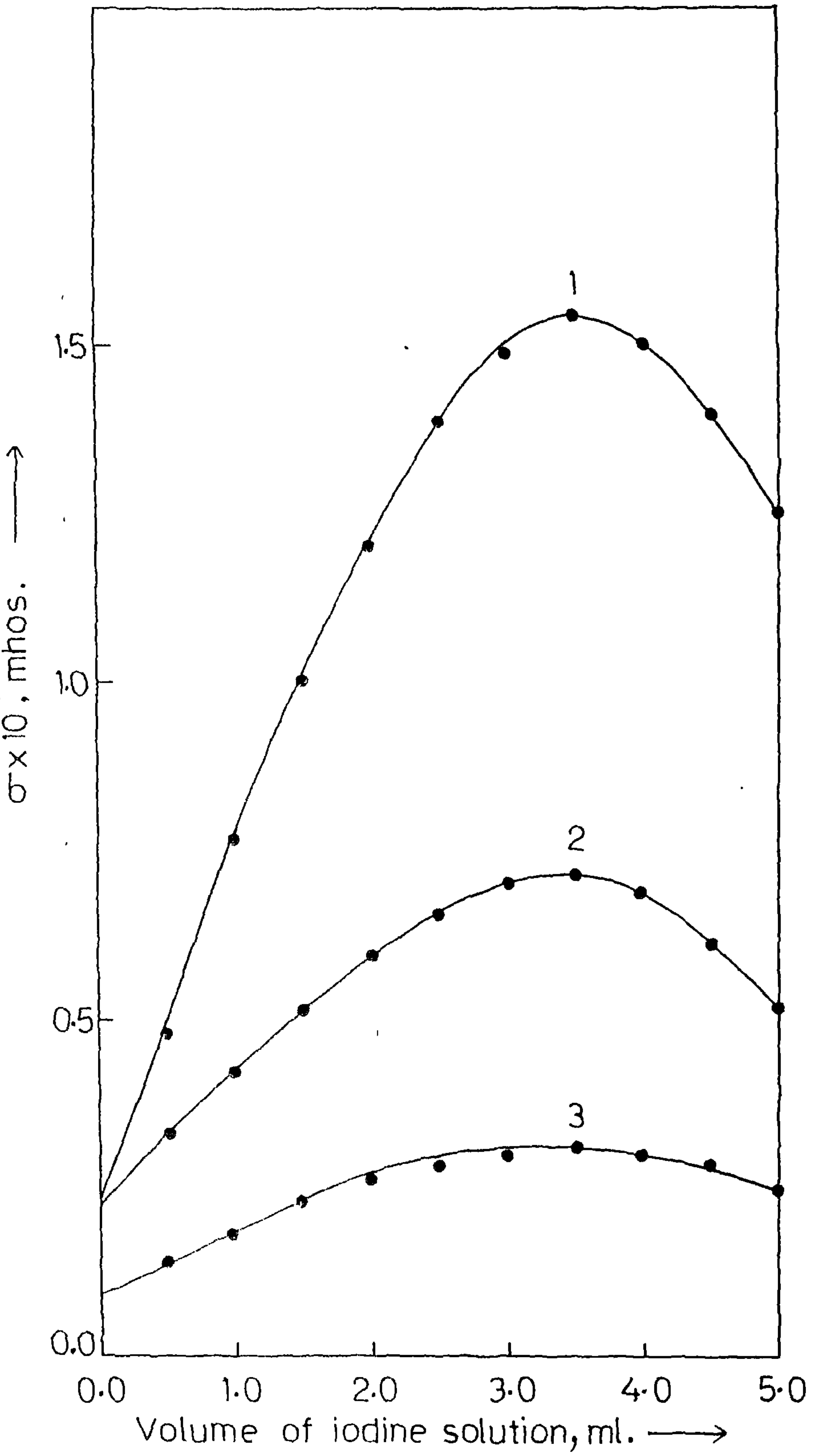

Fig. III. 3. Effect of Dielectric Constant of the Media on the Electrical Conductivity of Acetone-I_2 (Isomolar) System at 25 °C. Conc. = 0.01 M.
1. ϵ = 36.7; 2. ϵ = 30; 3. ϵ = 25.
Solvent :: Acetonitrile + Carbon Tetrachloride

carriers. These results are in harmony with our earlier findings where it has been shown that the rate of electron transfer in EDA complexes is enhanced by solvent polarity (ref. 2,7,27). A general trend of decrease in electrical conductivity with decrease in the dielectric constant of the media has been observed in all the cases we have studied.

It has been mentioned earlier that the conductivity of any solution depends on the number of charge carriers, the charge on the charge carriers and on the mobilities of charge carriers. In the present case (i.e., transformation of outer complex into inner complex) the number of charge carriers depend on the concentration of the complex and on the degree of dissociation of the complex (assuming the charge of the ion as one). As the concentrations of each of the donor as well as acceptor are increased from 0.005 M to 0.02 M the electrical conductivities (at the peak) increase from 0.95×10^{-4} Mho to 3.23×10^{-4} Mho at 25 °C. (Table III. 3 and Fig. III. 4). This increase in conductivity with the increase in concentration of the donor/acceptor is probably due to an increase in number of charge carriers.

The conductivity depends on the mobility of the charge carriers in addition to the number of charge carriers. When the temperature of the solution is increased, the

Table III. 3

Effect of Concentration on the Electrical Conductivity of Acetone-I_2 System at 25 °C

Solvent :: Acetonitrile

Volume of Acetone Solution (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^4 MHo*		
		0.005 M	0.01 M	0.02 M
0.0	5.0	0.83	1.25	2.86
0.5	4.5	0.87	1.40	3.03
1.0	4.0	0.91	1.51	3.17
1.5	3.5	0.95	1.54	3.23
2.0	3.0	0.91	1.49	3.04
2.5	2.5	0.80	1.39	2.67
3.0	2.0	0.71	1.20	2.35
3.5	1.5	0.62	1.00	1.89
4.0	1.0	0.46	0.77	1.35
4.5	0.5	0.30	0.48	0.77
5.0	0.0	0.10**	0.25**	0.36**

* Error Limit : ± 0.01; ** Extrapolated Value.

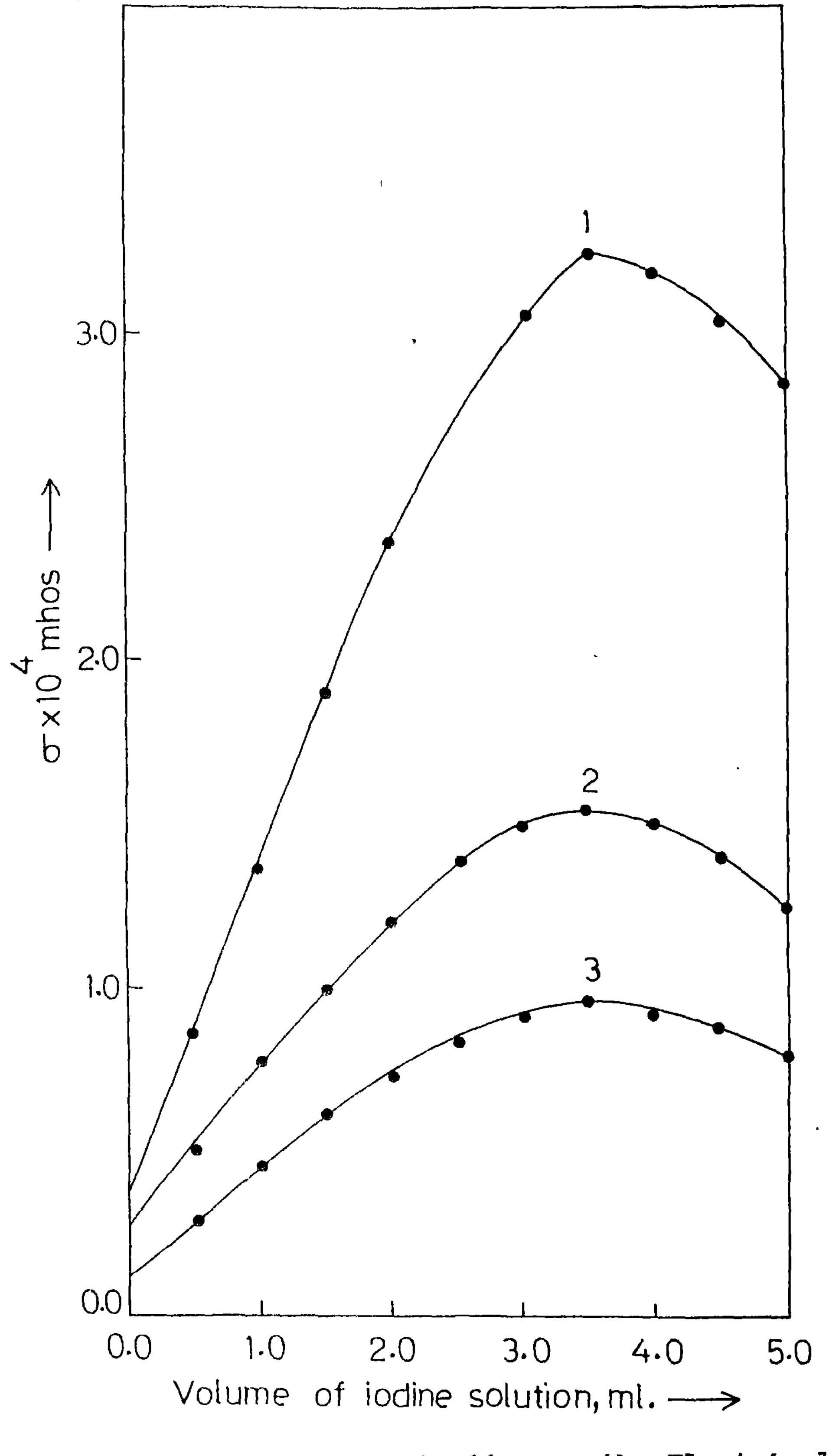

Fig. III. 4. Effect of Concentration on the Electrical Conductivity of Acetone-I_2 (Isomolar) System at 25 °C.

1. 0.02 M; 2. 0.01 M; 3. 0.005 M.

Solvent :: Acetonitrile.

number of charge carriers (due to the dissociation of the complex into free components) and the mobilities of the charge carriers will be affected. In the present case (i.e. in transformation of outer complex to inner complex) when the temperature of the system is increased, the equilibrium constant for the formation of complex decreases, i.e. the amount of complex formed will be less and hence the number of ions formed (from the complex) will be less (i.e., the number of charge carriers is reduced). However, the mobility of the charge carriers increases with temperature (assuming the solvation number and hence the size of the solvated ions do not change with temperature which may not be true always). So, the conductivity of the solution can increase or decrease depending upon which factor will be more predominant (as the temperature is increased). In acetone-iodine, we have observed an increase in conductance with increase in temperature (Table III. 4 and Fig. III.5). So it appears in the present case, increase in the mobility of the charge carriers is more responsible for the increase in conductance.

The electrical conductivities of iso-molar solutions of methyl ethyl ketone, *iso*-butyl methyl ketone, dimethyl sulphoxide-iodine complexes were also determined. at different temperatures (25, 30, 35 and 40 °C), at different

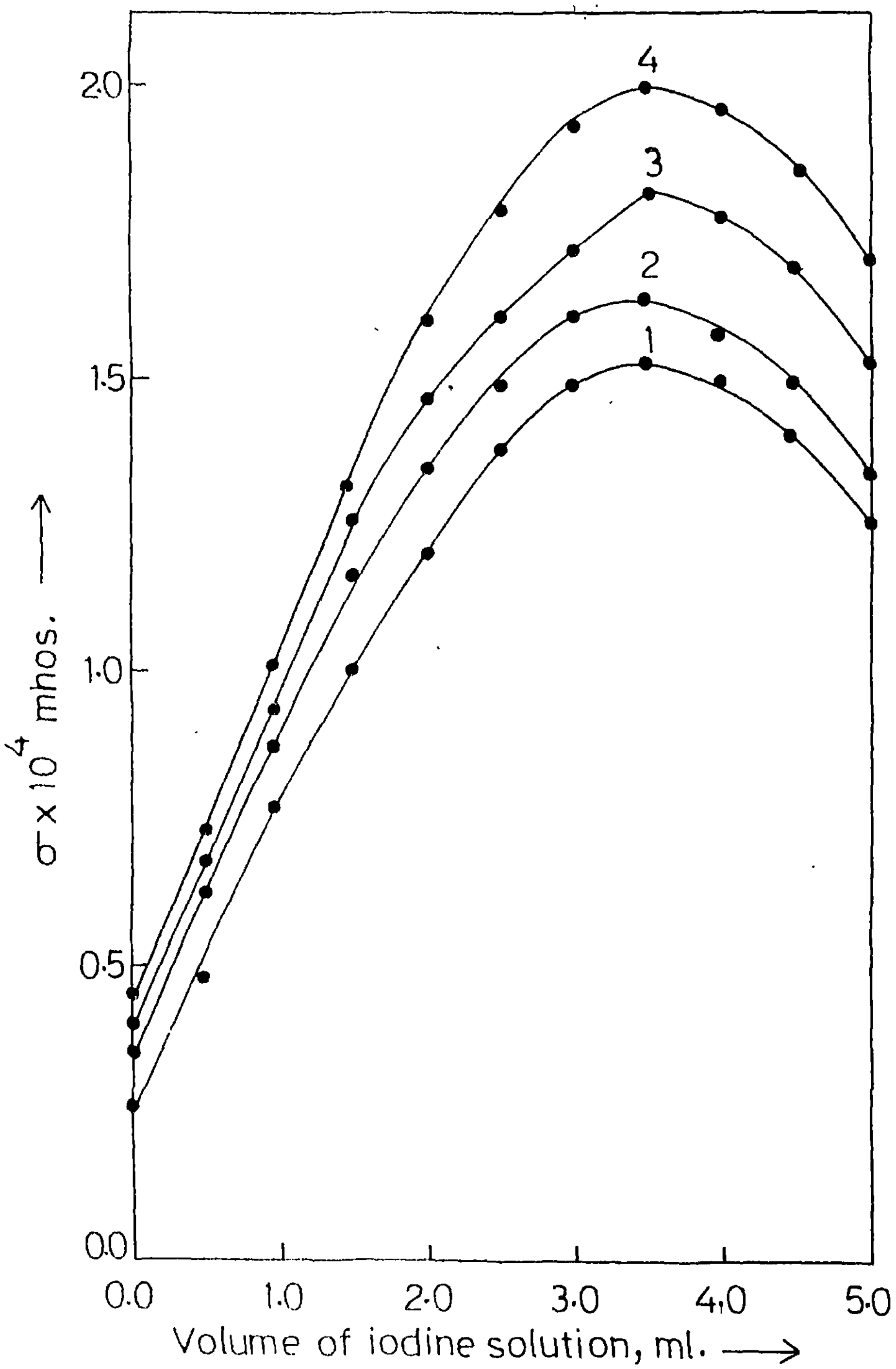

Fig. III. 5. Effect of Temperature on the Electrical Conductivity of Acetone-I_2 (Isomolar) System. Solvent :: Acetonitrile. Conc: 0·01M

1. 25 °C; 2. 30 °C; 3. 35 °C; 4. 40 °C.

Table III. 4

Effect of Temperature on the Electrical Conductivity of Acetone-Iodine System

Solvent :: Acetonitrile

Concn. of Iodine Solution = 0.01 M

Concn. of Acetone Solution = 0.01 M

Volume of Acetone Solution (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^4 Mhos*			
		25 °C	30 °C	35 °C	40 °C
0.0	5.0	1.25	1.33	1.54	1.72
0.5	4.5	1.40	1.47	1.70	1.85
1.0	4.0	1.51	1.58	1.79	1.96
1.5	3.5	1.54	1.64	1.82	2.00
2.0	3.0	1.49	1.61	1.72	1.92
2.5	2.5	1.39	1.49	1.61	1.79
3.0	2.0	1.20	1.35	1.47	1.59
3.5	1.5	1.00	1.18	1.26	1.31
4.0	1.0	0.77	0.87	0.91	1.00
4.5	0.5	0.48	0.59	0.65	0.69
5.0	0.0	0.25**	0.35**	0.39**	0.43**

* Error Limit : ± 0.01; ** Extrapolated Value.

concentrations and in different dielectric media. But for the sake of brevity the data at only one temperature and one concentration are reported in Table III.1. It can be seen from the Table III. 1 and Fig. III. 2 that methyl ethyl ketone, iso-butyl methyl ketone, dimethylsulphoxide also form $\approx 2:3$ complexes with iodine in acetonitrile. (However, in spectroscopic studies non-polar solvents have been used and the stoichiometries are reported to be 1:1). The electrical conductivities of methyl ethyl ketone-, iso-butyl methyl ketone-, dimethyl sulphoxide-iodine complexes at 25 °C for maximum deviation are 1.64×10^{-4}, 1.85×10^{-4} and 1.69×10^{-4} Mho respectively (conc. : 0.01M). The equilibrium constants and the other thermodynamic parameters show that the stabilities of the complexes vary in the order DMSO-$I_2 >$ iso-butyl methyl ketone-$I_2 >$ methyl ethyl ketone-$I_2 >$ acetone-I_2 in cyclohexane and the electrical conductivity of these complexes vary in the same order (except DMSO-I_2). However, one must be cautious before commenting on the stability of the complexes solely depending on the slight difference in the electrical conductivities of the solutions. It can be recalled that the equilibrium constant of formation of the complex depends on the nature of solvent. (Moreover, the enthalpy values reported in the literature do not have any such trend).

So it is not possible to compare conductivity data with that of thermodynamic data (which are obtained under different conditions).

Dimethyl sulphoxide forms an outer complex with iodine and under favourable conditions, the outer complex formed is transformed into inner complex,[14,28] (just like in the case of acetone-iodine complex). It is expected that the non-bonding electron of sulphur/oxygen will be taking part in the complexes. Klaboe et al[29] have reported that in DMSO-I_2 and acetone-I_2, the shift in IR frequency are $\Delta\bar{\nu}(C=S) = 30-60\ cm^{-1}$ and $\Delta\bar{\nu}\ (C=O) = 15-50\ cm^{-1}$, i.e., in both case the $\Delta\nu$, (that is, shift in $\nu_{C=S}$ and $\nu_{C=O}$) are nearly the same. So our present conductivity data go in parallel with those of Klaboe et al,[29] who has come to similar conclusion from the IR studies of DMSO-I_2 and acetone-I_2 complexes (but the medium was different) indicating that these complexes are probably of nearly the same strength. Moreover, the enthalpy values for both the complexes are also equal (-15.5 kJ/mole), eventhough the equilibrium constants are quite different.[29,30]

III. 3(ii) IODINE COMPLEXES OF TRIPHENYL PHOSPHINE, TRIPHENYL ARSINE AND TRIPHENYL STIBENE:

The conductance measurements of iodine complexes of triphenyl phosphine, triphenyl arsine and triphenyl stibene at different concentrations (0.02, 0.01 and 0.005M) were carried out in acetonitrile and acetonitrile-carbon tetrachloride mixtures (dielectric constants of 36.7, 30, 25 and 15) and at different temperatures (25, 30, 35 and 40°C). For the sake of brevity, as in earlier cases, the conductance data at one temperature and one concentration (0.01 M) are reported in Table III.5 and Fig. III.6. Triphenyl phosphine-iodine and triphenyl arsine-iodine systems have the conductance maxima at ~2:3 (lit. 1:1)[14] stoichiometry whereas triphenyl stibene-iodine has conductance maximum at ~1:4 stoichiometry. (The difference in stoichiometry of the complex may be due to solvent effect).

At 25 °C, the electrical conductivities (at the maximum point, i.e. at the approximate stoichiometry) of ϕ_3P-I_2, ϕ_3As-I_2 and ϕ_3Sb-I_2 complexes were 11.11 x 10^{-4}, 7.14 x 10^{-4} and 5.41 x 10^{-4} Mho respectively (conc. : 0.01 M), i.e., the electrical conductivities vary in the order $\phi_3P-I_2 > \phi_3-As-I_2 > \phi_3-Sb-I_2$. It will be interesting to note that the stabilities (i.e., enthalpies) of these complexes vary in the reverse order, i.e. $\phi_3P-I_2 < \phi_3As-I_2 <$

Table III. 5

The Electrical Conductivity Data of Iodine Complexes of Triphenyl phosphine, Triphenyl Arsine and Triphenyl Stibene at 25 °C

Solvent :: Acetonitrile

Concentration of Iodine Soln.: 0.01 M

Concentration of ϕ_3P/ ϕ_3As/ ϕ_3Sb : 0.01 M

Volume of ϕ_3P/ ϕ_3As/ ϕ_3Sb Soln. (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^{-4} Mhos*		
		ϕ_3P-I_2	ϕ_3As-I_2	ϕ_3Sb-I_2
0.0	5.0	1.25	1.25	1.25
0.5	4.5	4.55	3.57	3.51
1.0	4.0	7.41	5.88	5.41
1.5	3.5	9.09	6.67	4.17
2.0	3.0	11.11	7.14	3.70
2.5	2.5	9.52	6.45	3.33
3.0	2.0	8.00	5.88	3.03
3.5	1.5	5.88	5.00	2.63
4.0	1.0	4.17	4.00	2.08
4.5	0.5	2.27	2.13	1.25
5.00	0.0	1.0**	0.85**	0.50**

* Error Limit :: ± 0.01; ** Extrapolated Value.

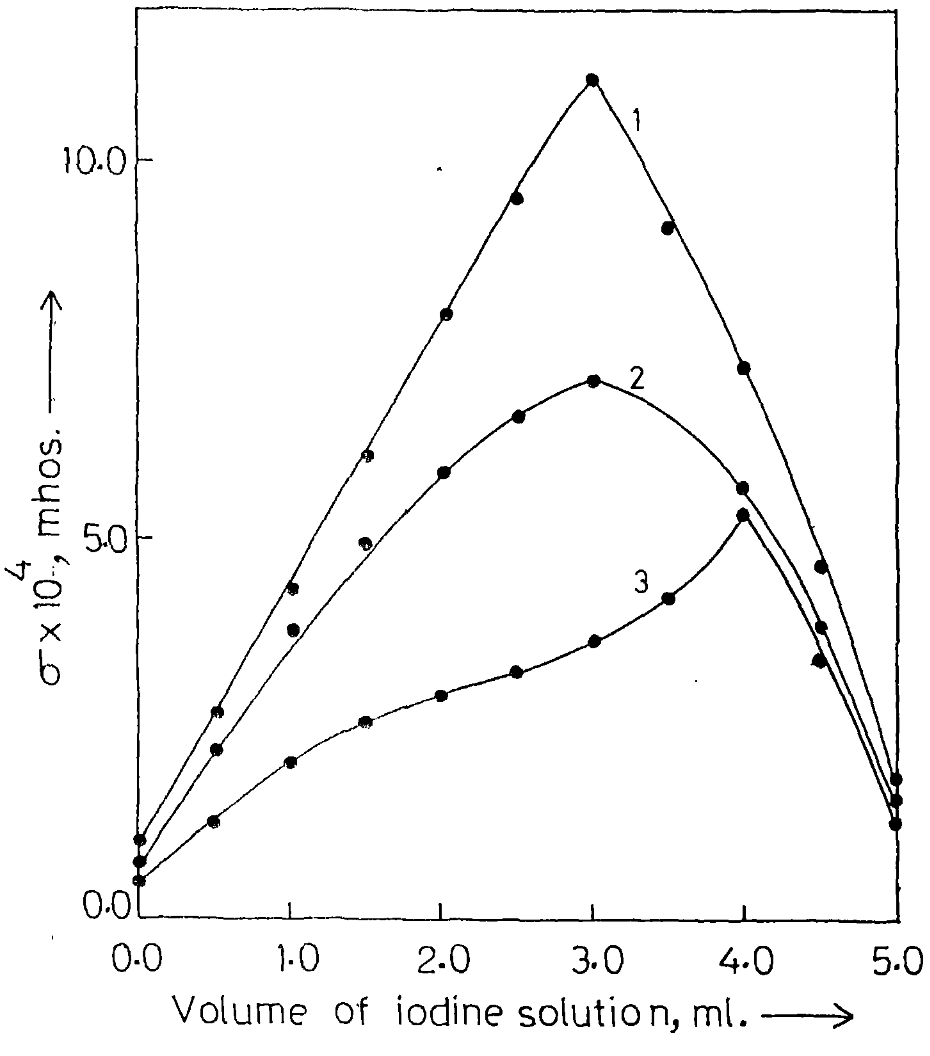

Fig. III. 6. Variation of Electrical Conductivity of ϕ_3P-I_2, ϕ_3As-I_2 and ϕ_3Sb-I_2 (Isomolar) Systems in Acetinitrile at 25 °C.

1. ϕ_3P-I_2; 2. ϕ_3As-I_2; 3. ϕ_3Sb-I_2.

Conc : 0·01M

ϕ_3Sb-I_2.[14] These data show that as the stability of the complexes increase the rate of transformation of outer to inner complexes decreases and due to the decrease in number of charge carriers, the electrical conductivity decreases. So our present electrical conductivity data are (in conformity with the expectation) as anticipated. For the sake of brevity, the effect of concentration, temperature and dielectric constant of media on iodine complexes of ϕ_3P are given in Table III. 6 (Fig. III. 6; III. 7 and III. 8). Triphenyl arsine and triphenyl stibene behave in similar way. The conductivities increase with increase in concentration (due to increase in the number of charge carriers), increase with increase in temperature (due to increase in mobility of charge carriers and also partly due to increase in dissociation rate), and decrease with decrease in dielectric constant of the medium (due to decrease in mobilities) as in the case of Ketones-I_2 complexes. However, in the case of ϕ_3As the stoichiometry of the complex changes from 2:3 to 1:4 as the dielectric constant of the media changes from 36.7 to 15 (Table III. 6d and Fig. III. 9. [Similar unusual observations were made (in our laboratory) in the case of pyridine-iodine and picolines-iodine]. It was difficult to obtain reliable value of conductivity data and hence the stoichiometry of the complex in low dielectric

Table III. 6a

Effect of Concentration on the Electrical Conductivity of Triphenyl phosphine-Iodine

Temp. : 25 °C Solvent : Acetonitrile

Volume of ϕ_3P Solution (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^4 Mhos*		
		0.005 M	0.01 M	0.02 M
0.0	5.0	0.83	1.25	2.86
0.5	4.5	2.56	4.55	7.14
1.0	4.0	4.17	7.41	11.76
1.5	3.5	5.13	9.09	13.33
2.0	3.0	6.06	11.11	14.29
2.5	2.5	5.71	9.52	13.33
3.0	2.0	5.26	8.00	11.76
3.5	1.5	4.17	5.88	10.53
4.0	1.0	2.94	4.17	8.00
4.5	0.5	1.54	2.27	4.76
5.0	0.0	0.10**	1.00**	1.90**

* Error Limit :: ± 0.01; ** Extrapolated Value.

Table III. 6b

Effect of Temperature on the Electrical Conductivity of Triphenyl phosphine-Iodine System in Acetonitrile Solvent

Concentration of Iodine Solution = 0.01 M

Concentration of ϕ_3P Solution = 0.01 M

Volume of ϕ_3P Solution (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^4 Mhos*			
		25 °C	30 °C	35 °C	40 °C
0.0	5.0	1.25	1.33	1.54	1.72
0.5	4.5	4.55	5.56	5.80	6.67
1.0	4.0	7.41	8.33	9.09	10.00
1.5	3.5	9.09	10.20	10.87	11.36
2.0	3.0	11.11	11.76	12.35	12.82
2.5	2.5	9.52	10.52	10.98	11.63
3.0	2.0	8.00	8.69	9.50	10.00
3.5	1.5	5.88	6.67	7.41	8.00
3.0	1.0	4.17	5.26	5.40	5.88
4.5	0.5	2.27	2.98	3.51	3.85
5.0	0.0	1.00**	1.40**	1.70**	2.20**

* Error Limit :: ± 0.01; ** Extrapolated Value.

Table III. 6c

Effect of Dielectricl Constant on the Electrical Conductivity of Triphenyl phosphine-Iodine System at 25 °C

Solvent :: Acetonitrile-Carbon tetrachloride

Concentration of Iodine Solution :: 0.01 M.

Concentration of ϕ_3P Solution :: 0.01 M.

Volume of ϕ_3P Solution (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^4 Mhos*			
		ϵ = 36.7	ϵ = 30	ϵ = 25	ϵ = 15
0.0	5.0	1.25	0.52	0.24	0.15**
0.5	4.5	4.55	1.72	1.43	0.30
1.0	4.0	7.41	2.78	2.25	0.45
1.5	3.5	9.09	3.64	2.78	0.53
2.0	3.0	11.11	4.35	2.94	0.56
2.5	2.5	9.52	3.85	2.78	0.54
3.0	2.0	8.00	3.23	2.38	0.53
3.5	1.5	5.88	2.56	1.92	0.48
4.0	1.0	4.17	2.13	1.52	0.36
4.5	0.5	2.27	1.67	1.28	0.24
5.0	0.0	1.00**	0.90**	0.75**	0.05**

* Error Limit :: ± 0.01 ; ** Extrapolated Value

Table III. 6d

Effect of Dielectric Constant on the Electrical Conductivity of Triphenyl arsine-Iodine System at 25 °C

Solvent :: Acetonitrile-Carbon tetrachloride

Concentration of Iodine Solution :: 0.01 M.

