ELECTROCHEMICAL AND OPTICAL PROPERTIES OF SOME PYRIDINYL COMPOUND: 1-ETHYL-4-CARBOMETHOXY PYRIDINIUM IODIDE

by

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TO MRS. ABU BAKAR'S FAMILY

IN THE NAME OF ALLAH

All Commendations to ALMIGHTY ALLAH who blessed me with intellect, resoluteness and determination to accomplish this assignment

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ABSTRACT

In order to gain information regarding the structure of charge transfer complex 1-ethyl-4-carbomethoxy pyridinium iodide (PyI) and to investigate the situation of ion-pairing, some proton magnetic resonance and conductance studies were carried out in various solvents. Proton magnetic resonance studies were extended to study the exchange reactions between PyI and Py ClO_4, and between pyridinium salt and tetra-butyl ammonium salts.

It was noted that proton chemical shifts arising from aromatic protons of salt under investigation were solvent dependent, and a correlation seems to exist between the solvent polarity parameter Z-value and chemical shift values of aromatic protons. The $\Delta\delta$ values were highest in chloroform $\Delta\delta = 1.17$; (Z = 63.2) and lowest in H_2O $\Delta\delta = 0.57$ (Z = 94.6).

An interesting phenomenon was observed during the course of study of exchange reactions between PyI and Py ClO_4 also, between Py ClO_4 and TBAI, was that instead of having two set of resonance lines, one for each PyI and $PyClO_4$, rather only one set was observed. It was concluded that there was extremely rapid exchange between iodide and perchlorate ion.

The conductance studies were carried out to investigate the ion-pairing phonomena and also effect of change of temperature and solvent polarity on the ion-pair dissociation constant. The magnitude of K was of the order of 10^{-2} to 10^{-3}, which suggested that pyridinium iodide exists essentially as ion-pairs. In different solvents under the similar conditions of temperature it was noted that ion-pair dissociation constant value decreases with the decrease in solvent polarity (dielectric constant ϵ). It has been observed for a particular solvent that the K value increases with the rise in temperature.

It was concluded that both temperature and dielectric constant of the solvent, affect the ion-pairing, such that the latter phenomenon is unfavoured by the increase in temperature or dielectric constant

value of the solvent.

Conductance studies were also carried out in $CHCl_3$ solvent but conductance data obtained showed variation, thus it was not possible to calculate the value of K and Λo from the experimental data. log Λc Vs. log c plots exhibited a minima, and it was concluded that triplet ions ($Py^+I^-Py^+$ and $I^-Py^+I^-$) may be existing.

CERTIFICATE

This thesis submitted by Mr. Tariq Mahmood is accepted in its present form by the Department of Chemistry as satisfying the thesis requirements for the degree of Master of Philosophy in Physical Chemistry.

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Chairman
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ISLAMABAD   Date_____

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INTRODUCTION

INTRODUCTION

Charge transfer phenomenon exhibited by certain compounds is of great importance in biological systems. It also finds wide application in photoelectrochemistry, where such charge-transfer complexes can be used in Solar energy conversion and storage. The role of charge transfer compound/complexes in biological systems and in photo electrochemistry is summarized below.

1.1 CHARGE TRANSFER COMPLEXES IN BIOLOGICAL SYSTEMS

In most of the biological systems the pyridinium ion is of particular importance and must be considered in relation to the behaviour of two key coenzymes, Nicotinamide Adenine Dinucleotide $(NAD^+, I, R = H$, alternatively called diphosphopyridine nucleotide = DPN) and Nicotinamide Adenine Dinucleotide phosphate $(NADP^+, I, R = OP (OH)_2$, alternatively called triphosphopyridine nucleotide TPN) and to the functioning of widely used herbicide, Paraquat.

In biochemical process involving NAD^+ $(I, R = H)$ in oxidation-reduction in which the pyridinium ring of NAD^+ $(II, R = riboxyl$ adenine phosphate residue) is reduced by hydride addition in the 4-position to give NADH $(III, R = riboxyl$ adenine phosphate residue). The coenzyme $NADP^+$ may be reduced in a similar way to NADPH.

Biochemical interest in these coenzymes had led to the study of simple model compounds containing the pyridinium part of these structures, in particular 1-alkyl pyridinium ions and various substituted derivatives.

I

II

III

CONH$_2$

+H$^-$ +H$^-$

H

H

CONH$_2$

R—N

R—N

HO

OH

CH$_2$—O

O$^-$—P=O

O

O$^-$—P=O

O—CH$_2$

HO

OR

N$^+$

C=O

NH$_2$
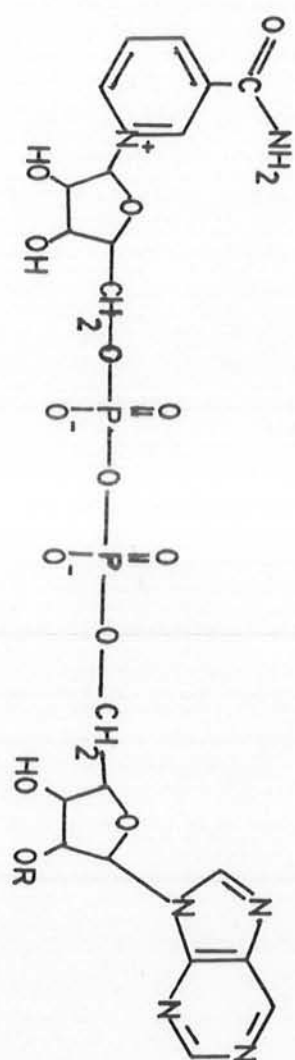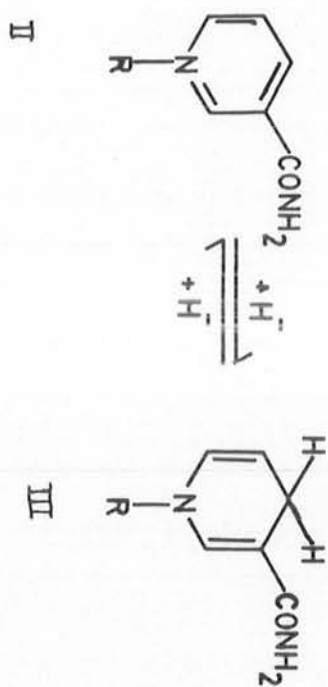
Kosower[2,3] and his coworkers after their extensive studies on such model compounds, were able to show that the products formed were in fact the intermolecular charge transfer complexes, in which the pyridinium ion acts as the electron acceptor and iodide ion as the donor species and he regarded such complexes essentially as ion pairs.

1.2 CHARGE TRANSFER PHENOMENON IN PHOTOELECTROCHEMISTRY

A great interest has developed in the field of photoelectro-chemistry, particularly in the applications of photoelectrochemical systems to the problem of solar energy conversion and storage, since with regards to   renewable energy, solar power remains a most important potential development both in developing and in the developed countries. The problem of developing new energy sources/to supplement is needed and eventually replace fossil fuels. Although serious consideration of photoelectrochemical systems for energy conversion is quite recent, research in this area has a rather venerable origin.

Photoelectrochemistry is based on the unique properties of the semiconductor - electrolyte junction[4,5,6]. Semiconductors are the basic raw materials used for the construction of all types of electronic components.   Semiconductors are now used in photo-electrochemical systems[4,5,7,9] and research and development have shown that extraordinary electrical and optical properties can be introduced into semiconductor material by controlling their impurity content. In the recent years organic charge transfer salts[10], using TCNQ as acceptors and various alkyl-substituted pyridinium cations as donor are being investigated as semiconductors. Semiconductors in photo-electrochemistry for the solar energy conversion are used as

electrodes in different type of photoelectrochemical cells, e.g. photoelectrolysis cells[11,13],electrochemical photovoltaic cells[12], and photogalvanic cells[27-31],and also in solar cells (solid state component).

1.2.1 PHOTOELECTROLYSIS CELLS

In the photoelectrolysis cells, optical energy is converted into chemical energy and most commonly decomposition of water into hydrogen and oxygen is preferred over other significant reactions which are also possible via photoelectrolysis.

Photoelectrolysis of water using sunlight is extremely attractive for several reasons. First, this type of solar energy conversion alleviates the energy storage problem since hydrogen can be stored much more easily than either electricity or heat. Second, hydrogen is valuable as a potential as fuel and energy carrier[11]; it is nonpolluting, renewable, inexhaustible, and very flexible with respect to the conversion to either form of energy (heat via combustion or electricity via fuel cells). Finally, hydrogen is valuable in its own right as a basic chemical feed stock used in large quantities for NH_3 synthesis and petroleum refining. Photoelectrosynthesis: in addition to the decomposition of water into H_2 and O_2 other important and interesting reactions, can be achieved in the photoelectrolysis cells. Frank and Bard[13] studied the photo-oxidation of many compounds such as ethanol, ethyl formate, hydroquinone, and p-aminophenol.

1.2.2 DYESENSITIZATION

The major part of the solar energy spectrum reaching   our

earth, falls in the visible region. Efforts have been made to increase the visible absorptivity of stable, wide band gap semiconductors, and hence to improve their conversion efficiency, by means of dye sensitization technique[14-24]. The dye molecules are adsorbed on the semiconductor surface, when they become excited by the absorption of visible light, charge transfer may occur from the excited state of the absorbed molecule to the semiconductors energy bands[4,25].

1.2.3 PHOTOVOLTAIC CELLS

In this type of photoelectrochemical cells optical energy is converted into electrical energy. The most common are the inorganic solar cells, a sandwich type device of the configuration, Al/mero-cyanine/Ag., have also been investigated[12].

1.2.4 PHOTOGALVANIC CELLS[27-31]

In this cell optical energy is also converted into electrical energy, but the light is absorbed by the dye molecules in the electrolyte. Charge transfer process to an electrode follows the absorption step whereas in photoelectrolysis cells and electrochemical photovoltaic cells the incident light is absorbed in semiconductor electrode.

A rigorous and detailed theory for photoelectrolysis has not yet been derived, and controvercy exist concerning the energetics, mechanism and upper limit conversion efficiency for photoelectrolysis.

A charge-transfer process to yield energy can be described

as (over-all process)

$$A^+B^- \xrightarrow{h\nu} A^\cdot + B^\cdot \qquad 1.1$$

$$A^\cdot \longrightarrow A^+ + e \qquad 1.2$$
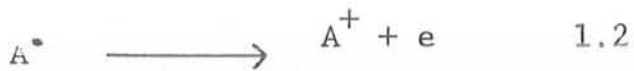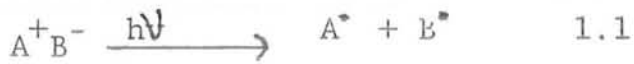
and if A^+ is electrochemically (reversi-bly) reduced

$$A^+ + e \rightleftharpoons A^\cdot$$

the E^o (or polarographic $E_{1/2}$) can be source of energy.

It is already mentioned above that Kosower[2,3,32] discovered charge-transfer phenomenon in some pyridinium iodides: the most extensively investigated compound being 1-ethyl-4-carbomethoxy pyridinium iodide. Based upon the charge-transfer properties of this compound, Kosower[34] proposed the solvent polarity parameter Z-value.

Kosower[32] showed that 1-ethyl-4-carbomethoxy pyridinium iodide (Py^+I^-), under the influence of light undergoes the following reaction:

$$Py^+I^- \xrightarrow{h\nu} Py^\cdot + I^\cdot \qquad (1.3)$$
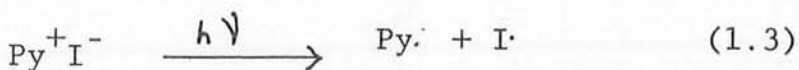
It is also shown that Py^+ can be electrochemically (reversibly) reduced[72].

$$Py^+ + \bar{e} \rightleftharpoons Py^\cdot \qquad (1.4)$$
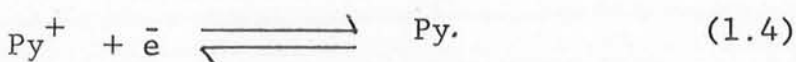
The $Py^\cdot$ formed photochemically can produce current following

$$Py^\cdot \longrightarrow Py^+ + e \qquad (1.5)$$
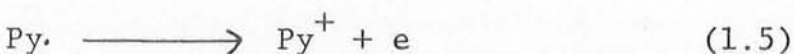
It is clear that processes 1.3 - 1.4 are over-all pictures; the photoelectrochemical reaction involves many steps, and many factors have to be taken into account e.g. recombination of Py· and I· to form Py^+I^-, bimolecular combination of I· to form I_2, reaction of Py· with oxygen if the experiment is carried out in open atmosphere etc. These various rates may be influenced by the nature of the charge-transfer in various solvents depending upon ion-pairing and solvation etc.

To study the phenomena of ion-pairing and solvation it was thought necessary to carry out some nuclear magnetic resonance, optical spectroscopic and conductance studies on the pyridinium salt under various conditions. The present work is concerned with such studies.

HISTORICAL
REVIEW

HISTORICAL REVIEW

This chapter consists of two sections. In the first section a brief review of photoelectrochemistry and the charge transfer complex under investigation is given, whereas the second section summarizes relevant aspects of NMR spectroscopy and electrolytic conductance. These latter-mentioned two techniques have been used in the present work.

SECTION - I

Photoelectrochemistry/Charge Transfer Complex

The pyridinium salt which is under present investigation is a charge transfer complex[33,34]. Its charge transfer property is invoked for understanding certain reactions of biological importance. Furthermore, charge transfer phenomena are considered not only important in understanding biological systems but also in the advancement of solar energy conversion and storage. Since solar energy is a major source of energy which is renewable, studies on charge transfer process can help in collecting information for the eventual utilization of these charge transfer complexes in solar energy conversion.

A) HISTORICAL DEVELOPMENT OF PHOTOELECTROCHEMISTRY

The first photochemical experiment was performed in 1839 by Becquerel[35], who demonstrated that a voltage and an electric current was produced when a silver chloride electrode, immersed in electrolytic solution and connected to a counter electrode, is illuminated. The origin of this photo-voltaic phenomenon called the "Becquerel

effect" was not well understood until Brattain and Garrett[36] launched the modern era of photoelectrochemistry in 1954. These pioneering workers showed how chemical reactions occurring at the surface of germanium semiconductors could be influenced by controlling the semiconducting properties of the germanium electrode, as well as by exposing the electrode to light. This development was a direct result of the advent, at that time, of semiconductor materials of controlled purity and the discovery of the extraordinary electrical and optical properties that could be introduced into semiconductor materials by controlling their impurity content.

It became apparent that the Becquerel effect was due to the presence of a semiconductor at the solid-electrolyte interface, and in particular, to the establishment of a semiconductor - electrolyte junction at the interface.

The pioneering work on the photoelectrochemistry of germanium was rapidly followed up with the studies of other semiconductor electrodes such as $Si, CdS, ZnS, CdSe, ZnSe, ZnTe, GaAs, GaP, ZnO, KTaO_3$, $Ta_2O_5, SrTiO_3$ and TiO_2.

These investigations have been extensively reviewed and summarised by several authors[4,5,37-40] who have covered the work upto 1970. In general these fundamental studies established the basic characteristic of the semiconductor-electrolyte junction. Of particular importance has been the work of Gerischer[4,5,7-9,41]. The kinetics and energetics of electron transfer across semiconductor-electrolyte junctions and nature of the spare charge lies in the semiconductor adjacent to the

semiconductor-electrolyte interface.

Other important early contributions to the basic understanding of photoelectrochemical phenomena were made by Turner[42,43], Boddy[44,45], Dewald [38,46], Williams[47], Morrison[48,49], Gomes[50,51], Freund[52], Memming[53,54] and Pleskov[55].

Whereas virtually all of the work in photoelectrochemistry prior to 1970 was of a rather fundamental nature. Honda and co-workers[56-60] beginning about 1970, were the first to point out the potential application of photoelectro-chemical systems to solar energy conversion and storage. Fujishima and Honda[60] using illuminated n-type semiconducting titanium oxide anodes, showed that the oxidation of water to oxygen could be achieved at a slightly more negative potential compared to standard redox potential of the H_2O/O_2 redox couple. Fujishima and Honda called this effect "Photosensitized electrolytic oxidation" and suggested that it be applied to the problem of using sunlight to split water into hydrogen and oxygen. This process is now generally known as photoelectrolysis.

Although the work of Honda and coworkers[56-60] appeared between 1969 and 1972, the first follow-up work did not appear until 1975[61-68]. Since then, there has been a large and rapidly growing international research and development effort concerned with both photoelectrolysis cells and electrochemical photovoltaic cells.

B) CHARGE TRANSFER SPECTRA AND PHOTOCHEMICAL ROUTE

Shortly after Mulliken formulated the theory of charge transfer spectra and complexes[69,70], Kosower and coworkers[2,3] discovered

the first example directly relevant to biochemical and biological problems. 1 - alkylpyridinium iodides absorbed light at wavelengths longer than expected for 1-alkylpyridinium ions; the intensity of the new absorption increased faster with concentration than expected for a linear concentration dependence. Further work indicated that the absorption wavelength varies as the electron-withdrawing power of the substituents on the pyridinium ring changes, with the absorption wavelength shifting to longer wavelength for the stronger electron-withdrawing groups. Replacing the iodide ion with bromide ion caused a shift of the new absorption to much shorter wavelengths. These observations corresponded precisely to what was expected for a charge transfer complex of iodide ion as donor and pyridinium ion as acceptor eq. 2.1

$$Py^+ + I^- \rightleftharpoons Py^+ , I^- \qquad (2.1)$$
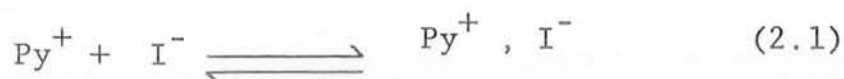
Absorption of light by the complex produces the equivalent of a radical pair in the excited state, which in this case is a combination of a pyridinyl radical and an iodine atom eq. 2.2.

$$Py^+ , I^- \xrightarrow{h\nu} Py^{\bullet} , I^{\bullet} \qquad (2.2)$$
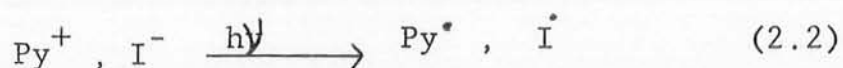
Kosower and Lindquist[47] have demonstrated by flash photolysis of 1-ethyl-4-carbomethoxypyridinium iodide that 1-ethyl-4-carbomethoxypyridinyl radical may be generated through the excitation process shown in Eq.2.2. Subsequent reactions between the radical and iodide atoms or iodine molecules return the systems with high efficiency to the starting pyridinium iodide.

The pyridinium ion is an acceptor of sufficient strength to make possible the formation of charge transfer complexes from a wide variety of donors, especially when the donor moieties are forced to be proximated to the pyridinium ring by a covalent link. Examples of intermolecular and intramolecular charge transfer bands are given by Kosower[71]. Particular attention has been paid to the wide variation in the transition energy required for the excitation process exemplified in eq.2.2. The wavelength at which the charge transfer maximum occurs is generally expressed in energy unit that is either Kcal/mole or cm^{-1}.

The frequent occurrence of charge transfer complexes of pyridinium ion suggests that the photochemical generation of pyridinyl radicals is always a possible chemical pathway..

C) SOLVENT POLARITY PARAMETER THE Z-VALUE

Kosower[34] has found that charge transfer light absorption band of 1-alkylpyridinium iodides is unusually sensitive to solvent (in fact, it is one of the most solvent-sensitive electronic transition known) and has derived a solvent polarity parameter called Z-value from the transition energies for 1-ethyl-4-carbomethoxy - pyridinium iodide. The Z-value for a solvent is the transition energy for the longest wavelength absorption band observed for 1-ethyl-4-carbomethoxy pyridinium iodide in that solvent. The defining equation is given as eq.2.3. The choice of kilocalories per mole as the energy unit is related to the usefulness of this quantity for comparisons to other chemical process.

$$Z = E_T \qquad \text{(Kilocalories / mole)} \qquad (2.3)$$

$$E_T = h\nu \qquad \text{(Ergs / molecule)} \qquad (2.4)$$

h = Plancks' constant = 6.624×10^{-27} Erg Sec.

ν = frequency of photon which produces transition.

$\nu = c/\lambda$ cycles per second

where c = velocity of light = 2.998×10^{10} Cm/Sec.

and λ = wavelength in cm.

Since " λ " is most commonly expressed in angstrom units, so the equation relating E_T in kilocalories/mole with λ in angstrom units can be derived in the following manner

$$\nu = \frac{C \times 10^8}{\lambda} \quad \text{(C.P.S)} \quad (\quad 10^8 \overset{o}{A} = 1 \text{ Cm}) \qquad (2.5)$$

$$\lambda \text{ expressed in } \overset{o}{A} \text{ units}$$

Using eq. (2.5) in eq. (2.4)

$$E_T = \frac{h.c.10^8}{\lambda} \qquad \text{(Ergs per molecule)}$$

$$= \frac{hcNx10^8}{\lambda \cdot 10^7} \qquad \text{(Joules per mole)}$$

Substituting the values of constants h,c,N; E_T in Kcals/mole is given by

$$E_T = \frac{2.859 \times 10^5}{\lambda}$$

when λ is in Angstrom

$$Z = E_T = \frac{2.859 \times 10^5}{\lambda \text{ (in Angstrom)}} \qquad \text{Kcals / mole} \qquad (2.6)$$

The Z-value is evaluated from the position of maximum in angstroms, by eq. 2.6

A process that transfers an electron to a pyridinium ring should be very sensitive to the substitution on that ring, since one should expect that substitution would affect markedly the acceptor ability of the ring. This substitution effect on the pyridinium was found to occur. The charge transfer spectra of the pyridinium iodide (1) have been determined in different solvents and it was observed that the longest wavelength band, which was the charge-transfer band shifts from 3416Å in methanol through 3591Å (Ethanol), 3747Å (Isopropanol) and 4005Å (Acetonitrile) to 4508Å in cis - 1,2- Dichlorethylene[1,2]. The above behaviour of high solvent sensitivity of charge transfer band of (1) can be explained in terms of charge transfer transition from the following discussion.

(I)   2.2
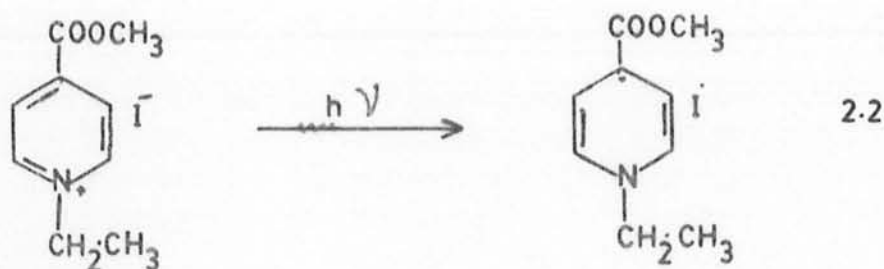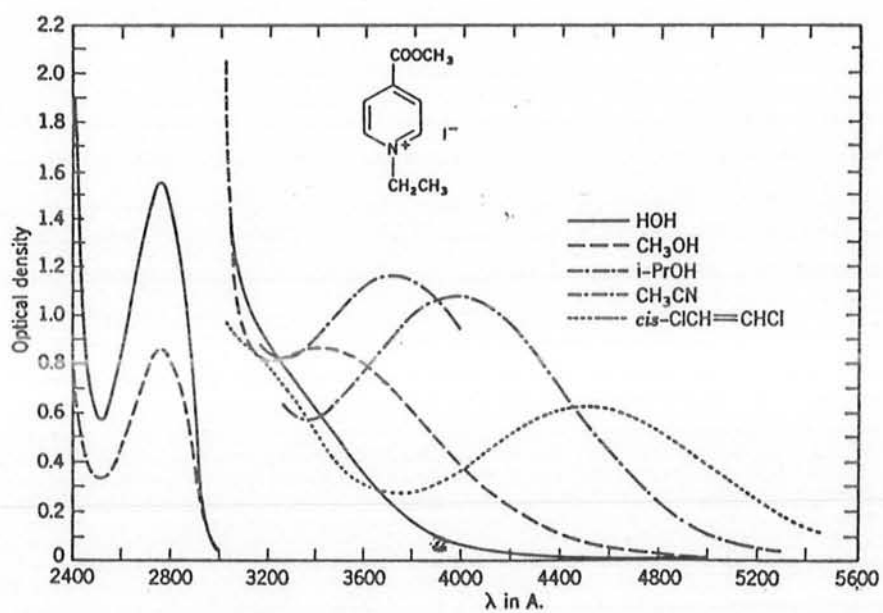
Fig. 2.1: Optical spectra of PyI in different solvents.

The special feature of the transition is that the dipole moment of the excited state does not vanish completely. The reason for this dipole moment of the excited state is that the ground state dipole is perpendicular to the plane of pyridinium ring whereas the dipole moment of the excited state is in the plane of the ring. The change in direction of dipole is known as "Dipole Flip". Dipole moment of solvent molecule surrounding the solute molecule (known as cybotactic region) would be parallel to the dipole moment of the ground state of the pyridinium iodide. The flip of the direction of the solute dipole upon excitation leads to an instantaneous situation in which the dipole moment of the solute is perpendicular to the dipole of the cybotactic region (See. fig. 2.2)

A list of Z-values based on the longest wavelength charge transfer band of PyI is given in table 2.1.

1-Ethyl-4-carbomethoxypyridinium iodide, used as a model compound for the model charge transfer process for the evaluation of Z-values that is the polarity parameter of solvent, has got two limitations on its use for the measurement of Z-values. The first limitation is that the salt is not soluble enough in certain non-polar solvents, such as hexane, for direct measurement of Z-value. The second limitation is that the longest charge transfer band moves to such short wavelengths in highly polar solvents that it cannot be observed underneath the much stronger transition of pyridinium ion.

Fig. 2.2:
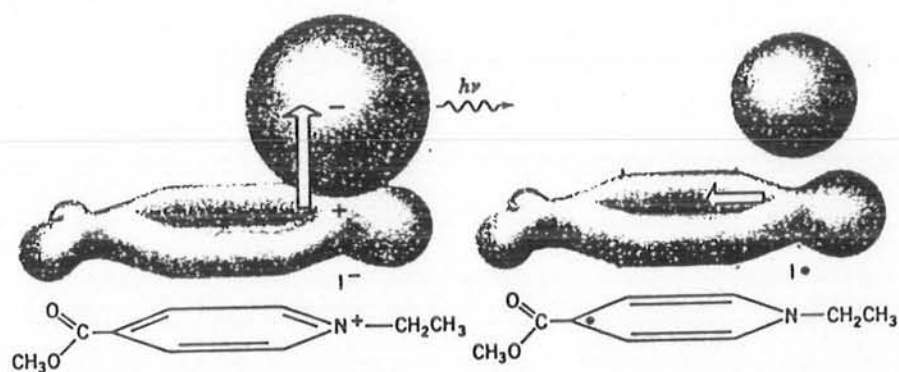
Dipole moment of the ground and excited state of the pyridinium iodide.
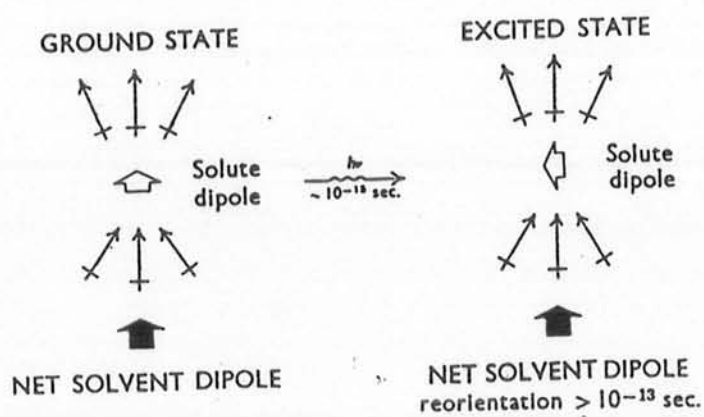
Dipole moment of solvent molecules surrounding the solute.

TABLE 1

Z-VALUES OF DIFFERENT SOLVENTS[2, 34]

SOLVENT	Z - VALUE (Kcal / mole)
Water	94.6
Methanol	83.6
Ethanol	79.6
1-Propanol	78.3
Isopropyl alcohol	76.3
Chloroform (0.13MEtoH)	63.2
Acetonitrile	71.3
Formamide	83.3
Dimethylformamide	68.5
Benzene	54.0
Tetrahydrofuran	56.8

The first limitation was overcome by changing/ modifying the compound pyridinium iodide (I) in order to record λ , e.g. pyridine-1-oxide was used to extend the Z-value scale to isoöctane, in which the salt is isoluble, but again there are limitations. Second limitation was for highly polar solvents; Z-values were determined by extrapola-ting Z-values measured for a mixture of solvents to zero concentration of second component of the mixture in a plot against the Grunwald Winstein Y-value. In this manner the Z-values of water have been determined.