Concentration of ϕ_3As Solution :: 0.01 M.

Volume of ϕ_3As Solution (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^4 Mhos*			
		$\epsilon = 36.7$	$\epsilon = 30$	$\epsilon = 25$	$\epsilon = 15$
0.0	5.0	1.25	0.52	0.24	0.15**
0.5	4.5	3.57	2.38	2.00	0.51
1.0	4.0	5.88	3.51	2.94	0.83
1.5	3.5	6.67	4.00	3.70	0.74
2.0	3.0	7.14	3.70	3.22	0.65
2.5	2.5	6.45	3.33	2.78	0.57
3.0	2.0	5.88	2.94	2.27	0.51
3.5	1.5	5.00	2.56	1.85	0.40
4.0	1.0	4.00	2.13	1.41	0.27
4.5	0.5	2.13	1.41	1.00	0.16
5.0	0.0	0.85**	0.65**	0.45**	0.05**

* Error Limit :: ± 0.01; ** Extrapolated Value.

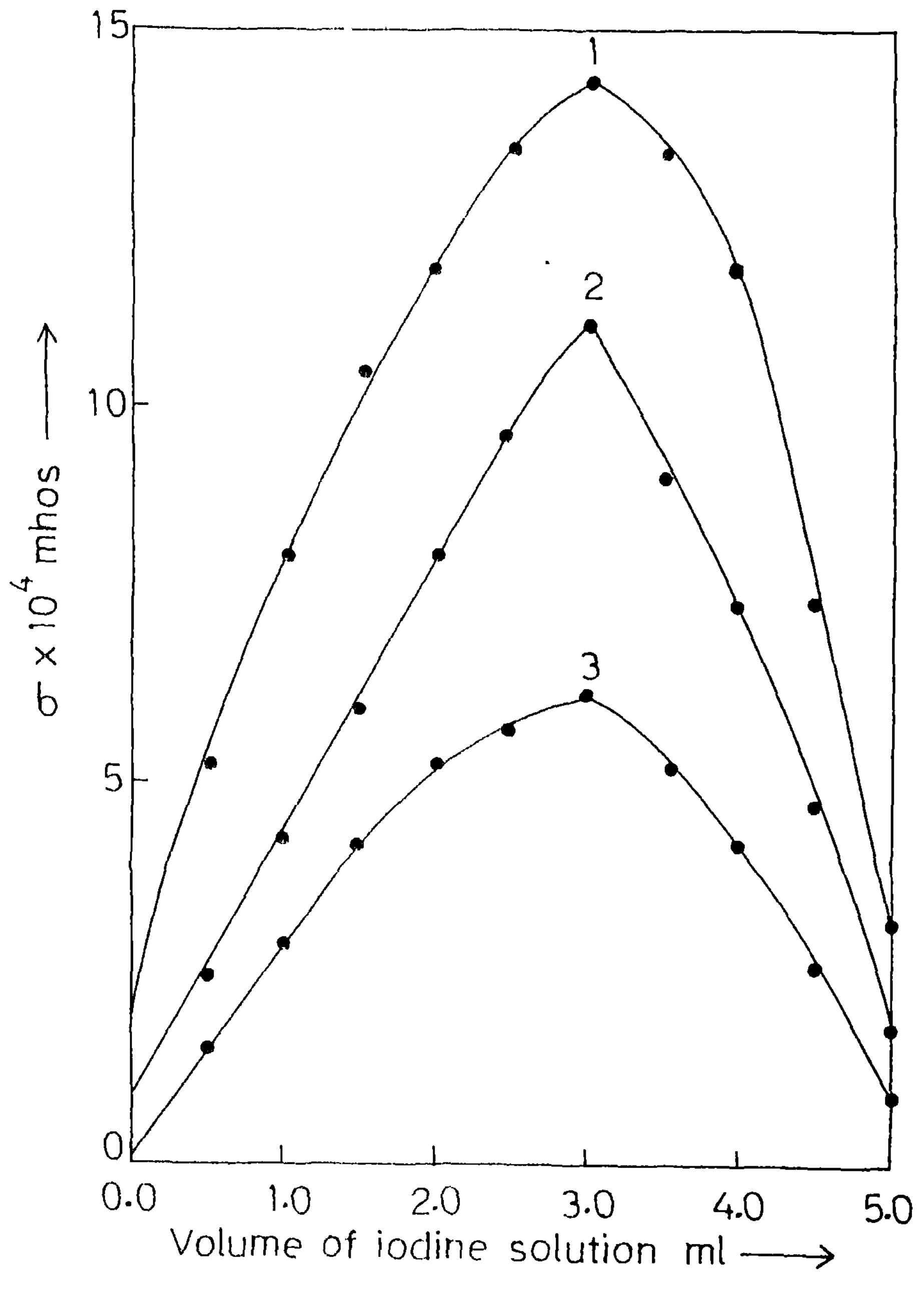

Fig. III. 7. Effect of Concentration on the Electrical Conductivity of ϕ_3P-I_2 System (Isomolar) at 25 °C.

Solvent :: Acetonitrile.

1. 0.02 ; 2. 0.01 M; 3. 0.005 M.

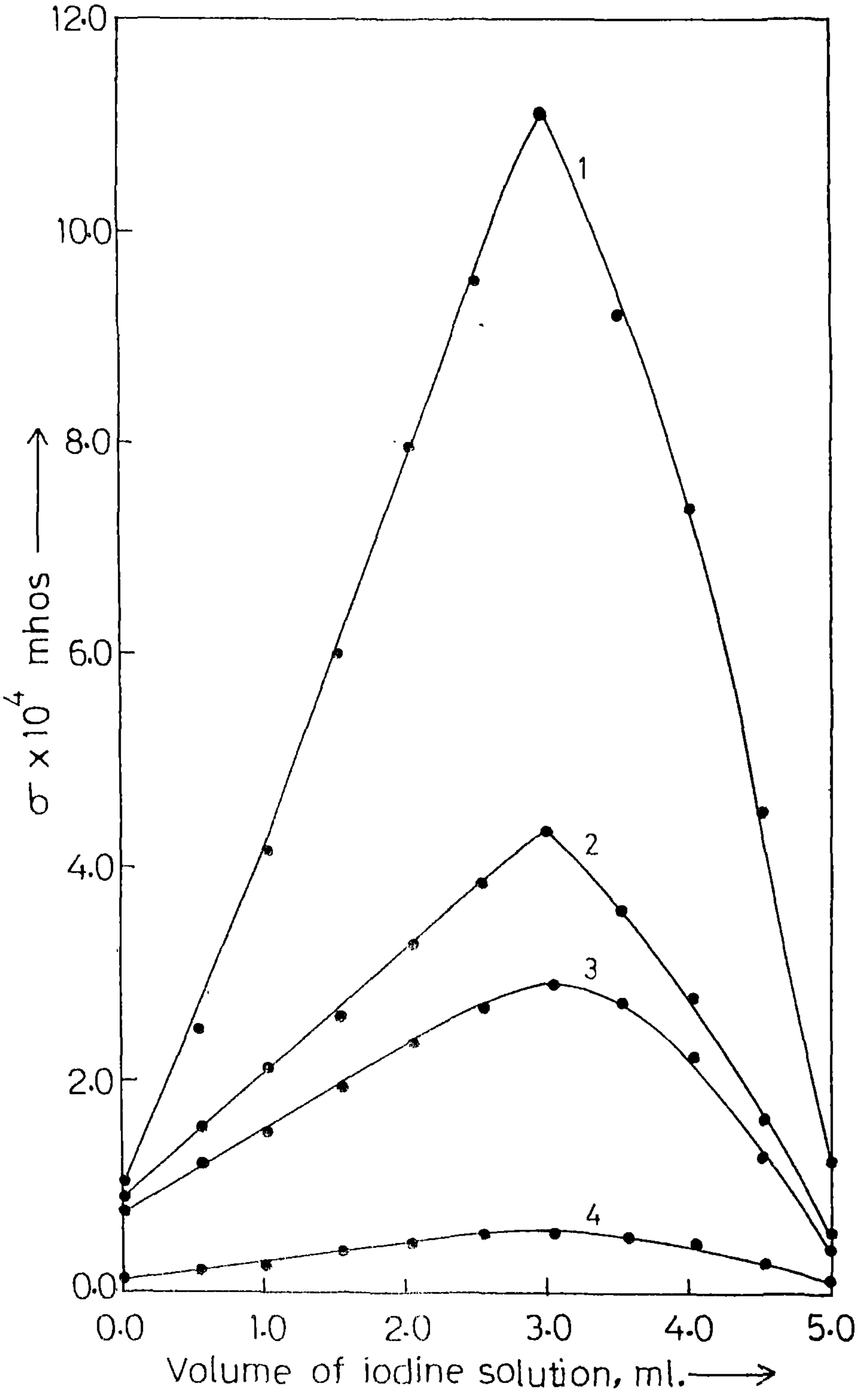

Fig. III. 8. Effect of Dielectric Constant of the Media on the Electrical Conductivity of ϕ_3P-I_2 System at 25 °C. Conc: 0·01 M

Solvent : Acetonitrile + Carbon Tetrachloride

1. $\epsilon = 36.7$; 2. $\epsilon = 30$

3. $\epsilon = 25$; 4. $\epsilon = 15$

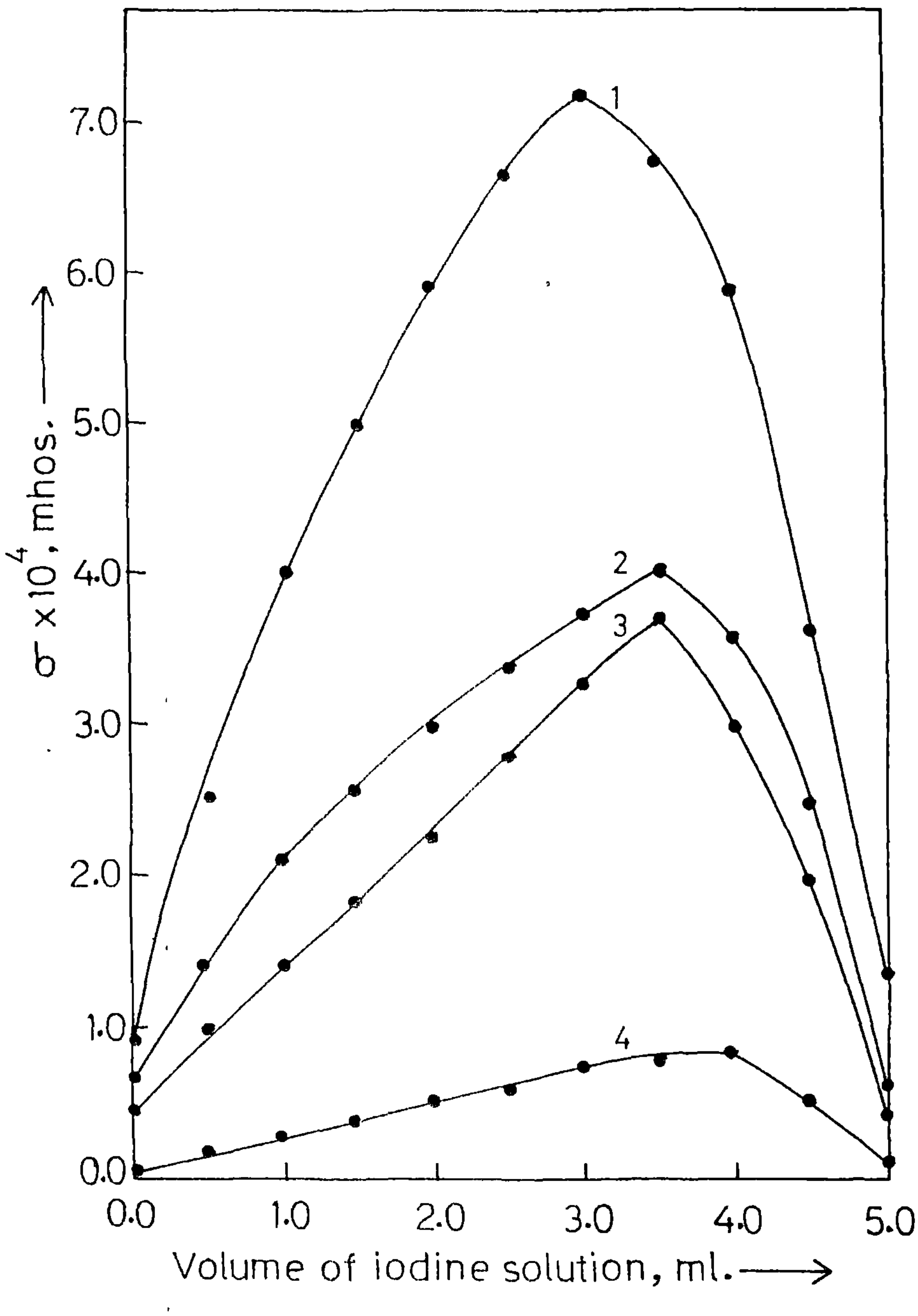

Fig. III. 9. Effect of Dielectric Constant of the Media (isomolar) on the Electrical Conductivity of ϕ_3As-I_2 System at 25 °C. Conc : 0'01 M

Solvent : Acetonitrile + Carbon Tetrachloride

1. $\epsilon = 36.7$; 2. $\epsilon = 30$;
3. $\epsilon = 25$; 4. $\epsilon = 15$.

media, as the conductivities were very low. As the polarity of the medium is decreased, the amount of iodine in the complex has increased. (Similar observations have been reported by Sahai et al[15] for triphenylphosphine-iodine, but their results could not be reproduced in our laboratory). This unexpected observation (for $\phi_3As\text{-}I_2$) cannot be explained with the existing model. One possibility is that, at reasonably low permittivity, the complex which exists as $\phi_3As^+ I^-$ might have combined with free iodine present in the solution and thus the iodine content in the complex might have been increased.

III. 3(iii) IODINE COMPLEXES OF METHANOL, ETHANOL AND n-PROPANOL:

The conductance measurements of the iodine complexes of methanol, ethanol and n-propanol were carried out at different concentrations (0.02, 0.01 and 0.005 M) at different temperatures (25, 30, 35 and 40 °C) and in different eielectric media (36.7, 30, 25 and 15). For the sake of brevity the conductance data at one temperature and one concentration are set out in Table III. 7 (Fig. III. 10). All these complexes have the conductance maximum at 2:3 (lit. 1:1)[31] stoichiometry. At 25 °C, the electrical conductivities (at the stoichiometry) of $MeOH\text{-}I_2$, $EtOH\text{-}I_2$ and

Table III. 7

The Electrical Conductivity Data of Iodine Complexes of Methanol, Ethanol and n-Propanol in Acetonitrile

Temp. : 25 °C; Concentration of Iodine : 0.01 M.

Concentration of n-Alcohols : 0.01 M.

Volume of n-Alcohol Solution (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^4 Mho*		
		$MeOH-I_2$	$EtOH-I_2$	n-$PrOH-I_2$
0.0	5.0	1.25	1.25	1.25
0.5	4.5	1.30	1.41	1.47
1.0	4.0	1.39	1.49	1.54
1.5	3.5	1.41	1.54	1.56
2.0	3.0	1.35	1.47	1.50
2.5	2.5	1.28	1.39	1.42
3.0	2.0	1.10	1.19	1.23
3.5	1.5	0.91	1.00	1.05
4.0	1.0	0.74	0.80	0.87
4.5	0.5	0.48	0.51	0.57
5.0	0.0	0.25**	0.31**	0.40**

* Error Limit :: 0.01; ** Extrapolated Value.

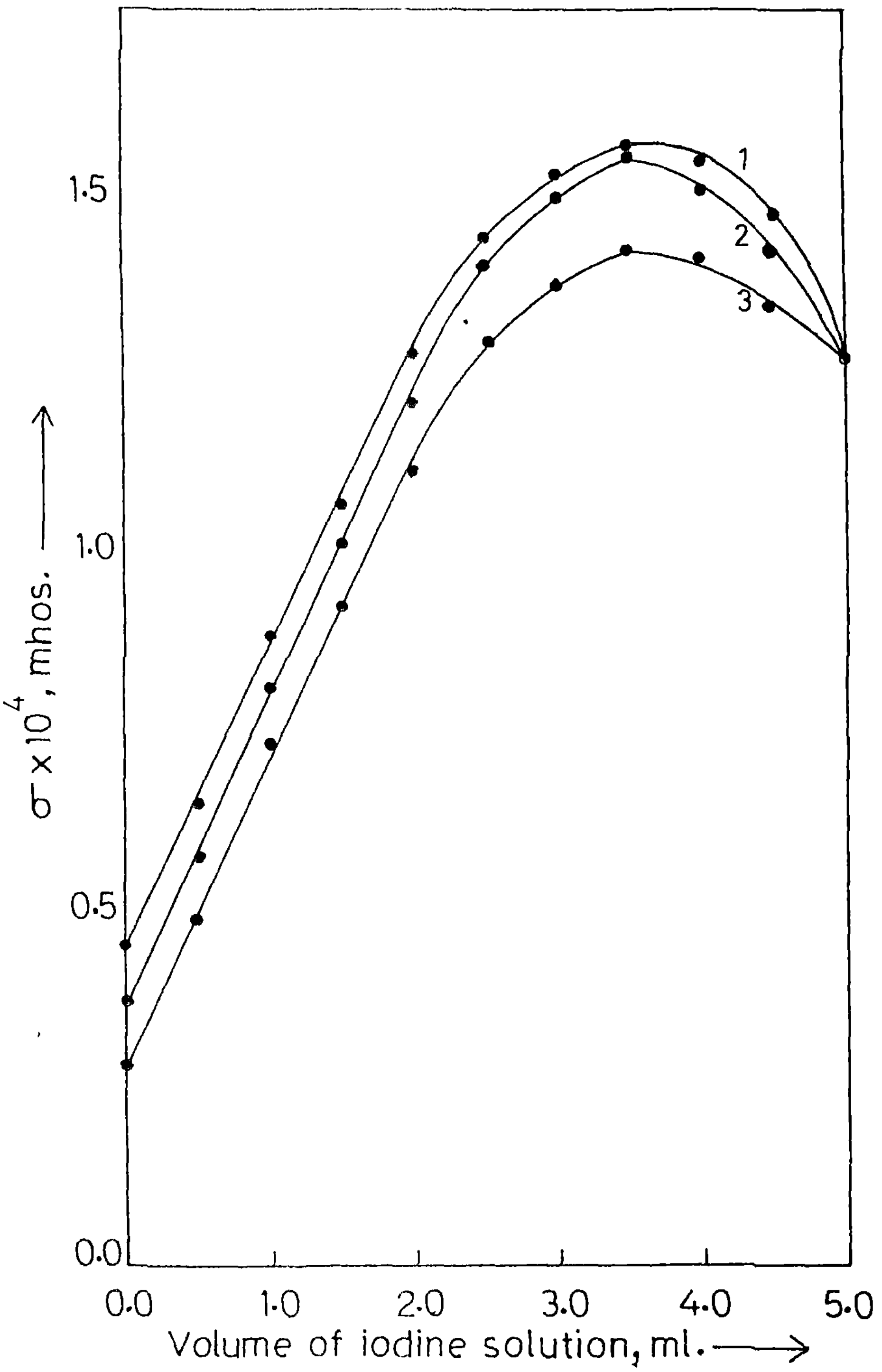

Fig. III. 10. Variation of Electrical Conductivity of $\underline{n}$-Alcohols-I_2 Systems at 25 °C(Isomolar).

Solvent :: Acetonitrile. Conc.; 0'01M

1. MeOH-I_2; 3. EtOH-I_2; 3. $\underline{n}$-PrOH-I_2.

n-PrOH-I_2 (of 0.01 M concentration) complexes awere 1.41 x 10^{-4}, 1.54 x 10^{-4} and 1.56 x 10^{-4} respectively. The effect of concentration, temperature and dielectric media on iodine complexes of MeOH are summarized in Table III. 8 and Figs. III. 11. The electrical conductivities of the solutions increase (0.111 x 10^{-4} to 3.51 x 10^{-4} Mhos) with increase in concentration (0.005 M to 0.02 M) and this is what has been expected. As the concentration of the alcohols increases, the concentration of the complexes increases, and due to ionization (of more complexes) the number of charge carriers increase, which in turn increases the electrical conductivity of the solutions. Here it should be noted that as the temperature of the system increases the interaction between alcohol molecules (i.e., hydrogen bondings-polymers) decreases.[31] So the nature of interaction between alcohols-I_2 may change with an increase in temperature. The increase in temperature causes an increase in conductivity (due to increase in mobility as well as increase in the nature of charge carriers). However, it is not possible to say which factor is more predominant. The decrease in electrical conductivity of iodine-MeOH with the decrease in dielectric constants must be due to the decrease in the mobility of the charge carriers as well as due to the formation of lesser number of "free" ions (in low dielectric media). The

Table III. 3a

Effect of Concentration on the Electrical Conductivity of MeOH-I_2 System at 25 °C

Solvent :: Acetonitrile

Volume of Methanol Solution (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^4 Mhos*		
		0.005 M	0.01 M	0.02 M
0.0	5.0	0.83	1.25	2.86
0.5	4.5	0.95	1.30	3.23
1.0	4.0	1.05	1.39	3.45
1.5	3.5	1.11	1.41	3.51
2.0	3.0	1.0	1.35	3.28
2.5	2.5	0.91	1.28	2.86
3.0	2.0	0.80	1.10	2.53
3.5	1.5	0.65	0.91	2.00
4.0	1.0	0.48	0.74	1.41
4.5	0.5	0.32	0.48	0.80
5.0	0.0	0.10**	0.25**	0.30**

* Error Limit :: ± 0.01; ** Extrapolated Value.

Table III. 8b

Effect of Temperature on the Electrical
Conductivity of Methanol-Iodine System
Solvent :: Acetonitrile
Concentration of Iodine Solution : 0.01 M
Concentration of MeOH Solution : 0.01 M

Volume of Methanol Solution (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^4 Mhos*			
		25 °C	30 °C	35 °C	40 °C
0.0	5.0	1.25	1.33	1.54	1.72
0.5	4.5	1.30	1.45	1.64	1.85
1.0	4.0	1.39	1.49	1.69	1.89
1.5	3.5	1.41	1.54	1.72	1.96
2.0	3.0	1.35	1.52	1.59	1.82
2.5	2.5	1.28	1.35	1.50	1.72
3.0	2.0	1.10	1.18	1.33	1.56
3.5	1.5	0.91	1.02	1.12	1.29
4.0	1.0	0.74	0.83	0.91	1.10
4.5	0.5	0.48	0.56	0.63	0.69
5.0	0.0	0.25**	0.35**	0.41**	0.43**

* Error Limit :: ± 0.01; ** Extrapolated Value.

Table III. 8c

Effect of Dielectric Constant on the Electrical Conductivity of Methanol-Iodine System at 25 °C

Solvent :: Acetonitrile-Carbon tetrachloride

Concentration of Iodine Solution :: 0.01 M

Concentration of Methanol Solution :: 0.01 M

Volume of Methanol Solution (ml)	Volume of Iodine Solution (ml)	Conductivity x 10^4 Mhos*			
		$\epsilon = 36.7$	$\epsilon = 30$	$\epsilon = 25$	$\epsilon = 15$
0.0	5.0	1.25	0.52	0.24	
0.5	4.5	1.30	0.57	0.28	Restistance of the the solution was too high (> 10^6 Ohm)
1.0	4.0	1.39	0.63	0.30	
1.5	3.5	1.41	0.67	0.32	
2.0	3.0	1.35	0.63	0.31	
2.5	2.5	1.28	0.59	0.29	
3.0	2.0	1.10	0.54	0.26	
3.5	1.5	0.91	0.46	0.22	
4.0	1.0	0.74	0.36	0.17	
4.5	0.5	0.48	0.24	0.12	
5.0	0.0	0.25**	0.12**	0.06**	

* Error Limit :: ± 0.01; ** Extrapolated Value.

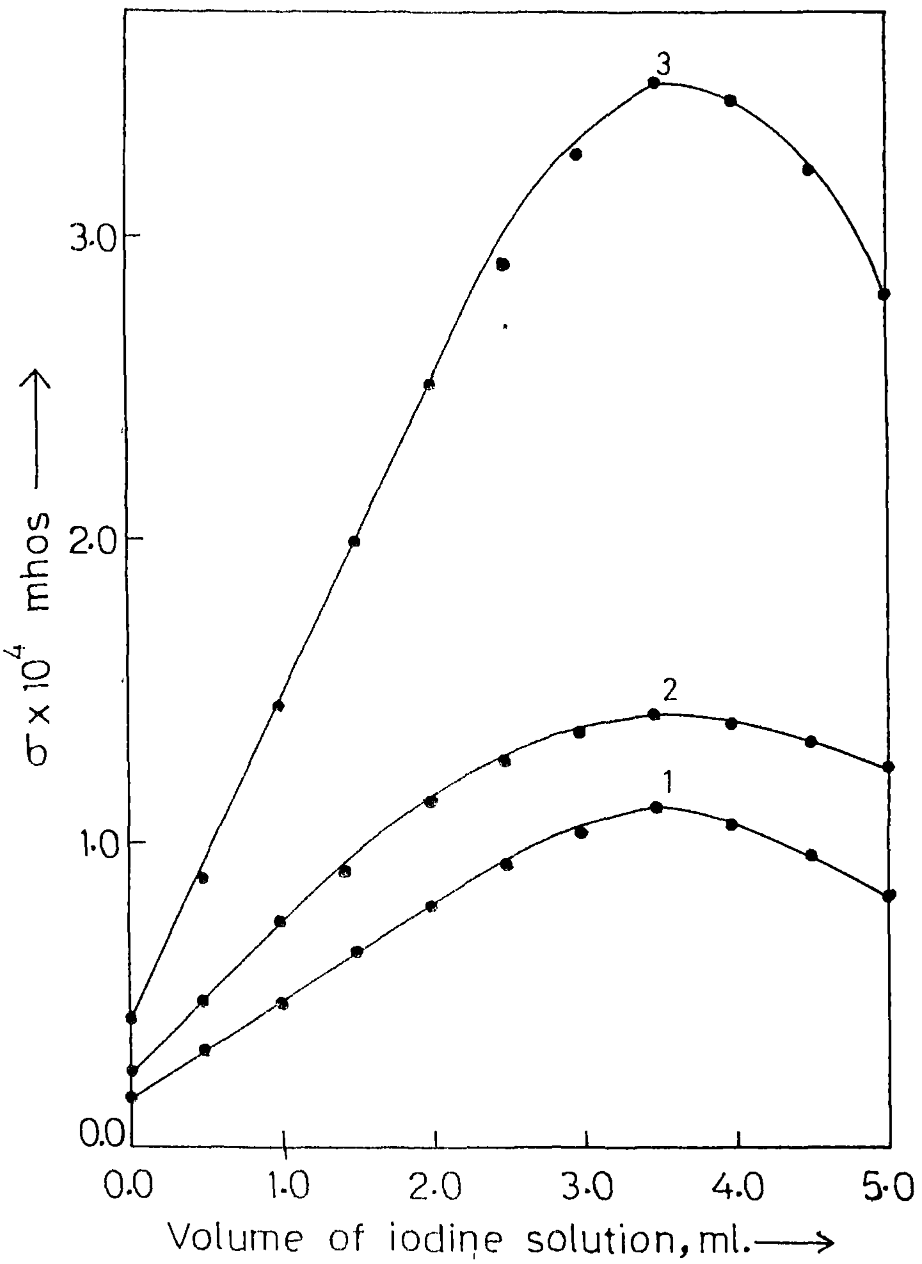

Fig. III. 11a. Effect of Concentration on the Electrical Conductivity of Methanol-Iodine System (Isomolar) at 25 °C.

Solvent :: Acetonitrile.

1. 0.005 M; 2. 0.01 M; 3. 0.02 M.

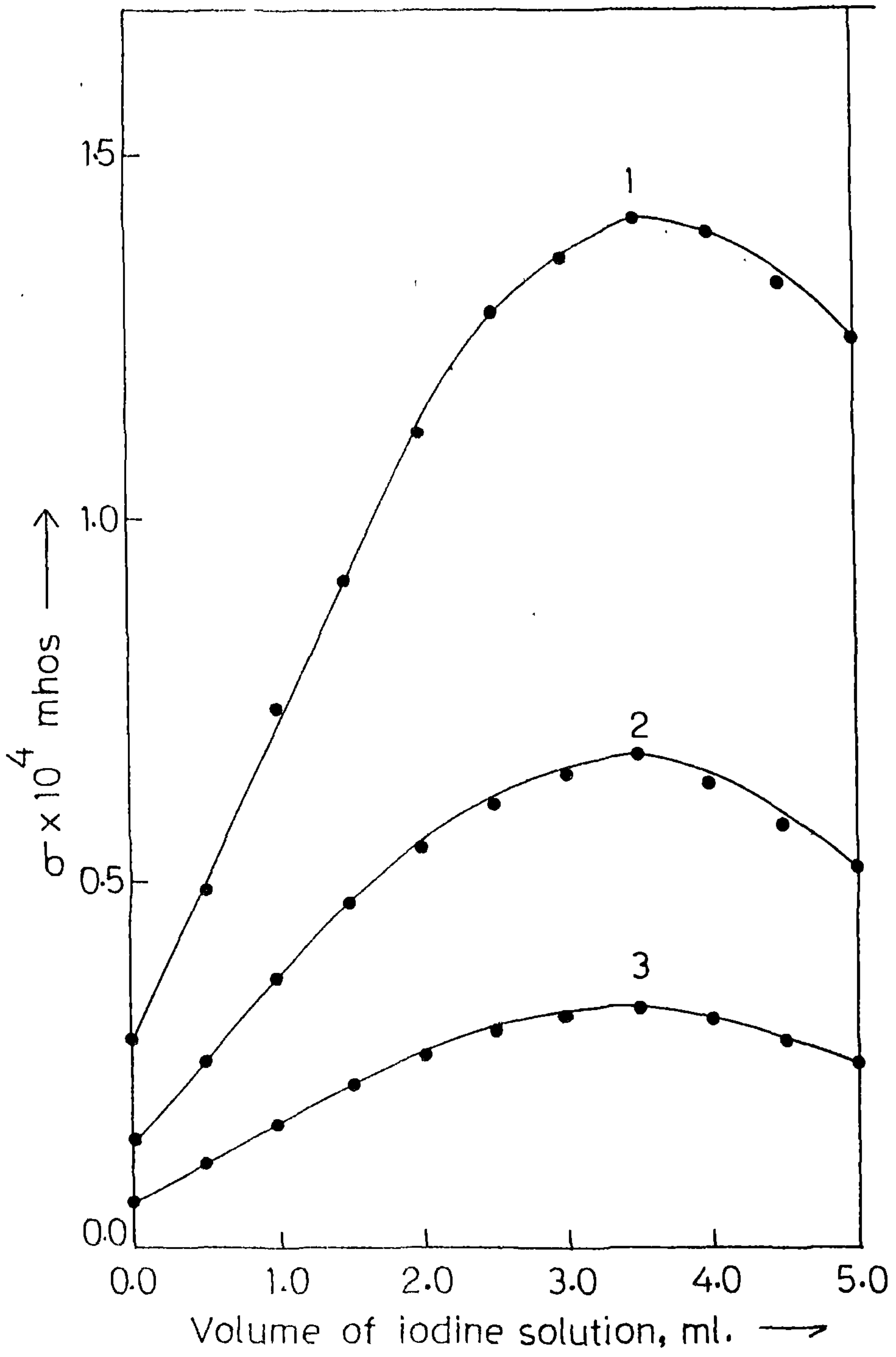

Fig. III. 11b. Effect of Dielectric Constant on the Electrical Conductivity of MeOH-I_2 (Isomolar) System at 25 °C. Conc. = 0.01 M.

Solvent : Acetonitrile + Carbon Tetrachloride.

1. $\epsilon = 36.7$; 2. $\epsilon = 30$; 3. $\epsilon = 25$.

stability of these complexes vary in the order n-PrOH-I_2 > EtOH-I_2 > MeOH-I_2, and the electrical conductivity vary in the same order. As mentioned earlier, it is not easy to interpret these conductivity data in terms of 'simple' stability data alone.

From these observations, we feel that conductometric titration (where the outer complex is transformed into inner complex which is assisted by the environmental cooperation) method can be conveniently used to determine the stoichiometry of the complex formed in polar media. However, if more than one type of complexes are formed, or if interaction between solute and solvent is considerable, then one has to be cautious in establishing the stoichiometry of the complex by this method. Moreover, if interaction between the molecules is weak, or if the permittivity of the medium is low, then this conductivity method will be of little help to determine the stoichiometry of the complexes in solution.

REFERENCES

1. R. S. Mulliken and W. B. Person, "Molecular Complexes", A Lecture and Note Volume, Wiley Interscience, New York, 1969.
2. S. N. Bhat and C. N. R. Rao, J. Am. Chem. Soc., 88, 3216 (1966).
3. C. Reid and R. S. Mulliken, J.Am.Chem.Soc., 76, 3869(1954).
4. a) R. Gopal and J. N. Srivastava, J. Ind. Chem. Soc., 29, 898 (1952).

   b) R. D. Srivastava, V. S. Mishra and P. N. Tripathi, Electrochimica Acta, 27, 863 (1982).

   c) R. D. Srivastava and P. C. Verma, Electrochimica Acta, 17, 2129 (1972).
5. M. V. Ramamamurthy and P. V. S. S. Prabhu, Electrochimica Acta, 27, 481 (1982).
6. a) F. Gutmann and M. Keyzer, Electrochimica Acta, 11, 555, 1163 (1966).

   b) J. P. Fargos and F. Gutmann, in "Modern Aspects of Electrochemistry", Ed. by Borkis and Conns, Plenum Publ.
7. B. Bhattacharjee, A. Varshney and S. N. Bhat, J. Ind. Chem. Soc., 60, 842 (1983).
8. L. F. Audrieth and E. J. Birr, J. Am. Chem. Soc., 55, 668 (1933).

9. a) J. J. Tondear and A. Borghese,
Electrochimica Acta, 22, 729 (1977).
b) A. E. Beezer, M. Orban and J. V. Tyrrel,
Acta Chem. Acad. Sci. Hungr., 99, 415 (1979);
CA, 91: 113227b.

10. P. C. Dwivedi, and A. K. Banga,
Electrochimica Acta, 24, 831 (1979).

11. P. C. Dwivedi, A. K. Banga and A. Gupta,
Electrochimica Acta, 28, 801 (1983).

12. Z. A. Siddiqui, N. A. Ansari, M. A. Lutfullah and
S. A. A. Zaidi, Ind. J. Chem., 20A, 30 (1981).

13. N. Chattopadhyay and R. Basu, J. Chim. Phys. Phys. Chim.
Biol., 76, 364 (1979); CA, 91: 56142u.

14. K. R. Bhaskar, S. N. Bhat, S. Sing and C. N. R. Rao,
J. Inorg. Nucl. Chem., 28, 1915 (1966).

15. R. Sahai, V. Singh and R. K. Verma,
Ind. J. Chem. 20A, 1017 (1981).

16. A. K. Trofimchuk, E. Y, Gorenbein,
Zh. Obshch. Khim., 41, 34 (1971); CA, 74: 146998f.

17. H. Gusten and L. Klasine, J. Phys. Chem., 76, 2452(1972).

18. C. Liu, G. Li and Y. Zhao,
Huaxue Xuebao., 42, 1 (1984); CA, 100: 109885b.

19. A. J. Popov and W. A. Deskin,
J. Am. Chem. Soc., 80, 2976 (1958).

20. V. S. Mishra, D. C. Tewari and P. N. Tripathi,
Electrochimica Acta, 29, 1335 (1984).

21. C. R. Das and A. N. Bose,
Bull. Chem. Soc. Japan., 46, 818 (1973).

22. H. A. Benesi and J. H. Hildebrand,
J. Am. Chem. Soc., 71, 2703 (1949).

23. C. N. R. Rao, S. N. Bhat and P. C. Dwivedi,
Appl. Spectros. Revs., 5, 1 (1972).

24. R. Foster, "Organic Charge-Transfer Complexes",
Academic Press, New York, 1969.

25. P. Job, Annls. Chim., 9, 113 (1928).

26. A. I. Vogel, "Text Book of Practical Organic Chemistry",
ELBS and Longman, 4th Ed., 1978.

27. a) V. P. Shedbalkar and S. N. Bhat,
Electrochimica Acta, 28, 359 (1983).
b) "Molecular Complexes", Vol. I and II, Ed. by
R. Foster, Elek. Science, London, 1973, 1977.

28. a) R. S. Drago, B. Wayland and R. L. Carlson,
J. Am. Chem. Soc., 85, 3125 (1963).
b) B. Musulin, W. J. Jones and M. J. Bleen,
J. Inorg. Nucl. Chem., 26, 239 (1964).

29. E.Augdahl amd P.Klaboe, Acta Chem. Scand., 18, 27 (1964).

30. H.Yamada and K. Koxima, J. Am. Chem. Soc., 82, 1543 (1960).

31. H.C. Tse and M. Tamres, J. Phys. Chem., 81, 1376 (1977).

CHAPTER IV

VISCOMETRY IN THE STUDY OF MOLECULAR COMPLEXES *

IV. 1. INTRODUCTION

There has been an increasing interest in the study of molecular complexes. The most common technique used in the study of molecular complexes is absorption spectroscopy in the visible and ultraviolet regions of the electromagnetic spectrum, as absorption spectra in these regions arise from electronic transitions in the molecules, modified by the vibrations of the molecules.[1-5] However, this technique can be hardly used when there is only slight perturbation of the donor or acceptor band due to weak interaction between donor and acceptor. In such cases it is not only difficult to get a correct stoichiometry of the complex formed, but also to get an accurate value of K and ϵ of the weak complexes by

---

* A paper based on this work appeared in the Proceedings of the Indian Academy of Sciences, (Chem. Sci.), 92, 147(1983).

the conventional spectral method alone. So in order to suppliment the spectral methods a number of different experimental procedures have been suggested to investigate the interaction between electron donors and electron acceptors with or without a third component. All the methods available to study the molecular structure and the nature of chemical bond also apply to molecular complexes. However, in spite of the fact that, in principle, the interaction between molecules and the composition of the complex formed can be established from the study of the characteristic abrupt departure of some physical properties from ideal behaviour, like dielectric constant, refractive index, optical absorption, surface tension, viscosity, etc., many of the methods are hardly used.[6-21] By a careful selection, one may find one or more suitable experimental methods for the investigation of all kinds of complexes. It must be emphasized, however, that a careful consideration is necessary as to whether the effects of complex formation are quantitatively reflected in the measured property. To choose an adequate method is a pre-requisite for obtaining reliable equilibrium constants. Recently, Bhat and coworkers[22-27] used non-spectral methods like surface tension, refractive index measurements, constant activity method etc. to study the interaction between the molecules in solutions, and demonstrated their applicabilities in obtaining the equilibrium constants even in the case of very weakly interacting systems directly. Although the measurements of various thermodynamic excess functions of binary solutions have been the subject of much research (from viscosity measurements) there is hardly any report on using viscosity measurement method for ternary systems.[28-35] It was therefore felt worthwhile to study the interaction of electron donors with electron acceptors, in suitable media, viscometrically and to obtain the equilibrium constant directly. The systems, chosen for the studies are benzene-, toluene-, o-xylene-carbon tetrachloride-cyclohexane.

IV. 2. MATERIALS AND METHODS

Cyclohexane, carbon tetrachloride, benzene, toluene and o-xylene, were purified by the standard procedures.[36]

Cyclohexane (IDPL B.N. 0010380), Benzene S(S.D.'s B.N. 070101007), Toluene (BDH B.N. 101/11/05101), xo-Xylene (IDPL, B.N. 0010477) were purified by shaking repeatedly with about 15 percent of their volumes of concentrated sulphuric acid in stoppered separating funnels until the acid layer become colourless (or very pale yellow) on standing. After each shaking the mixture was allowed to settle, and the lower layer of acid was drawn off. The upper layer was shaken with water for a couple of times to remove most of the acid, once with 10 per cent sodium carbonate solution, again with water and finally dried overnight over anhydrous calcium chloride and distilled. All the solvents were stored in tightly stoppered bottles over sodium wire. Benzene : B.P. 79 °C/662 mm (lit. 80 °C/760 mm); toluene : B.P. 108°C/662mm (lit. 110 °C/760 mm); o-xylene : 140 °C/662 mm (lit. 143 °C/760 mm); cyclohexane : 79 °C/662 mm (lit. 80-82 °C/760 mm).

Carbon tetrachloride was purified and dried by following the procedure given in Chapter III.

The densities and viscosities of pure samples and those of 'binary mixtures' of known composition (mole fractions) of benzene, toluene, o-xylene and carbon tetrachloride in cyclohexane were determined at 25, 30, 35 and 40 °C (± 0.1°C) using Ostwald's Viscometer (No. BS/IP/SL(S); No. 3) and the coefficients of viscosities were calculated. Similarly the densities and viscosities of ternary systems (of known compositions) of benzene-CCl_4-cyclohexane, toluene-CCl_4-cyclohexane and o-xylene-CCl_4-cyclohexane were determined. The experiments were repeated at least twice and the results were reproducible within the experimental error limit of ± 0.0150 millipoise.

The stoichiometry of the 'complex' was determined by Job's[37] Continuous Variation method.

The non linear plot of any physical property of a 'mixed solution' against the concentration of the components, i.e., the deviation from ideal behaviour of the pure components in solution, is an indication of the interaction between the two species, namely the donor D and the acceptor A (after deducting the solvent contribution). If one can assume that the deviation is entirely due to the complex alone, then the deviation should be proportional to the concentration of the complex. Baur et al[38] had developed a procedure for obtaining the equilibrium constant of a complex by studying the change in polarizability of the species. However, it is felt that the equilibrium constant K_c can be calculated by modifying the procedure of Yoshida and Osawa[39] which is of more general nature.

For an equimolar mixture of D and A (with total concentration C), the maximum deviation RS of any physical property, that is, (here η) from the additivities can be written as,

$$RS = \alpha x \qquad \ldots\ldots \qquad \ldots\ldots \text{IV. 1.}$$

where α is the proportionality constant and x is the concentration of the complex. When the total concentration is changed from C to C', then

$$R'S' = \alpha x' \quad \ldots\ldots \quad \ldots\ldots \text{IV.2.}$$

therefore,

$$\frac{RS}{R'S'} = \frac{\alpha x}{\alpha x'} = \frac{x}{x'} = k \ldots\ldots \text{IV. 3.}$$

In the present case, the K_x is given by,

$$K_x = x/\left[\left(\frac{C}{2} - x\right)\right]^2$$

$$= x'/\left[\left(\frac{C'}{2} - x'\right)\right]^2 \quad \ldots\ldots \text{IV. 4.}$$

Combining IV. 3. and IV. 4. and rearranging, we obtain,

$$K_x = 2\sqrt{k}\left\{\sqrt{k}\,(C + C') - (C + kC')\right\}/(C - kC')^2$$

$$\ldots\ldots \text{IV. 5.}$$

As the plot of $\Delta\eta$ vs mole fraction is not always symmetrical, k is actually the ratio of the area under the curves.

It was pointed out by Scott[40] that in dilute solutions even though in principle, the molar, mole fraction and molal scales are linearly related to one another, in practice the relationships are non-linear and become increasingly so as the solute concentrations increases. So the inconsistencies will arise if experimentally determined association constants are estimated as the concentration quotients. By following the suggestions of Foster[41], and Trotter and Hanna[42] (for reasonably low value of K), the following relationship was used to obtain K_c values:

$$K_x \approx K_c \cdot 1000d_s/M_s \qquad \text{.... IV. 6.}$$

where K_x and K_c are the equilibrium constants in mole fraction and concentration units, d_s is the density of the solvent in g/ml and M_s is the molecular weight of the solvent.

IV. 3. RESULTS AND DISCUSSION

The viscosities of benzene, toluene, o-xylene and carbon tetrachloride in cyclohexane were determined at 25, 30, 35 and 40 °C and these values agree with the literature values. The viscosities of benzene and alkyl benzenes in cyclohexane decrease with increase in concentration whereas that of carbon tetrachloride in cyclohexane increases with concentration. For the sake of brevity, the viscosity values of these binary systems, only at 25 °C are listed in Table IV. 1. Here it can be noted that benzene and alkyl benzenes are electron donors whereas carbon tetrachloride is an electron acceptor. Therefore, the interaction between benzene/alkyl benzenes and cyclohexane are of different nature. The viscosities of all the mixtures studied are lower than the expected values (Table IV. 2), i.e.,

Table IV. 1a

Viscosity Data and Grunberg and Nissan Parameters (d) for Benzene-, Toluene-Cyclohexane Binary System at 25°C

(i) Benzene-Cyclohexane Binary System

Mole fraction of Benzene	Calculated Viscosity millipoise	Observed Viscosity m poise	$\Delta\eta$ (= $\eta_{cal} - \eta_{obs}$	d
0.0	-	8.2678	-	-
0.1	8.0394	7.4789	0.5605	- 0.7550
0.2	7.8110	6.8998	0.9112	- 0.7236
0.3	7.5826	6.5130	1.0696	- 0.6771
0.4	7.3541	6.1939	1.1603	- 0.6645
0.5	7.1257	5.9435	1.1822	- 0.6736
0.6	6.8973	5.8710	1.0263	- 0.6181
0.7	6.6689	5.7621	0.9068	- 0.5524
0.8	6.4405	5.7507	0.6898	- 0.6524
0.9	6.2121	5.8198	0.3923	- 0.3923
1.0	-	5.9837	-	-

Error Limit :: ± 0.0150

Table IV. 1a contd..

Table IV. 1a (contd..)

((ii) Toluene-Cyclohexane Binary System

Mole fraction of Toluene	Calculated Viscosity millipoise	Observed Viscosity millipoise	$\Delta\eta$ (= $\eta_{cal} - \eta_{obs}$)	d
0.0	-	8.2678	-	-
0.1	7.9981	7.4115	0.5866	- 0.7762
0.2	7.7284	6.8106	0.9178	- 0.7183
0.3	7.4587	6.3384	1.1204	- 0.7014
0.4	7.1891	6.0309	1.1581	- 0.6565
0.5	6.9194	5.8444	1.0750	- 0.5979
0.6	6.6497	5.7457	0.9040	- 0.5293
0.7	6.3800	5.6079	0.7720	- 0.5325
0.8	6.1103	5.5455	0.5650	- 0.5222
0.9	5.8407	5.5342	0.3065	- 0.5123
1.0	-	5.5710	-	-

Error Limit :: ± 0.0150.

Table IV. 1b

Viscosity Data and Grunberg and Nissan Parameters for o-Xylene-, CCl_4-Cyclohexane Binary Systems at 25 °C

(i) o-Xylene-Cyclohexane System

Mole Fraction of o-Xylene	Calculated Viscosity millipoise	Observed Viscosity millipoise	$\Delta\eta = (\eta_{cal} - \eta_{obs})$	d
0.0	-	8.2678	-	-
0.1	8.1559	7.6911	0.4648	- 0.6419
0.2	8.0441	7.3090	0.7351	- 0.5886
0.3	7.9322	7.0598	0.8724	- 0.5445
0.4	7.8204	6.9115	0.9090	- 0.5043
0.5	7.7085	6.8373	0.8712	- 0.4692
0.6	7.5966	6.8280	0.7686	- 0.4338
0.7	7.4848	6.8040	0.6810	- 0.4433
0.8	7.3729	6.7910	0.5821	- 0.5030
0.9	7.2610	6.9750	0.2861	- 0.9241
1.0	-	7.1492	-	-

Error Limit = ± 0.0150

Table IV. 1b.contd.

Table IV. 1b

(ii) CCl_4-Cyclohexane System

Mole Fraction of CCl_4	Calculated Viscosity millopoise	Observed Viscosity mollipoise	$\Delta\eta = (\eta_{cal} - \eta_{obs})$	d
0.0	-	8.2678	-	-
0.1	8.3940	8.1764	0.2176	- 0.2817
0.2	8.5203	8.1890	0.3313	- 0.2375
0.3	8.6465	8.2386	0.4079	- 0.2199
0.4	8.7728	8.2720	0.5008	- 0.2347
0.5	8.8991	8.3778	0.5213	- 0.2314
0.6	9.0253	8.5583	0.4671	- 0.2114
0.7	9.1516	8.7031	0.4485	- 0.2294
0.8	9.2779	9.0140	0.2640	- 0.1705
0.9	9.4041	9.2791	0.1250	- 0.1390
1.0	-	9.5304	-	-

Error Limit = ± 0.0150.

Table IV. 2a

Excess Viscosities ($\Delta\eta = \eta_{cal} - \eta_{obs}$) of Benzene-, Toluene-Cyclohexane Binary Mixtures at Different Temperatures

(i) Benzne -Cyclohexane Binary System

Mole Fraction of Benzene	$\Delta\eta$, millipoise			
	25 °C	30 °C	35 °C	40 °C
0.1	0.5605	0.4986	0.4314	0.3350
0.2	0.9112	0.7653	0.7323	0.5850
0.3	1.0696	0.9329	0.8570	0.7230
0.4	1.1603	1.0037	0.9006	0.7979
0.5	1.1822	1.0364	0.9109	0.8230
0.6	1.0263	0.9118	0.8158	0.7646
0.7	0.9068	0.8076	0.7410	0.6686
0.8	0.6898	0.5902	0.5565	0.5535
0.9	0.3923	0.3821	0.3680	0.3491

Error Limit = ± 0.0150.

Table IV. 2a. contd....2/-

Table IV. 2a

(ii) Toluene-Cyclohexane Binary System

Mole Fraction of Toluene	$\Delta\eta$, millipoise			
	25 °C	30 °C	35 °C	40 °C
0.1	0.5866	0.5106	0.4758	0.4108
0.2	0.9178	0.8227	0.7106	0.5913
0.3	1.1204	0.9562	0.8175	0.6829
0.4	1.1581	0.9732	0.8291	0.7030
0.5	1.0750	0.9251	0.7755	0.6638
0.6	0.9040	0.7921	0.6727	0.5923
0.7	0.7720	0.6599	0.5370	0.4672
0.8	0.5650	0.4391	0.3858	0.3316
0.9	0.3065	0.2345	0.1962	0.1599

Error Limit = ± 0.0150.

Table IV. 2b

Excess Viscisities ($\Delta\eta = \eta_{cal} - \eta_{obs}$) of o-Xylene-, CCl_4-Cyclohexane Binary Mixtures at Different Temperatures

(i) o-Xylene-Cyclohexane Binary System

Mole Fraction of o-Xylene	$\Delta\eta$, millipoise			
	25 °C	30 °C	35 °C	40 °C
0.1	0.4648	0.4279	0.3967	0.3230
0.2	0.7351	0.6471	0.5646	0.4887
0.3	0.8724	0.7651	0.6670	0.5694
0.4	0.9090	0.7879	0.6850	0.5937
0.5	0.8712	0.7383	0.6496	0.5144
0.6	0.7686	0.6832	0.5920	0.4610
0.7	0.6810	0.5666	0.4550	0.3651
0.8	0.5821	0.4027	0.3288	0.2623
0.9	0.2861	0.2216	0.1827	0.1417

Error Limit = ± 0.0150.

Table IV. 2b. contd..../-

Table IV. 2b

(ii) CCl_4-Cyclohexane Binary System

Mole Fraction of CCl_4	$\Delta\eta$, millipoise			
	25 °C	30 °C	35 °C	40 °C
0.1	0.2050	0.1914	0.0530	0.0250
0.2	0.3439	0.2821	0.1145	0.0740
0.3	0.4079	0.3369	0.2892	0.1833
0.4	0.5008	0.3768	0.3382	0.2620
0.5	0.5213	0.4236	0.3844	0.3089
0.6	0.4671	0.3725	0.3157	0.2637
0.7	0.4485	0.3510	0.2193	0.1630
0.8	0.2640	0.2631	0.1512	0.0559
0.9	0.1250	0.1029	0.0750	0.0288

Error Limit = ± 0.0150.

$$\Delta\eta^E = \eta_s - (\eta_A X_A + \eta_B X_B) \quad .... \text{ IV. 7.}$$

where η_s is the observed viscosity of the mixtures and η_A and η_B are the viscosities and X_A and X_B are the mole fractions of the components A and B respectively. It can be seen from the table that the excess viscosity values ($\Delta\eta = \eta_{obs} - \eta_{cal}$) of the binary systems, are negative over the entire range of composition indicating that dispersion forces are dominant as expected. However, a well defined maximum occurs at X_1 (Cyclohexane) ≈ 0.5 for benzene-cyclohexane whereas for toluene-cyclohexane and o-xylene-cyclohexane it is at 0.6 mole fraction. These deviations from ideal behaviour indicate that there are interactions between benzene/alkyl benzenes and cyclohexane. Here it is worth mentioning that Singh and coworkers[17] have demonstrated the existence of interaction between benzene and xylenes. The other approaches to describe the viscosity of binary mixtures are of Grunberg and Nissan,[43] i.e.,

$$\ln \eta_{mix} = X_A \ln \eta_A + X_B \ln \eta_B + X_A X_B d$$

where d is proportional to W/RT where W being the interchange energy; and also those of Katti and Chaudhury[44] and Raman et al.[45] using Eyring concept of viscosity, i.e.,

$\ln \eta_s V_s = X_A \ln \eta_A V_A + X_B \ln \eta_B V_B + X_A X_B . \frac{W}{RT}$, where W is the energy of viscous flow. In all these cases, the parameter has the same significance as given by Guggenheim.[46]

in the treatment of his regular solution theory, and 'd' has been regarded as a better measure of the strength of interaction between the components in solution. However, as we were interested in the study of ternary systems we have used the equation IV. 7 (except for calculating 'd' in binary systems). Our present data go in parallel with the observations made by Islam and Ibrahim.[47] The maximum deviation in the plot of $\Delta\eta$, i.e., the differences in the calculated and observed viscosity, against the mole fraction of benzene in benzene-cyclohexane appears at 0.5 mole fraction of benzene whereas for toluene and o-xylene the excess viscosity maximum appears at 0.4 mole fraction indicating the presence of 2:3 complex (Table IV. 1). Similar observations were made by Lorimer and Jones,[48] and they are of the opinion that this is due to the resultant of specific and non-specific interactions. In addition, as Grunberg and Nissan's[43] parameter, d, is also negative for these systems; so, specific interactions are anticipated (Table IV. 1). However, the magnitudes of $\Delta\eta$ and those of d are not large; these low values indicate the weak nature of interaction — $\pi - \sigma$ type. As the temperature increases the magnitude of $\Delta\eta$ and d decreases, i.e., the systems tend towards ideal condition. Here it can be recalled that Islam and Ibrahim[47] from the excess volumes of cyclohexane and toluene have come to similar conclusions. As the deviation from the ideal behaviour is due to the interaction between the two different types of molecules, the relative deviation should be an indication of the relative strength of interaction between the molecules. From the present data (i.e., deviation from the ideal behaviour) it is clear that the strength of interaction between cyclohexane and alkyl benzenes vary in the order, benzene-cyclohexane $>$ toluene-cyclohexane $>$ *o*-xylene-cyclohexane (Fig. IV. 1). This trend is maintained at all the temperatures that we have studied. [Excess viscosities, i.e., $\Delta\eta$, of benzene-cyclohexane, toluene-cyclohexane, *o*-xylene-cyclohexane at different temperatures are listed in Table IV. 2]. This is an indication that the strength of the interaction not only depends on the polarizability (electron donating nature) of the molecule but also on the geometry (size) of the molecules. Even though polarizabilities of alkyl benzenes increase from benzene to *o*-xylene the shape/size of the molecules also vary, and probably these bulky groups may not allow cyclohexane to approach closely due to which the interaction becomes weaker. This trend is in good agreement with the observations made by Nigam et al[49] and others[50] for aromatic hydrocarbons-nitromethanes and

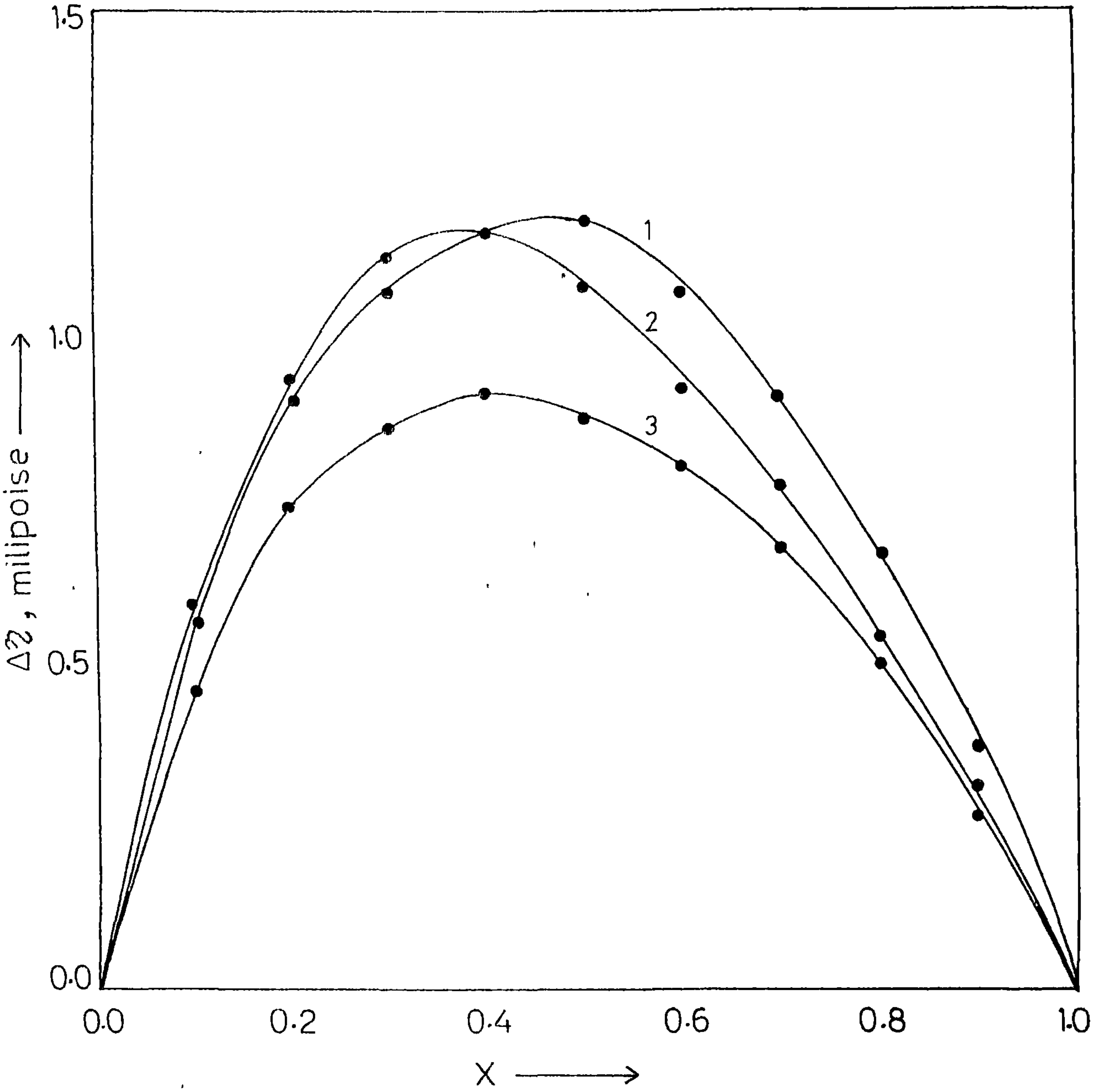

Fig. IV. 1. Variation of Δη, the Difference between η_{cal} and η_{obs}, with the Mole Fraction of Alkyl Benzenes at 25 °C.