If there exists such a property of charge transfer complex which is solvent dependent as well as directlyexperimentally observed without resorting to extrapolation, such a property could be worth further investigation. NMR chemical shift is such a property which is directly experimentally observed. NMR spectroscopic studies of such a charge transfer complex as 1-ethyl-4-carbomethoxy pyridinium iodide could of course be most interesting vis-a-vis Kosower Z-values. Eq. 2.2 clearly indicates that through continuous exposure of this charge transfer complex to the proper wavelength of light, sufficient concentration of a Py. radical can be built. At the same time Py^+ is known to/go a (reversible) one under electron reduction[72]

$$Py^+ + e \rightleftharpoons Py\cdot$$

giving pyridinyl radical Py.

Thus Py. can give off electron, via

$$Py\cdot \longrightarrow Py^+ + e$$
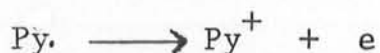
This source of electron supply can then, in principle be used as power or energy source, through solar energy conversion.

It is also well established that/ since C.T property and ion pairing are so closely related to each other to get more complete picture of a CT complex like PyI it is necessary to carry out studies on ion-pairing. The classical method of investigating the ion-pairing is electrolytic conductance; from this technique information can be gained about ion-pair formation and the equilibrium constant.

Thus it is now evident that proton magnetic resonance and conductance studies on the CT complex PyI in various solvents would give useful information regarding the structure of this class of compounds. Elements of NMR and conductance are discussed in the next section.

SECTION - II

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AND ELECTRO-LYTIC CONDUCTANCE

This section of the Chapter is divided into two parts. In the first part theory of NMR Spectroscopy is discussed while in the second part the theory of electrolytic conductance is given.

PART-I

NMR SPECTROSCOPY

The majority of nuclei have magnetic moment and when such a nucleus is placed in a magnetic field it takes up one of a number of quantized orientations with respect to that field. Each nuclear orientation corresponds to an energy level, the lowest corresponding to the orientation in which the nuclear magnetic moment is most closely aligned with the field. NMR spectroscopy consist in inducing transitions between such energy level by means of fluctuating magnetic field of the correct frequency, ν , so as to obey the Bohr relationship[73] $E = h\nu$, where h is Planck's constant.

A) MAGNETIC PROPERTIES OF ATOMIC NUCLEI

The nuclei of certain isotopes possess an intrinsic spin; that is, they are associated with an angular momentum. The quantum-mechanical expression for the total angular momentum is given by $I(I+1)h/2\pi$, where I is the quantum number for the spinning motion. Different nuclei have different half-integral values of the spin quantum number I. I may have the values, $I = 0, \frac{1}{2}, 1, 3/2, \ldots$ depending

upon the particular isotopic nucleus (I = 0 corresponds to a
nucleus which does not possess a spin and for such a nucleus no
nuclear magnetic reasonance transition is expected). Since atomic
nuclei are also associated with an electric charge, the spin gives
rise to a magnetic field such that one may consider a spinning
nucleus as a minute bare magnet, the axis of which is coincident
with the axis of spin. The magnitude of this magnetic dipole is
expressed as the nuclear magnetic moment μ , which has a charac-
teristic value for all isotopes for which I is greater than zero [74].

B) NUCLEAR RESONANCE

The nuclei of those isotopes for which the spin quantum
number I and magnetic moment μ are not equal to zero give rise to
magnetic resonance. Consider a bare nucleus such as a proton,
when such a nucleus is placed in a static uniform magnetic field
H_o it takes up one of (2I+1) orientations which are characterised
by energies dependent upon the magnitude of μ and H_o. Since the
bare nucleus has a spin quantum number I equal to one half, quantum
mechanics tells us that the tiny proton magnet is restricted to just
two possible orientations ((2I + 1) = 2), in the applied field and
these can be considered to be a low energy or parallel orientation
in which the magnet is aligned with the field, and a high energy or
anti-parallel orientation in which it is aligned against the field.
Since these two orientations correspond to two energy states it
should be possible to induce transition between them and the
frequency, ν , of the electromagnetic radiation which will affect
such transitions is given by the equation 2.7.

$$h\nu = \frac{\mu \, \beta_N H_o}{I} \qquad (2.7)$$

where β_N is a constant called the nuclear magneton. The equation (2.7) can be re-written as

$$\nu = \frac{\gamma H_o}{2\pi} \qquad (2.8)$$

where γ is known as gyromagnetic ratio and is characteristic of the nucleus.

The absorption or emission of the quantum of energy $h\nu$ causes the nuclear magnet to turn over or "flip" from one orientation to the other. For nuclei with spin quantum number greater than 1/2 there will be more than two possible orientations and in each case a set of equally spaced energy level results. The electromagnetic radiation of appropriate frequency can cause transitions between the various energy levels with certain selection rules that allow the transition between adjacent levels. Since the energy levels are equally spaced this selection rule requires that there is only one characteristic frequency for a given value of H_o. So one can say that in NMR spectroscopy the atomic nuclei of elements having (I=0) when placed in a strong magnetic field may absorb radio frequency radiation of discrete energy.

One may consider the classical picture of the absorption process which is more helpful in understanding the nuclear magnetic resonance and, also, is a helpful model for the experimental procedure. Consider a spinning nucleus oriented to an angle θ to the direction of applied field H_o (Fig. 2.3). The main field acts on the nuclear magnet so as to decrease the angle θ. However, because

Fig. 2.3

Fig. 2.3
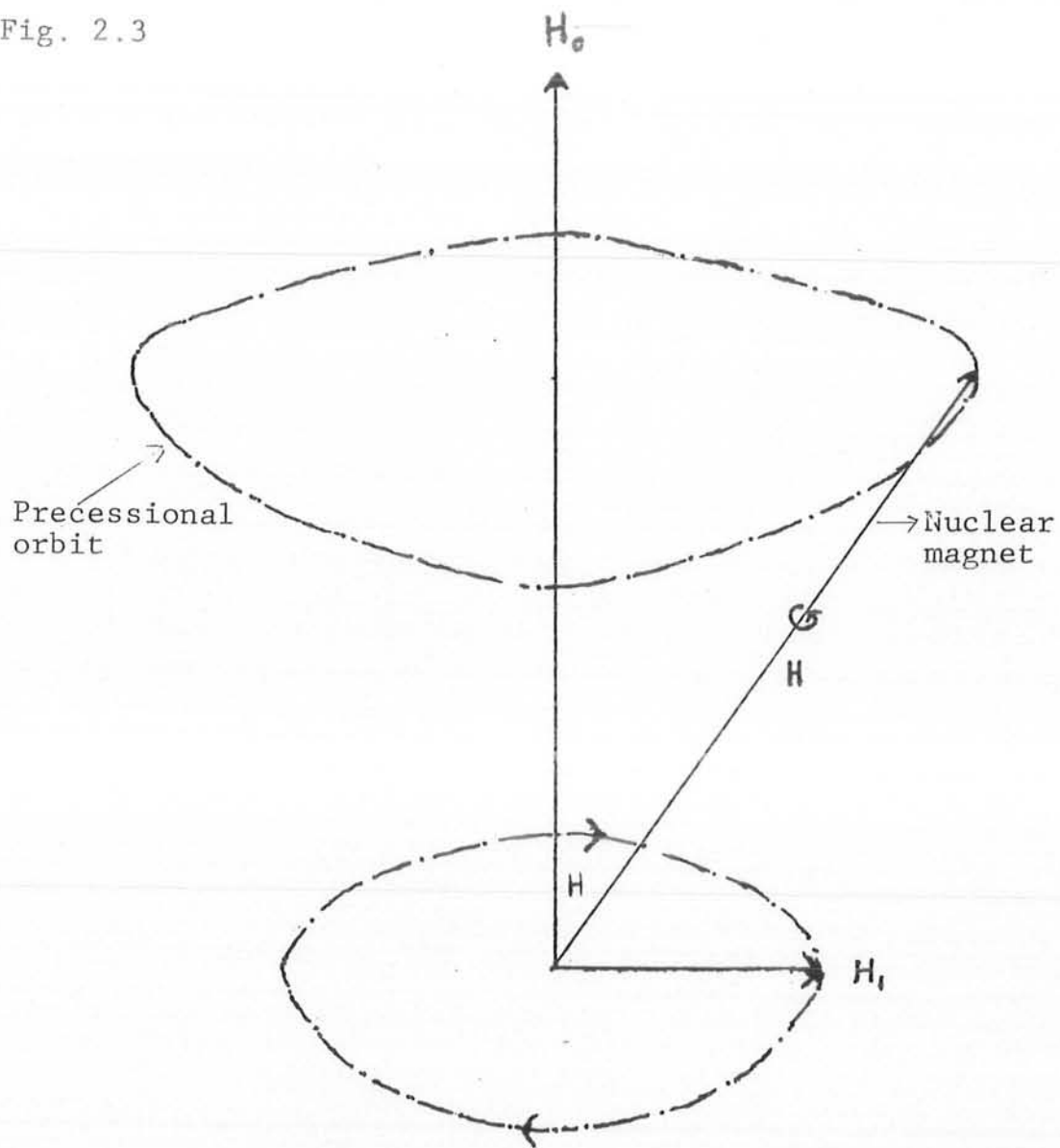
the nucleus is spinning, the net result is that the nuclear

magnet is caused to precess about the main field axis. The angular

velocity W_o, of this precessional motion is given by equation No.2.9.

$$W_o = \gamma H_o = 2\pi \nu \qquad\qquad (2.9)$$

The precessional frequency W_o is directly proportional to
H_o and to the gyromagnetic ratio γ , and is exactly equal to the
frequency of electromagnetic radiation which, on quantum mechanical
grounds, is necessary to induce a transition from one nuclear spin
state to an adjacent level. The act of turning over the nucleus
from one orientation to another corresponds to an alteration of the
angle θ. This can only be brought about by the application of mag-
netic field, H_1. Furthermore, if this new field, H_1, is to be conti-
nuously effective, it must rotate in a plane at right angles to the
direction of H_o in phase with the precessing nucleus. When these
conditions are met the rotating magnetic field and the precessing
nuclear magnet are said to be in resonance and absorption of energy
by the latter can occur[76].

So in order to obtain a physically observable effect it is
necessary to place the nucleus in a static field and then to subject
it to electromagnetic radiation in such a way that the magnetic
vector component of the radiation rotates with the appropriate
angular velocity in a plane perpendicular to the direction of the
field.

C) CHEMICAL EFFECTS IN NMR

1- CHEMICAL SHIFT

The separation of resonance frequencies of nuclei in different
structural environments from some arbitrarily chosen line position
is generally termed the chemical shift. So far from the discussion
in the previous section, more or less it is assumed that the
resonance frequency of a nucleus is simply a function of the applied
field and the gyromagnetic ratio of the nucleus. But, however, it
has been observed that the resonance frequency is, to a small degree,
dependent on its molecular environment. This is because extra-nuclear
electron magnetically screens the nucleus so that the magnetic field
felt by the nucleus is not the same as the applied field. Consider
a nucleus in a magnetic field of field strength (H_o), but the field
has been altered by the screening or shielding of the electron
surrounding the nucleus. Since electrons are magnetic particles
also, their motion is influenced by the imposition of an external
field; in general, the motion induced by an applied field is in a
direction so as to oppose that field (Lenz's Law)

$$H \ (\ Nucleus \ ) = H_o - \sigma H_o$$

$$= H_o \ (1 - \sigma) \qquad (2.10)$$

where σ is shielding constant and its magnitude depends on the
orientation of the molecule relative to the applied field. The
screening factor   is found to be small for protons $\sigma = 10^{-5}$ and
less than 10^{-3} for most of the other nuclei. NMR data are usually
measured in frequency units (Hertz) from a particular reference,

generally proton magnetic resonance (PMR) data is reported with respect to the internal reference of tetra-methyl silane (TMS) for non-aqueous solvents in which TMS is soluble and for aqueous solutions no single reference is predominant[75].

In cases where complex spectra occur or where spin-spin coupling constants are to be given, the results should be reported in frequency units as well. For chemical shifts, however, the use of frequency units has the disadvantage that the reported chemical shift is induced by the field. Hence it is customary and highly desirable to report chemical shift in the dimensionless units of parts per million (ppm), which is independent of radio frequency (rf), radiation (ν) or magnetic field strength (H). The relation can be arrived between the dimensionless scale and shielding constant (σ) as under.

The frequency (ν) at which a proton will resonate in the nuclear magnetic resonance (NMR) spectrum is given by the equation (2.11), in which H(nucleus) is the local field experienced by the proton and γ is a constant known as the gyromagnetic ratio. This equation (2.11) is also known as armor equation.

$$\nu_o = \gamma H_{(nucleus)} / 2\pi \qquad (2.11)$$

using equation 2.10 in equation 2.11 one gets

$$\nu_o = (\gamma / 2\pi) H_o (1 - \sigma) \qquad (2.12)$$

There are two main methods for scanning the NMR spectrum. In one method magnetic field (H) is held fixed and the frequency (ν) is varied and in the second procedure the radio frequency (ν_o) is

kept constant and magnetic field strength (H) is varied.

Now consider the scanning of a NMR spectrum when the magnetic field is held constant at H_o and the frequency (ν) is varied. Then the resonance frequency of the samples and reference are

$$\nu_s = (\gamma/2) H_o (1 - \sigma_s) \qquad (2.13)$$

$$\nu_R = (\gamma/2) H_o (1 - \sigma_R) \qquad (2.14)$$

The chemical shift on the dimensionless scale is usually given the symbol δ (delta).

The chemical shift is defined as

$$\delta = \frac{\nu_s - \nu_R}{\nu_R} \times 10^6 \qquad (2.15)$$

On substituting the values of ν_s and ν_R from equations (2.13) and (2.14) in equation (2.15) one obtains

$$\delta = \frac{\sigma_R - \sigma_s}{1 - \sigma_R} \times 10^6 \qquad (2.16)$$

If one makes the approximation that

$\sigma_R \ll 1$ in the equation (2.16), one gets δ as,

$$\delta = (\sigma_R - \sigma_s) \times 10^6 \qquad (2.17)$$

Another way of scanning NMR spectrum is to keep the frequency constant

and vary the magnetic field. The resonance of samples and reference will then be found at the values of the applied field given by

$$\nu_o = (\gamma/2) \, H_S \, (1 - \sigma_S) \qquad\qquad (2.18)$$

$$\nu_o = (\gamma/2) \, H_R \, (1 - \sigma_R) \qquad\qquad (2.19)$$

Again using the same analogy for the chemical shift as used in the equation (2.15)

$$\delta = \frac{H_R - H_S}{H_S} \times 10^6 \qquad\qquad (2.20)$$

On substitutions of equation (2.18) and (2.19) in equation (2.20) one gets, on simplification

$$\delta = \frac{\sigma_R - \sigma_S}{(1 - \sigma_S)} \times 10^6 \qquad\qquad (2.21)$$

Since $\sigma_S \lll 1$ so

$$\delta = (\sigma_R - \sigma_S) \times 10^6 \qquad\qquad (2.22)$$

From the above discussion one concludes that more highly shielded nucleus will show its resonance at higher applied field when the field is scanned, but at lower frequency when frequency is varied. Also, a sample that is less shielded than the reference will be assigned a larger value of chemical shift.

In defining equations 2.17 and 2.22 for chemical shift, both have had sample and reference reversed so that the value of chemical shift would increase with increasing shielding. Both conventions are

used for H^1 resonance. The protons in the reference compound, tetramethylsilane (TMS), proved to be more shielded than almost all other protons; hence the definition embodied in equations 2.17 and 2.22 is generally used, since it permits virtually all chemical shifts to be expressed as positive numbers. It is a convention used for H^1 resonance; a large chemical shift (measured with respect to TMS) implies that its protons are less shielded and hence resonate at lower field. Since it is often convenient to think of increasing chemical shifts in the direction of increasing rather than decreasing shielding, an alternative scale, the τ scale, is now widely used. This scale is a dimensionless scale that assigns to TMS (internal reference) the value 10.000 ppm. Chemical shifts are expressed in parts per million with decreasing number corresponding to decreasing shielding. The τ scale and δ scale as defined in equations 2.17 and 2.22 are related and values can be converted from one to other by the equation 2.23.

$$\tau = 10.000 - \delta \qquad (2.23)$$

The present studies will be concerned almost exclusively with the nuclear magnetic resonance of the hydrogen nucleus, that is, with proton magnetic reasonance (PMR), and the idea of structure on proton resonance frequencies can be gained by reference to figure 2.4. Tables of chemical shifts, expressed as τ or δ values are a prerequisite for the interpretation of nuclear magnetic resonance spectra. Tables of proton chemical shifts, given as τ and δ values can be found in NMR spectroscopy books[73,77]. Figure 2.4 gives a general idea of the proton chemical shifts for some common functional groups.
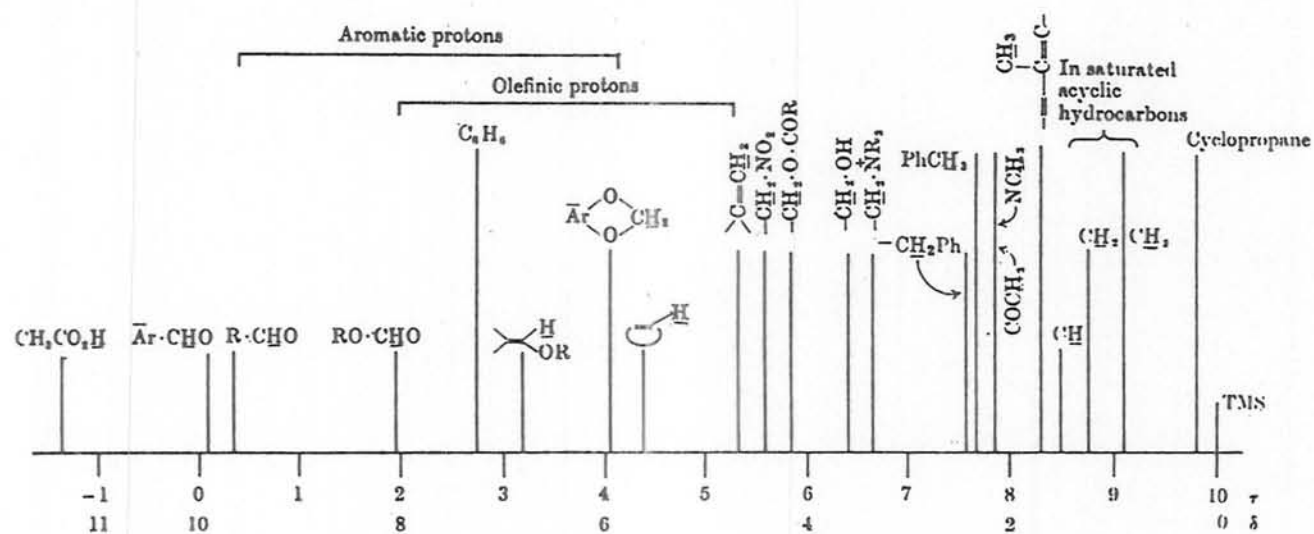
Fig. 2.4: Some common functions in organic compounds and their proton chemical shifts on the τ and δ scale.

Some regions overlap, for example, those where aromatic and olefinic proton lines appear, but in many cases chemical shifts are very characteristic of the chemical groups and/or their environment. Thus methyl groups in acyclic aliphatic compounds, and removed from other functional groups always have chemical shifts near to τ 9.1 (or δ 0.9). Methyl groups attached to aromatic or pseudo aromatic rings appear at τ 7-8 (δ 3-2). Also in the latter region one finds $N-CH_3$ and $CO.CH3$ lines. However, distinction between such possibilities is usually easy, especially with the help of chemical and other physical data.

Consider a few simple proton resonance spectra (i) p-xylene; Fig. 2.5 shows two lines, one at τ 7.7 (δ 2.3) from the protons of the methyl groups and one at τ 2.95 (δ 7.05) from those of benzene ring[78(a)]. The integrated intensities of these lines are in the ratio 6:4 respectively. (ii) The spectrum of toluene[78(b)] in deuterochloroform also shows two lines but with intensities of 5:3 (Fig.2.6). The line in the aromatic region of the spectrum is of course from the ring protons and that at a higher field is from the three equivalent protons of methyl substituent, so one can make assignments to the resonating signals in a NMR spectrum of any sample using the tables of proton chemical shifts and hence elucidate the structure of the compound under investigation.

One may consider another example; in the molecule of methyl β-amino-crotonate (III) there are four chemically distinct kinds of hydrogen nuclei (those hydrogen nuclei which are having different environment, also known as chemically non-equivalent), denoted as shown in III, by (A),(B),(C),(D) and these groups, having different
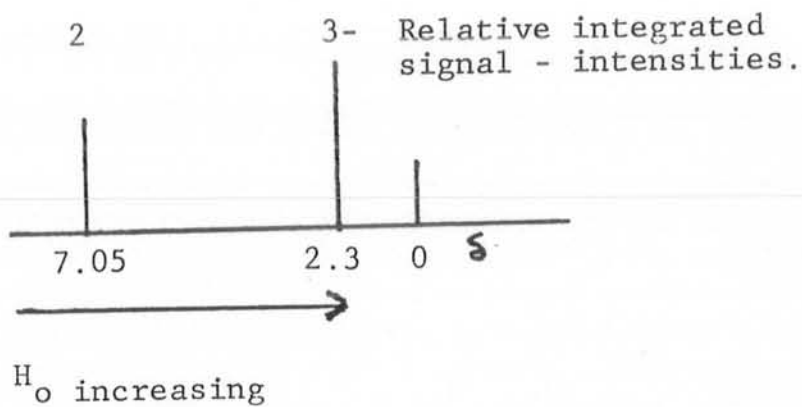
Fig. 2.5: Proton resonance lines from P-xylene in $CDCl_3$
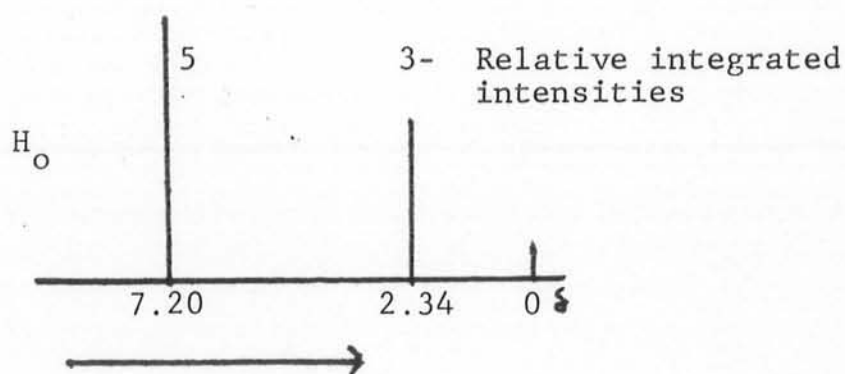
Fig. 2.6: Proton magnetic resonance of toluene in carbon tetrachloride.

chemical shifts, give

$$CH_3 \ (D) \diagdown \atop NH_2 \ (A) \diagup C = CH \ (B) - CO - OCH_3 \ (C)$$

<div align="center">III</div>
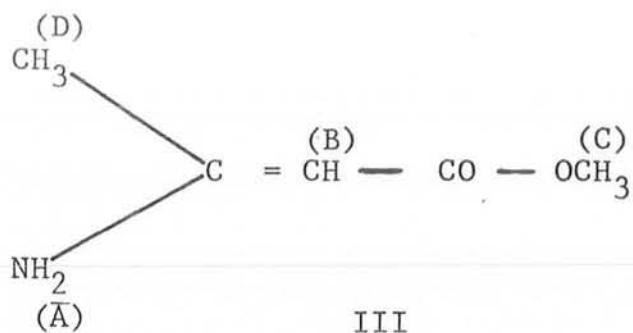
rise to a four line spectrum[79] Fig. 2.7. The assignments of the
signals as shown are readily made from the information of chemical
shifts and line intensities. As one observes   the signal (A)
from NH_2 group is of broad nature. So from the latter NMR spectrum
it is obvious that band shapes vary enormously and the height of
the lines cannot be used as an approximation for intensity; only the
integrated intensities (area) will be proportional to the number of
protons responsible for the signals, and signals whose position may
vary over a wide region of the spectrum are tabulated in the text[73].
There, special characteristics are listed which help in correlating
these signals with the possible functional groups, hydroxyl, amino,
amido, thiol, and acid functions.

II)   CHEMICAL SHIFT AND EXCHANGE PHENOMENA

Protons which exchange rapidly give sharp signals (as do non-
exchanging protons); their environments are well averaged. Protons
which exchange slowly are effectively in more than one environment
and may give rise to separate signals or to a brodened line,
depending on the residence time and rate of exchange. The proton
exchange phenomena are discussed later in this chapter under heading of
time dependance phenomena.
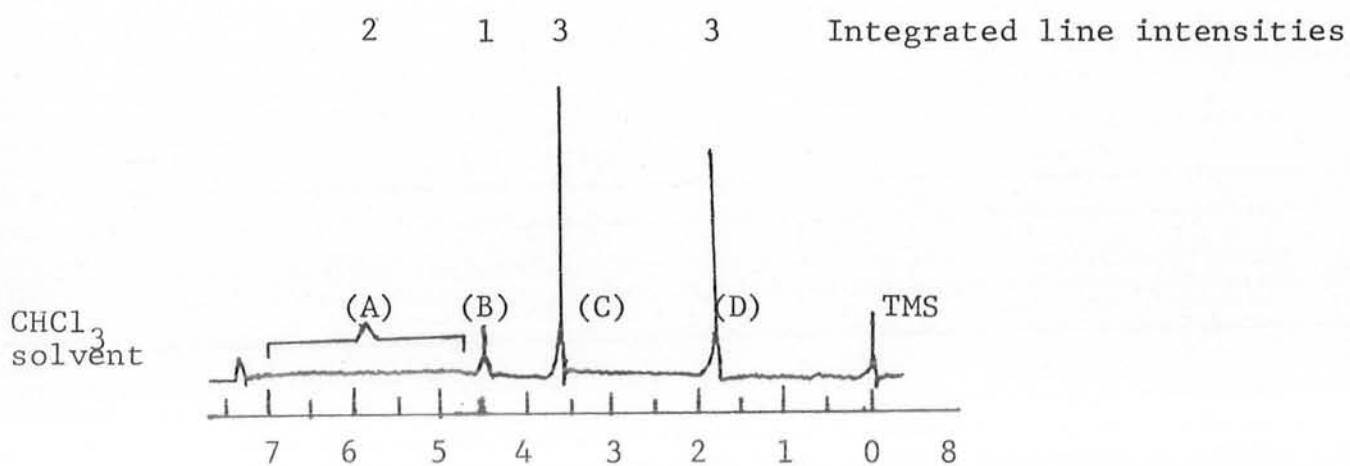
Fig. 2.7: The proton magnetic resonance spectrum of III, showing the assignment of the 4 lines to the 4 different groups of protons (A),(B),(C),(D).

III- EFFECT OF SOLVENT ON CHEMICAL SHIFT VALUES

If the solvent is a hydrogen compound (e.g. $CHCl_3$, dioxan, methanol, etc.) then its own resonance lines are added to the spectrum. The solvent lines are very intense because of the much greater effective molar concentration of solvent protons,compared to those of the solute. Very strong lines are always accompanied by side bands, and so a region of the spectrum, rather than a narrow band is effectively spoiled (Fig. 2.8). The interference is worse the higher the hydrogen content of the solvent molecule. To circumvent this nuisance deuterated solvents are employed. Sometimes it may be necessary to examine a compound in two different solvents which have their resonance lines in different parts of the spectrum, so that whole of the spectral range can be covered.

The side bands are of two types (Fig. 2.8). The spinning side bands result from amplitude modulation of the main resonance signal and appear in pairs centred about the main signal and spaced from it by the sample rotation frequency or integral multiple of this. Spinning side bands are easily recognized because of the symmetry of their arrangement about the main signal and the fact that the alteration of the speed of spinning of the sample causes them to move in the spectrum. Other side bands, sometimes observed in proton resonance spectra, are invariant in position with spinning rate. These are so-called carbon-13(^{13}C) satellites.