1. Benzene- Cyclohexane. 2. Toluene- Cyclohexane- 3. o-Xylene- Cyclohexane.

halomethanes. In addition, it can be seen from the data (Table IV. 1b) that carbon tetrachloride and cyclohexane also interact and form 1:1 complex. However, the interaction seems to be weaker compared to that between benzene-cyclohexane (i.e., the $\Delta\eta_i$ values are smaller) and the strength of interaction as expected decrease with increase *in temperature. Similar observations were made by Brown et* al[51] and Scatchard et al[52] by calorimetric studies. So from this data it is clear that even cyclohexane and carbon tetrachloride do interact to form $\sigma-\sigma$ type complexes. Now it is evident that viscometric studiesaare better than some of the conventional methods like spectroscopic methods in detecting the presence of interaction between such molecules. The activation energies for the viscosities of benzene, toluene, *o*-xylene, carbon tetrachloride and cyclohexane were 8.23, 9.25, 10.98 and 13.58 kJ mol^{-1} respectively. However, for the binary systems there is slight increase in the activation energy with increase in size of the molecule (10.39, 9.96, 10.79 and 11.69 kJ mol^{-1} respectively).

The viscosities of ternary systems, namely benzene-CCl_4- cyclohexane, toluene-CCl_4-cyclohexane, *o*-xylene-CCl_4-cyclohexane of different compositions were determined at different temperature (25. 30. 35 amd 40 °C). No maxima were found in the viscosity curves but the non-linear plot of the difference in viscosities of the mixed solutions (i.e., $\eta_{cal} - \eta_{obsd}$) against the concentration of benzene/alkyl benzenes in cyclohexane indicates the presence of a complex (Fig. IV. 2). For the sake of brevity, the viscosities of mixed solution of benzene/alkyl benzenes-carbon tetrachloride-cyclohexane only at 25 °C are listed in Table IV. 3 (Fig. IV. 3). A continuous variation plot of $\Delta\eta$, the difference in viscosity between the calculated and the observed values for the ternary systems - i.e., benzene-CCl_4-cyclohexane, shows the presence of only a 1:1 complex (i.e., maximum deviation at 0.5 mole fraction) in the experimental range of concentrations (Fig. IV. 2). (Similar observations were made by several workers from calorimetric studies[42]). As mentioned earlier, the deviation between the observed and calculated values is due to the interaction between the two species. From Fig. IV. 2 and the data (Table IV. 4 and IV. 5), it is clear that there is an interaction between the benzene and carbon tetrachloride (in cyclohexane) which decreases with increase in temperature (Table IV. 4). Similar trends are observed in the case of other alkyl benzenes. These observations indicate that the interaction between the alkyl benzenes and carbon tetrachloride decreases not only with the increase in temperature (which is expected) but also with the size and

Table IV. 3a

Viscosities of Mixed Solutions of Benzene-Carbon Tetrachloride in Cyclohexane at 25 °C

Total Concentration :: 1.0 mole

Benzene (in Cyclohexane) (mol)	CCl_4 (in Cyclohexane) (mol)	Calculated Viscosity (millipoise)	Observed Viscosity (m poise)	$\Delta\eta = \eta_{cal} - \eta_{obs}$ (m poise)
0.0	1.0	8.4031	8.1792	0.2239
0.1	0.9	8.3649	8.0636	0.3013
0.2	0.8	8.3271	7.9970	0.3301
0.3	0.7	8.2892	7.9302	0.3588
0.4	0.6	8.2514	7.8469	0.4045
0.5	0.5	8.2137	7.7620	0.4520
0.6	0.4	8.1756	7.6921	0.4835
0.7	0.3	8.1313	7.6114	0.5199
0.8	0.2	8.0924	7.5614	0.5310
0.9	0.1	8.0538	7.5110	0.5430
1.0	0.0	8.0249	7.4491	0.5758

Error Limit :: ± 0.0150

For the sake of convenience, the concentrations are expressed in molar units.

Table IV. 3a

Viscosities of Mixed Solutions of Benzene-Carbon Tetrachloride in Cyclohexane at 25 °C

Total Concentration :: 2 moles

Benzene (in Cyclohexane) (mol)	CCl_4 (in Cyclohexane) (mol)	Calculated Viscosity (milli poise)	Observed Viscosity (milli poise)	$\Delta\eta$ $(=\eta_{cal}-\eta_{obs})$ (milli poise)
0.0	2.0	8.5353	8.1830	0.3523
0.2	1.8	8.4599	7.9865	0.4735
0.4	1.6	8.3847	7.8462	0.5385
0.6	1.4	8.3102	7.7048	0.6054
0.8	1.2	8.2352	7.5617	0.6735
1.0	1.0	8.1604	7.4430	0.7174
1.2	0.8	8.0860	7.3423	0.7437
1.4	0.6	8.0118	7.2340	0.7778
1.6	0.4	7.9381	7.1161	0.8220
1.8	0.2	7.8645	6.9939	0.8706
2.0	0.0	7.7910	6.8695	0.9215

Error Limit :: ± 0.0150.

For the sake of convenience, the concentrations are expressed in molar units.

Table IV. 4

Excess Viscosities ($\Delta\eta = \eta_{cal} - \eta_{obs}$) of Mixed Solutions of Benzene-Carbon Tetrachloride in Cyclohexane at Different Temperatures

Total Concentration :: 1 mole.

Benzene (mol) 66666	Carbon Tetrachloride (mol)	$\Delta\eta$, millipoise			
		25 °C	30 °C	35 °C	40 °C
0.0	1.0	0.2239	0.2190	0.1948	0.1476
0.1	0.9	0.3013	0.2499	0.2460	0.1791
0.2	0.8	0.3301	0.2734	0.2720	0.1873
0.3	0.7	0.3588	0.2993	0.2850	0.2236
0.4	0.6	0.4045	0.3207	0.3000	0.2475
0.5	0.5	0.4520	0.3461	0.3380	0.2843
0.6	0.4	0.4835	0.3750	0.3470	0.3097
0.7	0.3	0.5199	0.3913	0.3697	0.3143
0.8	0.2	0.5310	0.4164	0.3880	0.3333
0.9	0.1	0.5430	0.4429	0.4130	0.3585
1.0	0.0	0.5758	0.4617	0.4286	0.3718

Error Limit :: ± 0.0150

For the sake of convenience, the concentrations are expressed in molar units.

Table IV. 5

Excess of Viscosities of Mixed Solutions of Benzene-CCl_4, Toluene-CCl_4, o-Xylene-CCl_4 in Cyclohexane

Temperature :: 25 °C; Total Concn. :: 1 mole

Benzene/ Alkyl benzenes (mol)	Carbon Tetra-chloride (mol)	$\Delta\eta$ SYSTEMS $(\eta_{cal} - \eta_{obs})$		
		Benzene-CCl_4-Cyclohexane	Toluene-CCl_4-Cyclohexane	o-Xylene-CCl_4-Cyclohexane
0.0	1.0	0.2239	0.2239	0.2239
0.1	0.9	0.3013	0.2850	0.2617
0.2	0.8	0.3301	0.3190	0.2963
0.3	0.7	0.3588	0.3469	0.3326
0.4	0.6	0.4045	0.3834	0.3572
0.5	0.5	0.4520	0.4269	0.3880
0.6	0.4	0.4835	0.4697	0.4122
0.7	0.3	0.5199	0.5070	0.4355
0.8	0.2	0.5310	0.5092	0.4532
0.9	0.1	0.5430	0.5390	0.4943
1.0	0.0	0.5758	0.5507	0.5121

Error Limit :: ± 0.0150

For the sake of convenience , the concentrations are expressed in molar units.

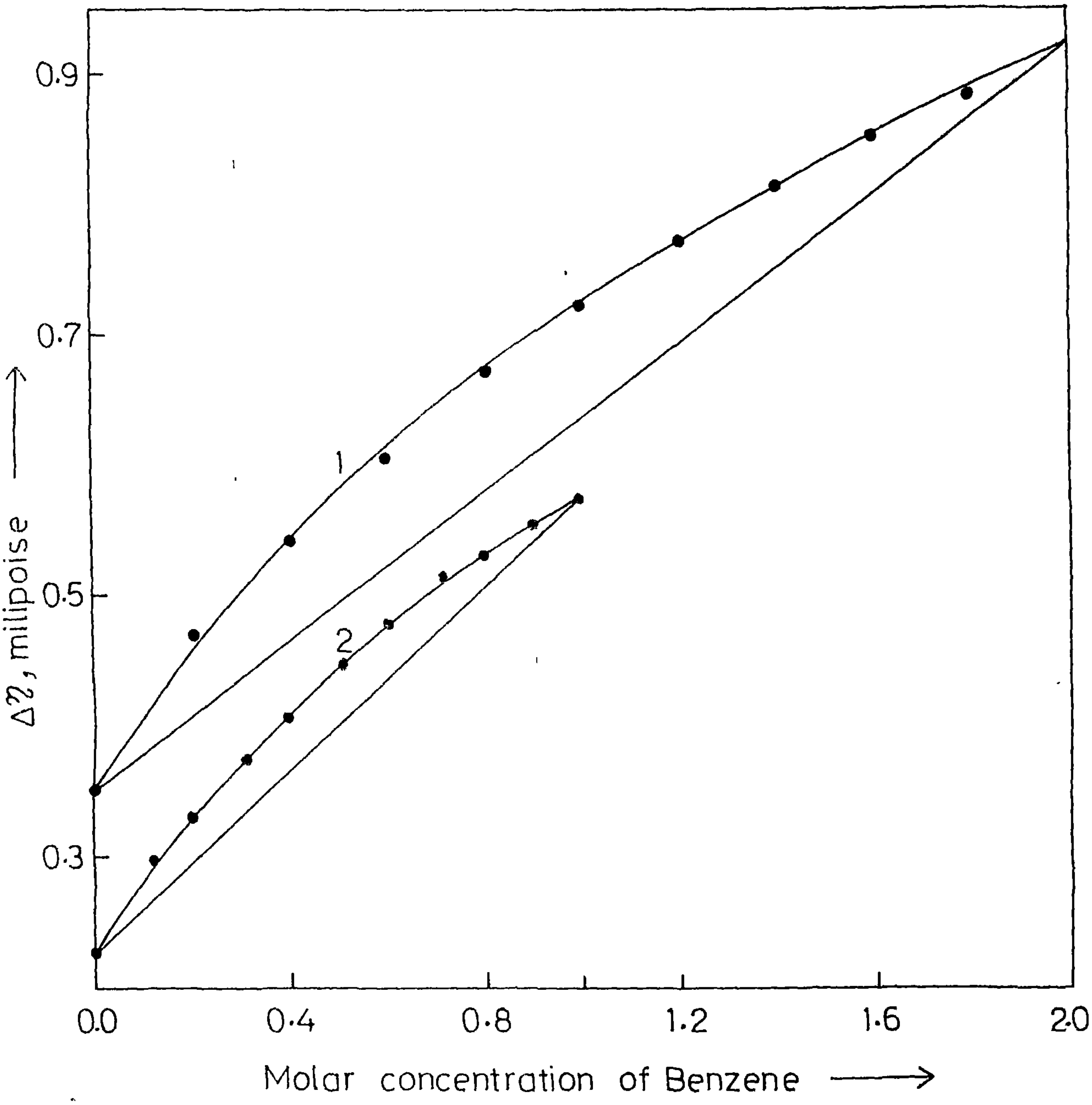

Fig. IV. 2. Variation of $\Delta\eta$ with the Molar Concentration of Benzene in Benzene-CCl_4-Cyclohexane System at 25 °C.

1. Total Concentration :: 2 Molar.

2. Total Concentration :: 1 Molar.

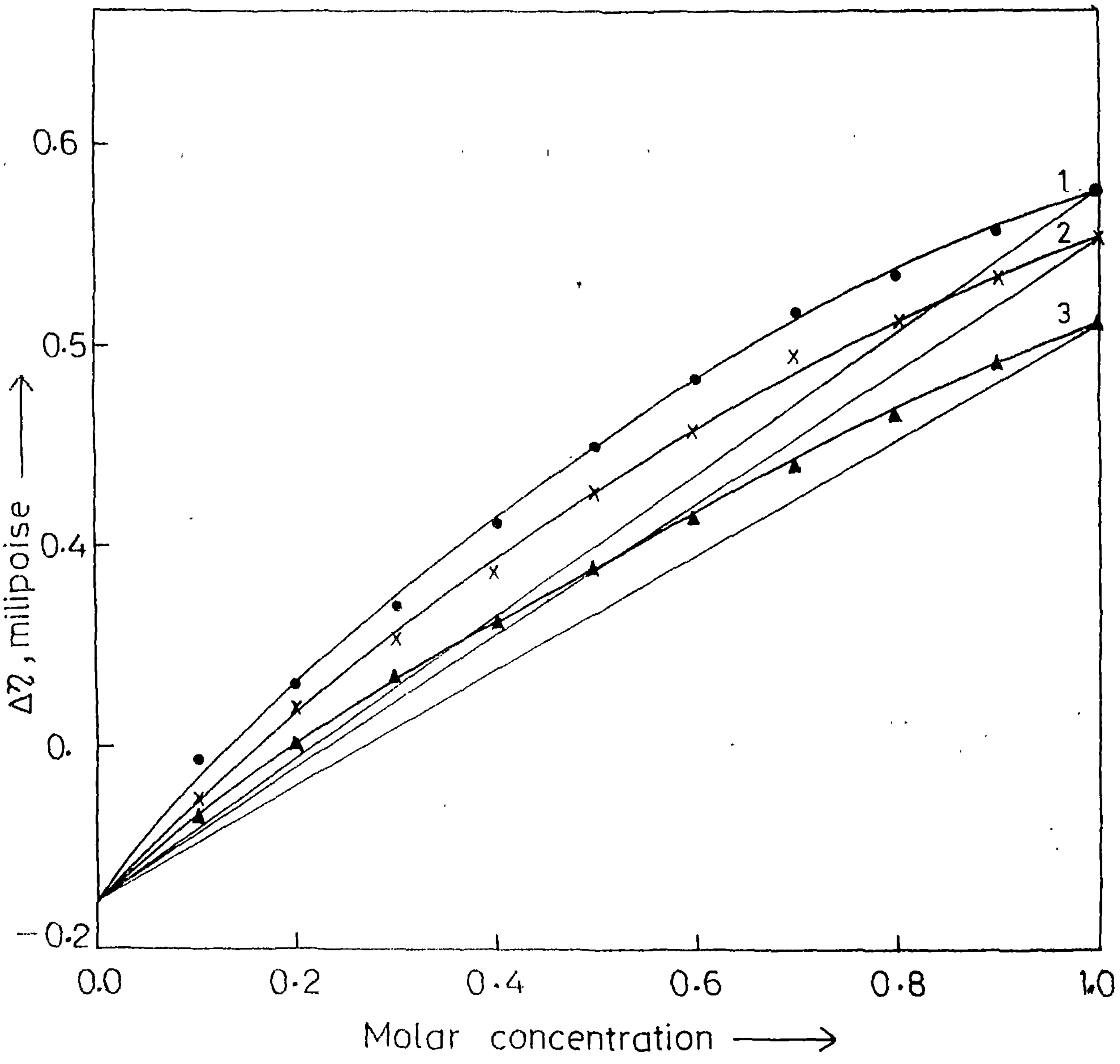

Fig. IV. 3. Excess Viscosity vs Molar Concentration of Benzene-, Toluene-, o-Xylene-CCl_4 in Cyclohexane at 25 °C.

1. Benzene-CCl_4 in Cyclohexane.
2. Toluene-CCl_4 in Cyclohexane.
3. o-Xylene-CCl_4 in Cyclohexane.

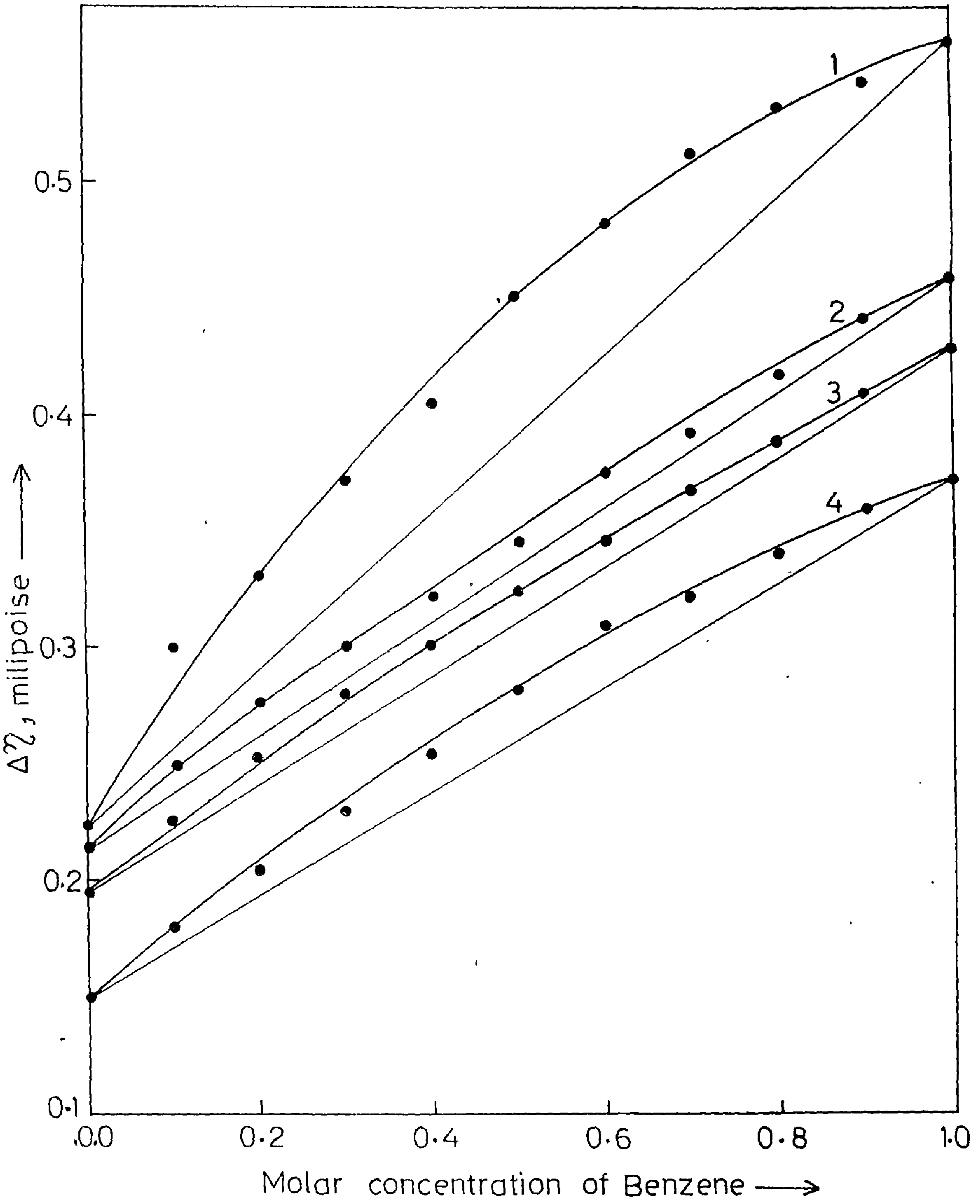

Fig. IV. 4. Excess Viscosity vs Molar Concentration of Benzene in Benzene-CCl_4-Cyclohexane System at 1. 25 °C; 2. 30 °C; 3. 35 °C; 4. 40 °C.

shape of the molecules (Fig. IV, 3). Equilibrium constants (calculated from using equations IV. 5 and IV. 6) and the other thermodynamic parameters of alkyl benzenes—carbon tetrachloride in cyclohexane are listed in Table IV. 6. It can be seen from the tables that the equilibrium constants obtained by viscometric method are higher than the literature data obtained by spectroscopic method. Here it can be recalled that Kohler[53] has rightly pointed that the thermodynamic properties of liquid mixtures are frequently influenced by association or complexation equilibria between certain molecular species. It is often possible to follow the shift in those chemical equilibria by spectroscopic methods. One of the difficulties in comparing thermodynamic and spectroscopic evaluation of complexation equilibria, frequently neglected in literature, is caused by the fact that thermodynamics is determined by the activities of the species whereas spectroscopic properties are determined by their concentrations. (Furthermore, intensity of spectral lines is not always proportional to concentration, but might be influenced by properties of surrounding liquids). Foster[41] has pointed out the limitations of various methods used in determining the equilibrium constants. Prue[54] has argued that even purely contact charge-transfer complex can give rise to equilibrium constant of the order of $K_c \approx$

Table IV. 6

Equilibrium Constants and Other Thermodynamic Parameters of ZAlkyl Benzenes-Carbon Tetra-Chloride in Cyclohexane

SYSTEM	K_c* M^{-1}				$-\Delta H^0$ # kJ/mole at 25°C	ΔG^0 ** kJ/mole at 25°C	$-\Delta S^0$ kJ/mole at 25 °C
	25 °C	30°C	35°C	40°C			
Benzene-CCl_4	0.34 (0.215)	0.29	0.26	0.23	20.6 (5.28)	2.66	0.078
Toluene-CCl_4	0.27 (0.413)	0.25	0.23	0.22	11.0 (4.35)	3.27	0.048
o-Xylene-CCl_4	0.25	0.23	0.22	0.21	9.7	3.39	0.044

* Error Limit :: ± 0.01

\# Error Limit :: ± 1.5

** Calculated from K_c Value at 25 °C.

The Values in parentheses refer to the literature data, J. Chem. Soc. A, 673 (1969).

0.3 l mol^{-1} and it is difficult to accept the lower values reported in the literature. However, recently Bhowmik and Paul[55] have carried out a (spectroscopic) study of interaction of aromatic hydrocarbons with halonils and the K values $\approx$ 0.07 for anthracene-CCl_4, etc. in heptane and ΔH are $\approx$ 8 kJ/mole. It must be noted that in all such systems the equilibrium constants are very low and one should look into the trend/relative values rather than the absolute values. So we feel that the equilibrium constants for alkyl benzenes-CCl_4 in cyclohexane obtained by viscometric method seem to be reasonable. Moreover, the results obtained by different methods may or may not agree as the experimental conditions may be different. Not only that, it is reported in the literature that even for the same system, the equilibrium constants obtained depend on the concentration range of the systems. So under such circumstances, we are not in a position to comment on the slightly higher/lower values of K_c obtained by viscometric method.

The equilibrium constant, K_c, value is decreasing from benzene-CCl_4 to o-xylene-CCl_4. ΔH^o values are also varying in the same order. The trend in our present data agree well with the literature data reported by calorimetric studies.[56] However, our values are high than the literature values. On the basis of polarizability/ionization potential, one would naturally expect that the interaction between benzene and carbon tetrachloride will be weaker compared to either toluene-CCl_4 or o-xylene-CCl_4. But from the present data it appears that the trend is reverse, i.e., the interaction between benzene and CCl_4 is stronger than that between toluene and CCl_4 which in turn is stronger than o-xylene-CCl_4. So, from these limited data we feel that, at least in the present case, the size and shape of the molecules (i.e., geometry) are more predominant factors compared to the polarizabilities in molecular interactions, as the shape of the molecule determines the "closeness" of the partners. It is already reported that o-xylene, due to its structure, cannot approach CCl_4 more closely compared to benzene. So one can rationalise this trend, i.e., the interaction between alkyl benzenes-CCl_4 in cyclohexane varies in the order o-xylene-$CCl_4 <$ toluene-$CCl_4 <$ benzene-CCl_4 (by looking into the structure/shape of molecules) The low positive ΔG^o values indicate the low values of K.

As it stands, the present viscometric procedure demands very careful measurements of viscosities involving long flow times to realise significant differences between solvent and dilute solutions. In addition, there are experimental difficulties, such as accurate measurements of flow times, large amount of solutions, precise temperature control, dust free materials, etc. Moreover, the measurements are time consuming. However, this method is useful where no other alternative is available.

REFERENCES

1. G. Briegleb, "Elektronen Donor-Acceptor Komplexes", Springer Verlgab, Berlin, 1961.
2. R. Foster, "Organic Charge-Transfer Complexes", Academic Press, New York, 1969.
3. J. Rose, "Molecular Complexes", Pergamon Press, Oxford, 1967.
4. C. N. R. Rao, S. N. Bhat and P. C. Dwivedi, Appl. Spectros. Revs., 5, 1 (1971).
5. "Spectroscopy and Structure of Molecular Complexes", Ed. by J. Yarwood, Plenum Press, New York, 1973.
6. J. R. Geoates, R. J. Sullivan and J. B. Ott, J. Phys. Chem., 63, 589 (1959).
7. C. V. Chaturvedi and S. Prakash, Acustica, 27, 248 (1972).
8. N. Prasad, O. Prakash, S. Singh and S. Prakash, Ultrasonics, 16, 77 (1978).
9. M. Karvo and A. Nissema, Finn. Chem. Lett., 132 (1979).
10. M. M. Chaudhury, V. N. Hendric, C. Abbott and M. Michael, J. Chem. Eng. Data, 25, 254 (1980).
11. T. S. Nguyen, U. V. Dang, H. H. Tran, T. H. Tran, B. B. Nguyen and N. T. Pham, Tap. Chi Hoa. Hoc., 18, 25 (1980); CA, 94 : 53697e.
12. M. Karvo, J. Chem. Thermodyn., 12, 635 (1980).
13. K. Masanao, Bull. Chem. Soc. Japan, 53, 1937 (1980); and P. Smith, Aust. J. Chem., 30, 23, 43 (1977).