^{13}C occurs naturally with 1% of the abundance of ^{12}C. The nucleus has a spin $1 = \frac{1}{2}$ and so causes splitting of the signal from an attached proton into two components, and these appear centred on the main proton signal some 120-200 cycles/sec(c/s)
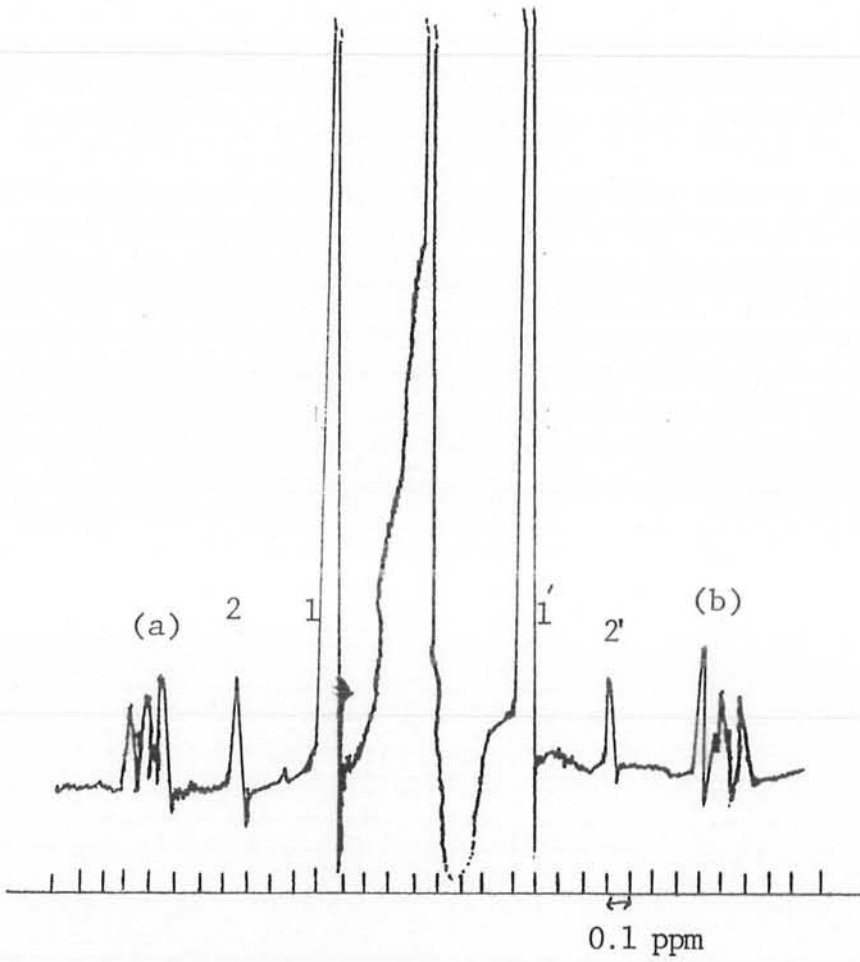
Fig. 2.8: Spinning side bands, 1,1´,2,2´ and C^{13}-H satellite signals, (a) and (b), surrounding the proton resonance line from liquid dioxan.

apart. The combined intensities of these satellite bands will be
1% of that of the main signal, corresponding to ^{13}C abundance in
the particular functional grouping. Only in special cases do these
satellite signals become appreciable in magnitude. That is so with
dioxan (IV) (Fig. 2.8) where,

$$\text{O}$$

H$_2$C   CH$_2$

H$_2$C   CH$_2$

$$\text{O}$$
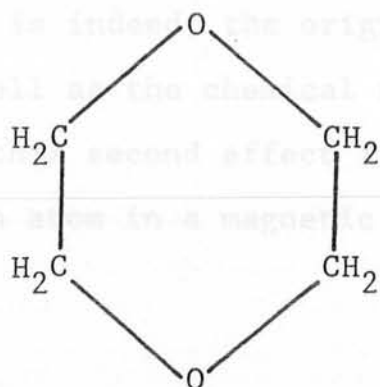
IV

because of the molecular symmetry, there is 4% chance of any one
molecule containing a ^{13}CH$_2$ group[76].

For a given solute, different solvents will give rise to
different sets of chemical shifts if the solvent molecules are not
chemically inert and magnetically isotropic (i.e. spherically
symmetrical in magnetic properties). Carbon tetra chloride (CCl$_4$) is
an ideal solvent.

IV- CAUSES OF CHEMICAL SHIFT

As discussed above that the field experienced by a nucleus in
an atom or molecule is not precisely equal to the applied field,
H$_o$, because the nucleus is to some extent shielded by the extra-
nuclear electrons associated with it and with neighbouring nuclei.
In principle, electrons can influence the field at a nucleus in one

that the motion of electrons differs from that in the field-free system by a common precession of frequency H_o e/4mc (where H_o = applied magnetic field, e = charge on electron; m = mass of electron; c = velocity with which electrons revolve around the nucleus). The physical significance of the theorem can be explained by reference to the Bohr model of hydrogen atom shown in Fig. 2.9. In the presence of   magnetic field the electron in the hydrogen atom circulates (with a frequency H_o e/4mc) in the direction shown (clockwise). The motion of the electron is equivalent to an electric current flowing in a closed loop and as such it is associated with a secondary magnetic field which is also depicted in Fig. 2.9. The secondary magnetic field opposes the applied field, H_o, at the nucleus which consequently experiences a total field which is slightly less than that predicted from the value of H_o and the magnetic constant of the proton. Equation 2.11 can therefore be modified to

$$\nu = \gamma H_o (1 - \sigma) 2\pi \qquad (2.24)$$

where σ is the shielding constant for hydrogen atom. An important result which follows from the above treatment is that the frequency of Larmor precession is proportional to H_o . Extention of the treatment of shielding in free atoms to that of atoms in molecules is complicated by several factors. An understanding of these factors is particularly important as they are related to the way in which molecular structure affects the chemical shift. It is customary

to separate the shielding arising from the electrons directly associated with the nucleus, into two terms. The first term relates to normal circulation in atoms and is a function of electron density. The second term takes into account the restriction imposed on circulation of electrons by chemical bonding. The two are referred to as local diamagnetic shielding and local paramagnetic shielding by electrons which are involved in the bonding of the proton in question to the rest of the molecule.

Local diamagnetic shielding makes an important contribution to the shielding of protons in organic molecules. Its magnitude will differ from that of the shielding in the hydrogen atom by virtue of changes in electron density in the immediate vicinity of the nucleus, which result when hydrogen atom is involved in chemical bonding. This type of shielding will be discussed in some detail later.

However, local paramagnetic shielding, for proton, is much less important than the diamagnetic term. In case of the hydrogen molecule it is approximately/an order of smaller magnitude[82], and its variation with molecular structure is negligible. So for proton, local paramagnetic shielding is most commonly neglected in the theoretical treatment of chemical shift.

In addition to the local shielding effects just considered, significant contributions to the shielding of protons may arise from the circulations of electrons associated with other atoms or groups in the molecule. Shielding of this type is called long-range shielding. Long-range shielding arises only if the magnetic polarizibility of the electrons is anisotropic, i.e. if the circulation

induced by the applied field is greater for some orientation of the molecule in the applied field than for others. Long-range shielding may arise from electron circulation about the neighbouring atom in the molecule in which case it is referred to a neighbouring paramagnetic shielding or, alternatively, circulation may occur about two or more atomic centres and this effect is known as interatomic diamagnetic shielding. An important feature of long-range shielding is that it can be either positive or negative depending on the geometric relation between the group of electrons responsible for the effect and the nucleus under consideration. The magnitude of the effect is such that it is important in the chemical shift of protons but of less significance for heavier nuclei for which the overall scale of chemical shifts is dominated by local paramagnetic shielding.

Chemical shifts of protons in organic compounds are almost invariably measured in liquid phase, usually as solutions in suitable solvents. A solvent can contribute to the shielding of a proton in a molecule by its influence on the electronic structure of the molecule and by direct magnetic field contributions in case of magnetically anisotropic solvents.

In summary, the shielding (σ) of a nucleus can be expressed as the sum of five terms

$$\sigma = \sigma_d^L + \sigma_p^L + \sigma_p^N + \sigma_d^N + \sigma_s \qquad (2.25)$$

which are the local diamagnetic and paramagnetic, neighbouring paramagnetic and interatomic diamagnetic and solvent shielding contributions respectively.

a) <u>LOCAL DIAMAGNETIC PROTON SHIELDING</u>

The relation between the local diamagnetic shielding of a proton and chemical structure involves the effect of electric fields on circulations of electrons around the proton, and of the electron density at the proton. It has been found from quantum mechanical treatment[83] that the contribution from local paramagnetic shielding is negligible.

The much more important factor determining the magnitude of local diamagnetic shielding is the local electron density. Indeed the relation between σ_d^L and the polarity of the C - H bonds, as inferred from several general criteria, forms the basis of the most useful means of predicting approximate proton chemical shifts in organic molecules.

Various attempts have been made to correlate proton chemical shifts with the electronegativities of the substituents. First attempt was made to correlate proton chemical shifts in substituted alkanes with the electronegativities of the substituents. These earliest attempts utilized data for monosubstituted methanes[84-86] and ethanes[84,85,87].

It was noted that there was an approximately linear relation between the shifts for the methanes and the differences (δ internal) in chemical shifts between the methyl and methylene protons of the ethanes and that both these quantities were linearly related to the electronegativities of the substituents. Accordingly, it was suggested by Dailey and Shoolery[84] that (δ internal) could be used to measure electronegativities, the relation between the two

being given[86] by equation 2.26.

$$Electronegativity = 0.684 \; \delta \; internal + 1.78 \qquad (2.26)$$

where δ internal is in parts per million (ppm).

The apparent success of the above correlations suggests that the shielding in alkanes is due solely to the local diamagnetic term (σ_d^L) which in turn is controlled by the inductive ($\pm I$) effect of the substituent. However, it is now clear that this was not the case. Inspection of the data for substituted methane, showed that chlorine, bromine, iodine and sulphur are anomalous. It has been shown that the shifts of α - protons in isopropyl chloride, bromide and iodide are in opposite order to that found for the corresponding methyl halides and α - protons of ethyl halides[89]. These findings cannot be explained simply in terms of the inductive effect of substituents. Spiesecke and Schneider[88] have considered the proton chemical shift data for substituted methanes and ethanes. They concluded that the long-range shielding was largely responsible for the anomalous results for the halogens and sulphur.

The proton chemical shift has also been correlated with parameters which reflect the effective electronegativity of the group to which the proton is attached. For instance, correlations of Hammett σ - constants for substituents have been attempted for aromatic protons in substituted benzenes[90,91] aldehyde protons in substituted benzaldehydes,[92] the methoxy protons in substituted methoxybenzenes[93], α - and β - protons in ethyl benzenes[94]. In general reasonable correlations are reported for p-substituents

but less satisfactory argument is obtained with the m-protons, for which long-range shielding contributions are expected to be more important.

In short the dependence of local diamagnetic shielding on electronegativity and Hammett-type substituent parameters clearly involves polarization of the C-H bond, the shielding being reduced as the $\bar{C}\overset{+}{H}$ character of the bond increases. Hence for a detailed understanding of the role of local diamagnetic shielding, all the factors which affect the polarity of C-H bond should be considered. These factors include , (i) direct electostatic effects of charges and dipoles, (ii) inductive effects, (iii) mesomeric effects, (iv) hybridization of the carbon to which the proton is attached, (v) van der Waal effects. The detail of these effects on the local diamagnetic shielding can be found in the texts[75,77].

b) LONG-RANGE/INTERATOMIC DIAMAGNETIC SHIELDING

Aromatic and pseudo-aromatic rings, with their cyclically delocalized π - electrons, allow the induced circulation of these electrons over all the ring atoms. The considerable ring currents thus induced produce correspondingly large magnetic fields. Such systems are far from being spherically symmetrical; indeed, they are markedly anisotropic, and so the effects of the induced field at a point in the surrounding space do not average to zero for all possible orientations of the ring with respect to the applied magnetic field. Aromatic rings therefore provide a strong source of long-range shielding and deshielding. The induced field and resulting shielding zones for the benzene molecule can be seen as in Fig. 2.10. The field arising from the induced circulation of π -electrons round the
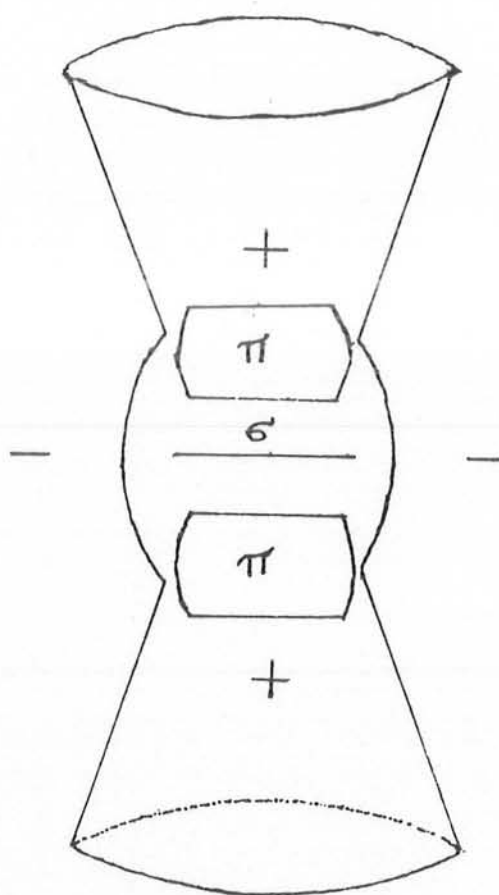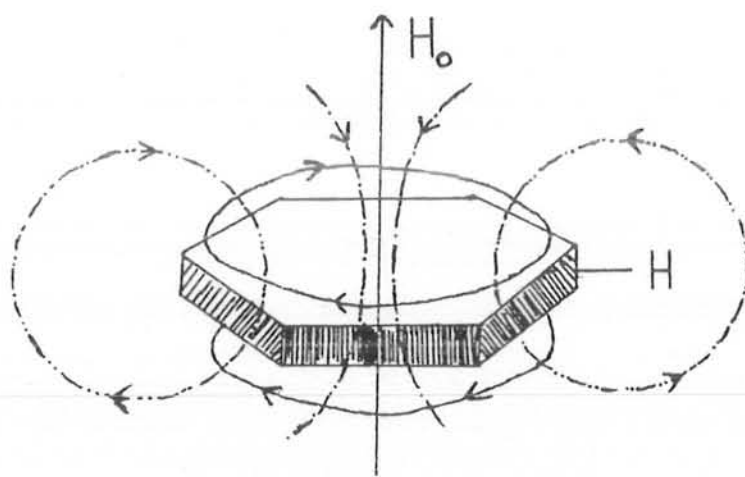
Fig. 2.10: The induced diamagnetic circulation of π-electrons
around a benzene ring and the resultant shielding
envelope.

ring is opposed to the applied field at the centre of the ring, but in the same direction outside, in the plane of the ring where the benzene protons lie. These are then deshielded (negatively shielded), because there the secondary induced field reinforces the applied field. The result is that the protons come to resonance at a correspondingly lower value of the applied field than would otherwise be required. The protons of benzene have a chemical shift of $\delta = 7.27$; on the other hand a nucleus held over the centre of the benzene ring is shielded, because in the region induced and applied fields are opposed. Thus, in the paracyclophane (V) one finds
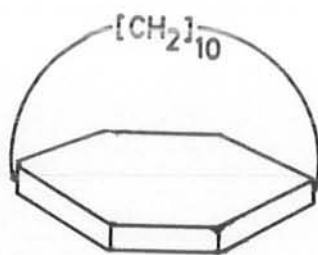
V

the central methylene protons of the bridging chain have $\delta = 0.80$ as compared with $\delta = 1.25$ in a normal aliphatic chain.

The induced magnetic field /does not really arise from induced circulations of electrons around bonds or rings. The electrons continue to move in their normal paths but additionally perform an induced precessional motion about the lines of force of the applied

field[96]. It is from the sum of their induced precessional motions
that the secondary magnetic field arises. The secondary induced
field has a distribution in the surrounding space such that it
could equally well have arisen from a prescribed circulation of
electrons within the bond. Thus, the induced secondary field about
a benzene molecule has the same form as if the π-electrons
circulated round in two superconducting loops (the π-lobes) one
above and one below the plane of σ-bond framework. The secondary
field can be calculated on such a basis. In this way the shielding
and deshielding zones surrounding the benzene molecule have been
computed by Johnson and Bovey[97]. These computations are of great
help in explaining the chemical shifts of groups held in proximity
to benzene rings or any other aromatic rings in the same molecule.

C) SPIN-SPIN COUPLING

Consider the low resolution spectrum of ethanol (Fig.2.11) which
consists of three bands as expected from the three types of protons
in the molecule . The intensities of these bands, as measured by the
areas they enclose, are in the ratio 1:2:3. This is to be expected
since the intensities of absorption bands are proportional only to
the number of protons responsible for the absorption.

Now if the ordinary ethanol's NMR spectrum is scanned at high
resolution, one finds a somewhat more complicated picture (Fig.2.12).
The bands associated with the methyl and methylene groups now appear
as multiplets, the total areas of which are still in the ratio of
3 : 2; the spacing of the three components of the methyl groups
triplet are found to be equal to that in the quartet from the methylene
group. Furthermore the areas of the components of each multiplet

The Low resolution spectrum of ethanol

Fig. 2.11

100   MHz   spectrum of ethanol containing a trace of acid.
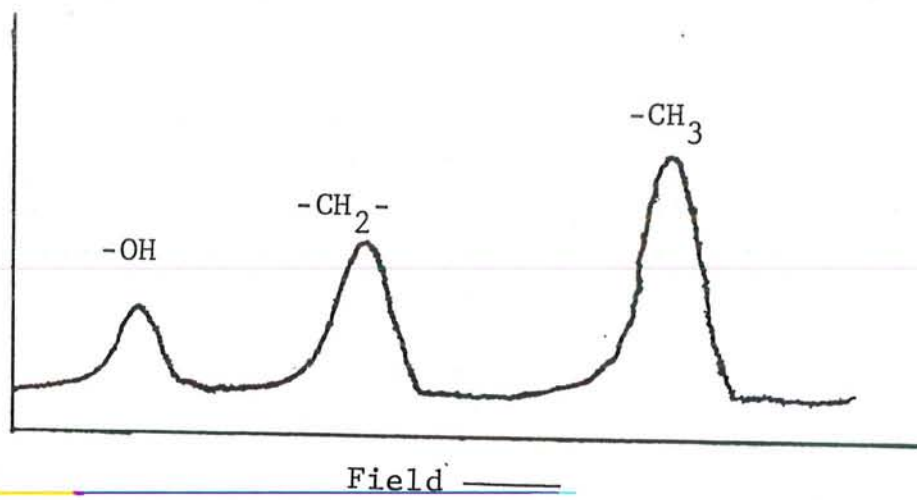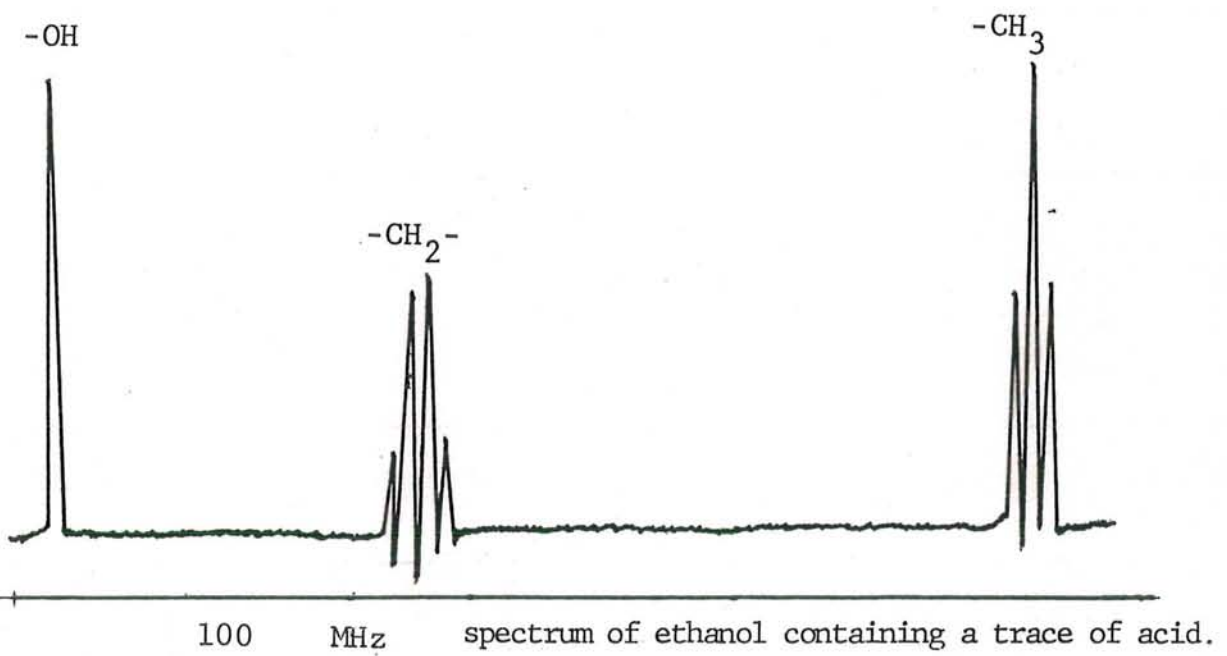
Fig. 2.12

approximate to simple integral ratios (1:2:1 for triplet and 1:3:3:1 for the quartet). These observations can be understood if one imagines that the field experienced by the protons of the one group is influenced by the spins of protons in the neighbouring group. Consider the methyl protons in relation to possible spin arrangement of the two methylene protons.

There are four spin arrangements for the methylene group. If one labels the two protons A&B then one has (1) A and B both in parallel spin states, (2) A & B both in anti-parallel spin states, (3) A parallel and B anti-parallel, and (4) A anti-parallel and B parallel. The arrangements (3) and (4) are equivalent. The magnetic effect of these arrangements is in some way transmitted to the methyl group protons so that these protons will experience one of three effective fields according to the instantaneous spin arrangements of methylene group. Thus for a collection of ethanol molecules there will be three equally spaced transition energies for the methyl protons. Since the probability of existence of each of four spin arrangements are, to a higher order of approximation, equal and taking into account the fact that (3) and (4) are equivalent, it follows that the intensities of the three transitions will be 1:2:1. These results are illustrated schematically in Fig. 2.13. Similarly one finds that the spins of methyl group can be arranged in eight ways of which there are two sets of three equivalent arrangements (Fig.2.14) thus accounting for the observed structure of the methylene multiplet. In this example, the spacing of adjacent lines in the multiplet is a direct measure of the spin-spin coupling of the protons of the methylene group with those of the methyl group, and is known as spin-spin coupling constant J^{80}.

Splitting arising from spin-
spin coupling with the protons
of the methylene group.
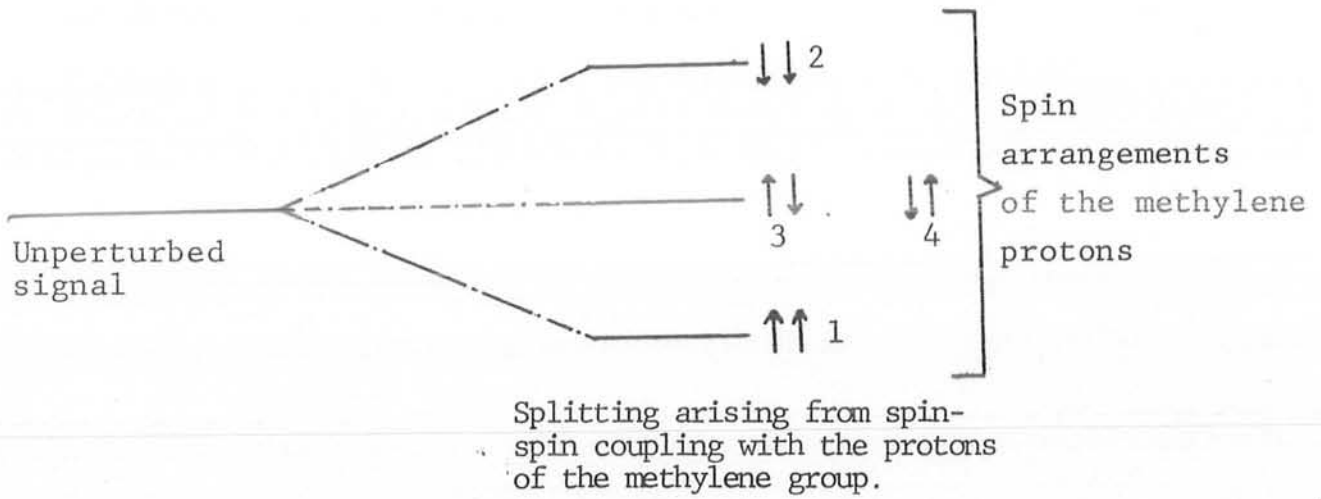
Fig. 2.13: The splitting of the signal from the methyl protons in
ethanol by spin-spin interaction with the protons of
methylene group.

Splitting arising from spin-spin
coupling with the protons of the
methyl group.
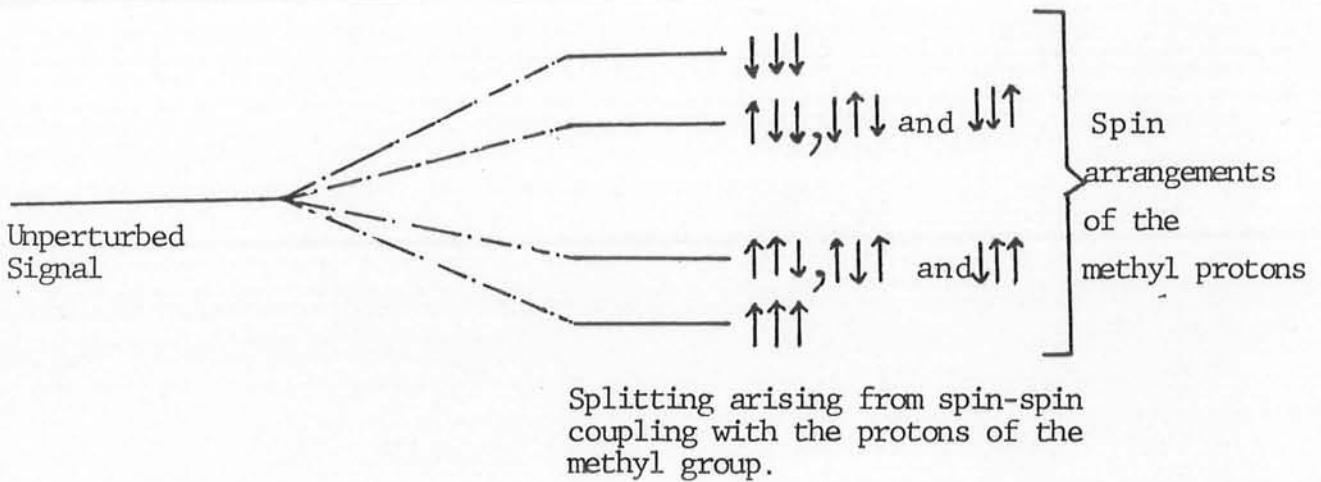
Fig. 2.14: The splitting of the signal from the methyl group protons
in ethanol by spin-spin interaction with the protons of the
methyl group.

d) SOLVENT EFFECT

Since all NMR measurements are made in the liquid phase, the position of a nuclear resonance line of a particular molecule in a liquid is affected by the surrounding molecules. In solutions the position of the resonance signal is often found to be concentration dependent. By extrapolation to infinite dilution, the effect of neighbouring solvent molecules can be observed separately. In general two different effects can be distinguished.

1. Shifts due to difference in the bulk diamagnetic susceptibility of the solute and solvent.
2. Shifts arising from intermolecular interaction between solute molecules or between solute and solvent molecules.

Theoretically definable effect arising from the solvent medium such as association between solvent and solute molecules, hydrogen bond between solvent and solute, such effects are particularly important in proton magnetic resonance, where intermolecular shielding is small.

The shielding contribution (σ_S) of the solvent to a proton in a solute molecule was accounted by Buckingham et al[98] in terms of five separate effects has been given by eq. 2.27.

$$\sigma_S = \sigma_B' + \sigma_W' + \sigma_a' + \sigma_E' + \sigma_c' \qquad (2.27)$$

Where the first four terms on the right side of the equation are associated respectively, with the effects of bulk magnetic susceptibility, van der Waals interactions, diamagnetic anisotropy

of solvent, and electrical polarization and polarizibility of
solvent, the fifth term includes weak interactions such as charge
transfer and hydrogen bonding, which lead to the some form of
complex in which the solute and solvent molecules are specifically
oriented with respect to each other.

In complex molecules it is often found that solvent effects
are selective. It has been observed that the chemical shifts of
different methyl groups in a steroi d[99] respond quite differently
to change of solvent. Systematic studies of variation in chemical
shifts of protons in well known location in large molecules have
shown considerable regularity in solvent effects.[100]

In general, the solute-solvent complex is best thought of as
a transitory species that biases the otherwise random distribution
of solvent molecules around the solute, rather than a distinct
separate species.

The fourth factor σ'_E arises from the effect of an electric
field on the nuclear shielding. Buckingham et al[98] has shown that
when a polar molecule or molecule containing polar group is dissolved
in a dielectric medium, it induces a "reaction field" the effect
of which is usually to reduce the shielding around the proton in
the solute which affects the chemical shift values of the shielded
proton of solute.

e) TIME-DEPENDENT PHENOMENA

Molecules often exist in two (or more) co-existing states or
subspecies which are in rapid equilibrium with each other.These may

be different conformations[101-107], different ionized forms, different positions of protonation[108], or complex forms. In the u.v and I.R. of such a molecule, one may expect to see the absorption peaks corresponding to both states. At the high frequency associated with the optical spectra (10^{13} -10^{15} sec^{-1}) one may expect the broadening of the absorption peaks if the life time of each form is very small, 10^{-14} -10^{-15} sec., or less. But broadening cannot be appreciable compared to the resolving power of optical spectrometer if the life time of the two forms is not small as mentioned above. However in nmr spectroscopy the observing frequency is one millionth as great; spectral lines may be only one cycle per second in width and those corresponding to interchanging subspecies may be only a few cycles/ second apart; very marked broadening, sufficient to merge the lines for each subspecies, may occur even when life times are as long as 10^{-1} to 10^{-3} sec. If their life times are much shorter than this, the two forms will give a single narrow peak and be entirely indistinguishable. These life-times, say 10^{-1} to 10^{-5} sec, correspond to a range of reaction and isomerization that is of great importance in chemistry.

One of the most commonly encountered reactions which may be fast on n.m.r time scale is intermolecular exchange of labile protons between groups such as -OH, -NH and -SH and kinetic n.m.r studies of these and related have been reviewed[109-112] by many authors.

The average spectrum corresponding to rapid exchange is generally encountered with high concentrations, with some polar solvents and in the presence of traces of acidic or basic catalysts, such as mineral acids. Becker and coworkers[113] studied the exchange

effects on the proton n.m.r. spectra of 1,3-dimethyl cytosin

hydrochloride (VI) and hydroiodide in SO_2 and at different

temperatures.
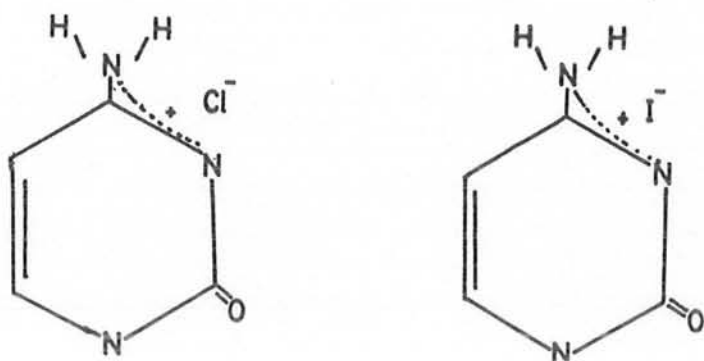
VI

The two $-NH_2$ protons are in different environments, thus

different chemical shift values were observed in the n.m.r. spectrum.

Further they observed that the values of the two NH_2 protons are

smaller in hydroiodide than in the hydrochloride showing that the

presence of different cations can exchange the environment and

hence change the chemical shift and δ values.

Suppose a given nucleus can exchange between two sites, A and

B, and that in these sites it has resonance frequencies ν_A and ν_B

respectively. If the life time at A and B are τ_A and τ_B seconds, the life time of the system is defined as $\tau = \tau_A \tau_B / (\tau_A + \tau_B)$. If one considers a special case in which the nucleus has equal probability of being in the two sites, in this case $\tau = \tau_A/2 = \tau_B/2$, one also assumes that the transverse relaxation times (T_2) for the nucleus in the two sites are the same and are large compared with $1/(\gamma_B - \gamma_B)$.

So the conditions in qualitative terms for which the nucleus gives rise to a single line at $(\gamma_A + \gamma_B)/2$ and a pair of lines at γ_A and γ_B, the former situation arises if $\tau \ll 1/(\gamma_B - \gamma_A)$ and similarly two lines at γ_A and γ_B are observed if $\tau \gg 1/(\gamma_B - \gamma_A)$, it being assumed that $\gamma_B > \gamma_A$. Of particular interest is the situation in which τ and $1/(\gamma_B - \gamma_A)$ are of the same order. The behaviour of the system under this condition was first deduced theoretically by Gutowsky, McCall and Slichter[114], and more simply, by McConnell[115]. The predicted behaviour is presented in Fig. 2.15. One notes that as the life time decreases through the critical range the two lines broaden and move together until they coalesce to a broad singlet. As the life-time decreases still further the broad singlet sharpens and eventually reaches a line width which is determined only by T_2. The life time corresponding to coalescence is given by equation 2.28

$$\tau = \sqrt{2} / 2\pi (\gamma_B - \gamma_A) \qquad (2.28)$$

Since the line shapes can be computed for any value of τ and $(\gamma_B - \gamma_A)$ and since $(\gamma_B - \gamma_A)$ can be determined directly from the spectrum observed under conditions of slow exchange, it follows that this phenomenon provides a method of determining the

$$\tau \ll \frac{1}{2\pi(\nu_B - \nu_A)}$$

$$\tau \fallingdotseq \frac{2}{\sqrt{2}\,\pi(\nu_B - \nu_A)}$$

$$\tau \gg \frac{1}{2\pi(\nu_B - \nu_A)}$$
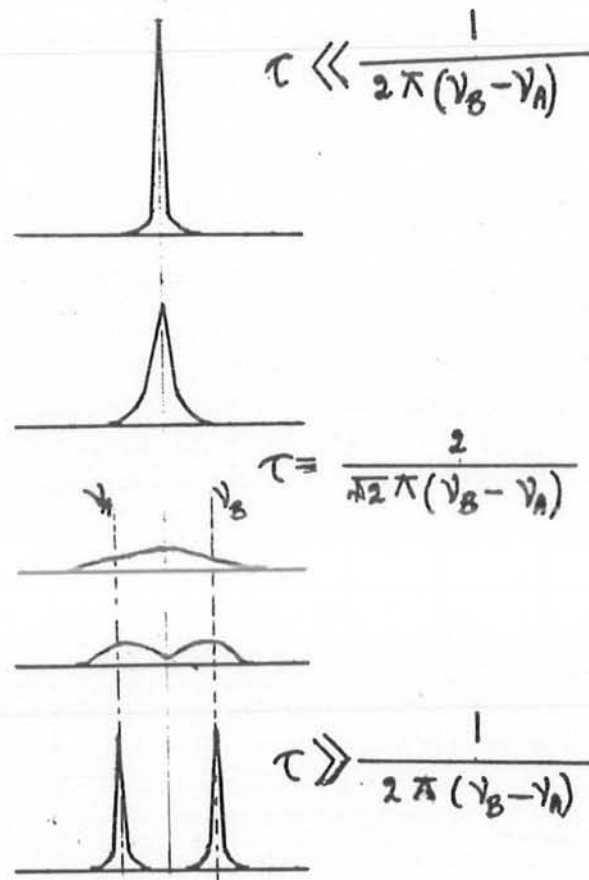
Fig. 2.15: Theoretical line shapes for nuclei exchanging
             between two equally populated sites.

rates of quite fast reactions. Since ($\nu_B - \nu_A$) is generally in the range 10-1000 Hz, life-times of the order of 10^{-2} -10^{-4} sec can be investigated. For the particular case with which we are dealing and with $T_2 \gg 1/(\nu_B - \nu_A)$, four approximate methods are available for extracting τ from spectra corresponding to partial coalescence. The first due to Gutowsky and Holm[116] takes advantage of a simple relation between the separation, $\Delta\nu$obs, of the two maxima in partially coalesced spectra equation 2.29

$$\frac{\Delta\nu_{obs}}{(\nu_B - \nu_A)} = \left[1 - \frac{1}{2\pi^2\tau^2[\nu_B - \nu_A]^2}\right]^{1/2} \qquad 2.29$$

The second method[117] relates life-time to the ratio of the peak maxima to the minimum between them equation 2.30

$$\tau = \pm\frac{\left[2r \pm 2(r^2-r)^{1/2}\right]^{1/2}}{2\pi(\nu_B - \nu_A)} \qquad 2.30$$

Where r = Max. intensity/Min.intensity. In the region where the two peaks are broadened but do not overlap equation 2.31[118,119] which is independent of peak separation can be applied.

$$\frac{1}{\tau} = 2\left[\frac{1}{T_2^{exch}} - \frac{1}{T_2^o}\right] \qquad 2.31$$

Where T_2^{exch} and T_2^o are found by multiplying π by the line widths found for exchange and in the absence of exchange respectively.

Line width measurements of coalesced spectra can also yield life-times through equation 2.32[119,120].

$$\frac{1}{\tau} = \pi^2 \left(\nu_B - \nu_A \right)^2 \left[\frac{1}{T_2^{exch}} - \frac{1}{T_2^o} \right] \qquad 2.32$$

It is stressed that the last four equations do not hold in the region of coalescence, i.e. when $\tau = \sqrt{2}/2\pi \ (\nu_B - \nu_A)$. In this region, and when $1/T_2$ and $(\nu_B - \nu_A)$ are of similar magnitude, the life-time can be determined by comparison with theoretically computed spectra[121].

EXPERIMENTAL

PART - II

THEORY OF ELECTROLYTIC CONDUCTANCE

The resistance of an electrolytic conductor to current passage is governed by the Ohms' Law to such conductors. However, instead of resistance, it is customary to speak of conductance, which is merely the reciprocal of electrical resistance. The resistance of any conductor is proportional directly to its length and inversely to its cross-sectional area, namely,

$$R = \rho \times \ell / A \qquad (2.33)$$

where R is resistance in Ohms, ℓ is the length in Cm, A is the area in square Cm and ρ the specific resistivity. The value of ρ depends on and is characteristic of the nature of the conductor. From eq. 2.33 the expression for the corresponding conductance L follows as

$$L = 1/R = 1/\rho \times (A/\ell)$$
$$L = L_S \ (A/\ell) \qquad (2.34)$$

where $L_S = 1/\rho$ is the specific conductance of the conductor. This quantity is defined as the conductance of one cm cube of material and is expressed in reciprocal Ohms or Mhos per Centimeter.

Although the specific conductance is a property of conducting medium, in dealing with solution of electrolytes a quantity of greater significance is the equivalent conductance, Λ . The equivalent conductance of an electrolyte is defined as the conduc-

tance of a volume of solution containing one equivalent weight of dissolved substance when placed between two parallel electrodes 1 cm apart and large enough to contain between them all of the solution. Λ is never determined directly but it is calculated from the specific conductance. If C is the concentration of a solution in gram equivalents per liter, then the concentration per cubic centimeter is C/1000, and the volume containing one equivalent of the solute is therefore, 1000/C cc. Since L_S is the conductance of a centimeter cube of the solution, the conductance of 1000/C cc, and hence Λ , will be

$$\Lambda = \frac{1000\ L_S}{C} \qquad (2.34)$$

Eq. 2.34 is the defining expression for the equivalent conductance, where C is the number of gram equivalents of solute per liter of solution.

PRINCIPLE OF CONDUCTIVITY MEASUREMENT

The problem of obtaining Λ values requires the determination of specific conductance of electrolyte, and this in turn, to the resistance of solution and use of eq. 2.34. For measuring resistance of the electrolytic solutions the wheatstone bridge method[125] is employed, schematic diagram of which is shown in Fig. 2.16; R_X, the unknown resistance whose value is to be determined, is placed in one arm of the bridge, a variable known resistance R_s in the other. AB is a uniform slide wire across which moves a contact point 'C'. To balance the bridge the contact is moved alongwith this resistance until no current from the battery 'E' flows through the galvanometer 'G'. When this condition is reached, R_s, the resistance from A to
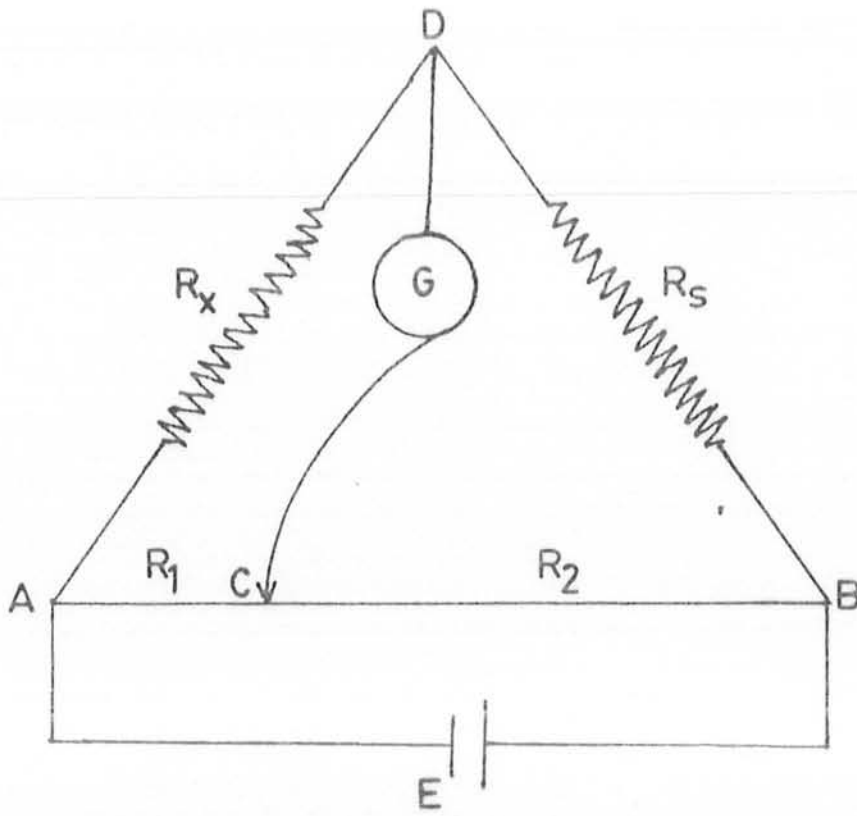
Fig. 2.16: Wheatstone Bridge

to C,R_1, and that from C to B, R_2, are noted. R_x is then calculated
from these resistances according to the following considerations.
When the current 'I' from the battery reaches point 'B' it divides
into two parallel paths and into two currents, I_1 and I_2. These
currents lead to potential drops across the resistances they traverse
The purpose of balancing the bridge is to find a point along AB,
namely C, such that the potential drops from B to C is equal to that
from B to D. When this point is found, D and C are at the same
potential and no current flows through the branch containing the
galvanometer. The condition for the bridge balance is, then,

$$R_s \; I_1 \; = \; R_2 \; I_2 \qquad (2.35)$$

But, when these 'IR' drops are equal, those from D to A and from
C to A must also be equal. Hence

$$R_x \; I_1 \; = \; R_1 \; I_2 \qquad (2.36)$$

Hence

$$R_x \; / \; R_s \; = \; R_1 \; / \; R_2$$

$$R_x \; = \; R_s \; (R_1 \; / \; R_2) \qquad (2.37)$$

Although the principle of Wheatstone bridge[124] just given
remains the same, several modifications in the techniques have been
made for the measurement of resistances of the electrolytic solu-
tions by this method. In the first place direct current is not used,
as it causes electrolysis and concentration changes at the electrodes.
To avoid these, alternating current is employed, usually at a
frequency of 500-2000 cycles per second, and supplied by either a

vibrating tuning fork or a vacuum tube oscillator. Since a current of this frequency is within the range of human ear the galvanometer can be replaced by a set of earphones. Passage of current through these produces a buzzing sound which decreases in intensity as balance is approached and is minimum when the balance point is reached. Theoretically the sound should be zero at balance, but due to capacitance introduced by the cells, such an ideal state is not attained. However, by placing a variable condenser across the standard resistance, it is possible to sharpen the balancing by adjusting the condenser to the capacitance of the cell, thus neutralizing the two to a degree. An alternate detecting device employed in some of instruments is the Cathoderay oscilloscope. By its use a balance of both resistance and capacitance can be obtained.

VARIATION OF CONDUCTIVITY WITH DILUTION

Although the actual conductivity of an electrolyte becomes smaller as the solution is progressively diluted, the molecular and equivalent conductivities increases[123] with dilution until a limiting value is reached. The dilution effect on equivalent conductance can be understood from Fig. 2.17., which is a plot of Λ vs. $\sqrt{c}$. It is apparent from Fig. 2.17., that equivalent conductance increases with the decrease in concentration. This limiting value of equivalent conductance is known as equivalent conductance at zero concentration and is represented by Λ_0 .

EQUIVALENT CONDUCTANCE AT INFINITE DILUTION

Kohlrausch[125] was the first to point out that when Λ for strong electrolytes is plotted against $\sqrt{c}$ the curve approaches
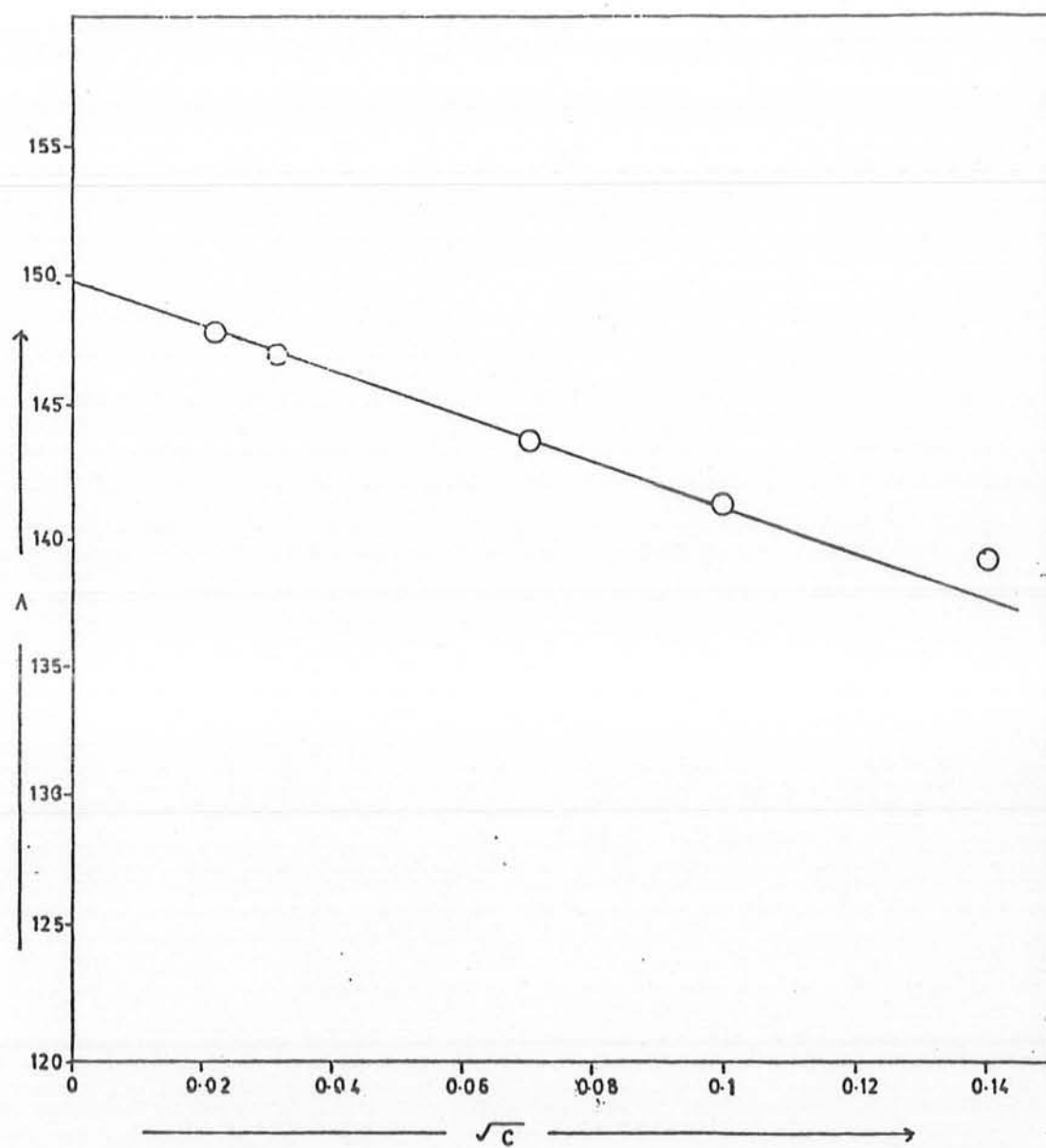
Fig. 2.17: Λ Vs. $\sqrt{c}$ plot of KCl in water at 25°C.

linearity in dilute solutions, that is, in dilute solutions

$$\Lambda = \Lambda_o - b\sqrt{c} \qquad (2.38)$$

where b is a constant. The validity of this finding may be seen from the plot of potassium chloride in figure 2.17. Consequently, to obtain Λ_o of such electrolytes the curve may be extrapolated to $\sqrt{c} = o$ and the intercept read, or the slope of the linear portion of the curve may be obtained from the plot, and Λ_o solved for from equation 2.38.

THE CONDUCTANCE RATIO/DEGREE OF IONIZATION (α)

The limiting value of Λ, at infinite dilution, or zero concentration, is represented by Λ_c or Λ_o respectively. The amount of current passing clearly depends upon the number of ions present in the solution, for they are the sole carriers of the current, and also upon their mobility, or the ease with which they get through the liquid. The two factors, then, upon which the conductivity of a solution will depend are (a) the number of ions and (b) their mobility. Arrhenius assumed that the latter did not vary with dilution, and so the only reason for the increased equivalent conductance must be in the formation of more ions. At infinite dilution, he reasonably supposed, that the electrolyte was completely dissociated. Since the current flowing is proportional to the number of ions present, the amount of dissociation at any dilution, v, or concentration, C, would be given by

$$\alpha = \frac{\Lambda_v}{\Lambda_c} \qquad \text{or} \qquad \alpha = \frac{\Lambda_c}{\Lambda_o} \qquad (2.39)$$

Arrhenius supposed that α measured the degree of ionic dissociation of the electrolyte, so that, for instance potassium chloride in one normal solution would be 76% ionized. For strong electrolytes however this is not true; the dissociation is complete, or nearly so, and is much greater than the value of α suggests. Therefore one prefer the non-committal phrase conductance ratio for $\alpha = \dfrac{\Lambda v}{\Lambda \alpha}$

EFFECT OF DIELECTRIC CONSTANT ON DISSOCIATION

Walden showed that a dissolved salt gives a definite value for the ratio Λ/Λ_0 at a dilution which is inversely proportional to the cube of dielectric constant of the solvent. Thus, if one chooses $\alpha = (\dfrac{\Lambda}{\Lambda_0}) = 0.5$, one will find the dilution required to give this value of α being inversely proportional to the cube of the dielectric constant. This relationship is only approximately true, and reaches this degree of accuracy only for strong electrolyte

It is found that only in liquids of fairly high dielectric constant, dissociation can take place. The dielectric constant of a substance is dependent upon its dipole moment, that is, upon the degree of assymmetry[122] of the arrangements of charges in the mole-cule. It is not surprising therefore to find that only those liquids with high dielectric constants, that is, very unsymmetrical fields, can bring about ionization.

The actual mechanism of ionization in solution, where the solid salt is not completely ionized before dissociation, is not understood. Some hold the view that a compound formation with the solvent is a necessary preliminary to further breakdown into ions.

The behaviour of salts in non-aqueous solvents is usually considerably different from that in water. Ionization in any solvent is governed largely by Fajan's rule. This states that ionization will be promoted by the presence of a small anion and a large cation.

Further, in solvents of dielectic constant less than 25, the dependence of the equivalent conductance on the concentration becomes complex. Plots of log Λ vs. log C, instead of being linear or slightly curved as they are in solvents of higher dielectric constant, contain minima which appear at lower concentrations the lower the dielectric constant. To explain these minima and the curves in general it has been suggested that in these solvents ions exhibit a tendency to associate into complexes[125] such as A^+B^-, $A^+B^-A^+$, and $B^-A^+B^-$, which decrease the number of ions available to carry current, and hence the conductance. These theories of association into complexes seem to account fairly well for the observed phenomena.

EFFECT OF TEMPERATURE ON CONDUCTANCE

The conductance of all electrolytes increases with temperature. The variation of Λo with temperature can be represented by the equation[125]

$$\Lambda_{o(t)} = \Lambda o(25^o c) \left[1 + \beta (t - 25) \right] \qquad (2.40)$$

where $\Lambda o(t)$ is the limiting equivalent conductance at $t^o c$, $\Lambda o(25^o)$ that at $25^o c$, and β a constant. For salts β is usually 0.022 to 0.025, for acids 0.016 to 0.019. Similar behaviour is exhibited

by the equivalent conductances of strong electrolytes in finite
concentration. However with weak electrolytes the variation of
Λ with temperature is not so regular, for in these not only do
the velocities of the ions and the interionic forces change, but
also the degree of dissociation.

OSTWALDS DILUTION LAW

The law of mass action finds a fruitful field of application
to ionic equilibrium. This application is especially instructive
because ions deviate more markedly from ideal behaviour than do the
neutral molecules, with the result that the activity corrections
are correspondingly more important.

Consider a simple type of ionic equilibrium involving the
dissociation of a neutral molecule (or ion pair) AB.

$$AB \; \rightleftharpoons \; A^+ + B^- \qquad (2.41)$$
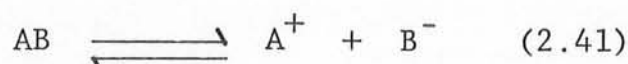
The condition of equilibrium is that the chemical potential
μ_{AB} of the undissociated molecule shall equal the sum of the chemical
potentials $\mu_A{}^+$ and $\mu_B{}^-$ of the ions. In solution sufficiently dilute
to justify the use of van't Hoff's Law one may express μ for each
species of the solute as $\mu^O + RT \ln C$, where 'C' is its equilibrium
concentration, and μ^O its chemical potential in a solution of unit
concentration. It follows that

$$\frac{(C_A{}^+) \, (C_B{}^-)}{(C_{AB})} = e^{-\mu/RT} = K \qquad (2.42)$$

where the constant K, though a function of temperature and pressure, is independent of the concentration, and $\Delta \mu^o$ is given by

$$\Delta \mu^o = \mu^o_{A^+} + \mu^o_{B^-} - \mu^o_{AB} \qquad (2.43)$$

Let the salt AB be dissociated to a fraction α, in a solution of concentration 'C'. Then the concentration of AB, A^+, and B^- is given as

$$[AB] = C(1 - \alpha), \text{ and } [A^+] = [B^-] = C\alpha \qquad (2.44)$$

Substituting the values of [AB] $[A^+]$ and $[B^-]$ from equation 2.44 in equation 2.42 one gets

$$K = \frac{\alpha^2 C}{(1-\alpha)} \qquad (2.45)$$

But according to Arrhenius (Eq. 2.39)

$$\alpha = \Lambda_c / \Lambda_o$$

where Λ_c = equivalent conductance when the concentration of solute = 'C' and Λ_o = equivalent conductance at infinite dilution.

Hence

$$K_c = \frac{C \Lambda^2_o}{\Lambda_o(\Lambda_o - \Lambda_c)} \qquad (2.46)$$

The above equation is known as Ostwald's dilution law.