14. M. Karvo, A. Nissema and T. Kaivamo, Finn. Chem. Lett., 137, 141 (1983); CA, 100 : 145959n; 100 : 145960f.

15. M. R. Nag and K. D. Nayer, J. Ind. Chem. Soc., 29, 250(1952).

16. H. A. Heintz and D. N. Hume, J. Phys. Chem., 61, 462(1957).

17. J. Singh, H. D. Pflug and G. C. Bensoo, J. Phys. Chem., 72, 1939 (1968).

18. I. Nagata and T. Ohta, J. Chem. Eng. Data, 28, 256 (1983).

19. H. M. N. Irving and J. S. Smith, J. Inorg. Nucl. Chem., 31, 159 (1969).

20. M. G. Prolongo, R. M. Masegosa, I. Hernandez Fuentes and A. Horta, J. Phys. Chem., 88, 2163 (1984).

21. L. Pikkarainen, J. Chem. Eng. Data, 28, 344, 381 (1983).

22. R. A. Singh, S. P. Mishra and S. N. Bhat, Proc. Ind. Acad. Sci. (Chem. Sci.), 89, 139 (1979).

23. R. A. Singh and S.N. Bhat, Can. J. Chem., 59, 1212 (1981).

24. R. A. Singh and S. N. Bhat, Bull. Chem. Soc. Japan, 55, 1623 (1982).

25. V. P. Shedbalkar and S. N. Bhat, Bull. Chem. Soc. Japan, 57, 852 (1984).

26. V. P. Shedbalkar and S. N. Bhat, J. Mol. Liquids, 31, 0000 (1985).

27. B.L. Marwein and S.N. Bhat, Acustica, 58, 0000 (1985).

28. R. Gopal, S. Agarwal and D. K. Agarwal, J. Ind. Chem. Soc., 55, 501 (1978); and Y.Marcuss, "introduction to Liquid State Chemistry, Wiley.

29. H. M. N. Irving, and J. S. Smith,
J. Inorg. Nucl. Chem., 31, 3163 (1969).

30. R.P. Shukla and B.P. Bhatnagar, J. Phys. Chem., 60, 809 (1956).

31. A. N. Campbell and F. M. Kartzmark,
J. Chem. Thermodyn., 5, 163 (1973).

32. W. I. Chien and R. L. Rowley,
J. Chem. Eng. Data, 29, 336 (1984).

33. M. Dizechi and E. Marschall, J. Chem. Eng. Data, 27, 358 (1982).

34. M. Palma and J. P. Morel, Can. J. Chem., 59, 3248 (1981).

35. P. Skubla, Collect. Czech. Chem. Commun., 46, 329 (1981);
CA; 94 : 145510s; 145511t.

36. A. I. Vogel, "A. Text Book of Practical Organic
Chemistry", 4th Ed., 1978.

37. P. Jobs, Ann. Chim., 9, 197 (1928).

38. M. E. Baur, D. A. Morsma, C. M. Knobler and P. Perz,
J. Phys. Chem., 73, 641 (1969).

39. Z. Yoshida and E. Osawa, Bull. Chem. Soc. Jpn., 38, 140 (1965).

40. a) R. L. Scott, Proc. Int. Conf. on Coordination
Compounds, Amsterdam, 1955, p. 265.
b) R.L. Scott, Rec. Trav. Chim., 75, 787 (1956).

41. R. Foster in "Molecular Complexes", Part II, Ed. by
R. Foster, Elek. Science,, London, 1974.

42. P.J. Trotter and M.W. Hanna, J. Am. Chem. Soc., 88, 3724 (1966).

43. L. Grunberg and A.H. Nissan, Nature (London), 164, 799 (1949).

44. P. K. Katti and M. Chaudhuri, J. Chem. Eng. Data, J. Chem. Eng. Data, 9, 442 (1964).

45. G. K. Raman, P. R. Naidu and V. R. Krishnan, Aust. J. Chem., 21, 2717 (1968).

46. E.A. Guggenheim, "Mixtures", Oxford Univ. Press, 1952.

47. N. Islam and M. Ibrabim, Ind. J. Chem., 21A, 1026 (1982).

48. J.W. Lorimer and D.E. Jones, Can. J. Chem., 55, 2980(1977).

49. R. K. Nigam, P. P. Singh, R. Mishra and M. Sing, Can. J. Chem., 58, 1468 (1980).

50. J. S. Rowlinson, "Liquids and Liquid Mixtures", Butterworth, London, 1971.

51. I. Brown and A. H. Ewald, Aust. J. Scient. Res., A3, 306 (1950); A4, 198 (1951).

52. G. Scatchard, S. E. Wood and J. M. Mochel, J.Phys. Chem., 43, 119 (1939); J. Am. Chem. Soc., 61, 3206(1939); ibid, 62, 712 (1940).

53. F.Kohler, J.Mol. Liquids, 30, 00C(1985); personal commn.

54. J. E. Prue, J. Chem. Soc., 7534 (1965).

55. a) B. B. Bhowmik and T. K. Paul, Spectrochimica Acta, 38A, 713 (1982).
    b) B. B. Bhowmik and T. K. Paul, Spectrochimica Acta, 40A, 601 (1984).

56. M. L. Glashan, D. Stubley and H. Watts, J. Chem. Soc. A, 673, (1969).

CHAPTER V

VISCOMETRIC STUDIES OF HYDROGEN BONDING[*]

V. 1. INTRODUCTION

Although the spectrophotometric method is probably the commonest method used for the determination of the association constants and other thermodynamic parameters of hydrogen bonded systems and charge transfer complexes, doubts have frequently been raised as to the significance of the values of K_c and ϵ, obtained by spectral method alone.[1-3] Even though, in principle, the formation of molecular complexes and hydrogen bonding can be detected and their composition can be established from a study of characteristic abrupt departures from ideal behaviour in some physical properties, e.g., vapour pressure, refractive index,

---

[*] A paper based on this work has appeared in the Proceedings of the Indian Academy of Sciences (Chem. Sci.), 94A, 461, 1985.

surface tension, etc., many of these methods are hardly used for the study of hydrogen bonding.[3-18] Recently attempts are being made, in our laboratory, to explore the possibilities of using various non-spectral methods like - surface tension, refractive index measurements, constant activity methods, etc., - for studying the interaction between the molecules in solutions to obtain K directly and their applicabilities in obtaining the equilibrium constant directly have been demonstrated.[19-23] It is heartening to note that even though the measurements of various thermodynamic excess functions of binary solutions have been the subject of much research, there is hardly any report on using viscometric method for the study of hydrogen bonding in ternary systems.[24-31] It was therefore felt that it may be worthwhile to make an attempt to study the interaction between proton donors and proton acceptors (i.e., hydrogen bonding/molecular complexes, or that is, between electron acceptors and electron donors) viscometrically, in suitable media and to obtain equilibrium constants "directly". The systems chosen for the studies are : methanol, ethanol, n-propanol and n-butanol as proton donors, acetone as proton accetpor and carbon tetrachloride as solvent. Here it can be mentioned that as "hydrogen bonding" is considered as molecular association/complexes, both the terms are used synonymously in the discussion.

V. 2. MATERIALS AND METHOD

Acetone, carbon tetrachloride, methanol, ethanol, n-propanol and n-butanol were purified by the standard procedures.[32]

Acetone : Purification procedure of acetone is given in Chapter III.

Carbon tetrachloride : Purification procedure of carbon tetrachloride is described in Chapter IV.

Purification of methyl alcohol and ethyl alcohol are given in Chapter II. n-Propyl alcohol (Sarabhai M Chemicals B. N. IJP810604) and n-butanol (SD's B.N. 031/61/22031) were also purified by the similar procedure. Boiling point: n-propanol : 93 °C/661mm (lit. 96 °C/760mm), and n-butanol : 113 °C/658 mm (lit. 116 °C/760 mm).

The densities and viscosities of pure samples and those of "binary mixtures" of known compositions (mole fractions) of methanol, ethanol, n-propanol, n-butanol and acetone in carbon tetrachloride were determined at 25, 30, 35 and 40 °C (± 0.1 °C) by using a pyknometer and Ostawald's Viscometer (No. BS/IP/SL(S) No. 3) respectively and the coefficients of viscosities were calculated; similarly the densities and viscosities of ternary systems (of known compositions) of alcohols-acetone-CCl_4 were determined. The experiments were repeated at least twice and the results were reproducible within the experimental error of ± 0.0150 millipoise.

The stoichiometry of the "associated species (complex)" was determined by Job's continuous variation process.[33]

The procedures for calculating the equilibrium constants and the other thermodynamic parameters of alcohol-acetone-CCl_4 are given in detail in Chapter IV.

V. 3. RESULTS AND DISCUSSION

The viscosities of methanol, ethanol, n-propanol, n-butanol, acetone and carbon tetrachloride and their solutions in carbon tetrachloride were determined at 25, 30, 35 and 40 °C. The viscosities of ethanol, n-propanol and n-butanol in carbon tetrachloride increase with increase in concentration whereas those of methanol in carbon tetrachloride and acetone in carbon tetrachloride decrease with increase in concentration (vide Table V. 1). The observed viscosity of methanol in carbon tetrachloride is higher than that of expected/calculated value [i.e., $\Delta\eta = \eta_{cal} - \eta_{obs} = (x_1\eta_1 + x_2\eta_2 - \eta_{obs})$ is negative] whereas

Table V. 1.

Observed Viscosity Data of MeOH-, EtOH-, n-PrOH-, n-BuOH- and Acetone-CCl_4 Binary Systems at 25 °C

Mole fraction of alcohols/ acetone	Systems				
	MeOH-CCl_4 η_{obs} m poise	EtOH-CCl_4 η_{obs} m poise	n-PrOH-CCl_4 η_{obs} m poise	n-BuOH-CCl_4 η_{obs} m poise	Acetone-CCl_4 η_{obs} m poise
0.0	9.5304	9.5304	9.5304	9.5304	9.5304
0.1	9.1188	9.1380	9.2455	9.4451	8.5907
0.2	8.9251	9.1398	9.3664	9.8004	7.9163
0.3	8.8163	9.2466	9.7378	10.4036	7.2726
0.4	8.6916	9.3640	10.3530	11.3846	6.6655
0.5	8.4879	9.6342	11.1959	12.8174	6.1150
0.6	8.2035	9.9281	12.1499	14.5598	5.5883
0.7	7.7798	10.2150	13.2538	16.6548	5.0811
0.8	7.1603	10.5164	14.4706	18.8728	4.6074
0.9	6.3787	10.7843	15.6995	21.0146	4.1231
1.0	5.4140	10.9760	16.7230	23.0350	3.6460

Error Limit :: ± 0.0150.

in all other alcohols and acetone in carbon tetrachloride they are lower (i.e., $\Delta\eta$ is positive). The deviation between the observed and calculated values in methanol-CCl_4 system, i.e. $\Delta\eta$, shows that there is interaction between methanol and carbon tetrachloride and maximum deviation is observed at 3:2 compositions and the stoichiometry is temperature independent (Table V. 2). As the observed values are higher than the expected values, it appears that due to "complexation/Association" (between CH_3OH and CCl_4 molecules) the viscosity of the system increased. Similarly, in the case of acetone-CCl_4 systems expected and observed values of η are different, which again indicate the existence of interaction between acetone and carbon tetrachloride. The maximum deviation in the plot of $\Delta\eta$ against the mole fraction of acetone in acetone-CCl_4 appears at 0.4 mole fraction of acetone indicating the presence of 2:3 complex. It is known in the literature that acetone and carbon tetrachloride do interact to form a complex.[34,35] Singh and Rao[36] have shown from infrared studies that methanol and ethanol formed dimers or trimers even in very dilute solutions (in CCl_4) ($\sim$0.01 M). An NMR study of methanol in CCl_4 showed the existence of trimers and octamers even in very dilute solutions.[37] Therefore, it is quite safe to assume that methanol etc.

Table V. 2

Excess Viscosity ($\Delta\eta = \eta_{cal} - \eta_{obs}$) Data and Grunberg and Nissan Parameters(d) of Alcohols-, Acetone-Carbon Tetrachloride Binary Mixtures at 25 °C

(i) Methanol-CCl_4, Ethanol-CCl_4 and Acetone-CCl_4 Systems:

Mole fraction of Alcohols/ Acetone	Systems					
	MeOH-CCl_4		EtOH-CCl_4		Acetone-CCl_4	
	$\Delta\eta$ m poise	d	$\Delta\eta$ m poise	d	$\Delta\eta$ m poise	d
0.1	-0.0646	0.1377	0.5360	-0.6241	0.3512	-0.0858
0.2	-0.2180	0.2967	0.6797	-0.4381	0.437	0.0413
0.3	-0.5208	0.4369	0.7177	-0.3457	0.4925	0.0851
0.4	-0.8077	0.5586	0.7445	-0.3087	0.5111	0.1117
0.5	-1.0157	0.6676	0.6190	-0.2391	0.4732	0.1467
0.6	-1.1429	0.7890	0.4697	-0.1827	0.4115	0.1779
0.7	-1.1309	0.9185	0.3270	-0.1404	0.3301	0.2078
0.8	-0.9230	1.0404	0.1703	-0.0908	0.2155	0.2616
0.9	-0.5531	1.1936	0.0472	-0.0388	0.1113	0.2988

Error Limit :: ± 0.0150.

Table V. 2. contd..../-

Table V. 2

(contd...)

(ii) n-PrOH-CCl_4 and n-BuOH-CCl_4 Systems:

Mole fraction of n-Alcohols	Systems			
	n-PrOH-CCl_4		n-BuOH-CCl_4	
	$\Delta\eta$ m poise	d	$\Delta\eta$ m poise	d
0.1	1.0042	- 0.9620	1.4360	- 1.0806
0.2	1.6025	- 0.8113	2.4309	- 0.9286
0.3	1.9504	- 0.7007	3.1782	- 0.8433
0.4	2.0544	- 0.5922	3.5476	- 0.7302
0.5	1.9308	- 0.4803	3.4652	- 0.5798
0.6	1.6961	- 0.3939	3.0734	- 0.4406
0.7	1.3114	- 0.3039	2.3288	- 0.2836
0.8	0.8139	- 0.2013	1.4613	- 0.1424
0.9	0.3042	- 0.0770	0.6699	- 0.0394

Error Limit :: ± 0.0150.

associate through hydrogen bonding even in carbon tetrachloride solutions. Scatchard and his colleagues[38] had studied the interaction between methanol and carbon tetrachloride calorimetrically and had come to similar conclusions. So when carbon tetrachloride molecule approaches alcohol molecules, there is a 'breaking' of hydrogen bonding between alcohol molecules and, formation of hydrogen bonding between (oxygen of) methanol and (chlorine of) carbon tetrachloride occurs.[39] Methanol is smaller molecule (compared to other alcohol molecules) and the dimerization energy in methanol is maximum and it decreases from methanol to n-butanol.[3] As the dimerization energy is more for methanol molecules, stability of "associated" species is higher. So naturally breaking of hydrogen bonding of methanol molecules (i.e., structure breaking effect) and then forming new hydrogen bonding (i.e., structure making effect) between MeOH and CCl_4 is less favoured compared to ethanol-, or n-propanol-, or n-butanol-CCl_4 systems and that is what has been observed.[36] From the data (Table V.2), it can be seen that the deviation, $\Delta\eta$, increases in the order MeOH-CCl_4 $<$ EtOH-CCl_4 $<$ n-PrOH-CCl_4 $<$ n-BuOH-CCl_4, indicating that MeOH-CCl_4 interaction is less favoured (negative values) compared to n-BuOH-CCl_4 (Fig. V. 1). This trend is maintained at all the temperatures, i.e., 25, 30,

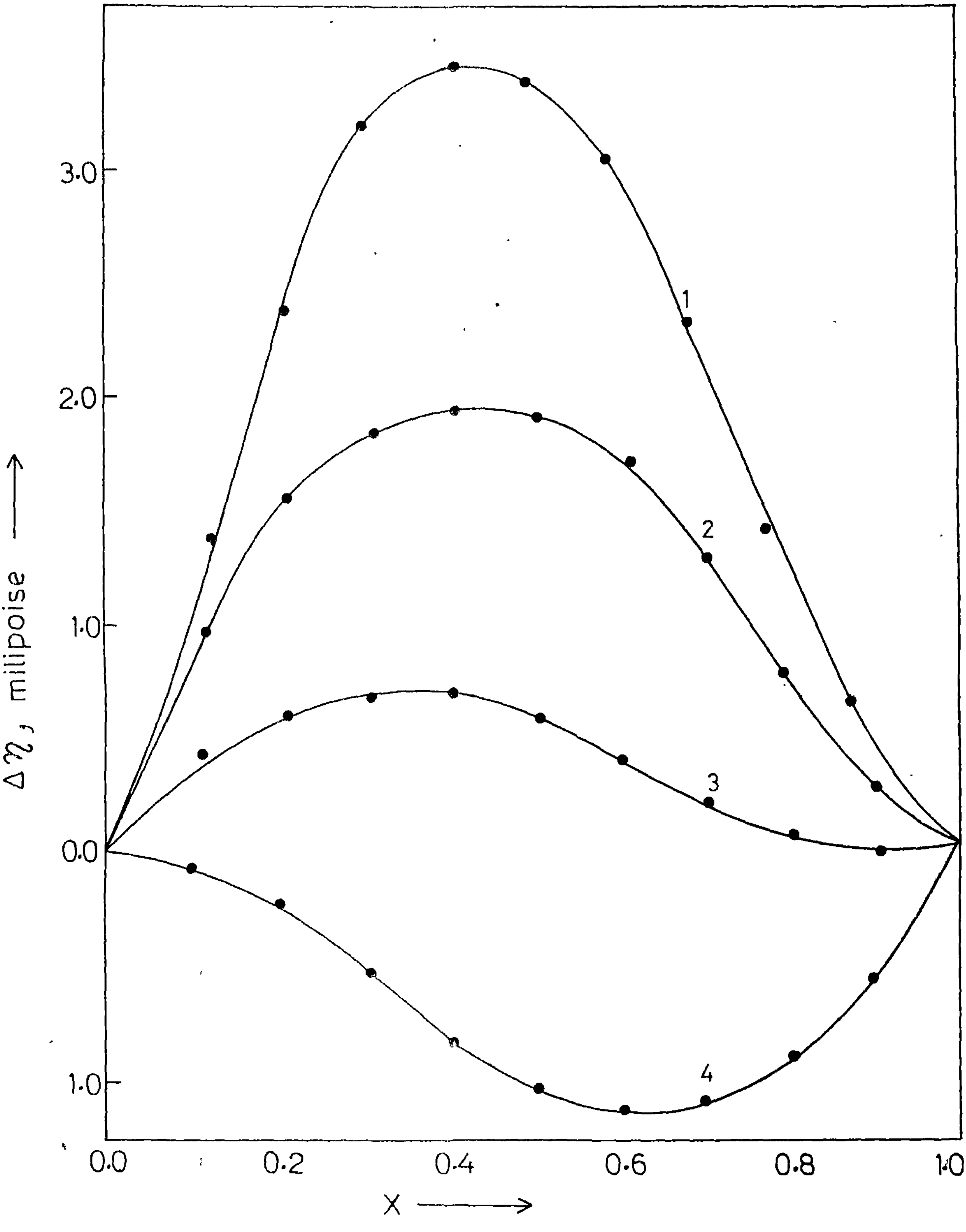

Fig. V. 1. Variation of $\Delta\eta$, the Difference between η_{cal} and η_{obs} with the Mole Fraction of n-Alcohols at 25 °C. 1. n-BuOH-CCl_4 2. n-PrOH-CCl_4 3. EtOH-CCl_4 4. MeOH-CCl_4

35, 40 °C, that we have studied (Table V. 3). As mentioned earlier, from the plot of $\Delta\eta$ against the mole fraction of alcohols (ethanol, propanol and butanol) (Job's method)[33] the maximum deviation appears at ~0.4 mole fraction of alcohol indicating the stoichiometry 2:3 in EtOH-CCl_4, n-PrOH-CCl_4 and n-BuOH-CCl_4; similar observations are reported in the literature for higher alcohols-dichloromethane.[40,41] The deviation decreases with increase in temperature showing that the interaction between n-alcohols-CCl_4 decreases with increase in temperature, which is expected in all the 'exothermic' equilibrium cases (Table V. 3). The energy of activation (for viscous flow) of pure components, namely, methanol, ethanol, n-propanol, n-butanol and acetone and carbon tetrachloride were 10.5, 16.9, 19.1, 21.0, 6.9 and 10.9 kJ mol^{-1} respectively, and for the binary mixtures of these respective alcohols in CCl_4 the values are 10.5, 11.9, 12.7, and 13.7 (± 0.01) kJ mol^{-1} respectively. From the present data, eventhough one would be tempted to conclude that the viscosity and energy of activation depends on the size/shape of the molecule, one has to be cautious in cases, like the present one, where one is dealing with already 'associated' species and there may be more than one H-bonded species between donor and acceptor molecules. It can be seen from the above data that the

Table V. 3.

Excess Viscosities of Alcohols-, Acetone-Carbon Tetrachloride Binary Mixtures at Different Temperatures

Temperature °C	Systems				
	MeOH*-CCl_4 $\Delta\eta$ (m poise)	EtOH#-CCl_4 $\Delta\eta$ (m poise)	n-PrOH#-CCl_4 $\Delta\eta$ (m poise)	n-BuOH#-CCl_4 $\Delta\eta$ (m poise)	Acetone#-CCl_4 $\Delta\eta$ (m poise)
25	- 1.1429	0.7445	2.0544	3.5476	0.5111
30	- 0.9919	0.6582	1.9357	2.9503	0.4124
35	- 0.9905	0.4743	1.4309	2.3751	0.2250
40	- 0.9074	0.3500	1.2267	1.9974	0.1782

* Mole fraction of MeOH = 0.6.

\# Mole fraction of EtOH, n-PrOH, n-BuOH, Acetone = 0.4.

Error Limit :: ± 0.0150.

energies of activation of the "mixtures" of alcohols-CCl_4 are lower than that of alcohol, which we are not in a position to explain as we are dealing with "complex"/"associated" molecules.

The viscosities of ternary systems, namely alcohols-acetone-carbon tetrachloride of different compositions are determined at different temperatures (25, 30, 35 and 40 °C). No maxima are found in the viscosity curves. But the non-linear plot of the difference in viscosities of the mixed solutions (i.e., $\eta_{cal} - \eta_{obs}$) against the concentration of acetone indicates the presence of hydrogen bonding/a complex. A continuous variation plot of $\Delta\eta$, the difference in viscosity between the "mixed solutions" and the calculated viscosities of the solutions shows the presence of 1:1 complex in the experimental range of concentration (Fig. V. 2). The viscosities of mixed solutions of n-alcohols-acetone-carbon tetrachloride at 25 °C are listed in Tables V. 4 and V. 5. From the Figure V. 2, it is clear that there is interaction between acetone and alcohol in CCl_4. The interaction (area under the curve in the plot) is increasing from MeOH-acetone-CCl_4 to n-BuOH-acetone-CCl_4 systems (Figure V. 3), and this indicates the relative strength of the "complexes", i.e., n-BuOH-acetone-CCl_4 > n-PrOH-acetone-CCl_4 > EtOH-acetone-CCl_4 > MeOH-acetone-CCl_4.

Table V. 4a.

Viscosities of Mixed Solutions of MeOH-Acetone in Carbon Tetrachloride at 25 °C.

Total Concentration :: 1 mole.

MeOH (mol)	Acetone (mol)	η_{cal} (millipoise)	η_{obs} (millipoise)	$\Delta\eta = \eta_{cal} - \eta_{obs}$ (millipoise)
1.0	0.0	9.1533	9.1066	0.0467
0.9	0.1	9.1359	9.0311	0.1048
0.8	0.2	9.1183	8.9847	0.1336
0.7	0.3	9.1006	8.8971	0.2035
0.6	0.4	9.0828	8.8449	0.2379
0.5	0.5	9.0649	8.8019	0.2630
0.4	0.6	9.0469	8.7507	0.2962
0.3	0.7	9.0287	8.7051	0.3236
0.2	0.8	9.0105	8.6565	0.3540
0.1	0.9	8.9922	8.6033	0.3889
0.0	1.0	8.9736	8.5760	0.3976

Error Limit :: ± 0.0150.

For the sake of convenience, the concentrations are expressed in molar units.

Table V. 4b.

Viscosities of Mixed Solutions of MeOH-Acetone in Carbon Tetrachloride at 25 °C

Total Concentration :: 2 mole.

Methanol (mol)	Acetone (mol)	η_{cal} (millipoise)	η_{obs} (millipoise)	$\Delta\eta = \eta_{cal} - \eta_{obs}$ (millipoise)
2.0	0.0	8.8143	8.9588	- 0.1445
1.8	0.2	8.7791	8.8344	- 0.0552
1.6	0.4	8.7433	8.7330	0.0102
1.4	0.6	8.7072	8.6399	0.0673
1.2	0.8	8.6706	8.5116	0.1590
1.0	1.0	8.6336	8.4171	0.2165
0.8	1.2	8.5961	8.3170	0.2791
0.6	1.4	8.5581	8.2251	0.3330
0.4	1.6	8.5197	8.1341	0.3856
0.2	1.8	8.4808	8.0698	0.4110
0.0	2.0	8.4413	8.0020	0.4393

Error Limit :: ± 0.0150.

For the sake of convenience, the concentrations are expressed in molar units.

Table V. 5.

Excess Viscosities of n-Alcohols-Acetone in Carbon Tetrachloride at Different Temperatures

Total Concentration :: 1 mole(1:1).

Temperature °C	Systems			
	MeOH-Acetone-CCl_4 $\Delta\eta$(m poise)	EtOH-Acetone-CCl_4 $\Delta\eta$(m poise)	n-PrOH-Acetone-CCl_4 $\Delta\eta$(m poise)	n-BuOH-Acetone-CCl_4 $\Delta\eta$(m poise)
25	0.2630	0.5308	0.7127	0.9520
30	0.1983	0.4375	0.6174	0.7833
35	- 0.0081	0.2091	0.3688	0.4940
40	- 0.0269	0.1641	0.3072	0.4629

Error Limit :: ± 0.0150.

For the sake of concenience, the concentrations are expressed in molar units.

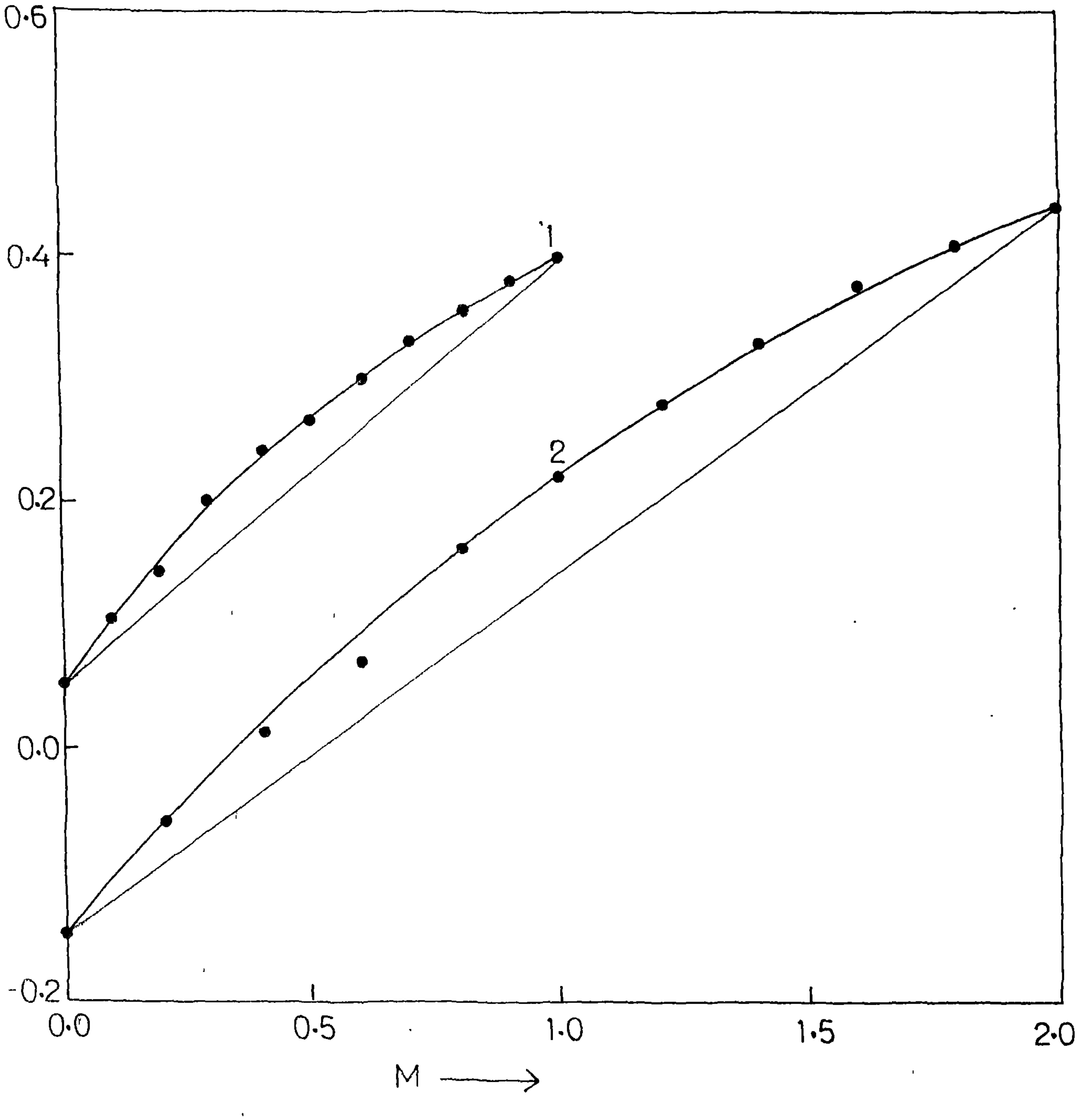

Fig. V. 2. Variation of $\Delta\eta$ with the Molar Concentration of Acetone in MeOH-Acetone-CCl_4 System at 25 °C.