To apply this equation one rearranges it as suggested by Kraus (1922) into the form

$$C \Lambda_c = - K_c \Lambda_o + \frac{K \Lambda_o^2}{\Lambda_c} \qquad (2.47)$$

so that, by plotting $C \Lambda_c$ as a function of $1/\Lambda_c$, one obtains a straight line, with an y-intercept of $-K \Lambda_o$ and a gradient of $K \Lambda_o^2$. So in this way one gets two equations with two unknowns, k and Λ_o which are evaluated by solving them simultaneously. As an example, the data of McInnes and Shedlovsky (1932) on acetic acid in water at 298.16 $\overset{o}{K}$ have been analysed in this way (Fig.2.18). One finds $K \Lambda_o = 7.00 \times 10^{-3}$ and $K \Lambda_o^2 = 2.74$, which follows that $\Lambda o = 391.6$ and that $K = 1.787 \times 10^{-5}$ equivalents per liter. Both values have been confirmed by independent experiments.
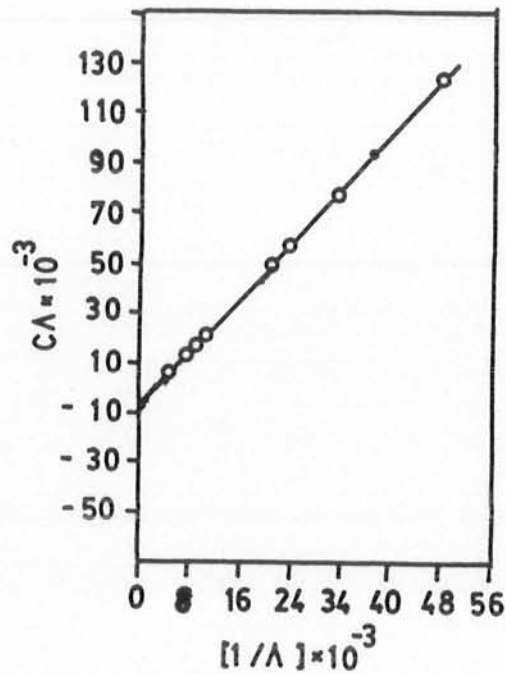
Fig. 2.18: Determination of the ionization constant of acetic acid in aqueous solution at 25°C from conductivity measurements.

EXPERIMENTAL

During the present investigation, two experimental techniques N.M.R. spectroscopy and conductance measurements were employed.

N.M.R. spectra of PyI and $PyClO_4$ were recorded under various conditions (e.g. change in solvent etc.), whereas conductance studies were carried out in different solvents and at different temperatures. These observations were obtained to gain information regarding charge transfer phenomena, ion pairing and its dissociation constants etc.

CONDUCTIVITY MEASUREMENTS

Conductance measurements of PyI in different solvents and at different temperatures were carried out. The conductance measurements were carried out under inert atmosphere and an assembly was self-designed in order to produce inert atmosphere. Nitrogen gas was used for inert atmosphere production and was purified after passing through the traps containing pyrogallol and then through a trap containing the   solvent under study.

A) INSTRUMENTATION

For conductivity measurements, conductivity bridge set Model MC1 MKV, Electronic Instruments Limited, Chertsey, Surrey, England was used. The instrument is designed for quick and accurate conductivity measurements to be made over a wide measuring range having the following specifications:

Fig. 3.1:   Composition MCI MKV conductivity bridge.
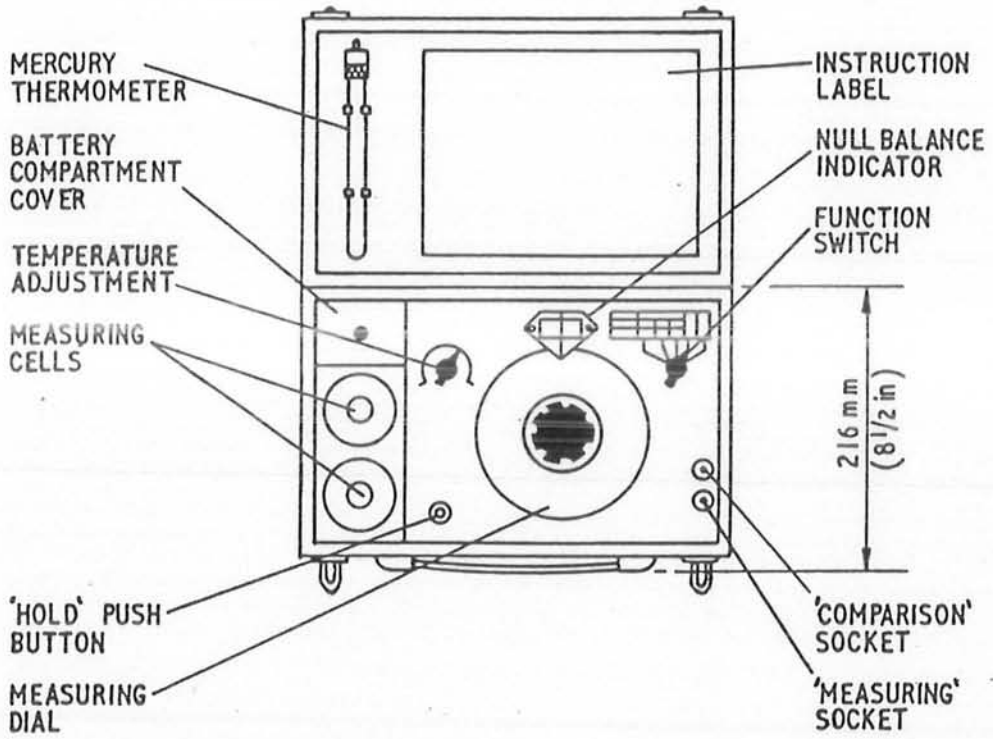
Fig. 3.2: Panel diagram MCI MKV.

a) <u>Measuring Ranges</u>:

$0.01 - 100 \mu S / cm$
(micromhos/cm)
$1-10^4 \mu S/cm$
$10-10^5 \mu S/cm$

In three switched ranges.
Using a Cell with constant
$K = 0.1$

$0.1 - 10^3 \mu s/cm$

$10 - 10^5 \mu s/cm$

$100 - 10^6 \mu S/cm$

In three switched ranges
using a cell with constant
$K = 1.0$

b) <u>Accuracy</u>:

$\pm$ 1% of reading at centre scale
(1.0 on dial)

$\pm$ 3% of reading at normal scale ends.
(0.1 and 10 on dial)

$\pm$ 10% of reading outside normal scale.
(0.01 - 0.1 and 10.0 - 100
of dial range)

c) <u>Power Supply</u>:

9 V PP 7 battery, or equivalent. Battery life
6-12 months; dependent on climate and usage.

d) <u>Preliminary Procedure</u>:

Before making the measurements the measuring cells
were cleaned. Also a brief test procedure was carried
out on the instrument to check calibration and battery
condition.

i) <u>Cleaning the Cells</u>:

The plastic bung was removed from the bottom of
the beaker cell; using the bottle brush, the cell's

bore was scrubbed with a 50% water/detergent solution and was rinse thoroughly with distilled water. Surplus water was shake out and the cell was examined to ensure that the electrodes and interior surfaces were evenly wetted (i.e. there were no grease deposits); if they were not, the cleaning procedure was repeated and plastic bung was replaced.

ii) Calibration of the Instrument etc:

The function switch was set to the test position and the HOLD ON push button was depressed. The large calibration dial was rotated until the null balance indicator pointer coincided with the cursor line above it, the dial reading opposite the cursor was at 1.0 mark.

The battery condition was checked by setting the function switch to any one of the three measuring ranges, and HOLD ON push button was depressed. The null balance indicator showed a full scale deflection showing that the battery was in working condition.

B) MEASUREMENT

The instrument used was provided with two beaker type cells of cell constant 0.1 K and 1.0 K. For conductivity measurements of a sample the cell with a cell constant 0.1 K was used, since this cell had a greater precision through out the measuring range over the cell of cell constant 1.0 K as mentioned by the manufacturer of the instrument.

Movable inner tube
connected to N$_2$ gas
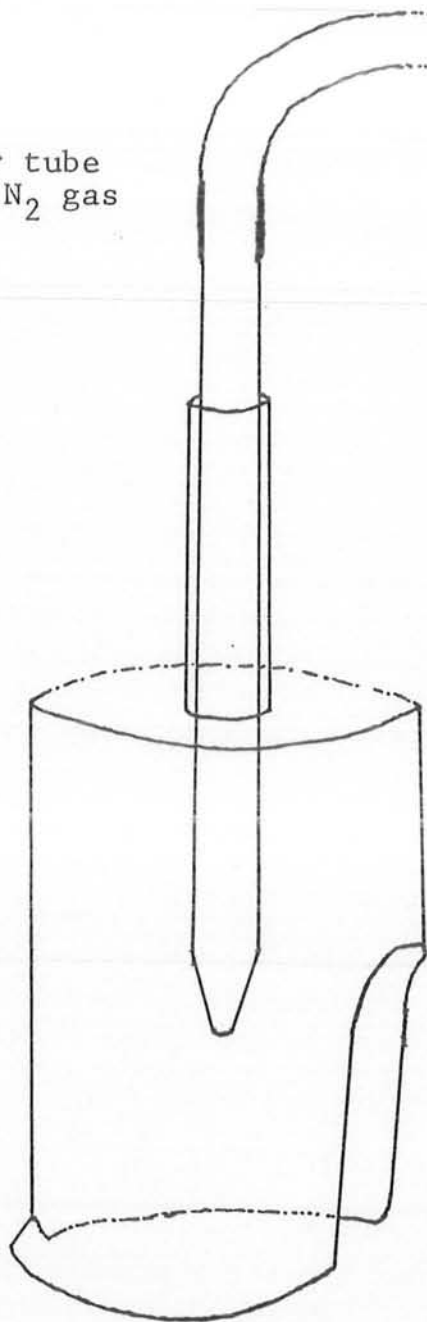
Fig.3.3: Assembly used for N$_2$ atmosphere during conductance
measurements

The measuring cell was filled with the sample; the connecting cables were plugged into the measuring socket. The temperature of the sample was measured using the thermometer provided and the temperature knob was adjusted to read the value as measured by the thermometer. The thermometer was then removed from the cell containing the sample. The housing made up of glass (see fig.3.3) was placed on the cell, which provided a continuous flow of nitrogen gas from the sample and hence the nitrogen atmosphere was generated. The function switch was adjusted to the anticipated range of measurement, then HOLD ON button was depressed and graduated dial was slowly rotated until the edgewise balance indicator showed centre scale precisely. The dial setting at which this occured was read off and multiplied by the range factor for the appropriate function switch position and cell constant. Temperature of the sample solution was also noted after conductance measurement; this was done in order to observe the temperature fluctuations, if any. From the value of specific conductances for samples of solute thus obtained, concentration ranging from 2×10^{-2}M to 2×10^{-4}M the values of equivalent conductance (Λ_c), ion pair dissociation constant K, and equivalent conductance at infinite dilution (Λ_o), were determined as described in chapter two.

N M R SPECTROSCOPY

i) Instrument

NMR studies were carried out on NMR spectrometer Model JNM-PM-60 JEOL CO., JAPAN. This spectrometer is specially designed
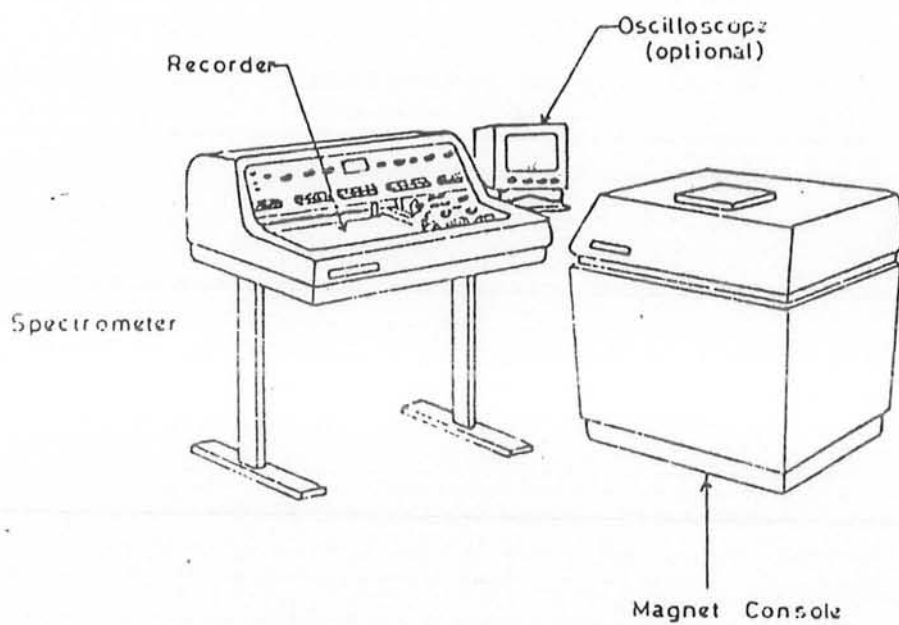
COMPOSITION   JNM-PMX- 60

Fig. 3.4:

BLOCK DIAGRAM JNM - PMX-60

Fig.3.6:

POWER

POWER

AMPLITUDE

POWER

PHASE

SIGNAL INTENSITY

INTEGRATOR

FIELD COARSE

FIELD ZERO

Power Phase Coarse Amplitude Reset Balance Hold (KHz) Field Zero

Hi LEVEL FILTER (Hz) MODE Auto SWEEP WIDTH(Hz) OFFSET(Hz)

Lock SD

STAT

Hi LEVEL FILTER MODE SWEEP WIDTH OFFSET
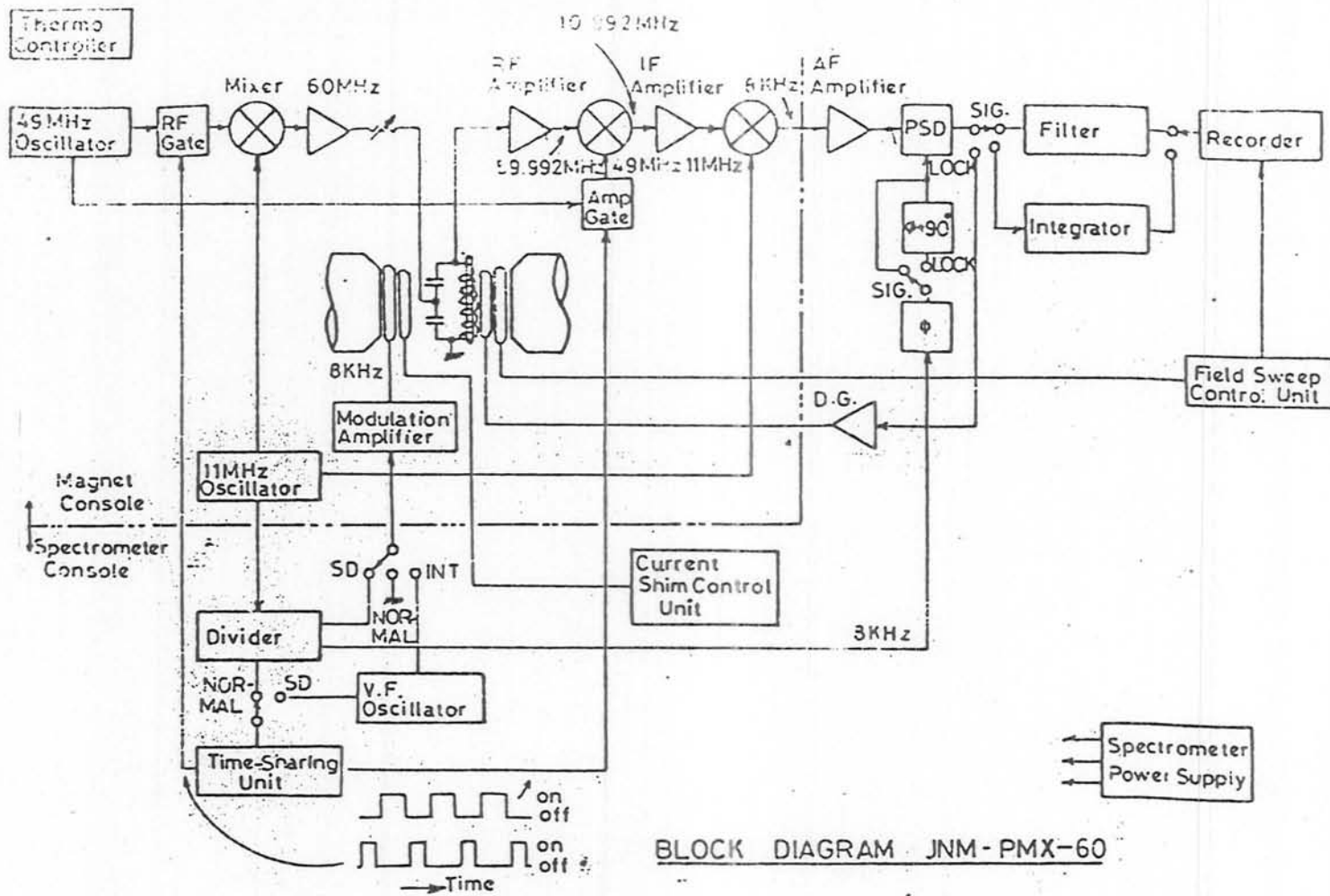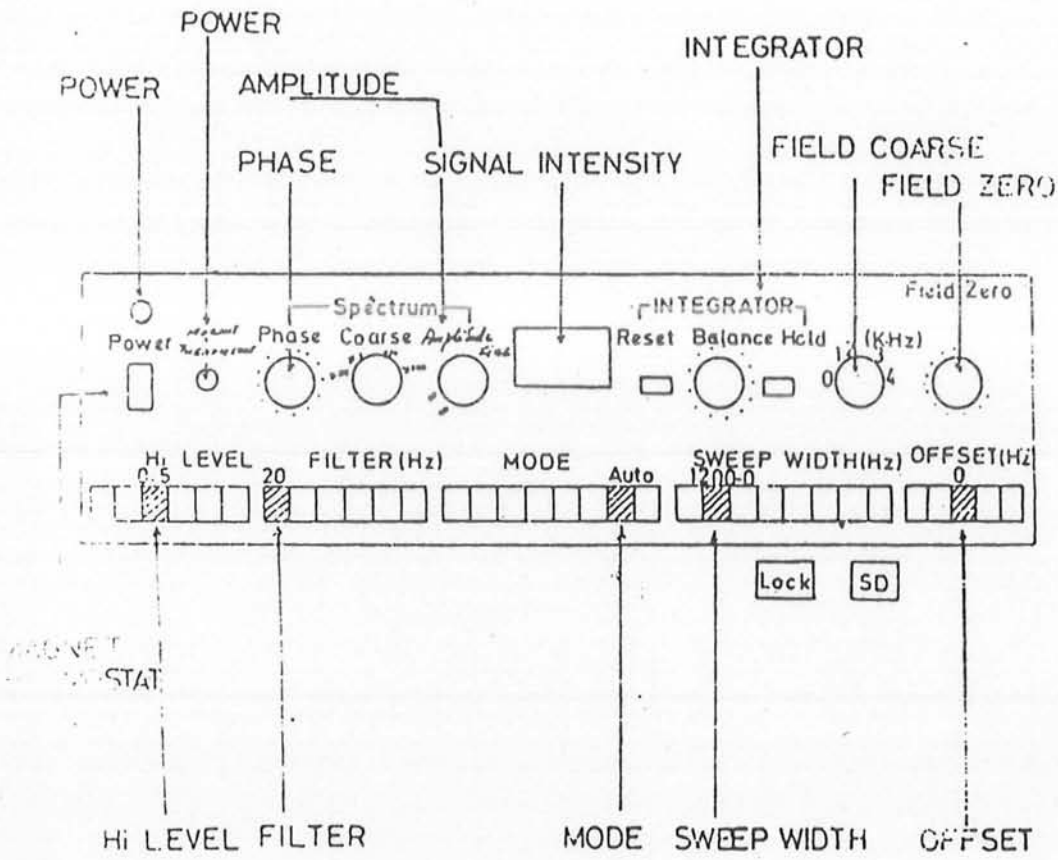
PANEL DIAGRAM JNM - PMX - 60

Fig. 3.5:

for measurements of hydrogen nuclei resonance, that is for proton
magnetic resonance (PMR) studies. It has the following specifications

STANDARD FREQUENCY	=	60 MHz
FIELD INTENSITY	=	14092 Gauss
RESOLUTION	=	0.4 Hz
SAMPLE TUBE SIZE	=	5.mm(Outer diameter)
SAMPLE VOLUME	=	0.3 ml
RECORDER	=	Plane XY

ii) Procedure

For the scanning of PMR spectra first the solutions of PyI
(Concentration ranging from 0.05M to 0.4M) and $PyClO_4$ (concentration
ranging from 0.1M to 0.2M) in the required solvent were prepared.
The sample tubes were properly washed and dried. For recording
the spectra the sample tubes were filled approximately one third
of their capacity and encapped wiped with the tissue paper and were
completely cleaned from the outer sides (since some attached
impurities may generate some undesired signals). The samples were
preheated to a temperature/as same that of sample holder compartment.
This preheating was done by placing the sample tubes in the sample
holding compartment (which is a part of magnet console where the
sample is placed for scanning the NMR spectra) for approximately
five minutes as recommended by the manufacturer of the instrument.
After preheating the sample, tube was placed in sample holder and
the PMR spectra was recorded. This was repeated twice.

CHEMICALS

1-Ethyl-4-Carbomethoxy Pyridinium iodide (PyI)

The impure sample of 1-ethyl-4-carbomethoxy pyridinium iodide was available in the laboratory. It was purified by recrystallizing thrice. The recrystallization[126] of the sample was done by dissolving the given impure sample in hot acetone, until a saturated solution was obtained at elevated temperature, the solution was filtered off while hot. The solution in a sealed earlenmeyer flask, was kept in the freezer compartment of refrigerator, the solid that separated out was orange-coloured crystalline pure 1-ethyl-4-carbomethoxy pyridinium iodide. This orange crystalline powder was filtered off and was dried in the vacuum desiccator for fortyeight hours. The melting point was found $109^{\circ}C$ (literature $110^{\circ}C$). The salt is hygroscopic, its purification is necessary for the accurate and precise results of the experiments with particular reference to Z-values measurements.

1-Ethyl-4-Carbomethoxy Pyridinium Perchlorate (PyClO$_4$):

1-ethyl-4-carbomethoxy pyridinium perchlorate was prepared from PyI and AgClO$_4$ using the following procedure[126]:

Equimolar solutions of AgClO$_4$ and PyI were mixed in methanol. The resulting AgI was digested for one hour and AgI was filtered off. The filtrate was evaporated at room temperature and reduced pressure.

Four crystallizations from hot methanol gave white crystals. Further purification of the above white crystals of 1-ethyl-4-carbomethoxy pyridinium perchlorate was carried out by washing it with anhydrous ether and dried in vacuum desiccator at room temperature for two days at 1 m.m. Hg pressure.

SILVER PERCHLORATE (AgClO₄)

Silver perchlorate of BDH chemicals Laboratory reagent was used directly for the preparation of 1-ethyl-4-carbomethoxy pyridinium perchlorate from PyI and AgClO₄.

TETRA BUTYL AMMONIUM IODIDE: (TBAI)

Tetra butyl ammonium iodide of BDH chemicals Ltd., was used directly.

SOLVENTS:

N,N-Dimethyl Formamide:(DMF)

Reagent grade N,N-Dimethyl Formamide of Merck Ltd., of Fischer reagent grade was used. For purification[127] particularly for the removal of water, drying was carried out by molecular sieves type 4-A (heated at 250°C for 4-5 hours and cooled in vacuum desiccator) and finally vacuum distilled.

Acetone:

Acetone of Merck reagent grade was used and was further purified[127] according to the following method. Acetone was refluxed

with small portion of $KMnO_4$, and small portion of $KMnO_4$ were added
to acetone at reflux until the violet colour persists, followed
by drying with type 4-A Linde molecular sieve, and distilled.

Acetonitrile

Acetonitrile of Fischer reagent grade was used. It was dried[127]
on molecular sieve type 4-A. After drying it was stirred with CaH_2
until no further hydrogen was evolved. The acetonitrile was dis-
tilled after an hour's reflux with 0.5-1% (w/v) P_2O_5 in the dis-
tillation flask.

Isopropanol

Isopropanol used was of ZEELZE-HANNOVER (GERMAN) chemicals.
Isopropanol was dried with CaH_2 and then it was vacuum distilled.

Mathanol

Methanol of Merck reagent grade was used. Drying was carried
out with type 4-A Linde molecular sieve and distilled.

Chloroform: $(CHCl_3)$

Laboratory reagent Chloroform of BDH Chemicals was used
directly.

Formamide

Formamide of BDH reagent grade was directly used.

RESULTS
AND
DISCUSSION

RESULTS AND DISCUSSION

Some proton magnetic resonance and conductance studies on
1-ethyl-4-carbomethoxy pyridinium iodide were carried out. Proton
magnetic studies were performed under various conditions such
as changing the solvent, change of concentration of PyI in a parti-
cular solvent, and also by adding tetra alkyl ammonium salts. The
conductance studies on 1-ethyl-4-carbomethoxy pyridinium iodide
were carried out in different solvents to gain information about
ion-pairing.

The present investigations were carried out in order to study
the nature of ion-pairing and exchange reactions in presence of
salts under the conditions mentioned above, also to determine any
correlation between Z-values and chemical shifts and ion-pair
dissociation constant with the solvent polarity.

The proton magnetic resonance spectrum of 1-ethyl-4-carbomethoxy
pyridinium iodide(I)

(I)

$$COOCH_3 \quad (9)$$

$$(5) \quad (3) \quad I^-$$
$$(6) \quad N \quad (2)$$
$$CH_2 - CH_3$$
$$(7) \quad (8)$$
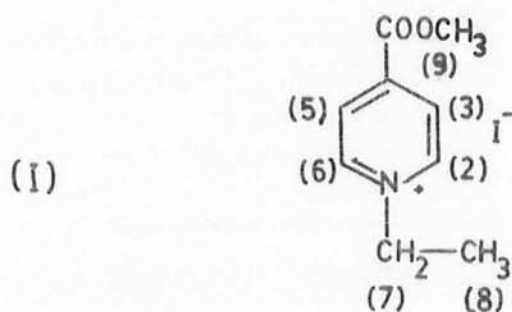
consist of two doublets for aromatic protons (2,6)and(3,5) between
δ = 8 to 10.00 ppm. , the quartet for CH_2(7) and triplet of

CH_3 (8), between (1.7 - 2.20 δ), with a singlet about δ = 4.0 - 5.5 ppm., which is labelled as due to CH_3 (9.) of carbomethoxy group. Some other peaks were also observed such as $CHCl_3$ signal. the resonance signal due to proton of chloroform appeared at 7.37 δ, when chloroform was used, a quartet, a triplet and a singlet were also observed, and they were labelled for CH_2, CH_3 and OH of ethanol, since a 2% V/V ethanol is always present in $CHCl_3$ acting as a stabilizer. Chloroform was used as a solvent in counter ion study and in the investigation if there exists any concentration dependence of PyI on its N.M.R. spectrum.

Proton magnetic studies on 1-ethyl-4-carbomethoxy pyridinium iodide were made to determine the solvent effect on chemical shift values. It has been observed that the line position of aromatic protons change in such a way that the difference between two doublets $\Delta\delta$, varies with the change of solvent in a manner that $\Delta\delta$ decrease with the increase of solvent polarity. That is, a correlation exists between $\Delta\delta$ and Z-value of the solvent. This value ($\Delta\delta$) was found to be highest, $\Delta\delta$ = 1.17 for chloroform (Z = 63.2); and decreases from dimethylformamide; $\Delta\delta$ = 1.01, (Z = 68.5); isopropanol; $\Delta\delta$ = 0.92, (Z = 76.3); ethanol, $\Delta\delta$ = 0.76 (Z = 79.6); formamide; $\Delta\delta$ = 0.62, (Z = 83.3). The lowest value for water $\Delta\delta$ = 0.57, (Z=94.6).

Previously (Kosower[34]) the Z-value for water had been obtained by extrapolating the Z-values measured for aceton-water, ethanol-water and methanol-water mixtures to zero organic component in a plot against Grunwald-Winstein y-value. This indirect procedure was adopted due to the limitation, since the largest charge transfer

band of PyI moves to such a shorter wavelength in highly polar solvents that it cannot be observed underneath the much stronger $\pi \longrightarrow \pi^*$ transition of pyridinium ion. Whereas the present experimental observable $\Delta\delta$ was found independent of such a limitation and $\Delta\delta$ values were obtained from the NMR spectrum of PyI in water. These $\Delta\delta$ values calculated from the spectra of PyI in different solvents could be related with the Kosower's Z-values of the respective solvents. The information about the relationship between Z-values of solvent and $\Delta\delta$ can thus be gained.

NMR investigations were also carried out on the solution of PyI and $PyClO_4$ in different ratios, 5:1, 1:2, 2:1 etc. The results of such studies are collected in table 3.

An interesting behaviour has been observed, that is instead of two separate spectra/each for PyI and $PyClO_4$, only the spectrum
consisting the two doublets arising from aromatic protons and a CH_2 quartet, a CH_3 triplet and one CH_3COO singlet (with a quartet, triplet and singlet due to ethanol present in $CHCl_3$ as stabilizer)/observed,
whereas the separation between doublets, that is/values of aromatic protons decreases with the increase in the concentration of $PyClO_4$ in the solutions. This effect that is, the decrease in $\Delta\delta$ values of aromatic protons with the increase in $PyClO_4$ concentration can be explained on the argument that perchlorate may be pushing iodide ion
farther /from the pyridinium ring in the solutions of mixtures of PyI and $PyClO_4$. However, there were no broadening or coalesceing of the line. This behaviour can be attributed to a rapid exchange (phenomena) of iodide to perchlorate (and vice versa) to the pyridinium ring, such that the exchange is higher than the n.m.r. time scale. NMR studies

on the solutions of PyI in $CHCl_3$, with different concentration (0.05M-0.4M) were carried out (table-4). It can be concluded from observed $\triangle\delta$ values of aromatic protons, that $\triangle\delta$ value is independent of PyI concentration for a particular solvent.

SALT EFFECT

The effect of addition of tetrabutylammonium iodide (TBAI) on the spectrum of $PyClO_4$ was investigated and/are collected in table 3.
results

NMR spectrum of $PyClO_4$ and TBAI in chloroform with the variation of the concentration ratio of the two were recorded. It was observed that as the concentration of TBAI was increased, the value of $\triangle\delta$ value for the aromatic protons increased. In this case as may be noted that, if there is rapid exchange, four species would be present: PyI, $PyClO_4$, TBAI, and TBAP. Since one does not observe two sets of resonance lines, one each for the pyridinium iodide and perchlorate, rather only one set is observed, it can be concluded that there is extremely rapid exchange between iodide and perchlorate ion.

CONDUCTANCE STUDIES

ION-PAIR DISSOCIATION CONSTANTS

Conductance studies on PyI were carried out in solvents, acetonitrile (CH_3CN), dimethyl formamide (D.M.F), methanol (CH_3OH), acetone (($CH_3)_2$ CO) and chloroform ($CHCl_3$). The conductance studies were also carried out at different temperatures for $40^{\circ}C$, $30^{\circ}C$ and $25^{\circ}C$ in the same solvent. The conductance data for PyI in the above solvents are collected in tables 6-21.

The values of ion-pair dissociation constant K were calculated using Onsager and Kraus method and are collected in table 5.

The K^d values obtained using Onsager method are collected in fifth column and K^e due to Kraus method in seventh column of table 5. It is apparent from the magnitude of K values that the PyI exists essentially as ion-pair in these solvents.

The aim of the present study was/ also to investigate (i) the influence of solvent polarity parameters (ε dielectric constant and Z-values) on K, and (ii) the temperature dependence of K.

The K values for PyI in a specific solvent are recorded alongwith the solvent polarity parameter (ε) values. In general the increase in temperature causes shift in equilibrium (eq.4.1) towards left,

$$Py^+, I^- \xrightleftharpoons{K} Py^+ + I^- \qquad 4.1$$
$$\text{(ion-pair)}$$
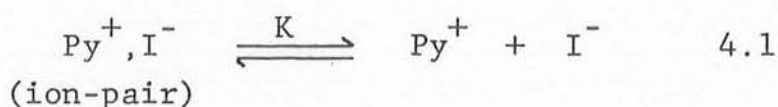
that is, ion-pairing would not be favoured by the increase in temperature. However, at the same time the dielectric constant of the solvent which plays an important role in the dissociation/ association of the ion-pair, decreases with the increase in temperature[34]. The latter role of solvent on the other hand favours the ion-pair formation and causes the equilibrium (eq.4.1) to shift towards right and hence a low value to K.

Solvent polarity parameter e.g. dielectric constant decreases with temperature according to the relationship[128] $\epsilon = \epsilon_0 \exp(-LT)$. Values of ϵ_0 and L are available for some solvents like methanol, ethanol, acetone and chloroform. The same should be valid for acetonitrile. The observed values of K^d for PyI are, in $CH_3CN = 1.88 \pm 0.27 \times 10^{-2}$, D.M.F $= 2.27 \pm 0.86 \times 10^{-}$ (within the limits of error, this value of K^d is of same order of magnitude as that of K^d in CH_3CN, which is expected, since the difference in the dielectric constant values for the two solvents is small) $CH_3OH = 1.70 \pm 0.20 \times 10^{-2}$, and $(CH_3)_2 CO = 6.27 \pm 1.39 \times 10^{-3}$, in the tempetature range $33^\circ C - 35^\circ C$. From the data given above it is apparent that the ion-pair dissociation constant decreases with the decrease in dielectric constant (ϵ) of the solvents, which is expected in more polar solvents, dissociation is increased resulting in the increased K^d values (Table 5).

Again for the same solvent the magnitude of ion-pair dissociation constant should be a resultant of two effects namely (i) temperature effect (ii) solvent effect. The increase in temperature causes the ion-pair to dissociate more and hence a larger value of K is expected i.e. decrease in ion-pair formation. At the same time this increase in temperature affects the solvent polarity in a manner/so as to cause the solvent polarity value to decrease as mentioned above. As a result of decreased solvent polarity the ion-pair dissociation value should decrease due to increase of ion-pairs.

The K^d values for PyI in acetonitrile were determined for three temperatures, that is for $34.5^\circ \pm 1^\circ C$, $28.0^\circ \pm 1^\circ C$ and $25.0^\circ \pm 2^\circ C$. The magnitude of K^d was found to be greatest for the temperature $34.5^\circ \pm 1^\circ C$ and lowest for $25^\circ \pm 2^\circ C$, whereas the K^d value for $28.0 \pm 1^\circ C$ lies in between the two. This behaviour or K^d, i.e. to increase with the rise in temperature suggests that temperature effect on the disso-ciation of ion-pair is large compared to the decrease in solvent

polarity (ϵ).

For PyI in dimethylformamide the K^d values were determined for two different temperatures. The K^d values obtained are of the same magnitude within the limits of error, hence no decrease in ion-pair formation/with the increase of temperature.

occurs

In methanol K^d values were determined at three temperatures, $40^\circ \pm 3^\circ C$, $30^\circ \pm 1^\circ C$, & $25^\circ \pm 2^\circ C$, the behaviour of K^d for first two temperatures was anomalous. The average K^d value at the temperature $25^\circ \pm 2^\circ C$, is $2.02 \pm 0.09 \times 10^{-2}$, which considering the limits in error, is of the same magnitude as that at $30^\circ \pm 1^\circ C$ $(2.14 \pm 0.76 \times 10^{-2}$ but of higher magnitude as compared to that at $40^\circ \pm 3^\circ C$ $(1.70 \pm 0.20 \times 10^{-2})$. If the solvent polarity be the sole cause then the value of K^d at $25^\circ C$ should be higher than that at $40^\circ C$, since at $25^\circ C$ the methanol's polarity is high compared to its polarity at $40^\circ C$.

In acetone the value of K^d is smallest of K^d observed in other solvents, which is quite obvious, since acetone has got the lowest ϵ - value of the solvents used in the conductance determination. Here the temperature effect on the dissociation of PyI ion-pair seems dominant

The discussion has been centred upon the Onsager K^d values. However, in general, the same conclusions can be drawn from Kraus K^e values (table 5 column 7) except in case of methanol ($40^\circ C$) and acetone. Considering the experimental error and random error in the two cases the values of K^d and K^e are overlapping .

The difference in the K^d and K^e values in the case of CH_3OH (40°C) and $(CH_3)_2CO$, it may be noted that Λo are different in the two cases. This shows the difference in curve fittings of the data. Without more extensive studies and perhaps, under very rigorous and controlled conditions of impurity (probably water), temperature etc. one could not make a case in favour of one or the other.

Conductivity data of/PyI in $CHCl_3$ is collected in tables 20-21. When the $C \Lambda c$ Vs. $1/\Lambda_c$ and Λc Vs. $\sqrt{c}$ plots were drawn they showed an anomalous behaviour, from (showing) a linear relationship. Also, for an electrolyte / which exists as ion-pair in solution, $\log \Lambda_c$ Vs. $\log C$ plot is linear, but linearity is dependent on the polarity of solvent used. The $\log \Lambda_c$ Vs. $\log C$ plot exhibits a minima, if the conductance measurements are carried out in solvents of dielectric constant values less than 15. The same behaviour is observed when $\log \Lambda_c$ Vs. $\log C$ plots were drawn for PyI in CHC_3 (see Fig.4.16) The minima in such curves is explained by the ionic association theory[129] The ion-pairs (Py^+, I^-) are electrically neutral and do not contribute to the equivalent conductivity which therefore falls as more pairs are formed. As the solution becomes still more concentrated, triple ions, either $(Py^+ I^- Py^+)$ or $(I^- Py^+ I^-)$, are formed from some of the ion/pairs, and since these triplets bear a net charge, they contribute to the conductivity, which therefore increases from its minima value. The quantitative theory of these effects has not yet been worked out, although attempts is being made[130].

TABLE - 2

NMR. DATA OF PyI^a AND $PyClO_4^b$ IN DIFFERENT SOLVENTS

S.No.	Concentration of PyI^a/$PyClO_4^b$	Solvent	Z-Value KCal./mole.	(2,6)H	(3,5)H	$\Delta\delta$	$-CH_2$(7)	$-COOCH_3$ (δ)	$-CH_3$(9)
1	$0.2MPyI^a$	$CHCl_3$	63.2	9.83,9.72	8.63,8.53	1.19	5.33,5.21, 5.09,4.97	4.09	1.97,1.84, 1.73
2	$0.2MPyI^a$	D.M.F.	68.5	9.22,9.11	8.23,8.06	1.01	4.74,4.63, 4.50,4.38	3.60	C
3	$0.1MPyI^a$	ISOPROPANOL	76.3	9.57,9.47	8.66,8.53	0.92	C	C	C
4	$0.2MPyI^a$	Ethanol	83.6	9.44,9.34	8.66,8.56	0.77	C	C	C
5	$0.1MPyClO_4^b$	Ethanol	83.6	9.25,9.14	8.57,8.47	0.67	C	C	C

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) 1-Ethyl-4-carbomethoxy pyridinium perchlorate.

c) Unable to find out or lable their resonance signals in their spectra.

TABLE - 3

NMR DATA OF PyI^a- PyClO$_4^b$ AND PyClO$_4^b$ - TBAI^c MIXTURES IN CHLOROFORM

SALT	=CH(2,6)	=CH(3,5)	$\Delta \delta$	-CH$_2$(7)	C$\underline{H}_3$COO(9)	-CH$_3$(8)
PyI	9.73,9.63	8.56,8.46	1.17	5.23,5.13,5.00,4.86	4.03	1.89,1.76,1.66
PyClO$_4$	9.05,8.95	8.44,8.38	0.58	4.91,4.82,4.67,4.54	3.98	1.82,1.67,1.57
PyI:PyClO4						
5 : 1	9.8,9.7	8.69,8.60	1.10	5.34,5.23,5.1,4.99	4.16	2.0,1.87,1.76
2 : 1	9.62,9.50	8.56,8.46	1.04	5.22,5.09,4.97,4.85	4.05	1.92,1.79,1.67
1 : 2	9.34,9.24	8.57,8.47	0.77	5.12,4.99,4.87,4.75	4.07	1.93,1.79,1.67
PyClO4:TBAI						
1 : 5	9.97,9.87	8.57,8.47	1.40	5.27,5.17,5.03,4.9	4.03	d
1 : 1	9.48,9.38	8.5,8.4	0.97	5.10,5.0,4.9,4.8	d	d
5 : 1	9.33,9.23	8.53,8.43	0.79	5.25,4.95,4.83,4.73	4.03	d

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) 1-Ethyl-4-carbomethoxy pyridinium perchlorate.

c) Tetrabutyl ammonium iodide

d) Unable to find out or lable their resonance signals in their spectra.

TABLE - 4

NMR DATA OF PyI[a] IN CHLOROFORM AT DIFFERENT CONCENTRATIONS

S.No.	Salt Conc.	CH(2,5)	CH(3,5)	$\Delta\delta$	$-CH_2(7)$	$\underline{CH}_3COO(9)$	$-CH_3(8)$
1	0.4MPyI[a]	9.79,9.69	8.57,8.47	1.21	5.25,5.14,5.02,4.90	4.03	1.87,1.76,1.65
2	0.3MPyI[a]	9.80,9.70	8.59,8.49	1.21	5.35,5.16,5.04,4,93	4.06	1.93,1.80,1.68
3	0.2MPyI[a]	9.83,9.72	8.63,8.53	1.19	5.33,5.21,5.09,4.97	4.09	1.97,1.84,1.73
4	0.1MPyI[a]	9.76,9.65	8.61,8.51	1.14	5.27,5.16,5.04,4.92	4.06	1.92,1.80,1.68
5	0.05MPyI[a]	9.85,9.74	8.67,8.56	1.17	5.41,5.27,5.14,5.02	4.14	1.97,1.88,1.76

a) 1-Ethyl-4-carbomethoxy pyridinium iodide

TABLE - 5

K and Λ_o VALUES FOR PyI^a IN DIFFERENT SOLVENTS FROM CONDUCTANCE MEASUREMENTS

S.No.	SOLVENT	Temp.$^{\circ}C$	ϵ	$K^d \times 10^2$ (Equiv./liter)	Λ_c^d (mho Cm^2 equiv.$^{-1}$)	$K^e \times 10^2$ (equiv./liter)	Λ_o^e (mho Cm^2 equiv.$^{-1}$)
1	Acetonitrile	$34.5\pm1^{\circ}C$	-	1.88 ± 0.27	194.6	2.20 ± 0.01	188.14
2	Acetonitrile	$28.0\pm1^{\circ}C$	-	1.21 ± 0.56	213.5	1.87 ± 0.01	203.47
3	Acetonitrile	$25.0\pm2^{\circ}C$	37.5^b	1.18 ± 0.29	186.31	1.65 ± 0.01	177.63
4	Dimethylformamide	$33^{\circ}\pm1^{\circ}C$	-	2.27 ± 0.86	97.6	2.00 ± 0.01	99.19
5	Dimethylformamide	$25\pm1^{\circ}C$	36.7^b	2.10 ± 0.86	86.07	2.5 ± 0.03	88.98
6	Methanol	$40\pm3^{\circ}C$	29.17 ± 0.47^c	1.70 ± 0.20	140.7	2.05 ± 0.01	133.65
7	Methanol	$30\pm1^{\circ}C$	30.79 ± 0.16^c	2.14 ± 0.76	122.07	2.41 ± 0.02	118.14
8	Methanol	$26\pm1^{\circ}C$	32.6^b	2.13 ± 0.58	114.6	1.91 ± 0.01	118.22
9	Methanol	$25\pm3^{\circ}C$	32.6^b	1.97 ± 0.22	116.73	2.20 ± 0.01	109.47
10	Methanol	$25\pm1^{\circ}C$	32.6^b	2.21 ± 0.50	111.5	1.92 ± 0.03	114.72
11	Methanol	$25\pm1^{\circ}C$	32.6^b	2.17 ± 0.50	110.5	3.53 ± 0.01	104.93
12	Acetone	$33\pm2^{\circ}C$	19.95 ± 0.02^c	0.63 ± 0.14	145.8	0.19 ± 0.01	210.67
13	Acetone	$25\pm2^{\circ}C$	20.7^b	0.62 ± 0.14	128.6	0.15 ± 0.01	206.97
14	Acetone	$26\pm3^{\circ}C$	20.7^b	0.48 ± 0.16	165.52	0.67 ± 0.03	159.16

a) 1-Ethyl-4-carbomethoxy pyridinium iodide

b) The dielectric constant values for $25^{\circ}C$.

c) Dielectric constants calculated from $\epsilon = \epsilon_o \exp(-LT)$ [128].

d) K and Λ_o values calculated using Onsager method.

e) K and Λ_o values calculated using Kraus method.

TABLE - 6

CONDUCTIVITY DATA OF PyI[a] IN ACETONITRILE[c] AT $34.5^{\circ} \pm 1^{\circ}C$

S.No.	Conc. (Equiv/ Liter) $C \times 10^3$	Corrected specific conductance[b] (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 Equiv^{-1})	$C \Lambda_c$ (mhos Cm^{-1} /1000) $\times 10^1$	$1/\Lambda_c$ (mho^{-1} Cm^{-2} equiv) $\times 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_0^d}$	$K^e = C\alpha^2/ (1-\alpha)$ (equiv./ liter) $\times 10^2$
1	20.0	24.45±0.20	122.25±1.00	24.45±0.20	8.18±0.07	0.6282±0.0051	2.09±0.06
2	10.0	13.75±0.10	137.5 ±1.0	13.75±0.10	7.28±0.05	0.7066±0.0050	1.71±0.05
3	5.0	7.77±0.07	155.3± 1.5	7.77±0.07	6.44±0.06	0.7981±0.0077	1.66+0.01
4	2.5	4.28±0.04	171.2± 1.6	4.28±0.04	5.84±0.05	0.8798±0.0082	1.64±0.15
5	1.25	2.31±0.02	184.8± 1.6	2.31±0.02	5.42±0.04	0.9747±0.0167	2.31±0.41

a) 1-Ethyl-4-Carbo. ethoxy Pyridinium iodide.
b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.
c) Specific conductance of Acetonitrile used $(L_s) = 4.68 + 0.05 \times 10^{-6}$ mho Cm^{-1}
d) The value of Λ_0 has been determined from entrapolation to $\sqrt{c} = o$ in a Λ_c Vs. $\sqrt{c}$ plot (Fig 4.12(a))

$$\Lambda_0 = 194.6 \text{ mho Cm}^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant $K = 1.88 \pm 0.27 \times 10^{-2}$ equiv/liter.(Onsager method)

TABLE - 7

CONDUCTIVITY DATA OF PyI^a IN ACETONITRILE^c AT $28^\circ C \pm 1^\circ C$

S.No.	Conc. (Equiv/ Liter) $C \times 10^3$	Corrected specific conductance[d] (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 $Equiv^{-1}$)	$c\Lambda_c$ (mhos Cm^{-1} /1000) $X\ 10^1$	$1/\Lambda_c$ (mho^{-1} Cm^{-2} equiv) $X\ 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o}$	$K^e = C\alpha^2/ (1-\alpha)$ (equiv./ liter) $X\ 10^2$
1	20.0	26.12±0.24	130.58±1.22	26.12±0.24	7.62±0.11	0.6119±0.0057	1.96±0.06
2	6.0	9.07±0.10	151.17±1.66	9.07±0.10	6.62±0.07	0.7084±0.0078	1.05±0.09
3	2.0	3.39±0.03	169.5±1.5	3.39±0.03	5.90±0.05	0.7943±0.0070	0.62±0.03
4	0.6	1.30±0.13	216.67±21.66	1.30±0.13	4.67±0.46	-	-
5	0.2	0.56±0.02	282.5±7.5	0.57±0.02	3.55±0.09	-	-

a) 1-Ethyl-4-carbonethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of Acetonitrile used $(L_S) = 3.50 \pm 0.04 \times 10^{-6}$ mho Cm^{-1}

d) The value of Λ_o determined from entrapolation to $\sqrt{c}$ = o in a Λ_c Vs. $\sqrt{c}$ plot (Fig 4.12(b))
$$\Lambda_o = 213.5 \text{ mho } Cm^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant $K = 1.21 \pm 0.56 \times 10^{-2}$ equiv./liter

TABLE - 8

CONDUCTIVITY DATA OF PyI[a] IN ACETONITRILE[c] AT $25°C \pm 2°C$

S.No.	Conc. (Equiv/Liter) $C \times 10^3$	Corrected specific conductance[d] (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 $Equiv^{-1}$)	$C\Lambda_c$ (mhos Cm^{-1} 1000) $\times 10^1$	$1/\Lambda_c$ (mho^{-1} Cm^2 equiv) $\times 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o^d}$	$K^e = C\alpha^2/(1-\alpha)$ (equiv./liter) $\times 10^2$
1	20.0	21.41±0.21	107.05±1.05	21.4±0.2	9.34±0.09	0.5746±0.0056	1.55±0.05
2	10.0	12.05±0.12	120.5 ±1.2	12.05±0.12	8.30±0.08	0.6468±0.0064	1.19±0.05
3	6.0	8.68±0.10	144.67±1.66	8.68±0.10	6.91±0.08	0.7765±0.0089	1.62±0.1
4	5.0	6.81±0.08	136.2±1.6	6.81±0.08	7.35±0.08	0.7311±0.0085	1.00±0.05
5	2.5	3.76±0.04	150.4±1.6	3.76±0.04	6.65±0.07	0.8078±0.0090	0.95±0.40
6	2.0	3.24±0.03	162.00±1.50	3.24±0.03	6.18±0.05	0.8696±0.0080	1.17±0.09
7	1.25	2.02±0.02	163.2±1.6	2.04±0.02	6.13±0.06	0.8759±0.0085	0.78±0.06
8	0.6	1.08±0.03	180±5	1.08±0.03	5.56±0.15	0.9662±0.0268	4.67±3.82
9	0.2	0.54±0.01	272.5±7.5	0.55±0.01	3.67±0.10	-	-

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of Acetonitrile used (L_S) = 3.34±0.04 $\times 10^{-6}$ mhos Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c}$ = o in a Λ_c Vs. $\sqrt{c}$ plot (Fig.4.12(c))
$$\Lambda_o = 186.31 \text{ mho } Cm^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pairs dissociation constant. K = 1.18± 0.29 $\times 10^{-2}$ equiv./liter

TABLE - 9

CONDUCTIVITY DATA OF PyI^a IN DIMETHYLFOR MAMIDE^c AT $33^\circ \pm 1^\circ C$

S.No.	Conc. (Equiv/ Liter) $C \times 10^3$	Corrected specific conductance^d (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 $Equiv^{-1}$)	$c\Lambda_c$ (mhos Cm^{-1}/ 1000) $\times 10^1$	$1/_1\Lambda_c$ (mho^{-1} Cm^{-2} equiv.) $\times 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o}$	$K^e = C\alpha^2/ (1 - \alpha)$ (equiv./ liter) $\times 10^2$
1	20.0	13.57+0.10	67.85+0.50	13.57+0.10	14.74+0.11	0.6952+0.0051	3.17+0.1
2	6.0	4.57+0.10	76.17+1.67	4.57+0.10	13.14+0.29	0.7804+0.0170	1.68+0.20
3	2.0	1.69+0.05	84.5+2.5	1.69+0.05	11.85+0.36	0.8659+0.0255	1.18+0.28
4	0.6	0.58+0.02	96.67+3.34	0.58+0.02	10.36+0.36	0.9904+0.0341	3.06+0.19
5	0.2	0.25+0.03	125.00+15	0.25+0.03	8.12+0.98	-	-

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of dimethyformamide used (L_S) = 3.05+0.03 x 10^{-6} mho Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c}$ = o in a Λ_c Vs.$\sqrt{c}$ plot (Fig.4.13(a))
Λ_o = 97.6 mho Cm^2 equiv.$^{-1}$

e) Average value of ion-pair dissociation constant. K = 2.27+0.86 x 10^{-2} equiv./liter.

TABLE - 10

CONDUCTIVITY DATA OF PyI^a IN DIMETHYLFORMAMIDE^c AT $25° \pm 1°C$

S.No.	Conc. (Equiv/Liter) $C \times 10^3$	Corrected specific conductance^d (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 $Equiv^{-1}$)	$C\Lambda_c$ (mhos Cm^{-1})/ 1000) $X\ 10^1$	$1/\Lambda_c$ (mho^{-1} Cm^{-2} equiv) $X\ 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o}$	$K^e = C\alpha^2/$ $(1 - \alpha)$ (equiv./ Liter $X\ 10^2$
1	20.0	12.07±0.10	60.35±0.50	12.34±0.37	16.57±0.14	0.7012±0.0058	3.29±0.12
2	6.0	4.05±0.10	67.50±1.67	4.05±0.10	14.83±0.36	0.7842±0.0194	1.73±0.24
3	2.0	1.50±0.05	75.00±2.5	1.50±0.05	13.35±0.44	0.8714±0.0290	1.27±0.36
4	0.6	0.51±0.02	85.00±3.33	0.51±0.02	11.78±0.46	0.9876±0.0387	-
5	0.2	0.223±0.003	112.5±2.5	0.230±0.005	8.89±0.19	-	-

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of dimethylformamide used $(L_S) = 2.71 \pm 0.03 \times 10^{-6}$ mho Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to to $\sqrt{c} = o$ in a Λ_c Vs. $\sqrt{c}$ plot(Fig.4.13(b))

$$\Lambda_o = 86.07 \text{ mho } Cm^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant. $K = 2.10 \pm 0.86 \times 10^{-2}$ equiv./liter.

TABLE - 11

CONDUCTIVITY DATA OF PyI[a] IN METHANOL[c] AT $40° \pm 3°C$

S.No.	Conc. (Equiv/ Liter) $C \times 10^3$	Corrected specific conductance[d] (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 $Equiv^{-1}$)	$C\Lambda_c$ (mhos $Cm^{-1}/1000$) $\times 10^1$	$1/\Lambda_c$ (mho^{-1} Cm^{-2} equiv.) $\times 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o}$	$K^e = C\alpha^2/(1-\alpha)$ equiv./ liter $\times 10^2$
1	20.0	17.45±0.15	87.28±0.93	17.46±0.19	11.46±0.12	0.6203±0.0066	2.04±0.08
2	10.0	9.65±0.09	96.55±0.85	9.66±0.09	10.36±0.09	0.6863±0.0060	1.51±0.05
3	6.0	6.45±0.09	107.59±1.42	6.46±0.09	9.30±0.13	0.7647±0.0101	1.49±0.10
4	2.5	3.09±0.02	123.8±0.6	3.10±0.02	8.08±0.04	0.8799±0.0043	1.73±0.18
5	2.0	2.53±0.02	127.25±0.25	2.54±0.02	7.86±0.02	0.9044±0.0018	1.71±0.04
6	1.25	1.57±0.04	126.0±2.8	1.58±0.04	7.94±0.02	0.9417±0.0888	-
7	0.63	0.77±0.08	124.00±12	0.78±0.08	8.14±0.79	-	-
8	0.6	0.73±0.08	122.5±12.5	0.74±0.08	8.25±0.84	-	-
9	0.2	0.26±0.03	132.5±12.5	0.27±0.03	7.62±0.72	-	-

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of methanol used $(L_S) = 1.49\pm0.15 \times 10^{-5}$ mhos Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c} = o$ in a Λ_c Vs. $\sqrt{c}$ plot (Fig.4.14(a)).
$$\Lambda_o = 140.7 \text{ mho } Cm^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant. $K = 1.70\pm0.20 \times 10^{-2}$ equiv./liter.

TABLE -12

CONDUCTIVITY DATA OF PyI[a] IN METHANOL[c] AT $30° \pm 1°C$

S.No.	Conc. Equiv/ Liter) $C \times 10^3$	Corrected specific conductance[d] (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 $Equiv^{-1}$)	$c\Lambda_c$ (mhos Cm^{-1}/ 1000) $X\ 10^1$	Λ_c (mho^{-1} Cm^{-2} equiv) $X\ 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o^d}$	$K^e = C\alpha^2/(1-\alpha)$ equiv./ liter $X\ 10^2$
1	20.0	16.4±0.5	82.08±2.48	16.42±0.49	12.20±0.37	0.6727±0.0203	2.79±0.34
2	10.0	8.81±0.1	88.15±0.95	8.82±0.10	11.35±0.13	0.7225±0.0078	1.89±0.09
3	6.0	5.79±0.06	96.59±0.92	5.80±0.06	10.34±0.10	0.7916±0.0075	2.05±0.34
4	2.5	2.51±0.29	100.6±11.8	2.52±0.30	10.08±1.18	0.8245±0.0967	3.78±1.09
5	2.0	2.19±0.02	109.75±0.75	2.20±0.02	9.11±0.06	0.8996±0.0062	1.62±0.12
6	1.25	1.39±0.04	111.6±2.8	1.40±0.04	8.97±0.23	0.9147±0.0230	1.35±0.43
7	0.63	0.724±0.017	116.0±2.4	0.73±0.02	8.63±0.18	0.9509±0.0198	1.39±0.60
8	0.60	0.70±0.02	117.5±2.5	0.71±0.02	8.52±0.19	0.9630±0.0205	2.23±1.29
9	0.20	0.28±0.01	142.5±2.5	0.29±0.01	7.02±0.12	-	-

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of methanol used $(L_S) = 8.6\pm0.3 \times 10^{-6}$ mhos Cm^{-1}.