1. Total Concentration :: 1 Molar.

2. Total Concentration :: 2 Molar.

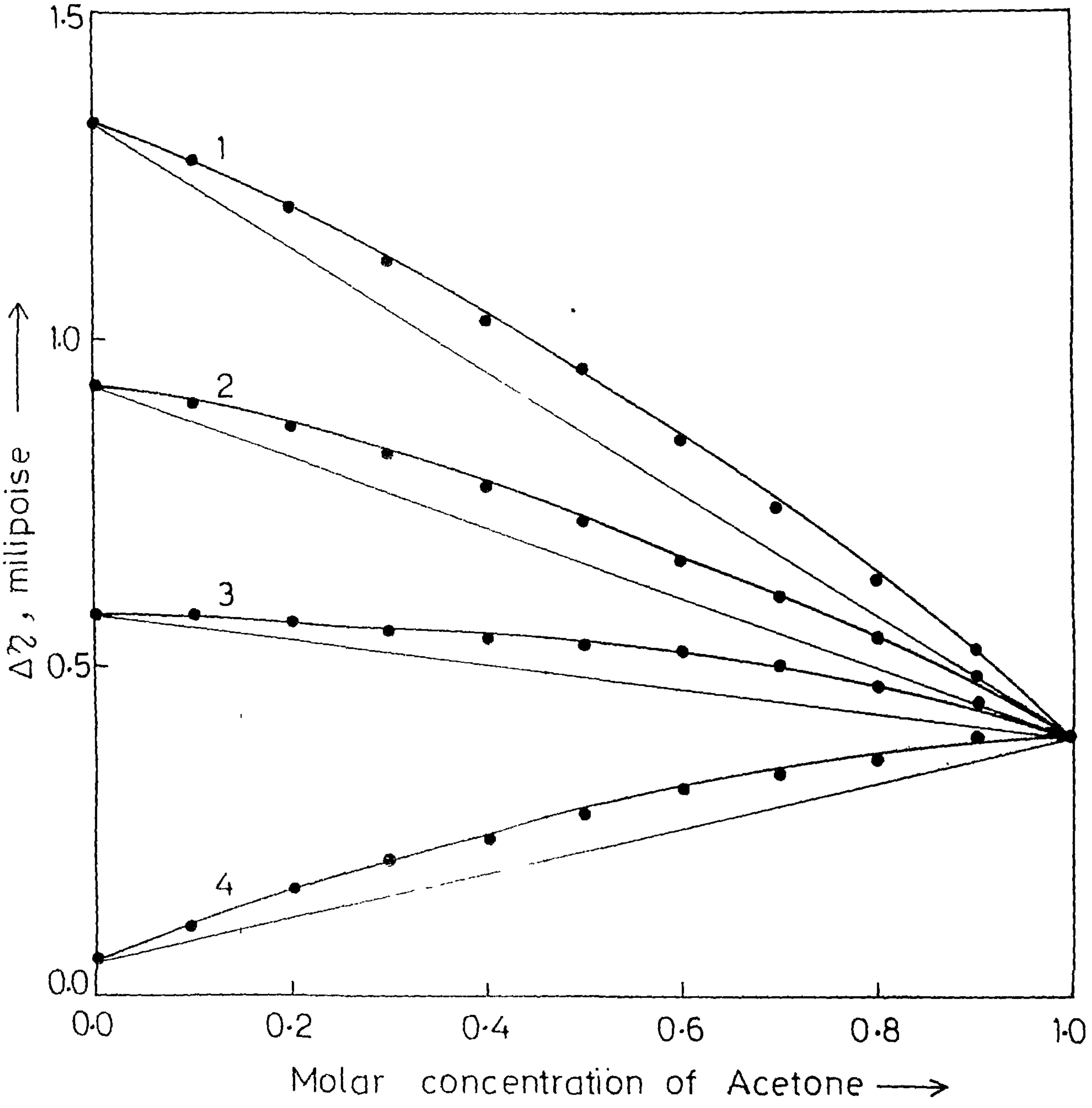

Fig. V. 3. Excess Viscosity vs Molar Concentration of Acetone in n-Alcohols-Acetone-CCl_4 System at 25 °C.

1. Acetone-n-Butanol-CCl_4.
2. Acetone-n-PrOH-CCl_4.
3. Acetone-EtOH-CCl_4.
4. Acetone-MeOH-CCl_4.

The equilibrium constants were calculated (from concentration of the species rather than activities) by using the equation given in Chapter IV. 6 and at 25 °C, they are 0.22, 0.30, 0.38 and 0.52 M^{-1} ($\pm$ 0.01) for MeOH-acetone, EtOH-acetone, n-PrOH-acetone and n-BuOH-acetone in CCl_4 respectively. Here it is worth mentioning that Tamres and Strong[42] have rightly pointed out that even contact charge-transfer complexes should have K values of the order of 0.11 M^{-1}. So our present values of K seem to be reasonable. Equilibrium constants and other thermodynamic parameters of n-alcohols-acetone in carbon tetrachloride are listed in Table V. 6. From the data it is clear that the formation constants (of hydrogen bonding formation) increases from MeOH-acetone to n-BuOH-acetone (assuming that the standard enthalpy of formation ΔH^o of the H-bond in a complex A—H.....B and its standard entropy of formation are independent of temperatures). The heat of formation of these hydrogen bonded systems were obtained from the plot of log K_c vs 1/T and these values are slightly higher than normal ($-\Delta H^o$ for MeOH-acetone, EtOH-acetone, n-PrOH-acetone and n-BuOH-acetone in CCl_4 are 63.4, 46.5, 40.7 and 37.5 kJ/mole respectively), and the trend is reverse compared to the equilibrium constants. However, similar observations were made in literature for purine-H_2O-DMSO,[43] heterocyclic

Table V. 6.

Equilibrium Constants and the Other Thermodynamic Parameters of n-Alcohols-Acetone in Carbon Tetrachloride

System	K_c^*, M^{-1} #				$-\Delta H^o$ ** kJ/mole at 25 °C	ΔG^o kJ/mole at 25 °C	$-\Delta S^o$ kJ/mole
	25 °C	30 °C	35 °C	40 °C			
MeOH-Acetone	0.22	0.16 (2.51)	0.09	0.07	63.5	3.1	0.22
EtOH-Acetone	0.30	0.22	0.17	0.12	46.5	2.9	0.17
n-PrOH-Acetone	0.38	0.25	0.21	0.17	40.7	2.7	0.15
n-BuOH-Acetone	0.52	0.41 (2.04)	0.31	0.26	37.5	1.6	0.13

\# Error Limit :: ± 0.01.

** Error Limit :: ± 1.5.

Values in the parenthesis refer to the literature data : J. Indian Chem. Soc., 58, 320 (1981).

compounds-phenol,[44] malamine cyanourate.[45] Here it can be recalled that the large enthalpies ($\sim$60 kJ/mole) of formation of hydrogen bonding of nitro-phenols with picric acid has been explained in terms of formation of 1:1 proton transfer complexes in preference to the 1:1 H-bonded complexes.[3] However in the present case neither we are able to account for such high values of ΔH nor for such reverse trend compared to the equilibrium constants. Most of the time, the literature data are for binary systems, and here we have all ternary systems. The values for the heats of complexation/hydrogen bonding must be considered as representing a composite result for alcohol-acetone-CCl_4 systems of different alcohol aggregation,[46] rather than individual binary systems. The process of self association and preferential solvation will result in a complex which seems to consist of acetone molecule interacting with an aggregate containing many alcohol molecules. The number of alcohol molecules in the aggregate is concentration dependent because of different degrees of self association and solvation. It is possible that the donor strength of the alcohol may change after association. Molecular orbital calculations on the association of water, methanol and other hydrogen bonded molecules show that the charge distribution of the polymeric molecules is different from that of the monomers.[47-50]

The negative charge on the oxygen atom in the molecule acting as the proton donor increases when the hydrogen bond is formed, and increases still more if a trimer is formed; this in turn causes more positive charge on proton and the interaction between proton and oxygen of acetone will be stronger. For an exothermic reaction, ΔG^o will be negative. However, in the present case ΔG^o is positive ($K < 1$); and ΔS^o is negative and this is possible because of large negative ΔH^o.

As mentioned earlier, the present procedure demands very careful measurements of viscosities involving long flow times in order to realise significant difference between solvent and dilute solutions. So even though the viscometric method can be used for studying the interaction between the molecules in solution (H-bonding), this method may be more applicable where no alternative is available.

REFERENCES

1. J. D. Childs, S. D. Christian, J. Grundness and S. R. Roach, Acta Chem. Scand., 25, 1679 (1971).
2. J. D. Childs, S. D. Christian and J. Grundness, J. Am. Chem. Soc., 94, 5657 (1972).
3. S. N. Vinogaradov and R. H. Linnel, 'Hydrogen Bonding', Van Nostrand Reinhold Co., New York, 1971.
4. J. R. Geoates, R. J. Sullivan and J. Bott, J. Phys. Chem., 63, 589 (1959).
5. C. V. Chaturvedi and S. Prakash, Acustica, 27, 248 (1972).
6. N. Prasad, O. Prakash, S. Singh and S. Prakash, Ultrasonics, 16, 77 (1978).
7. M. Karvo and A. Nissema, Finn. Chem. Lett., 65, 132 (1979); CA; 91 : 192625f.
8. M. M. Chaudhury, V. N. Hendric, C. Abbott and M. Michael, J. Chem. Eng. Data, 25, 254 (1980).
9. T. S. Nguyen, U. V. Dang, H. H. Tran, T. H. Tran, B. B. Nguyen and N. T. Pham, Tap. Chi. Hoa Hoc., 18, 25 (1980); CA; 94 : 53697e.
10. M. Karvo, J. Chem. Thermodyn., 12, 635 (1980).
11. K. Masanao, Bull. Chem. Soc. Jpn., 53, 1937 (1980).
12. M. Karvo, A. Nissema and T. Kaivamo, Finn. Chem. Lett., 137, 141 (1983); CA; 100 : 145959n 145960f.

13. I. Nagata and T. Ohta, J. Chem. Eng. Data, 28, 256(1983).

14. F. Smith, Aust. J. Chem., 30, 23, 43 (1977).

15. Y. Marcuss, "Introduction to Liquid State Chemistry", Wiley Science, New York.

16. "Chemical Thermodynamics", Vol. 2, Ed. by M. L. McGlashan - The Chemical Society, London, 1978.

17. R. H. Stokes and M. Adamson, J. Chem. Thermodynamics., 8, 683, 709 (1976).

18. L. Pikkarainen, J. Chem. Eng. Data, 28, 344, 381 (1983). CA; 100 : 127614s.

19. a) R. A. Singh and S. N. Bhat, J. Phys. Chem., 82, 2322 (1978).
    b) ibid, Can. J. Chem., 59, 1212 (1981).

20. R. A. Singh, S. R. Mishra and S. N. Bhat, Proc. Ind. Acad. Sci. (Chem. Sci.), 89, 139 (1980).

21. B. Bhattacharjee and S. N. Bhat, Proc. Ind. Acad. Sci. (Chem. Sci.), 92, 147 (1983).

22. a) V. P. Shedbalkar and S. N. Bhat, Bull. Chem. Soc. Jpn., 57, 852 (1984).
    b) ibid, J. Mol. Liquids, 31, 0000 (1985).

23. B. L. Marwein and S. N. Bhat, Acustica, 58, 0000 (1985).

24. H. M. N. Irving and J. S. Smith, J. Inorg. Nucl. Chem., 31, 159, 3163 (1969).

25. R. P. Shukla and R. P. Bhatnagar,
J. Phys. Chem., 60, 809 (1956).

26. A. N. Campbell and F. M. Kartzmark,
J. Chem. Thermodynamics, 5, 163 (1973).

27. W. I. Chien and R. L. Rowley,
J. Chem. Eng. Data, 29, 336 (1984).

28. M. Dizechi and E. Marschall, J. Chem. Eng. Data,
27, 358 (1982); CA; 97 : 28874q.

29. M. Palma and J. P. Morel, Can. J. Chem., 59, 3248 (1981).

30. P. Skubla, Collect. Czech. Chem. Commun.,
46, 329 (1981); CA; 94 : 145510s; 145511t.

31. K. Noda, Kagaku Kogaku Ronbeenshu, 9, 237 (1983).

32. A. Weissberger, Ed., "Techniques of Chemistry", Vol. IV,
"Organic Solvents", Wiley Interscience, New York, 1970.

33. P. Job, Anals. Chim., 9, 197 (1928).

34. C. N. R. Rao, S. N. Bhat and P. C. Dwivedi,
Appl. Spectros. Revs., 5, 1 (1972).

35. J. S. Rowlinson, "Liquid and Liquid Mixtures",
Butterworths, London, 1971.

36. S. Singh and C. N. R. Rao, J. Phys. Chem., 71, 1074 (1967).

37. W. P. Dixon, J. Phys. Chem., 74, 1396 (1970.

38. a) G. Scatchard and L. B. Ticknor,
J. Am. Chem. Soc., 74, 3724 (1952).
b) G. Scatchard and F. G. Satkiewiet,
J. Am. Chem. Soc., 86, 130 (1964).

39. L. K. Patterson and R. M. Hanmaker,
Spectrochim Acta, 23A, 2333 (1967).

40. N. M. Chaudhury and P. R. Naidu,
Can. J. Chem., 59, 2210 (1981).

41. K.S. Reddy and P.R. Naidu, Can. J. Chem., 55, 76(1977).

42. M. Tamres and R. L. Strong, "Molecular Association",
Ed. by R. Foster, Academic Press, New York, 1979.

43. F. I. Kanbour, J. K. Ahmed and G. A. W. Derwish,
J. Solution Chem., 12, 763 (1983).

44. O. V. Sverdlova and N. L. Vatolina, Spektrokhim.
Vnutri-Mezhmol Vzaimodeistvii, 3, 168 (1983);
CA; 100 : 85172p, 120357b.

45. A. I. Finkel'shtein and O. S. Rukerich, Zh. Prikl.
Spektrosk, 38, 327 (1983); CA; 98 : 160088m.

46. H. C. Tse and M. Tamres, J. Phys. Chem., 81, 1376(1977)

47. J. R. Hoyland and L. B. Kier,
Theor, Chim. Acta, 15, 1 (1969).

48. A. S. N. Murthy, R. E. Davis and C. N. R. Rao,
Theor. Chim. Acta, 13, 81 (1969).

49. A. S. N. Murthy, S. N. Bhat and C. N. R. Rao,
J. Chem. Soc. A, 1251 (1970).

50. H. Marita and S. Nagakura,
Theor. Chim. Acta, 27, 325 (1972).

CHAPTER VI

STUDY OF MOLECULAR COMPLEXES BY INFRARED SPECTROSCOPY*

VI. 1. INTRODUCTION

The charge-transfer theory developed by Mulliken[1] predicts the perturbation of donor, acceptor bands and appearance of new bands, depending on the strength of interaction between the donor and acceptor. If the interaction between donor and acceptor is weak, there will be only perturbation of donor/acceptor bands and if the interaction is strong, new band(s) may appear in addition to the perturbation of constituent molecular bands. So the "amount of perturbation" in donor/acceptor band (and appearance of new band(s)) is an indication of the strength of interaction, i.e., weak, medium or strong.[2]

---

* A paper based on this work is communicated to Indian Journal of Chemistry, 1985.

The formation of D—A bonds, between donor and acceptor molecules, usually leads to considerable changes in the vibrations of the systems in addition to the appearance of new intermediate vibrations due to vibrational motions of atoms and atom groups relative to the D—A bond and sometimes due to the allowed transitions, as a result of changes in molecular symmetry; moreover, the intensity of the bands may be affected considerably. So the direct information on the properties of D—A bonds can be best provided by studying new intermolecular vibrations (and the perturbed bands of the donor and acceptor too), mainly of the valence vibrations of the donor-acceptor bands themselves. It is surprising to note that even though large number of papers on infrared and Raman spectra of $\underline{n}$-σ complexes have been published, hardly any IR spectral studies on $\underline{n}$-π and π-π complexes have been reported (ref. no. 2-18). Moreover, most of the researchers, it appears, were interested in the spectra of halogens (acceptor) rather than on the spectra of complexes. So we have made an attempt to investigate the interaction of a few n donors (which can behave as π donors also) with σ and π acceptor to understand the mode of interactions between the donors and acceptors. For this purpose, we have chosen pyridine, α-, β-, γ-picolines and 2-amino pyridine (which can behave as **n** as well as π donors) and iodine (σ-acceptor), chloranil, bromanil and iodanil (π-acceptors).

VI. 2. MATERIALS AND METHODS

VI. 2(i). MATERIALS

The electron donors, namely, pyridine, α-picoline, β-picoline, γ-picoline and 2-amino pyridine and electron acceptors iodine and chloranil were available commercially and were purified following the standard procedures.[19] The other two electron acceptors, bromanil and iodanil were synthesized and purified following the recommended procedures.[20]

Pyridine (IDPL B. N. 0030980), α-picoline (IDPL B. N. 0010770, β-picoline (IDPL B. N. 0010177), γ-picoline were refluxed with KOH for 4 to 5 hours and then distilled. (Care was taken to any passage of moisture) and collected in stoppered bottles. B. P. of Pyridine 111 °C/672 mm (lit. 113 °C/760 mm), α-picoline 122 °C/670 mm (lit. 125 °C/760 mm), β-picoline 144 °C/670 mm (lit. 146 °C/760 mm), γ-picoline 138 °C/670 mm (lit. 140 °C/760 mm).

2-Amino pyridine (SD's B. N. 18032/37135) was recrystallized from benzene. M. P. 56 °C. (lit. 57.5 °C).

Iodine (SM B. N. 9GP 9192) (10 g) was mixed thoroughly with 4 g of KI and the mixture was resublimed thrice. The resublimed iodine was collected and stored in a coloured bottle.

Commercially available Chloranil (Loba, B.N. 100) was recrystallized several times from toluene. M. P. of chloranil 288 °C (lit. 290 °C).

Bromanil : 25 grams of hydroquinone (SISCO B. N. B/705262) suspended in 150 ml of glacial acetic acid and was treated with 200 g (6 mol) of bromine (~64.5 ml at 20 °C) and the mixture was kept over night. To the mixture was then added an equal volume of water and concentrated HNO_3 and heated on the steam bath till bromine was no longer evolved. Bromanil was recrystallized from ethanol. M. P. 299 °C (lit. 300 °C).

Iodanil : 12.5 grams of bromanil mixed with 11.5 g of potassium iodide and 125 ml of alcohol were heated on a steam bath (with a condenser) for two hours. The reddish brown diiodo bromoquinone obtained in this way, after being washed with water and alcohol, was transferred into a round bottom flask containing about 50 ml of alcohol and 20 g of potassium iodide and was heated for about 2 hours on a steam bath. Iodanil, thus formed, was recrystallized from benzene. M. P. 284 °C (lit. 290 °C).

VI. 2(ii). PREPARATION OF 1:1 COMPLEXES

a). Pyridine-Iodine Complex : 0.508 g (2 m mol) of iodine and 0.158 g (2mmol) of pyridine were weighed in a stoppered weighing bottle; few drops of methanol as solvent were added and the mixture was kept at 0 °C for ~ 24 hours. Care was taken to avoid the condensation of moisture. The solid separated was washed with cold methanol and dried and stored in a desciccator.

b). Picolines-Iodine Complexes : 0.186 g (2 m mol) of picolines (α-, β-, γ-picoline) and 0.508 g (2mmol) of iodine were weighed in a stoppered weighing bottle; few drops of methanol, as solvent, were added; the mixtures were stirred well and kept overnight (at 0 °C). Solid (reddish black) crystals separated were washed with methanol and then with dry carbon tetrachloride and dried and stored in desciccator.

c). 2-Amino pyridine-Iodine Complex : 0.190 g (2 mmol) of 2-amino pyridine and 0.508 g (2 m mol) of iodine were weighed separately and mixed throughly in a mortar.

d). Pyridine-Halonils Complexes : 0.158 g (2 m mol) of pyridine and 0.4920 g (2 m mol) of chloranil or 0.848 g (2 m mol) of bromanil or 1.224 g (2 m mol) of iodanil were taken in a well stoppered bottle to which few drops of methanol were added and kept overnight (at 0 °C). Care was taken to avoid moisture. The solid complexes formed were separatded, washed and dried and stored in a desciccator.

e). Picolines-Halonils Complexes : 0.246 g of chloranil (1 m mol)/0.424 g (1 m mol) of bromanil/0.612 g (1 mmol) of iodanil were taken in a well stoppered standard flask (10 ml), where 0.0931 g (1 m mol) of picolines (α-, β-, γ-picolines) were taken previously. The mixture was shaken well (after adding few drops of methanol) and kept overnight (at 0 °C). Care was taken to avoid any passage of moisture. Reddish brown complexes were separated. The solid products were washed, dried and stored in a desciccator.

f). 2-Amino pyridine-Halonils Complexes : 0.190 g (2 m mol) of 2-amino pyridine and 0.492 g (2 m mol) of chloranil/0.848 g (2 m mol) of bromanil/1.224 g (2 m mol) of iodanil were weighed separately and mixed throughly in a mortar.

VI. 2(iii). METHOD

The infrared spectra of pure components and their solid complexes, as prepared above, (in nujol mull and KBr media) were recorded (4000-600 cm^{-1}) on a Perkin-Elmer model 297 IR spectrophotometer. The error limit was ± 2 cm^{-1}.

VI. 3. RESULTS AND DISCUSSION

VI. 3(i). Pyridine-, Picolines-, and 2-Amino pyridine-Iodine Complexes :

The infrared spectra of pyridine, picolines, 2-amino pyridine and their iodine complexes in nujol/KBr were recorded over the range of 4000-600 cm^{-1} and the main spectral bands are set out in Table VI. 1. However, for the sake of convenience the spectra in the region between 1800 and 600 cm^{-1} are shown in the figures (Fig. VI. 1 to VI. 4). The vibrational spectra of pyridine-, picolines-iodine in mulls are generally quite different from those of equimolar solutions of these complexes in non-polar solvents. The broad absorption band between 3400 and 3600 cm^{-1} (Table VI. 1) is probably due to moisture present in the air (all the earlier workers had also observed such broad bands).[21-29] As we are interested in the "shift" of the donor bands after complexation, we have not assigned these bands.

As mentioned earlier, even though the IR spectra of halogens in the complexed state in polar and non-polar media (in far infrared region) have been studied by Ginn[30], Haque and Wood[12,13,14] and other workers exhaustively, little attention has been paid to the spectra of donors and their

Table VI. 1.

Important Infrared Spectral Bands of Iodine Complexes of Pyridine, α-, β-, γ-Picolines and 2-Amino Pyridine (in nujol mull)

Pyridine cm^{-1}	Pyridine-Iodine cm^{-1}	α-Picoline cm^{-1}	α-Picoline-Iodine cm^{-1}	β-Picoline cm^{-1}	β-Picoline-Iodine cm^{-1}	γ-Picoline cm^{-1}	γ-Picoline-Iodine cm^{-1}	2-Amino Pyridine * cm^{-1}	2-Amino-Pyridine-Iodine* cm^{-1}
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
3400m,br		3400w	3400w	3400w				3450m,br	3438m
								3340sh	3340sh
								3180sh	
3142m									
3080s		3080s	3090vw	3080m		3070s	3072m		
		3065m	3067vw						
				3060sh					
3050m		3040w							
3035s						3030s			
		2855w	2855w			2855s	2855s		
2850m	2850s			2850m	2850s				
2830m				2740m					
						2835s			
		2720sh				2685w			
		2610w		2610m					
2600w						2600m			
				2465w		2460s	2465w		
2450m									
				2390w		2400m	2400sh		
						2295m			
2290m						2220m			
2210w				2200m					
						2190w			
2130w						2020m			
1987m				1970w				1955	

Table VI. 1. ...... contd-.../-

Table VI. 1. (contd...)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1950w		1950w		1950w		1935s		1915w	
1921m				1912w					
		1910w							
1875m		1870w		1870w		1850m	1850w		
				1840w				1835sh	
				1770m					
			1725w						1670s
1682w						1665m			
1630m								1632s 1600s} d	
		1610w	1610sh		1610m	1605s			1600s
1600s		1595s		1600s					
	1590m		1586						
1582s				1582s	1580m				
	1568m	1570s				1562s 1595s	1565w	1565s	1565s
								1485s	1485s
1480s		1478s	1475s	1478s	1470s				
1440vs	1468m 1450s	1450m 1432s	1440m	1450m		1450s		1440s	
				1414s		1415s	1418s		
	1380s	1380s	1384m		1380s	1380s	1370w	1385w	1385w
1355m								1340s 1325s	1320s

Table VI. 1. contd....../-

Table VI. 1. (contd...)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1294m		1295s	1295w	1295s				1280s	1265s
	1245w	1240s	1235m	1240w 1225s	1242w	1225s 1210s			
1220s							1205m		
			1160m	1190s	1192s			1160s 1140s } d	1165m 1155m } d
1150s	1150w	1150s							1130m, br
		1100s	1100w	1120s 1100s	1120m				
1070s	1060s				1090w 1060sh	1070s	1070m 1060s	1071m	
1030s		1050s		1050m 1030s		1040s	1028s	1040m, br	1025w 1015s
	1010s 1004s	1000s	1020s	1000m				1010s	
990s						995s		990s	
983m		975m		975m		972s	972w	960s	950w
942vw 885w		940w 885w		940w 885w				860s 850s } d	845s 820w
810vw		800m 760s	800s 765s	800s	814m	800s	815s 800sh	775s	765w

Table VI. 1. contd....../-

Table VI. 1. (contd.../-)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
	755s			752s					
750s			745w					740s	
		730s		730s		730s	725s		725w
	725m								
		720w		712s		712w	710s		
		710w							
	705w								
703vs									
	690s					670m	670s	670w	
675w									
									645L
653w			645w		643w				
	640m		640m						
			637s						
	630m	630s		630s			628w	630m	
		624m							
	621s								
	615s								
606s									

* IR spectra of 2-amino pyridine and its complex with Iodine was taken in KBr media.

v, very; s, sharp; m, medium; w, weak; sh, shoulder; br, broad.