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c} = o$ in a Λ_c Vs. $\sqrt{c}$ plot (Fig.4.14 (b))

$$\Lambda_o = 122.07 \text{ mho } Cm^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant $K=2.14\pm0.76 \times 10^{-2}$ equiv./liter.

TABLE - 13

CONDUCTIVITY DATA OF PyI[a] IN METHANOL[c] AT $26° \pm 1°C$

S.No.	Conc. (Equiv/Liter) $C \times 10^3$	Corrected specific conductance[d] (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance Λ_c = L.1000/C (mho Cm^2 Equiv.$^{-1}$)	$C \Lambda_c$ (mhos Cm^{-1}/1000) $\times 10^1$	$1/\Lambda_c$ (mho^{-1} Cm^{-2} Equiv.) $\times 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o^d}$	$K^e = C\alpha^2/(1-\alpha)$ (equiv./Liter) $\times 10^{-2}$
1	20.0	16.22±0.20	81.08±0.97	16.22±0.19	12.34±0.14	0.7075±0.0085	3.43±0.18
2	10.0	8.64±0.08	86.35±0.85	8.64±0.08	11.58±0.11	0.7535±0.0074	2.31±0.12
3	6.0	5.54±0.16	92.25±2.75	5.54±0.16	11.17±0.32	0.8050±0.240	2.04±0.37
4	5.0	4.67±0.04	93.3±0.9	4.67±0.04	10.72±0.10	0.8142±0.0078	2.00±0.31
5	2.5	2.57±0.02	102.6±1.0	2.57±0.02	9.75±0.09	0.8953±0.0087	1.93±0.20
6	2.0	2.07±0.01	103.25±0.75	1.07±0.01	9.69±0.07	0.9010±0.0065	1.52
7	1.25	1.12±0.03	89.2±2.8	1.12±0.03	11.22±0.35	0.9671±0.0364	1.71
8	0.63	0.795±0.023	127.2±4.0	0.79±0.03	7.87±0.25	-	-
9	0.60	0.665±0.02	110.84±4.16	0.67±0.02	9.04±0.35	-	-
10	0.20	0.256±0.007	127.5±2.5	0.26±0.01	7.85±0.15	-	-

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of methanol used $(L_S) = 8.50 \pm 0.26 \times 10^{-6}$ mhos Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c} = o$ in a Λ_c Vs $\sqrt{c}$ plot (Fig.4.14(c))
$$\Lambda_o = 114.6 \text{ mho Cm}^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant $K = 2.13 \pm 0.58 \times 10^{-2}$ equiv./liter.

TABLE - 14

CONDUCTIVITY DATA OF PyI[a] IN METHANOL[c] AT $25° \pm 3°C$

S.No.	Conc. (Equiv/ Liter) $C \times 10^3$	Corrected specific conductance[d] (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 Equiv^{-1})	$C \Lambda_c$ (mhos Cm^{-1}/ 1000) $\times 10^1$	$1/\Lambda_c$ (mho^{-1}Cm^{-2} Equiv.) $\times 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o^d}$	$K^e = \dfrac{c\alpha^2}{(1-\alpha)}$ (equiv./ liter) $\times 10^2$
1	20.0	14.28±0.19	71.4±0.9	14.20±0.10	13.99±0.12	0.6118±0.0077	1.93±0.09
2	10.0	7.87±0.09	78.7±0.9	7.87±0.09	12.71±0.15	0.6744±0.0077	1.74±0.40
3	6.0	5.27±0.09	87.83±1.5	5.27±0.09	11.39±0.20	0.7527±0.0129	1.43±0.07
4	2.5	2.52±0.02	100.8±0.8	2.52±0.02	9.92±0.08	0.8638±0.0068	1.37±0.09
5	2.0	2.07±0.02	103.5±1.0	2.07±0.02	9.67±0.10	0.8871±0.0084	1.40±0.13
6	1.25	1.28±0.03	102.4±2.4	1.28±0.03	9.77±0.23	-	-
7	0.63	0.623±0.075	99.68±12.00	0.62±0.08	10.18±1.20	-	-
8	0.60	0.605±0.075	100.83±12.5	0.61±0.08	10.07±1.25	-	-
9	0.20	0.221±0.025	110.5±12.5	0.22±0.03	9.17±1.04	-	-

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of methanol used (L_S) = 1.22±0.15 x 10^{-5} mhos Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c}$ = o in a Λ_c Vs $\sqrt{c}$ plot (Fig.4.14(d))
$$\Lambda_o = 116.73 \text{ mho Cm}^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant K = 1.57 ± 0.22 X 10^{-2} equiv./liter.

TABLE - 15

CONDUCTIVITY DATA OF PyI[a] IN METHANOL[c] AT $25° \pm 1°C$

S.No.	Conc. (Equiv/ Liter) $C \times 10^3$	Corrected specific conductance[d] (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 Equiv^{-1})	$c\Lambda_c$ (mhos Cm^{-1}/ 1000) $\times 10^1$	$1/\Lambda_c$ (mho^{-1} Cm^{-2} equiv.) $\times 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o^d}$	$K^e = C\alpha^2/$ $(1 - \alpha)$ (Equiv./ liter $\times 10^2$
1	20.0	15.38+0.457	76.9+2.3	15.38+0.46	13.02+0.39	0.6897+0.0206	3.10+0.39
2	10.0	8.26+0.087	82.6+0.9	8.26+0.09	12.11+0.13	0.7408+0.0081	2.12+0.11
3	6.0	5.47+0.057	91.17+1.0	5.47+0.06	10.97+0.12	0.8182+0.0095	2.21+0.16
4	2.5	2.32+0.297	92.4+12.4	2.33+0.30	11.02+1.48	0.8287+0.1112	2.07+0.39
5	2.0	1.54+0.483	77.0+24	1.54+0.48	14.39+4.49	-	-
6	1.25	1.40+0.037	112.0+3.2	1.40+0.04	8.94+0.26		-
7	0.63	0.660+0.020	105.6+3.2	0.66+0.02	9.44+0.34	0.9471+0.0287	1.55+0.91
8	0.60	0.655+0.017	109.17+2.5	0.66+0.02	9.17+0.21	-	-
9	0.20	0.0261+0.01	130.5+0.5	0.26+.001	7.66+0.03	-	

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of methanol used (L_S) = $8.00 \pm 0.3 \times 10^{-6}$ mho Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c}$ = o in a Λ_c Vs. $\sqrt{c}$ Plot (Fig.4.14(e))

$$\Lambda_o = 111.5 \text{ mho Cm}^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant K = $2.21 \pm 0.50 \times 10^{-2}$ equiv./liter.

TABLE - 16

CONDUCTIVITY DATA OF PyI^a IN METHANOL^c AT $25° \pm 1°C$

S.No.	Conc. (Equiv/ Liter $C \times 10^3$	Corrected specific conductance^d (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 $Equiv^{-1}$)	$C \Lambda_c^{-1}$ (mhos Cm^{-1}/ 1000) $\times 10^1$	$1/\Lambda_c^{-2}$ (mho Cm^{-2} equiv.) $\times 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o^d}$	$K^e = CX^2/(1-X)$ (equiv./ liter) $\times 10^2$
1	20.0	15.6±0.20	78.1±1.0	15.62±0.20	12.81±0.16	0.7068±0.0090	3.22
2	10.0	8.319±0.087	83.2±0.9	8.32±0.09	12.06±0.09	0.7530±0.0081	2.30±0.12
3	6.0	5.34±0.16	89.00±2.83	5.34±0.17	11.25±0.36	0.8054±0.0256	2.06±0.39
4	5.0	4.50±0.05	98.8±1.00	4.5±0.05	11.11±0.13	0.8145±0.0090	1.79±0.13
5	2.5	2.47±0.03	98.8±1.2	2.47±0.03	10.13±0.12	0.8914±0.0136	1.87±0.29
6	2.0	1.99±0.01	99.5±1.0	1.99±0.02	10.05±0.10	0.9005±0.0091	1.79±0.34
7	1.25	1.08±0.03	86.4±3.2	1.08±0.04	11.59±0.43	0.9653±0.0302	6.97±6.17
8	0.625	0.766±0.024	122.4±4.0	0.77±0.02	8.18±0.27	-	-
9	0.6	0.641±0.021	106.67±3.33	0.64±0.02	9.38±0.29	-	-
10	0.2	0.241±0.007	122.5±2.5	0.25±0.01	8.17±0.16	-	-

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of methanol used (L_S) = 8.19±0.25 x 10^{-6} mho Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c}$ = o in a Λ_c Vs. $\sqrt{c}$ plot (Fig. 4.14(f))
$$\Lambda_o = 110.5 \text{ mho } Cm^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant K = 2.17±0.**50** X 10^{-2} equiv./liter.

TABLE - 17

CONDUCTIVITY DATA OF PyI^a IN ACETONE^c AT $33° \pm 2°C$

S.No.	Conc. (Equiv/ Liter) $C \times 10^3$	Corrected specific conductance^b (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 $Equiv^{-1}$)	$C \Lambda_c$ (mhos Cm^{-1}/ 1000) $\times 10^1$	$1/\Lambda_c$ (mho^{-1} Cm^{-2} equiv) $\times 10^3$	$\alpha = \dfrac{\Lambda_c}{\Lambda_o^d}$	$K^e = C\alpha^2/(1-\alpha)$ (equiv./ liter) 10^3
1	20.0	10.91±0.09	54.54±0.47	10.91±0.09	18.34±0.16	0.3740±0.0033	4.47±0.10
2	10.0	7.67±0.07	76.65±0.75	7.67±0.07	13.05±0.13	0.5258±0.0052	5.83±0.18
3	5.0	5.13±0.04	102.5 ±0.9	5.13±0.04	9.76±0.08	0.7030±0.0062	8.33±0.32
4	2.5	2.81±0.02	112.2 ±1.0	2.82±0.04	8.91±0.08	0.7696±0.0069	6.44±0.30
5	1.25	1.69±0.05	135.6± 3.6	1.69±0.05	7.38±0.20	0.9300±0.0247	18.5±6.7

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific donductance of Acetone used $(L_s) = 9.5 \pm 0.3 \times 10^{-6}$ mho Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c} = o$ in a Λc Vs. $\sqrt{c}$ Plot (Fig 4.15(a))
$$\Lambda_o = 145.8 \text{ mho } Cm^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant $K = 6.27 \pm 1.39 \times 10^{-3}$ equiv./liter.

TABLE - 18

CONDUCTIVITY DATA OF PyI[a] IN ACETONE AT $25° \pm 2°C$

S.No.	Conc. (Equiv/ Liter) $C \times 10^3$	Corrected specific conductance[b] (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 Equiv^{-1})	$C \Lambda_c$ (mhos^{-1} Cm^{-1}/ 1000) 10^1	$1/\Lambda_c$ (mho^{-1} Cm^{-2} equiv.) 10^3	$\alpha = \dfrac{\Lambda_c}{\Lambda_o^d}$	$K^e = C\alpha^2/ (1-\alpha)$ (equiv./ liter) 10^3
1	20.0	9.610±0.001	48.04±0.02	9.61±0.01	20.82±0.01	0.3735±0.0002	4.46±0.00
2	10.0	6.71±0.03	67.05±0.25	6.71±0.02	14.92±0.05	0.5214±0.0020	5.68±0.07
3	5.0	4.51±0.05	90.1±0.9	4.51±0.45	11.10±0.11	0.7006±0.0070	8.21±0.36
4	2.5	2.48±0.03	99.0±1.0	2.48±0.02	10.10±0.1	0.7699±0078	6.45±0.35
5	1.25	1.49±0.05	119.6±3.6	1.49±0.05	8.37±0.25	0.9300±0280	17.87±9.43

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of Acetone used $(L_S) = 8.4 \pm 0.3 \times 10^{-6}$ mho Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c} = o$, in a Λ_c Vs. $\sqrt{c}$ plot (Fig.4.15(b))
$$\Lambda_o = 128.6 \text{ mhos Cm}^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant $K = 6.20 \pm 1.36 \times 10^{-3}$ equiv./liter.

TABLE - 19

CONDUCTIVITY DATA OF PyI^a IN ACETONE^c AT $26° \pm 3°C$

S.No.	Conc. (Equiv/Liter) $C \times 10^3$	Corrected specific conductance^b (mho Cm^{-1}) $L \times 10^4$	Equivalent conductance $\Lambda_c = L.1000/C$ (mho Cm^2 Equiv^{-1})	$c\Lambda_c$ (mhos Cm^{-1}/1000) 10^1	$1/\Lambda_c$ (mho^{-1} Cm^{-2} equiv.) 10^3	$\alpha = \dfrac{\Lambda_c}{\Lambda_o^d}$	$K^e = c\alpha^2/(1-\alpha)$ (equiv./liter) 10^3
1	20.0	14.33±0.01	71.65±0.50	14.33±0.10	13.96±0.09	0.4329±0.003	6.61±0.13
2	6.0	5.83±0.09	97.17±1.66	5.83±0.10	10.29±0.18	0.5870±0.0101	5.02±0.29
3	2.0	2.23±0.01	111.5±1.0	2.23±0.62	8.97±0.08	0.6736±0.006	2.78±0.10
4	0.6	1.03±0.02	171.67±5.0	1.03±0.03	5.83±0.17	-	-
5	0.2	0.59±0.02	300 ± 10	0.60±0.02	3.34±0.11	-	-

a) 1-Ethyl-4-carbomethoxy pyridinium iodide.

b) The corrected specific conductance of PyI solutions were obtained by subtracting the specific conductance of solvent to that of solution.

c) Specific conductance of Acetone used (L_S) = $7.2 \pm 0.2 \times 10^{-6}$ mho Cm^{-1}

d) The value of Λ_o has been determined from extrapolation to $\sqrt{c}$ = o in a Λ_c Vs. $\sqrt{c}$ plot (Fig.4.15(c))
$$\Lambda_o = 165.52 \text{ mho Cm}^2 \text{ equiv.}^{-1}$$

e) Average value of ion-pair dissociation constant, K = $4.80 \pm 1.57 \times 10^{-3}$ equiv./liter

TABLE - 20

CONDUCTIVITY DATA OF PyI^a IN $CHCl_3^b$ AT $36.5° \pm 1°C$

S.No.	Conc. (Equiv./ Liter) $C \times 10^3$	Specific conductance (mhos/Cm) $L_c \times 10^7$	Equivalent conductance $\Lambda_c = 1000\ L_c/C$ 10^2	Log Λ_c 10^2	Log C
1	20.0	30.2±0.90	15.10±0.45	-82.13±1.29	- 1.69
2	20.0	18.0±0.20	18.00±0.20	-74.48±0.48	- 2.00
3	5.0	3.99±0.04	7.98±0.08	-209.69±0.55	- 2.30
4	1.0	0.75±0.08	7.50±0.80	-112.74±4.65	- 3.00
5	0.5	0.33±0.03	6.60±0.60	-118.23±3.95	- 3.30
6	0.2	0.10±0.01	5.00±0.50	-130.32±4.36	- 3.69

a) 1-Ethyl-4-carbomethoxy pyridinium iodide

b) Specific conductance of $CHCl_3$ used 1×10^{-8} mho Cm^{-1}

TABLE -21

CONDUCTIVITY DATA OF PyI^a IN $CHCl_3^b$ AT $26.5 \pm 2°C$

S.No.	Conc. (Equiv/Liter) $C \times 10^3$	Specific Conductance (mhos/Cm) $L_c \times 10^7$	Equivalent conductance $\Lambda_c = 1000\ L_c/C$ 10^2	Log Λ_c 10^2	Log C
1	20.0	28.0±0.80	14.0±0.4	- 85.41±1.25	- 1.69
2	10.0	10.4±1.40	10.4±1.4	- 98.69±5.88	- 2.00
3	7.0	4.73±0.19	9.14±2.6	-105.78±1.30	- 2.16
4	5.0	2.52±0.08	5.04±0.16	-129.78±1.3	- 2.30
5	2.0	1.69±0.05	8.45±0.25	-107.34±1.28	- 3.00
6	0.6	0.45±0.05	7.5± 0.83	-108.28±7.6	- 3.30
7	0.2	0.18±0.02	9.0±1.00	-108.45±8.45	- 3.69

a) 1-Ethyl-4-carbomethoxy pyridinium iodide

b) Specific conductance of $CHCl_3$ used 1×10^{-8} mhos Cm^{-1}
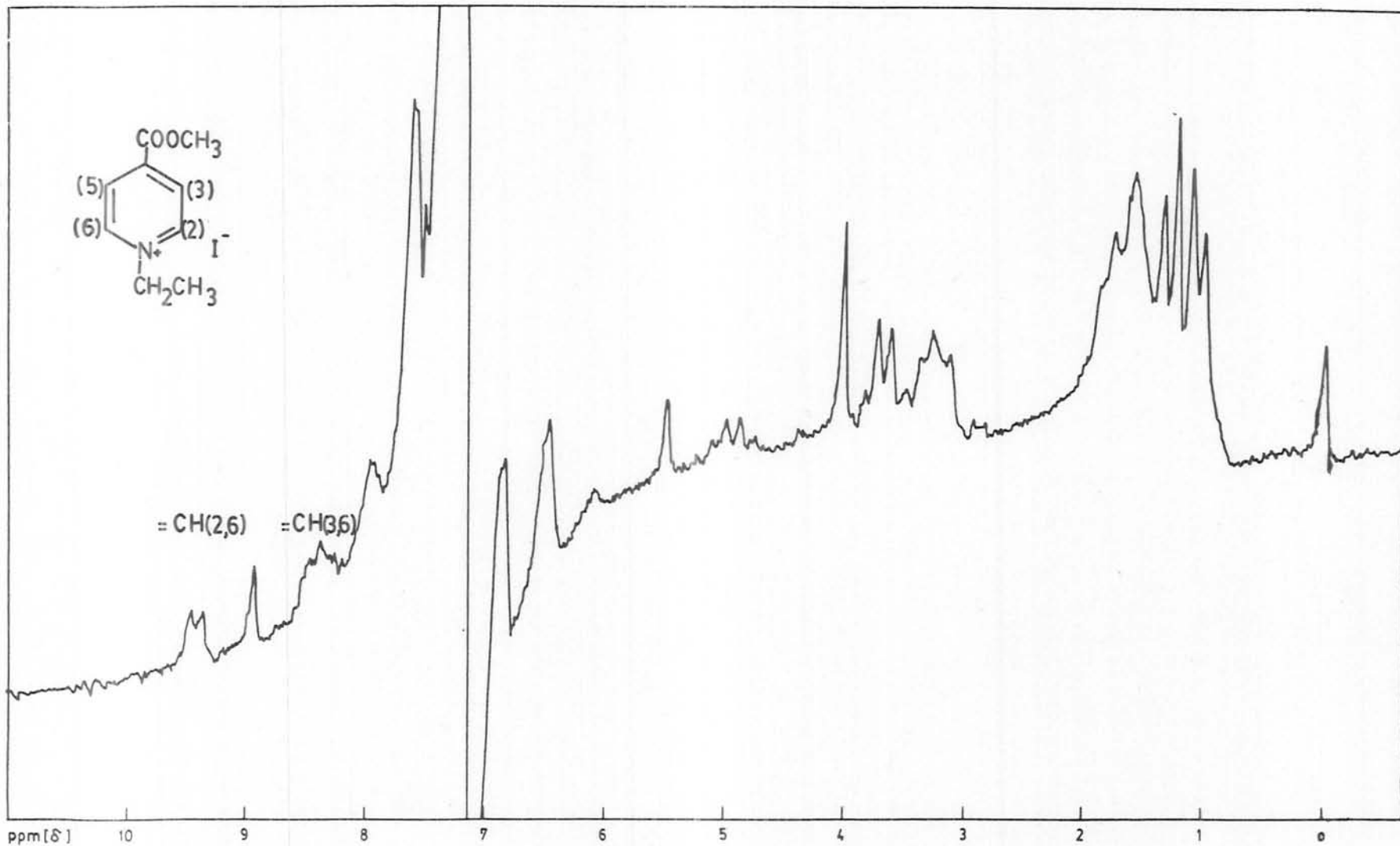
Fig. 4.1 NMR Spectrum of PyClO$_4$: TBAI   Solvent: Chloroform; Reference TMS.

0.1M : 0.1M

H$_1$Level 0.5; Filter 20(Hz); Sweep Width (Hz) 600 ; Sweep Time (Sec) 250; Amplitude 10 x 9
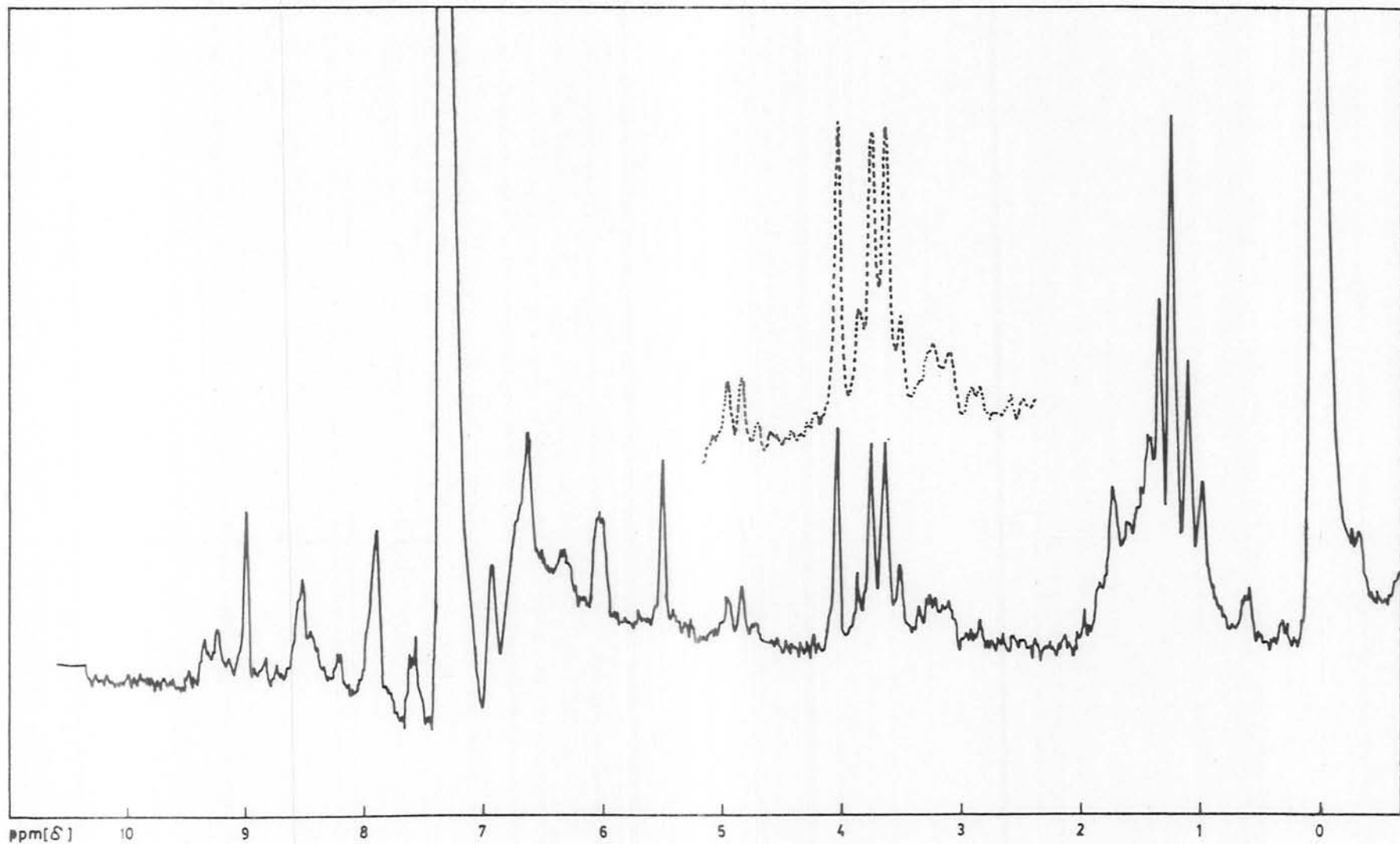
Fig. 4.2 NMR Spectrum of PyClO$_4$: TBAI Solvent Chloroform; Reference TMS.