Bands at 3030-2860 cm^{-1}, ~1460 cm^{-1} and ~1374 cm^{-1} in cases (1) to (8) have been omitted due to superimposition by nujol bands.

complexes, probably due to the difficulties involved in accounting the spectral changes.[2] Many factors may bring changes in donor molecules (when complexed with acceptors). One of the factors is that the change in the symmetry on complex formation can cause vibrations which are isolated in the independent molecules resulting in the sufficient change of the spectrum. Due to the interaction between donor and acceptor, the bond length within the participating molecule may increase or decrease resulting in a decrease or increase in the vibrational frequency of the components. Sometimes, it is possible that the position of bands may be influenced by so many factors which are not directly related to the changes in the electronic structure of the donor molecule because of charge transfer during coordination. The increase in the vibrational frequency may be related to the kinematic effect of the interaction of the vibrations of the donor and the vibrations of the DA bonds with the same type of symmetry.[28] This effect is so important that the appearance of additional bands may change the internal field of force of the donor molecule leading to changes in the vibrational frequencies. It can be seen from the Table IV. 1. and Figures VI.1, VI.2 and VI.3 that the ring stretching vibrations of pyridine are observed at 1600, 1580, 1480 and 1440 cm^{-1} and these are very sensitive to

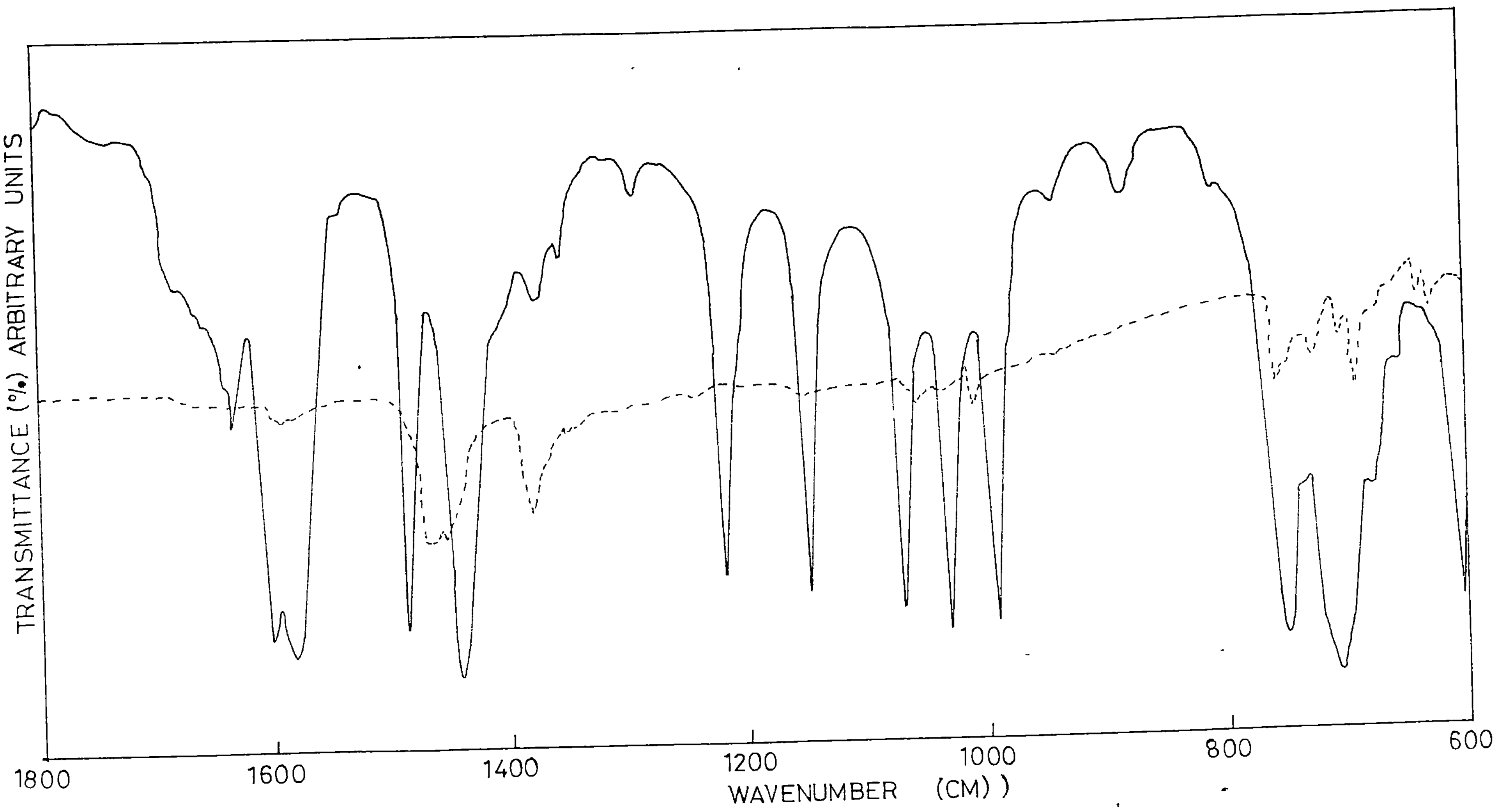

Fig. VI. 1. Infrared Spectra of Pyridine (.........)
and Pyridine-Iodine Complex (---------)
(in nujol mull).

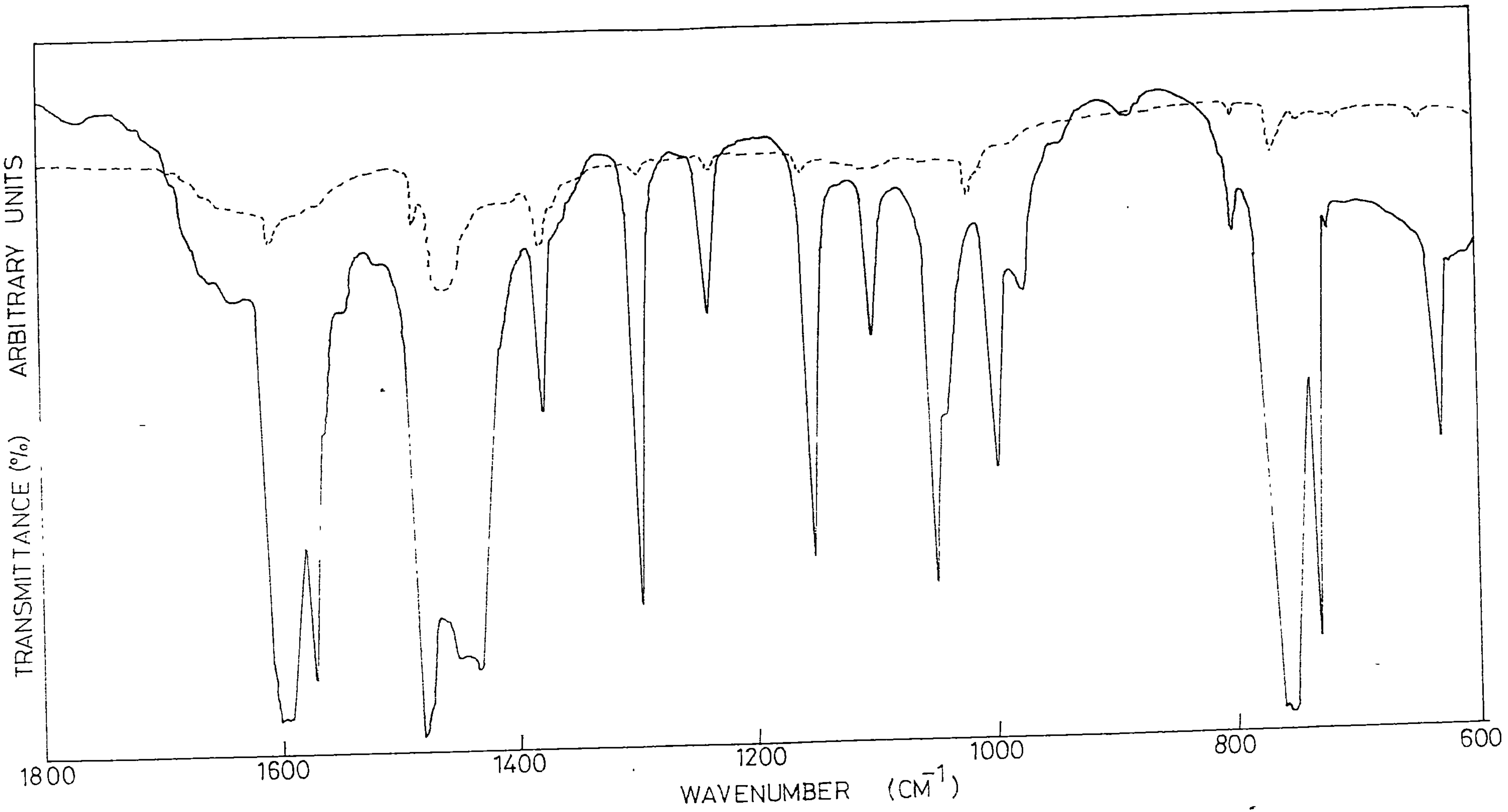

Fig. VI. 2a. Infrared Spectra of α-Picoline (.......) and α-Picoline-Iodine Complex (--------) (in nujol mull).

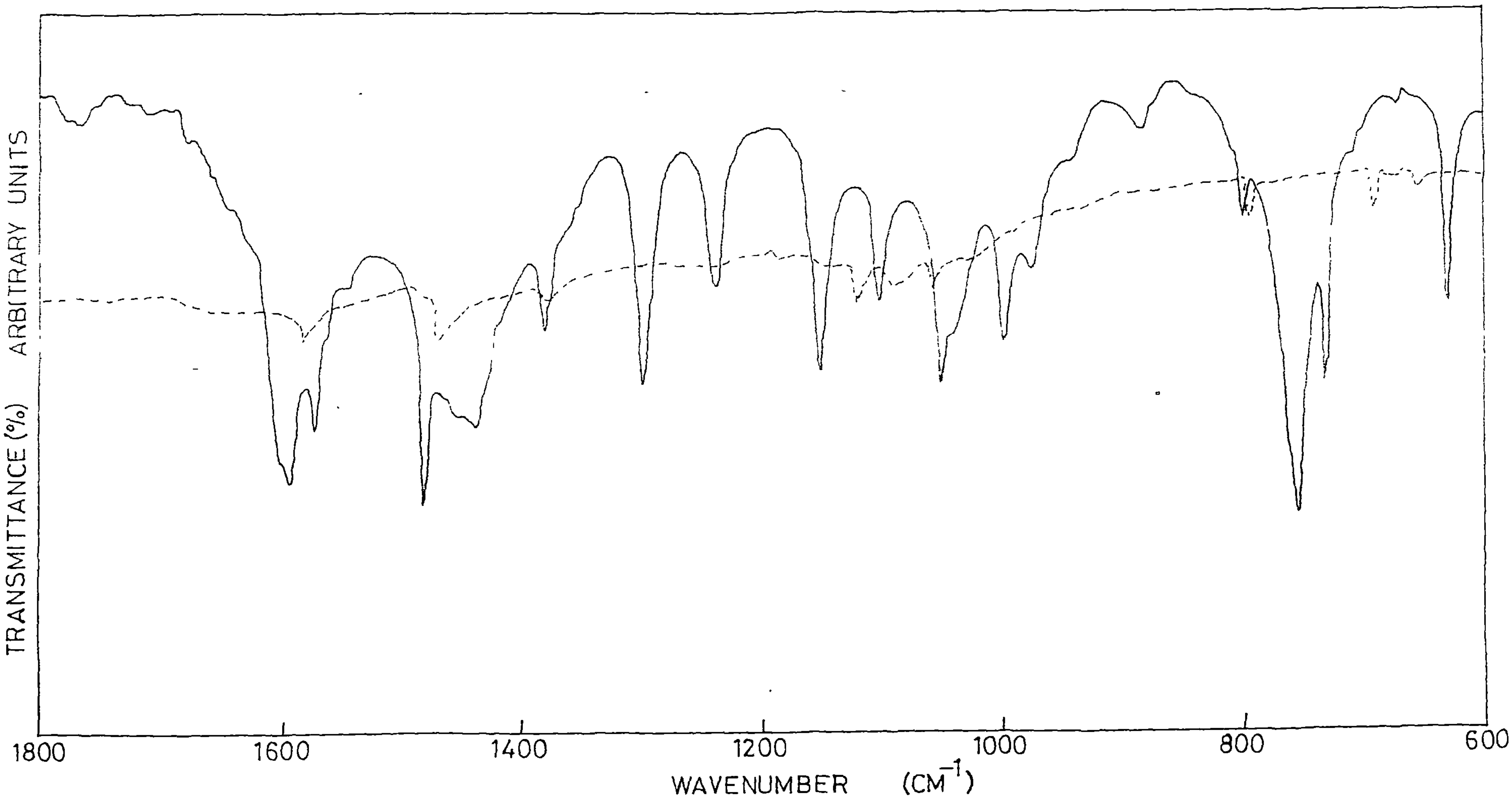

Fig. VI. 2b. Infrared Spectra of β-Picoline (........) and β-Picoline-Iodine Complex (---------) (in nujol mull).

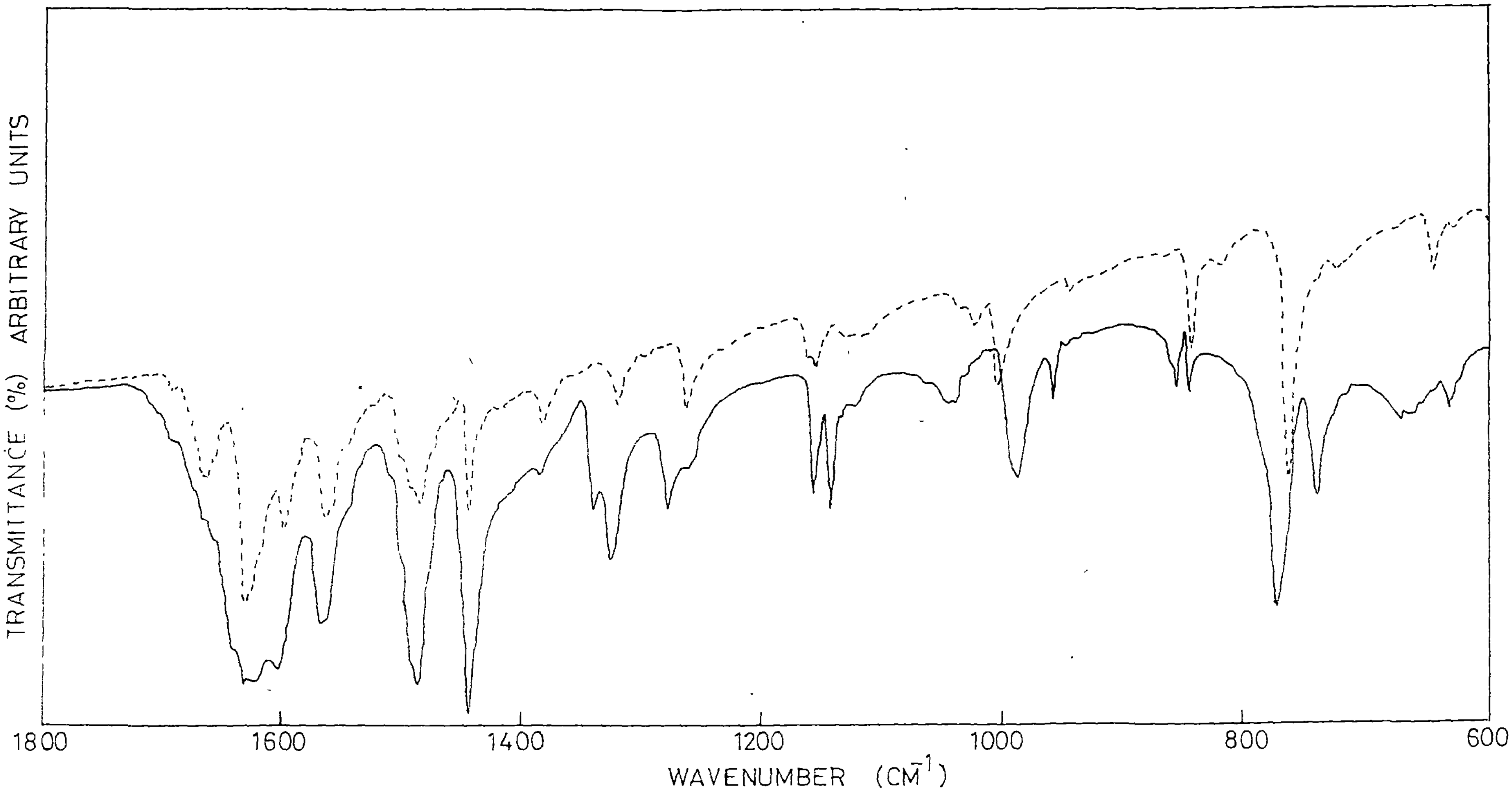

Fig. VI. 2c. Infrared Spectra of γ-Picoline (.......)
and γ-Picoline-Iodine Complex (--------)
(in nujol mull).

substitutions and positions (e.g., picolines and 2-amino pyridine). In the case of pyridine and picolines, the characteristic patterns of absorption of the ring stretching vibrations, probably results from the complete interaction of the C=C and C=N vibrations and therefore, it becomes very difficult to isolate the different vibrations. When pyridine or picolines interacts with iodine and forms a complex, there is redistribution of charges (however small it may be) which leads to frequency and intensity changes. In the present case, there is interaction between iodine and nitrogen (i.e., non-bonded electrons of nitrogen) and this is expected to affect the $\nu_{C=C/C=N}$ to certain extent and this is what has been observed. In pyridine-iodine, pyridine bands (i.e., 1600, 1580 and 1480 cm^{-1}) shift to lower frequencies (i.e., 1590, 1568 and 1468 cm^{-1} respectively and the 1440 cm^{-1} band is shifted to higher frequency, i.e. 1450 cm^{-1}) (Fig. VI. 1); the $\nu_{C=C/C=N}$ bands of α-picoline were perturbed and shift to slightly lower frequencies, i.e. from 1595, 1570 and 1478 cm^{-1} to 1585, and 1475 cm^{-1} respectively. However, the 1432 cm^{-1} band is shifted to higher frequency, i.e., to 1440 cm^{-1}. It is difficult to explain the absence of band ~ 1560 cm^{-1} in the complex. The same trend is observed in the case of β- and γ-picolines (Figures VI. 2). (Haque et al[12-14] had reported that they could isolate 3 distinct types of solids between γ-picoline and iodine,— (γ-pic-I)$_n^+$ I$^-$ —, but we could obtain only one type of complex, 1:1, probably may be due to different experimental conditions and procedure). The small shifts of the bands (or perturbations) towards the lower frequencies indicate that this change may be due to vibronic effects which may arise as a result of charge transfer interactions and/or classical electrostatic effects (dipole-dipole and dipole-induced dipole interactions).[32] Here it can be mentioned that the vibrational coupling effects can be quite loose. So one is tempted to attribute the small shift due to "back bonding" from the halogen molecule rather than neglecting the contribution due to vibrational mixing. In absence of Normal Coordinate Analysis it is not possible to account for this change. The above mentioned effects affect the "intensity" of the band but it is not possible to "quantify" the effect on intensity in solid state spectra. The C=C/C=N bands are slightly perturbed (weakened) due to the interaction between nitrogen (non-bonded electrons of nitrogen) and iodine. Here it should be noted that as the shift is about 5-15 cm^{-1}, one should look into the trend rather than the absolute values because the π electrons of C=C and C=N in pyridine and picolines are delocalized (electrons). Nevertheless the unambiguous shift towards the lower frequency indicates that pyridine and picolines do interact with iodine and the bond strength is decreased. Due to limitations of our instrument (i.e., range 4000-600 cm^{-1}), we could not detect either the $\nu_{N.....I}$ nor $\nu_{I.....I}$ band in the far infra-red region. These bands would have thrown more light on the relative strengths of interaction between the donor molecules (i.e., pyridine and picolines) and iodine.

The C-H in plane and out of plane deformation bands which appear in the region 1250-1030 and 850-700 cm^{-1} (for pyridine and picolines) are not affected much after complexation. However, the band around 991 cm^{-1} is very much shifted to higher frequency ($\sim$1000 cm^{-1}). We are not able to compare our present results with the literature data as the literature data mostly refers to solution spectra of complexes whereas ours is in solid state (i.e., the physical conditions are different). In the absence of Normal Coordinate Analysis, we are not able to properly interpret the frequency and intensity changes after complexation. This observation seems reasonable since the primary effect on complex formation is at nitrogen lone pair electrons. These electrons in the complex are in the modified form and some degree of interaction between the nitrogen sp^2 and $p\pi$ electrons distribution will take place. However, such effects being small in themselves are either not transmitted to the C–H bonds or are so weakly transmitted that the present method is too insensitive for detection. Similar observations were made for pyridine–ICl complex.[2,16] Haque and coworkers[12-14] feel that the band at ~1000 cm^{-1} may be due to $(D_2I)^+$ ion. They claim that picoline forms an inner complex with iodine and the band around 1000 cm^{-1} is due to $(py_2I)^+$. It can be recalled here that the nature of the complex formed depends on the 'environmental' conditions and cooperations' (excess of reactant/solvent) and mode of preparation of the complex. It is possible that our method of preparation of the complex may be different from those of Haque et al[12-14] due to which they might have observed bands due to $(pic_2\text{-}I)^+$ where as we could observe bands due to neutral species only. It has been reported in the literature that the nature of solvent used in obtaining the solid complex may affect the crystal structures and new bands/signals may appear even in IR/ESR spectra.[33] However, we could not detect any band around 360 nm (in electronic spectra) and this rules out the existence of I_3^-, and in turn, the possibility of the existence of $(D_2I)^+$.[12b] The absence of I_3^- band indicates that the complex is neutral and not ionic. The formation of I_3^- or $(py_2I)^+$ which Haque et al had observed is probably due to the following process:

$$py + I_2 \rightleftharpoons pyI_2; \quad pyI_2 \rightleftharpoons pyI^+ . I^-$$

$$pyI^+ + py \rightleftharpoons (py_2I)^+; \quad \text{and}$$

$$I^- + I_2 \rightleftharpoons I_3^- .$$

The formation of $(D_2I)^+$ is generally faciliated with the environmental assistance (particularly in polar media, i.e. excess of pyridine/picolines). It can be noted here that the study of changes of vibrational band shape (half band width) could provide a great deal of information about the molecular interaction. But as we are interested in solid state spectral studies, we could not compare the present band widths with the literature values as the environment can sufficiently influence the band position as well as band intensities.

VI. 3(ii). 2-Amino Pyridine-Iodine System :

In dilute solution the symmetric and antisymmetric stretching vibrations of $-NH_2$ group of 2-amino pyridine are observed at 3415 and 3520 cm^{-1}. As the concentration increases, the peak of 3415 and 3520 decrease while broad bands appear at 3450, 3340 and 3180 cm^{-1} which are due to intermolecular hydrogen bonding.[34,35] The two broad bands at 3340 and 3180 cm^{-1} are probably due to the Fermi doublet caused by the resonance between the hydrogen bonded N-H stretching vibration and the overtone of the NH_2 bending vibration at 1630 cm^{-1} in the $\underset{H}{N}$—H.....N hydrogen bonded system. The band around 1600 cm^{-1} can be due to N–H deformation whereas the band at ~1300 cm^{-1} is due to C—N stretching. When 2-amino pyridine interacts with iodine to form a complex, the electron density around nitrogen is perturbed. The band at 3450 cm^{-1} is shifted to 3438 cm^{-1} (i.e., the mean H—N.....H stretching frequency is lowered), 3340 cm^{-1} band is not affected whereas 3180 cm^{-1} band disappeared and a new band appeared at 1670 cm^{-1} (Table VI. 1 and Fig. VI. 3). This band is not due to skeletal stretching. This shift of H—N—H stretching to lower frequency and appearance of a band at 1670 cm^{-1} can be assigned to the cation of 2-amino pyridine. In the case of 2-amino pyridine-HCl[35] complex, the H—N—H stretching frequency decreases by about 70 cm^{-1} and H—N—H scissoring frequency increases by about 50 cm^{-1}. On comparison, it appears that the charge transfer is certainly less in 2-amino pyridine-iodine complex compared to 2-amino pyridine-HCl.[35] The doublets at 1160 and 1140 cm^{-1} are shifted to higher frequencies, i.e., to 1165 and 1155 cm^{-1} and the band at 1040 cm^{-1} shifts to lower region, i.e., 1025 cm^{-1}. The most sensitive band 990 cm^{-1}, shifts to 1015 cm^{-1}. Similarly, the band ~630 cm^{-1} is shifted to 645 cm^{-1} and, the shifts in 2-amino pyridine-iodine complex are more

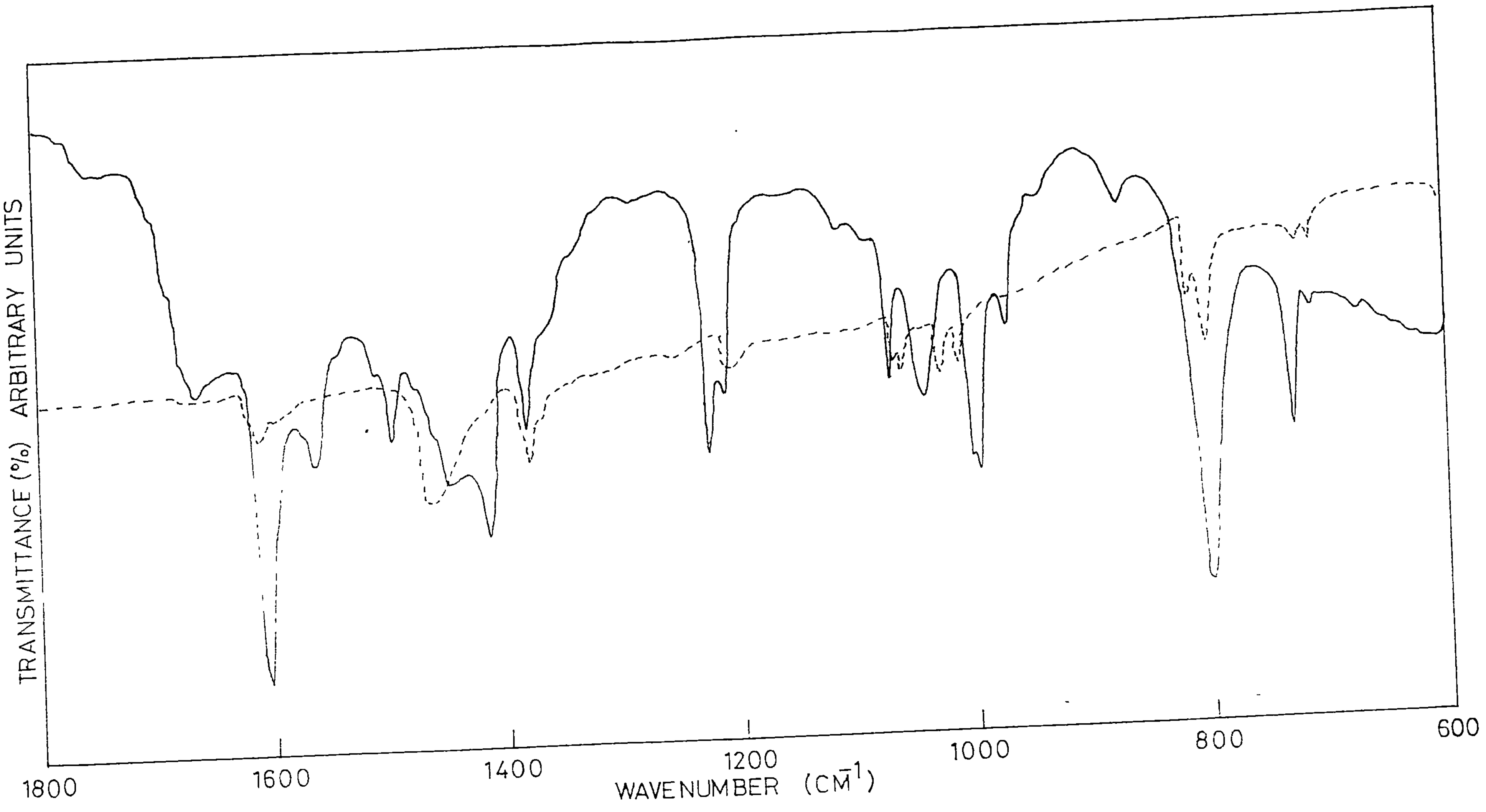

Fig. VI. 3. Infrared Spectra of 2-Amino Pyridine (.........) and 2-Amino Pyridine-Iodine Complex (————) (in KBr media).

compared to pyridine-iodine or picolines-iodine systems. Thus qualitative aspects of the data show that 2-amino pyridine-iodine is a stronger complex compared to pyridine complex.

2-amino pyridine-iodine complex absorbs at $\sim$360 nm, which is due to I_3^-. As mentioned earlier, the existence of I_3^- is possible only if the complex exists as an inner complex (ionic) rather than an outer complex (neutral) or if there is an equilibrium between inner and outer complex. Similar cases have been reported in the literature for picolines-IX system[2]. The new band, around 1670 cm^{-1}, may be ascribed due to (2-amino pyridine-I)$^+$, i.e., due to $\overset{+}{N}H_2$ scissoring. So, from the IR and electronic spectral data it appears that 2-amino pyridine-iodine is a stronger complex and it is ionic in the ground state.

As has been pointed out earlier, the vibrational changes which occur on complexation should lead to frequency and intensity changes and new 'bands' should appear if the interaction is strong. So the frequency shift can be used to compare interaction "strengths" within a closely related series of complexes (where normal coordinate changes might be expected to be similar in each case). In the present case, the strength of interaction should vary in the order 2-amino pyridine-iodine $>$ α-, β-, γ-picolines-iodine $>$

pyridine-iodine. (The heat of formation of 2-amino pyridine-iodine $>$ α-, β-, γ-picolines-iodine $>$ pyridine-iodine in n-heptane). In fact such trend has been observed in solution spectra of pyridine and picolines (i.e., α-, β-, γ-picolines-iodine $>$ pyridine-iodine).[12-14] But it is not easy to observe such trend in solid state spectra probably except in single crystal polarization IR spectra.

VI. 3(iii). Pyridine-, Picolines- and 2-Amino Pyridine-Halonil Complexes :

The infrared spectra of chloranil, bromanil and iodanil (π-acceptors) and their complexes with pyridine, picolines and 2-amino pyridine (n/π donors) were recorded over the range of 4000-600 cm $^{-1}$ and the significant spectral bands of pyridine-halonils, picoline-halonils and 2-amino pyridine-halonils complexes are summarised in Tables VI.2-6 and Fig. VI. 4 (pyridine-halonils). It can be seen from the Tables that chloranil, bromanil and iodanil have strong characteristic absorption at 1690, 1673 and 1658 cm^{-1} due to $\nu_{C=O}$. The bands at 1572, 1565 and 1515 cm^{-1} are due to $\nu_{C=C}$ and the bands at 1260, 1115; 1215, 1066, and 1172, 1012 are due to ν_{C-C}.[36] These values agree well with those of Iida[37] and Matsunaga.[38]

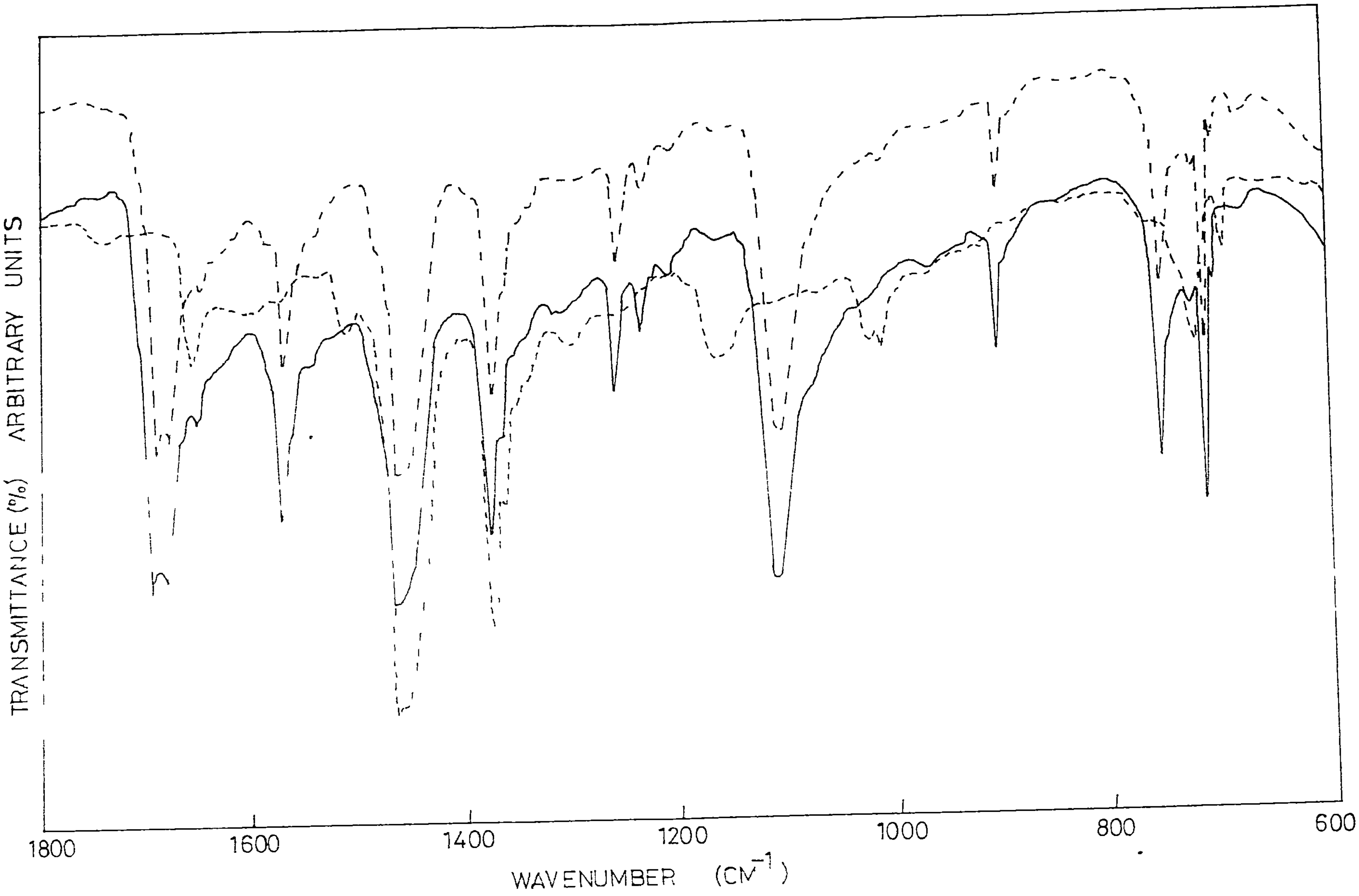

Fig. VI. 4. **Infrared Spectra of Pyridine Complexes of Chloranil, Bromanil and Iodanil in Solid State (in nujol mull).**
1. Pyridine-Chloranil; **2. Pyridine-Bromanil;**
3. Pyridine-Iodanil.

Table VI. 2.

Important Infrared Spectral Bands of
Pyridine-Halonil Complexes (in nujol mull)

Pyridine cm^{-1}	Chloranil cm^{-1}	Pyridine-Chloranil cm^{-1}	Bromanil cm^{-1}	Pyridine-Bromanil cm^{-1}	Iodanil cm^{-1}	Pyridine-Iodanil
(1)	(2)	(3)	(4)	(5)	(6)	(7)
3400m, br	3360 3360m	3355m	3340w	3360m	3400m,br	3400m
3142m						
3080s						
3050m						
3035s						
2850m		2845sh	2850s	2850sh	2855sh	
2830m						
2600w						
2450m						
2290m						
2210w						
2130w						
1987m						
1950w						
1921m						
1875m						
1682w	1690s	1691s		1692s		
	1681s	1680s	1681s 1673s	1680s	1659s	1659s
1630m	1650m	1650m	1642w	1650m		

Table VI, 2. contd..../

Table VI. 2 (contd....)

(1)	(2)	(3)	(4)	(5)	(6)	(7)
1600s						
1582s	1572s	1571s	1565s	1572s		
			1549s	1545w		
					1515m	1515m
1480s	1490sh					
1440vs						
1355m						
				1300w		1300w
1294m						
	1260m	1265m	1260m	1260s		
	1238m	1237m		1240m		
1220s	1210w	1210w	1215s	1218m		
					1192sh	1192sh
		1170w			1172m	1175m
					1156w	1158m
1150s	1115s	1112s	1110m	1112s		
1070s			1066s			
			1054s			
1030s			1030m		1027w	
		1010w			1012m	1015s
990s						
983m						
942vw	908m	905m		908s		
885w			880m			
			869s			
					840w	
					835w	
					824w	
810vw						
750s	755s	752s	753w	755s		
					721s	721s
	715s	712s	715m	715s	712sh	
703vs	708w	705w	705s	708m		
			695m		695s	693s
		680m, br			682m	
675w						
653w			645m			
606s						

Table VI. 3

Important Infrared Spectral Data for α-Picoline-Halonil Complexes(in nujol null)

α-Picoline cm^{-1} (1)	Chloranil cm^{-1} (2)	α-Picoline-Chloranil cm^{-1} (3)	Bromanil cm^{-1} (4)	α-Picoline Bromanil cm^{-1} (5)	Iodanil cm^{-1} (6)	α-Picoline Iodanil cm^{-1} (7)
3400w					3400m,br	3400m
	3360m					
		3355m				
			3340w	3340m		
3080s						
3065m						
3040w						
2855w					2855sh	
		2850s	2850s	2850sh		2850s
2720sh						
2610w						
1950w						
1910w						
1870w						
	1690s	1690s				
	1681s		1681s	1681s		
		1680s				
			1673s			
				1671s		
						1660s
					1659s	
	1650m	1650w				
			1642w	1642w		
1610w						
1595s						
	1572s					
		1571s				
1570s						
			1565s	1565m		
			1549s			
				1545m		
						1518m
					1515m	
	1490sh					
1478s						
1450m						
1432s						
1380s						
1295s						
	1260s	1260s	1260m			
1240s						
	1238m					
		1232m				
			1215s	1215s		
	1210w	1210w				
						1193sh
					1192sh	
						1174s
					1172m	

Table VI. 3. contd..../-

(1)	(2)	(3)	(4)	(5)	(6)	(7)
					1156w	
1150s						
	1115s	1110s	1110m	1110w		
1100s				1068s		
			1066s			
			1054s			
				1052s		
1050s						
			1030m	1030w		
					1027w	
						1014m
					1012m	
1000s						
975m						
940w						
	908m					
		903m				
885w						
			880m	880sh		
				870s		
			869s			
					840w	
						838w
					835w	
					824w	
800m						
760s						
	755s					
			753w			
		752s				
730s						
				723m		
					721s	
720w						
	715s		715m			
					712sh	
710w		710s				
	7082					
				706s		
			705s			
		701w				
			695m	695w	695s	695s
					682m	
			645m	645m		
	630w					

s, sharp; m, medium; w, weak; v, very; sh, shoulder.

Bands at 3030-2860, ~1460, ~1375 cm^{-1} have been omitted due to superimposition by nujol bands.

Table VI. 4

Important Infrared Spectral Data of β-Picoline-Halonil Complexes (in nujol mull)

β-Picoline cm^{-1}	Chloranil cm^{-1}	β-Picoline Chloranil cm^{-1}	Bromanil cm^{-1}	β-Picoline Bromanil cm^{-1}	Iodanil cm^{-1}	β-Picoline Iodanil cm^{-1}
(1)	(2)	(3)	(4)	(5)	(6)	(7)
3400w	3360m	3355m	3340w	3340m	3400m	3400sh
3080m						
3060sh						
2850m		2855s	2850s	2840sh	2855sh	2855s
2740m						
2610m						
2465w						
2390w						
2200m						
1970w						
1950w						
1912w						
1870w						
1840w						
1770m						
	1690s	1692s				
	1681s	1680s	1681s	1680s		
			1673s	1673s	1659s	1660s
	1650m	1650w	1642w			
1600s						
1582s	1672s	1671s	1565s	1562s		
			1549s	1550m	1515s	1520s
1478s	1490sh					
1450m						
1414s						
1295s					1300w	

Table VI. 4. contd..../-

Table VI. 4. contd.

(1)	(2)	(3)	(4)	(5)	(6)	(7)
	1260s	1260m	1260m			
				1255m		
1240w						
	1238m					
		1237m				
1225s						
				1218s		
			1215s			
	1210w	1210w				
						1193w
					1192sh	
1190s						
						1175s
					1172m	
					1156w	
1120s						
	1115s	1114s				
			1110m			
1100s						
				1068s		
			1066s			
			1054s			
				1052s		
1050m						
1030s			1030m	1030w		
					1027w	
						1015s
					1012m	
1000m						
975m						
940w						
	908m	907m				
885w						
			880m	875w		
				870s		
			869s			
					840w	
					835w	
					824w	
800s						
	755s	755s				
			753w			
752s						
730s						
				725s		
					721s	721w
	715s		715m			
712s		712s			712sh	
	708w			708s		
		705w	705m			
			695w	695w	695s	695s
					682m	
				647m		
			645m			
630s	630w					

s, sharp; m, medium; w, weak; v, very; sh, shoulder.

Bands at 3030-2860, ~1460 and ~1375 cm^{-1} have been ommitted due to superimposition by nujol bands.

Table VI. 5

Important Infrares Spectral Bands of

γ-Picoline-Halonil Complexes (in nujol mull)

γ-Picoline cm^{-1} (1)	Chloranil cm^{-1} (2)	γ-Picoline-Chloranil cm^{-1} (3)	Bromanil cm^{-1} (4)	γ-Picoline Bromanil cm^{-1} (5)	Iodanil cm^{-1} (6)	γ-Picoline Iodanil cm^{-1} (7)
3340m	3360m	3355m	3340w	3340w	3400m	3400sh
3070s						
3030s						
2855s		2850s	2850s	2855s	2855sh	2855s
2735s						
2685w						
2600m						
2460s						
2400m						
2295m						
2220m						
2190w						
2020m						
1935s						
1850m						
	1690s	1689s		1682s		
	1681s	1680s	1681s			
1665m			1673s	1673s	1659s	1661s
1615s	1650m	1638s	1642w			
1562s	1672s	1671m	1565s	1565w		
			1549s	1547m		
1496s	1490sh				1515s	1520s
1450s						

Table VI. 5. contd...../-

Table VI. 5 contd...

(1)	(2)	(3)	(4)	(5)	(6)	(7)
1415s						
1380s						
					1300w	
	1260s	1260m	1260w			
	1238m	1238w				
1225s						
				1217s		
			1215s			
1210w	1210w					
		1209m				
					1192sh	1194w
					1172m	1178m
		1165w				
					1156w	
	1115s			1115w		
		1114s				
			1110m			
1070s						
				1068s		
			1066s			
				1055s		
			1054s			
		1045sh				
1040s						
			1030m	1030sh		
					1027w	
						1018s
					1012m	
995s		995sh				
972s						
	908m					
		907s				
			880m			
				870s		
			869s			
					840w	841w
					835w	
		805m, br				
800s						
	755s	755s				
			753w			
730s						
					721m	723w
				720w		
	715s		715m			
712w		712s			712sh	
	708w			708m		
		705w	705s			
			695w		695s	695s
					682m	
670m						
			645m	645m		
	630w					

s, sharp; m, medium; w, weak; sh, shoulder; br, broad;

Bands at 3030-2860, ~1460 and ~1375 cm^{-1} have been omitted due to superimposition by nujol bands.

Table VI. 6

Infrared Spectral Data of 2-Amino Pyridine-Halonil Complexes (in KBr media)

2-Amino-pyridine cm^{-1}	Chloranil cm^{-1}	2-Amino-pyridine-chloranil cm^{-1}	Bromanil cm^{-1}	2-Amino-pyridine-Bromanil cm^{-1}	Iodanil cm^{-1}	2-Amino-pyridine-Iodanil cm^{-1}
(1)	(2)	(3)	(4)	(5)	(6)	(7)
3450m, br					3400m, br	3400sh
3340sh	3360m	3360vw	3340w	3340vw		
3180sh						
		3150w		2930w		
		2920w	2850s		2855sh	
1955w						
1915w						
1835sh						
	1690s	1690s				
	1681s	1680vw	1681s	1682s		
		1665s	1673s	1674s		1665s
	1650s		1642w		1659s	
1632s 1600s } d		1625m		1625m, br		1620m
	1572s	1571m		1568w		
1565s			1665s			1565m
			1549s	1550m		
		1515m			1515s	1515m
1485s	1490sh					1485m
	1470sh		1475w	1475w		
1440s						1445m
		1420vw				1420w
	1380m	1380w	1385m	1385m	1388w	1385w
1340sh						1360sh
1325s	1320w	1330w		1325w		1325m

Table VI. 6.....contd../-

Table VII. 6. (contd.)

(1)	(2)	(3)	(4)	(5)	(6)	(7)
1280s			1280w			
	1260s	1260m	1260w			
	1238m					
		1235w				
			1215s	1215m		
	1210w					
					1192sh	
					1172m	
		1170m, br		1170w		1170m, br
1160s 1140s } d	1115s					
		1110s				
1071m						
		1070w		1070s		
			1066s			
				1055s		
			1054s			
1040m, br						
			1030m			
					1027w	
						1025vw
						1015m
					1012m	
		1000w				1000sh
990s						
960s						
	908m	908w				
			880m			
				870m		
			869s			
860s 850s } d						
					840w	
					835w	
775s						
		770s		770m		
						765m
	755s					
			753w			
		750m				
740s						
						725w
					721m	
	715s		715m			
		712s		712sh		
	708w					
		705vw	705s	705s		
			695w	695w	695s	695m
					682m	
670w						
			645s	645s		
630m	630w					
				628vw		
		625w				625w

s, sharp; m, medium; w, weak, sh, shoulder; br, broad; v, very.

Chloranil, bromanil and iodanil are π-acceptors and their electron afinities are nearly the same (~ 2.1 ev).[17,39] Pyridine, picoline and 2-amino pyridine have non-bonded electron as well as π electrons. It is well known that pyridine, picolines and 2-amino pyridine are n-donors towards iodine. However, it is not known whether these donors behave as n-donors and π-donors towards π-acceptors, (like halonil), and it is not easy to speculate the geometry of the complex, eventhough one would like to opt for π-π complex model rather than n-π complex (as the electronic effects of interaction are unlikely to be localized). Vibrational spectroscopy has principally been used in order to distinguish neutral "outer" complex, D—A, from the radical ion pair, D^{+}-$A^{\dot{-}}$, formed from electron transfer. This distinction is easily made by a comparison of the spectra of the "free" components, the complex and the ions (like alkali metal salt of the acceptor); the latter is being regarded as a model for the situation in which complete electron transfer has taken place. Hall et al[40] have studied the solid molecular complexes of hexamethylbenzene and TCNE. They suggested that the complex consists of species which contains sequences of D-A-D-A-D-....... It can be seen from the Table (VI. 2-6) that the spectra of the complexes are almost the super-imposition of those of donors and acceptors. In the present case because of the similar nature of substituted pyridines, it is difficult to uncover any systematic spectral changes (of donors) during complex formation. For this reason, emphasis is placed on any significant change occuring in the spectra of halonils. Had there been the formation of n-π complex, one would have expected considerable change in frequency shift of the $\nu_{C=N}$ of donor (as the charge on nitrogen would have decreased due to charge transfer) and a new frequency corresponding to $\nu_{N.....Cl}$ of halonils. The acceptor exhibits absorption at ~1690, ~1682 and ~1660 cm^{-1} respectively. The lithium salt of p-chloranil absorbs at 1518, 1594 and 1028 cm^{-1} respectively. (Similarly for bromanil and iodanil ions). But we could not detect any absorption bands in these regions. So the absence of bands around 1518, 1594 and 1028 cm^{-1} in chloranil, bromanil and iodanil complexes indicates that the complexes are not ionic but they are neutral in the ground state. In addition, there is hardly any change either in the position or in the intensity of ν_{N-H} band of 2-amino pyridine-halonil complexes. This rules out the possibility of interaction of halonils with nitrogen of 2-amino pyridine (as 2-amino pyridine is already hydrogen bonded system).

It can be seen from the tables that the ν_{C-C} bands of chloranil, bromanil and iodanil shift from 1260, 1215 and 1172 to 1265, 1218 and 1175 cm^{-1} respectively in the complex, whereas the lithium salt of chloranil has absorption band at 1176 cm^{-1} (ν_{C-C}). As there is hardly any shift in the band position of ν_{C-C} of halonils in the complexed state it appears that there is hardly any change in electron density around C-C; this indicates that there is not much interaction between halonils and pyridine, picolines and the complexes are neutral in the ground state.

From these infrared spectral studies it is clear that pyridine, picolines and 2-amino pyridine do interact with iodine, chloranil, bromanil and iodanil. 2-amino pyridine is a better electron donor (towards iodine) compared to pyridine and picolines, and 2-amino pyridine-iodine forms an ionic complex in the ground state whereas others are neutral. Halonils form $\pi-\pi$ complexes with pyridine and picolines rather than $\underline{n}-\pi$ complexes.

REFERENCES

1. a) R. S. Mulliken and W. B. Person, "Molecular Complexes" - A lecture and Reprint Volume, Wiley Interscience, New York, 1969 and the references therein.

2. "Spectroscopy and Structure of Molecular Complexes", Ed. by J. Yarwood, Plenum Press, London, 1973 and the references therein.

3. a) J. Yarwood and W. B. Person, J. Am. Chem. Soc., 90, 594, 3930 (1968).

   b) J. Yarwood, Trans Farad. Soc., 65, 934 (1969).

   c) J. Yarwood, Spectrochim. Acta, 26A, 2079 (1970).

4. C. N. R. Rao, S. N. Bhat and P. C. Dwivedi, Appl. Spectros. Rev., 5, 1 (1971) and references therein.

5. M. Bugeanu, Bull. Inst. Politeh, "Gheorghe Gheorgheu-Dej", Buccuresti Ser. Chim-Metal, 44, 19 (1982); CA; 99 : 61082u.

6. E. E. Ferguson, J. Chem. Phys., 25, 577 (1956).

7. G. Junghawhnel and W. Paetz, Z. Chem., 4, 157, 192 (1964); CA; 61 : 3819d, 3819e.

8. a) W. B. Person, C. F. Cook and H. B. Friedrich, J. Chem. Phys., 46, 2521 (1967).

   b) Y. Yagi, A. I. Popov and W. B. Person, J. Phys. Chem., 71, 2439 (1967).

9. A. D. Nikolic, N. L. Kobilarov and A. N. Brzic,
J. Mol. Structure, 99, 179 (1983).

10. A. G. Maki and E. K. Plymer, J. Phys. Chem., 66, 766(1962).

11. P. Jacques, R. Paul and K. Roger,
Compt. Rend., 259, 1121 (1964); CA; 61 : 16179h.

12. a) I. Haque and J. L. Wood, J. Phys. Chem., 72, 2438(1965).
b) I. Haque and J.L. Wood,
Spectrochim. Acta, 23A, 959, 2523 (1967).
c) I. Haque and J. L. Wood,
J. Mol. Structure, 2, 217 (1968).

13. S. G. W. Ginn, I. Haque and J. L. Wood,
Spectrochim. Acta, 24A, 1531 (1968).

14. I. Haque, N. N. Dass and T. Bora,
Ird. J. Chem., 12, 70 (1974).

15. R. F. Lake and H. W. Thompson, Proc. R. Soc.,
A297, 440 (1967); Spectrochim. Acta, 24A, 1321 (1968).

16. a) K. Sasaki and K. Aida,
J. Inorg. Nucl. Chem., 42, 13 (1980).
b) K. Kato, K. Sasaki and K. Aida,
Spectrochim. Acta, 38A, 1011 (1982).
c) K. Kato, N. Yoshio and K. Aida,
Spectrochim. Acta, 38A, 373 (1984).
d) K. Aida, K. Yoshida and K. Kato,
Polyhedron, 4, 527 (1985).

17. A. K. Das and R. Basu, Ind. J. Chem., 21A, 1120 (1982).

18. Dynes Cook, Can. J. Chem., 42, 2523 (1964).

19. a) A. I. Vogel, "A Text Book of Practical Organic Chemistry", 4th ed., ELBS and Longman, London, 1978.

b) A. I. Vogel, A Text Book of Quantitative Inorganic Analysis", 4th ed., ELBS and Longman, London, 1978.

c) "Dictionary of Organic Compounds", Vol. 2, Eyre and Spottiswoode Publ. Ltd., E & F N Spon Ltd., London, 1965.

20. C.L. Jackson and E.K. Bolten, J. Am. Chem. Soc., 36, 305 (1914).

21. L. Corrsin, B. J. Fax and R. C. Lord, J. Chem. Phys., 21, 1170 (1953).

22. J. K. Wilmshurst and H. J. Bernstein, Can. J. Chem., 35, 1183 (1957).

23. N. S. Gill, R. H. Nuttall, D. E. Scaife and D.W.A.Sharp, J. Inorg. Nucl. Chem., 19, 79 (1961).

24. S. S. Singh, Labdev, 10A, 14 (1972); CA; 78 :103912p.

25. M. S. Afifi, A. A. Shabana, Analysis, 10, 239 (1982); CA; 97 : 14245y (1982).

26. C. V. R. Rao, C. Jacob and A. K. Chandra, Indian. J. Chem., 22A, 183 (1983).

27. A. R. Katritzky, C. R. Palmer, F. J. Swinbourne, T. T. Tidwell and R. D. Topsom, J. Am. Chem. Soc., 91, 636 (1969).

28. I. S. Perelygin and M. A. Klimchuk, Zh. Prikl. Spektrosk., 24, 65 (1976); CA; 84 : 128235g (1976).

29. A. V. Chekunov, Zh. Prikl. Spektrosk, 17, 922 (1972); CA; 78 : 50051y (1973).

30. S. G. W. Ginn and J. L. Wood, Trans. Farad. Soc., 62, 777 (1966).

31. D. T. Brown, R. S. Drago and T. F. Bolles, J. Am. Chem. Soc., 90, 5706 (1968).

32. J. Lewis, J. R. Miller, R. L. Richards and A. Thompson, J. Chem. Soc., 5850 (1965).

33. Z. Yoshida and E. Osawa, Bull. Chem. Soc. Jpn., 38, 140 (1965).

34. H. Sugeta, Bull. Chem. Soc. Jpn., 54, 3706 (1981).

35. a) E. Spinner, J. Chem. Soc., 3119 (1962).

36. C. N. R.. Rao, "Chemical Applications of Infrared Spectroscopy, Academic Press, New York, 1963.

37. Y. Iida, Bull. Chem. Soc. Jpn., 43, 345 (1970).

38. Y. Matsunaga, J. Chem. Phys., 41, 1609 (1964).

39. L. Lyons, Aust. J. Chem., 29, 1919 (1976).

40. B. Hall and J. P. Devlin, J. Phys. Chem., 71, 465 (1967).

SUMMARY

The field of molecular complexes (including hydrogen bonding) has been a subject of extensive investigations in recent years. A number of reports have appeared in literature in which the results of donor—acceptor systems (particularly in the case of weak donor-acceptor complexes) do not confirm the theoretical predictions. So, questions were raised about the reliability of the spectral and thermodynamic parameters of such systems obtained by spectral methods alone. Therefore, an attempt has been made to use some non-spectral methods to obtain the necessary informations on the nature of interactions between electron donors and acceptors.

The present dissertation contains the studies on molecular complexes/hydrogen bonded systems by using the less familiar methods, conductometry, viscometry, in addition to the usual infrared spectroscopy.

Various aspects of molecular complexes/hydrogen bonded systems, which are relevant to the studies reported in this thesis have been briefly reviewed in Chapter I.

The application of conductometry in the study of transformation of outer charge transfer complexes into inner complexes constitutes the subject matter of Chapter II. The donors used are methanol, ethanol, water and acetonitrile where as iodine is used as an acceptor. The transformation of outer complexes into inner complexes are found to follow the first order rate law. The effects of temperature and concentration on the rate of transformation have been studied. The results indicate that the rate of transformation vary in the order $H_2O-I_2 > MeOH-I_2 >$ $EtOH-I_2$. So, it has been felt that the ease with which the transformation proceeds depends on the relative magnitudes of enthalpy of formation of the outer charge-transfer complexes.

The formation of charge-transfer complexes can also be followed by measuring the changes in the electrical conductivity of a solution (e.g., donor in inert solvent of sufficiently high permittivity) on addition of another suitable solution (i.e., an acceptor). In effect, this amounts to a conductometric titration. Chapter III of the thesis deals with the applicability of conductometric titration for determination of the stoichiometry of charge transfer complexes (where outer charge transfer complex is transformed into inner complex) in polar media. The systems studied are : Iodine complexes of acetone, methyl ethyl ketone, iso-butyl methyl ketone, triphenyl phosphine, triphenyl arsine, triphenyl stibene, methanol, ethanol and n-propanol. The stoichiometry of the complexes (in highly polar media) are found to be $\approx 2:3$ (except in the case of triphenyl stibene where the stoichiometry is $\approx 1:4$). The effects of temperature, concentration and dielectric constants of the media on conductivities and stoichiometry of the complexes have been reported. The present results show that the electrical conductivities of the complexes in solution depend on temperature, concentration and dielectric constant of the medium, whereas the stoichiometry is almost independent of the dielectric constant. The limitations of conductometric titrations of molecular complexes have been pointed out.

Chapter IV deals with the technique based on the viscosity measurement in the study of weakly interacting systems. The viscometric method has been found to be applicable not only for detecting the presence of interaction between the donor and acceptor but also to determine the stoichiometry and equ-ilibrium constants and other thermodynamic parameters of weakly interacting systems. The systems which are studied by viscometric method include benzene-CCl_4-cyclohexane, toluene-CCl_4-Cyclohexane and *o*-Xylene-CCl_4-cyclohexane. The equilibrium constants (at different temperatures) and other thermodynamic parameters of these systems have been evaluated and compared with the literature data. The results show that the strength of the complexes vary in the order : Benzene-CCl_4-cyclohexane $>$ toluene-CCl_4-cyclohexane $>$ *o*-Xylene-CCl_4-cyclohexane. The possible reasons for such reverse trend have been given. The limitations of viscometric method have been pointed out.

The applicability of viscometric method in the studies of hydrogen bonding forms the subject matter of *Chapter V*. The systems, which are studied by viscometric methods, are: methanol-acetone, ethanol-acetone, *n*-propanol-acetone and *n*-butanol-acetone in carbon tetrachloride (ternary systems). The equilibrium constants (at different temperatures) and the other thermodynamic parameters have been determined. The strengths of the hydrogen bonding follow the order: Methanol-acetone-carbon tetrachloride $<$ ethanol-acetone-carbon tetrachloride $<$ *n*-propanol-acetone-carbon tetrachloride $<$ *n*-butanol-acetone-carbon tetrachloride. However, the heats of formation of the complexes obtained by this method were high. An attempt has been made to explain this in terms of breaking of hydrogen bonding and formation of new hydrogen bonding.

The studies of molecular complexes by infrared spectroscopy is the subject matter of Chapter VI. Pyridine, α-, β-, γ-picolines, 2-amino pyridine interact with iodine and halonils to form 1:1 solid molecular complexes. Infrared spectral data show that (except 2-amino pyridine-iodine complex) all these complexes are neutral in the ground state. It is inferred from the present studies that 2-amino pyridine is a better electron donor (towards iodine) than pyridine and picolines. Halonils form π-π complexes with pyridine and picolines rather than *n*-π complexes.