0.5M : 0.1M

H$_1$ Level 0.5 ; Filter 20(Hz);Sweep Width (Hz) 600; Sweep Time (Sec)250; Amplitude ——— 10 x 9
.... 100 x 2
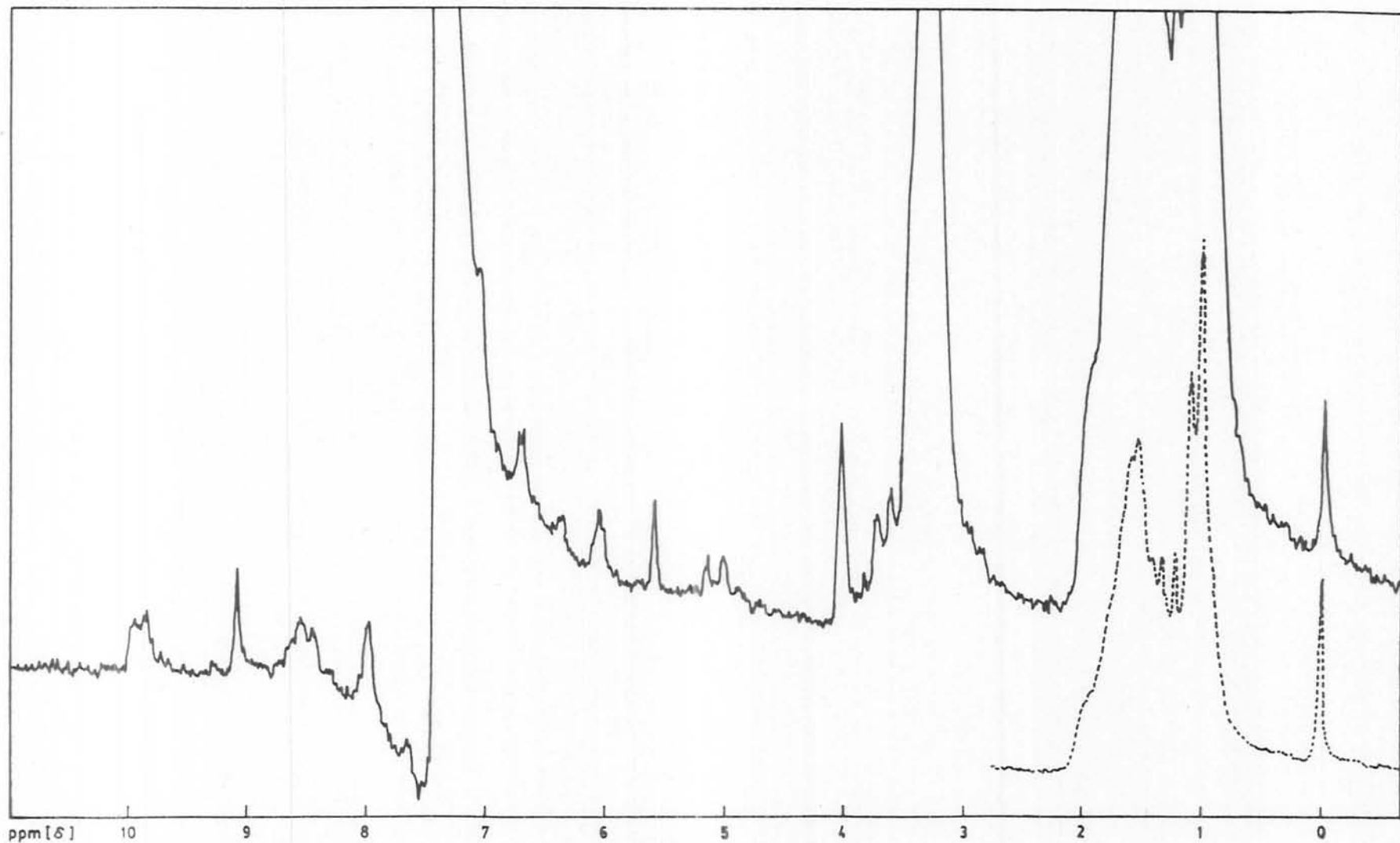
Fig. 4.3 NMR Spectrum of PyClO$_4$: TBAI Solvent Chloroform; Reference TMS.
0.1M : 0.5M

H$_1$ Level 0.5; Filter 20(Hz);Sweep Width (Hz) 600; Sweep Time (Sec)250; Amplitude ——— 10 x 9
.... 10 x 2
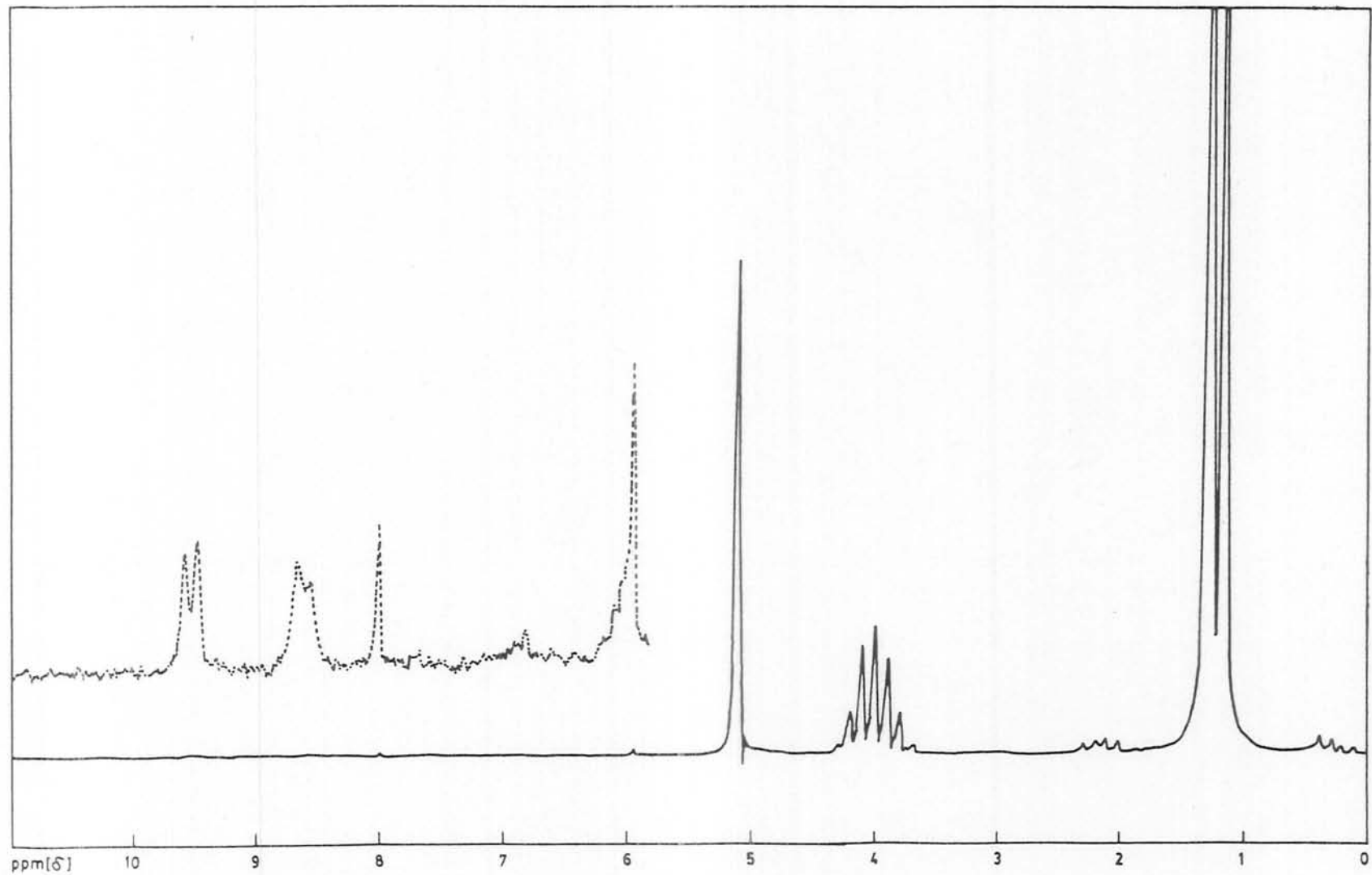
Fig. 4.4 NMR Spectrum of 0.1M PyI. Solvent Isopropanol

H_1 Level 0.5; Filter 20(Hz); Sweep width (Hz) 600; Sweep Time(Sec) 250;

Amplitude ———— 1 x 2

..... 1 x 10
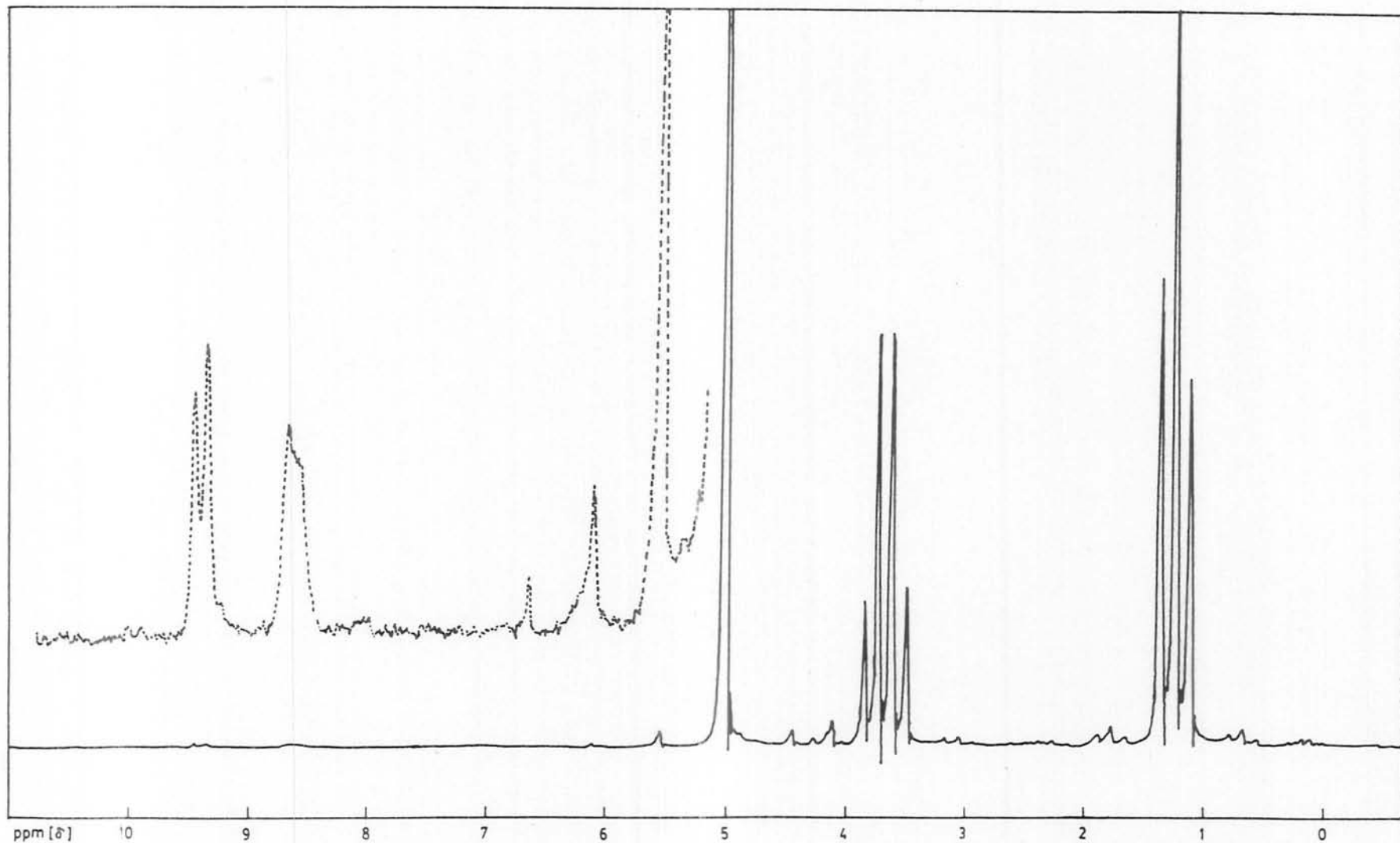
Fig. 4.5   NMR Spectrum of 0.2M PyI Solvent Ethanol.

H_1 Level 0.5; Filter 20 (Hz), Sweep width (Hz) 600; Sweep Time (Sec) 250;

Amplitude ——— 1 x 2
..... 10 x 3
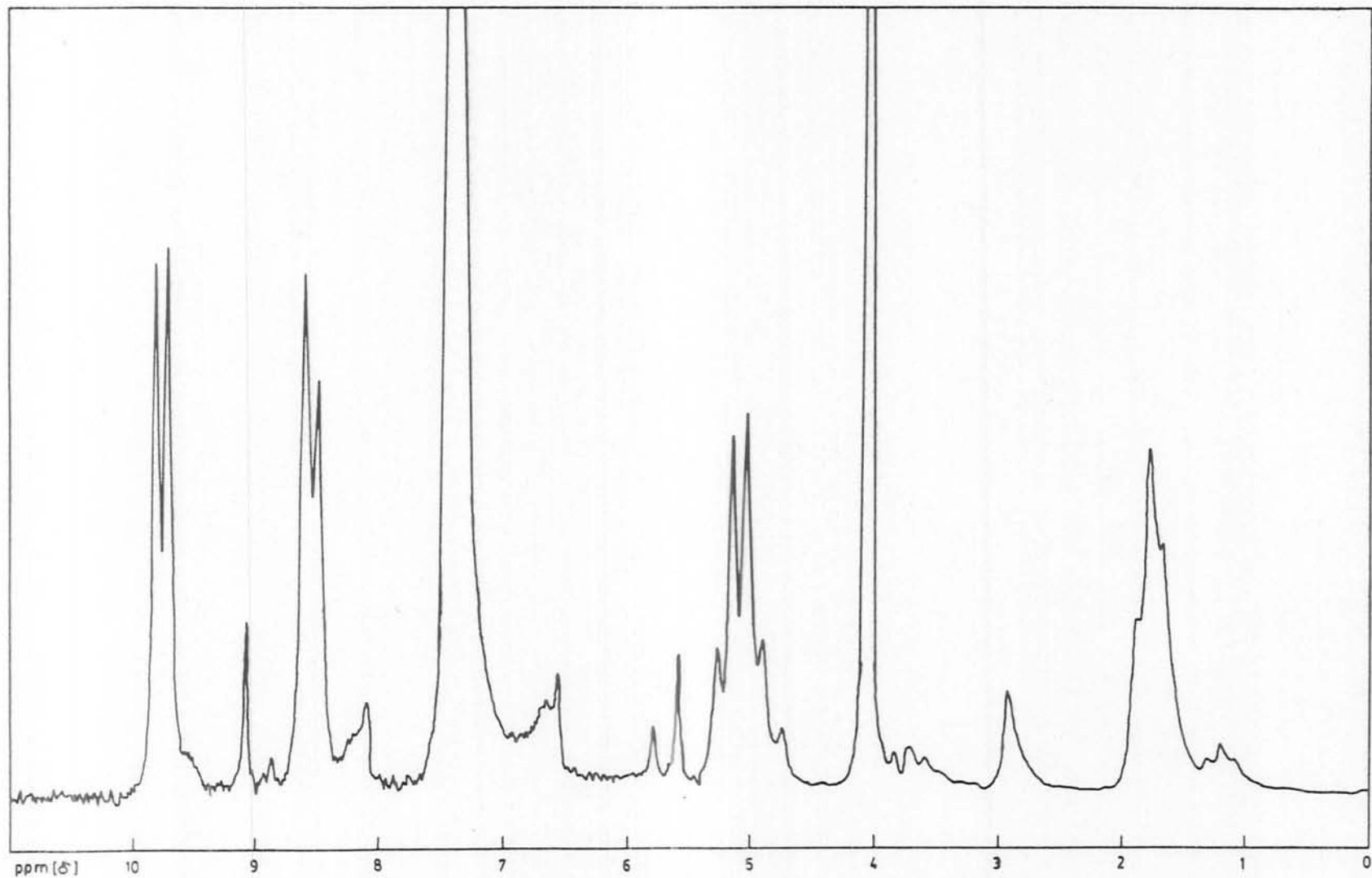
Fig. 4.6:   NMR Spectrum of 0.4M PyI Solvent Chloroform.

H_1 Level 0.5 ; Filter 20 (Hz); Sweep Width (Hz) 600; Sweep Time (Sec) 250
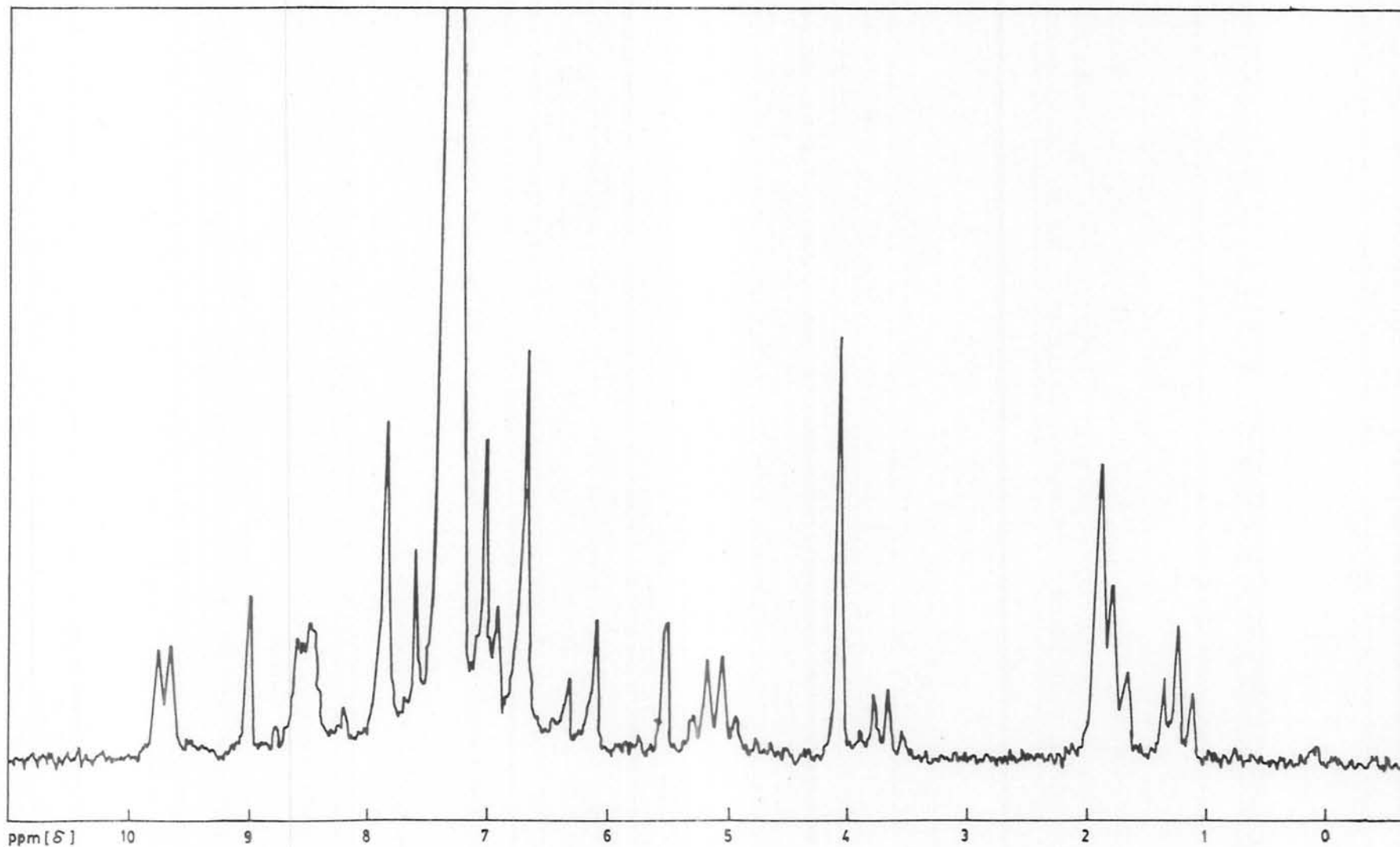
Amplitude ——— 10 x 10

Fig. 4.7: NMR Spectrum of 0.05M PyI; Solvent Chloroform.

H$_1$ Level 0.5; Filter 20 (Hz); Sweep width (Hz) 600; Sweep Time (Sec) 250;

Amplitude ——— 10 x 10.
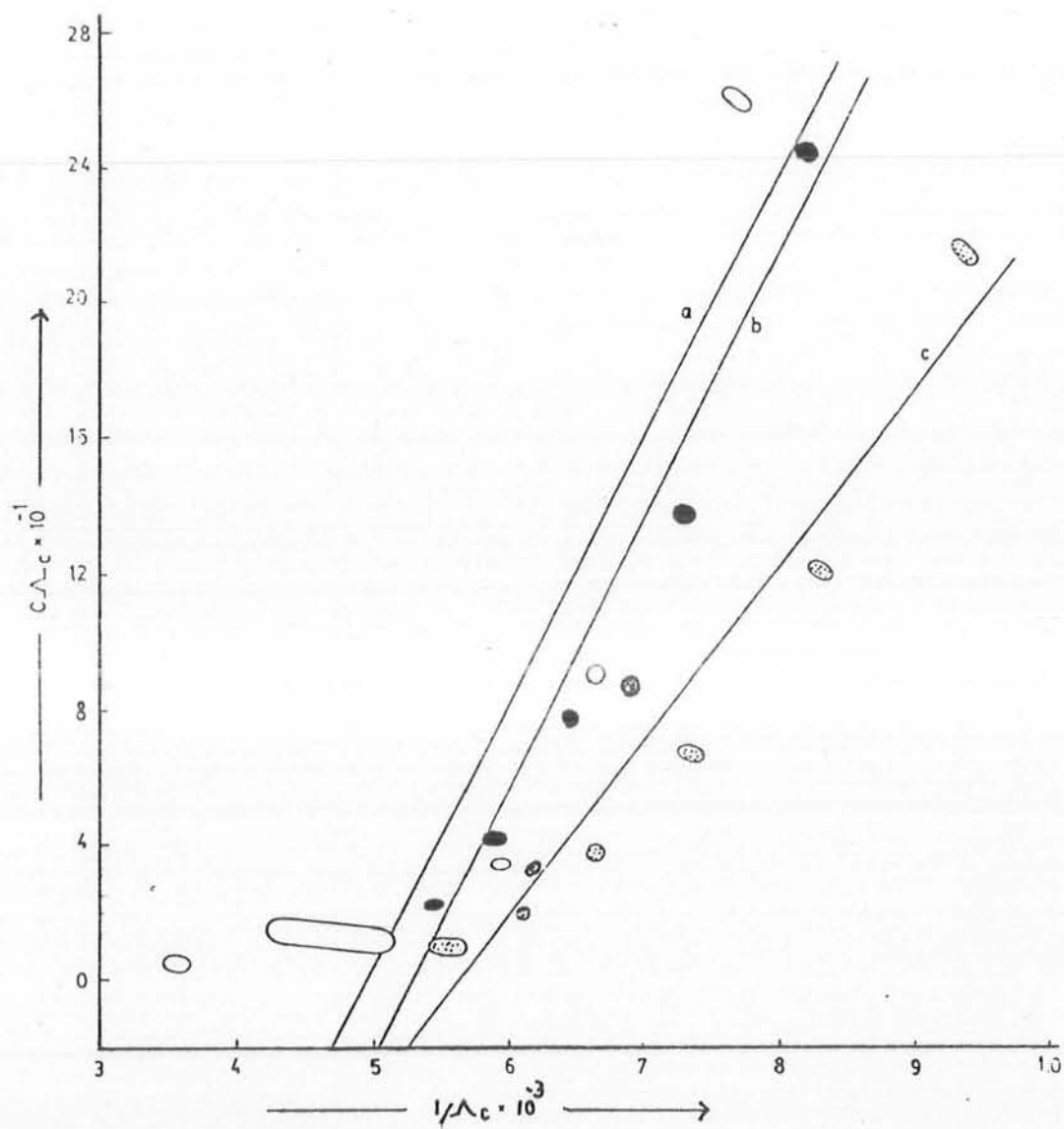
Fig. 4.8: Plots of C Λc   Vs. 1/ Λc for PyI in acetonitrile
at temperatures,

a) $34.5^{\circ} \pm 1^{\circ}C$

b) $28^{\circ} \pm 1^{\circ}C$

c) $25^{\circ} \pm 2^{\circ}C$
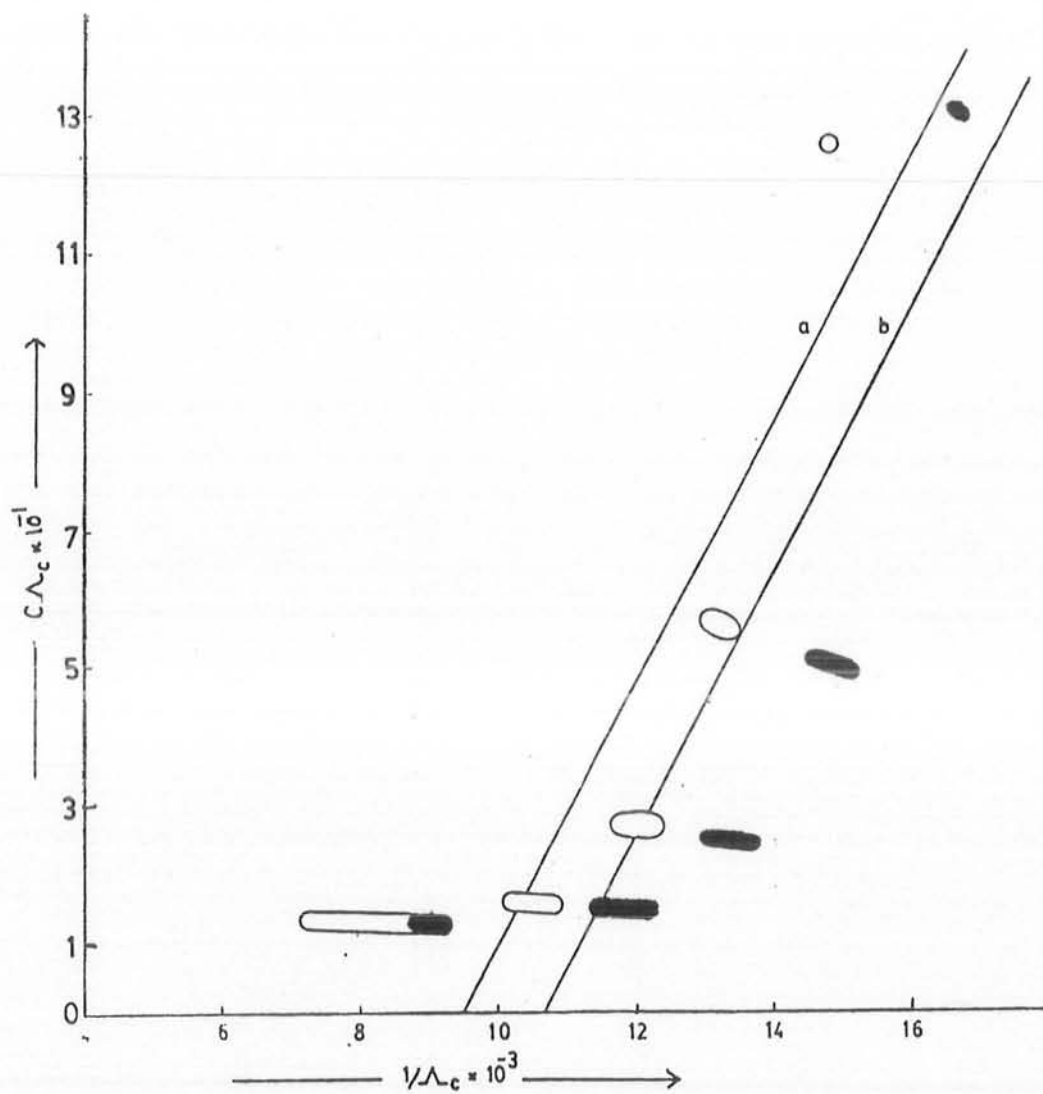
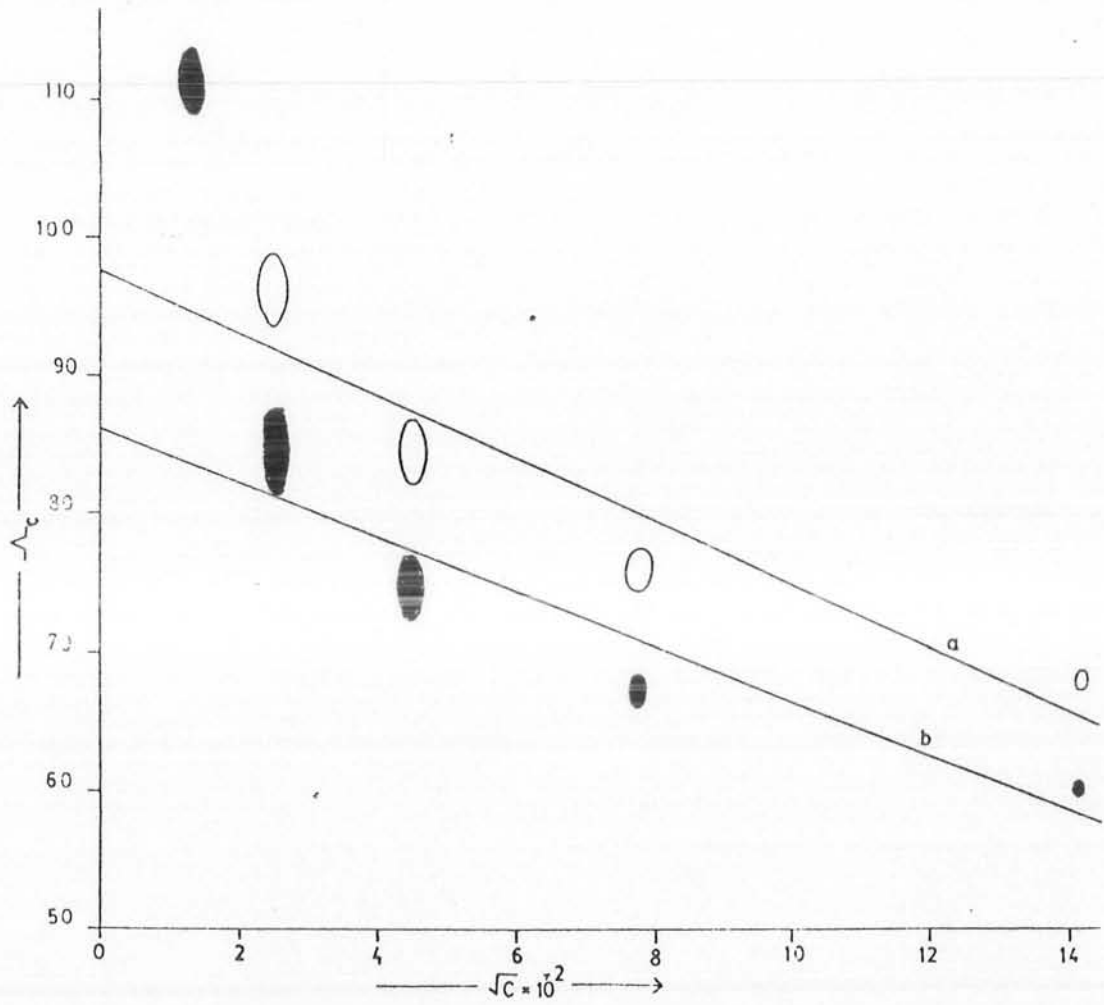Fig. 4.9: Plots of C Λc Vs. 1/Λc for PyI in D.M.F. at temperatures,

a) $33^{\circ} \pm 1^{\circ}C$

b) $25^{\circ} \pm 1^{\circ}C$

Fig. 4.10: Plots of C Λc Vs. 1/Λc for PyI in methanol
at temperatures,

a) $40^\circ \pm 3^\circ C$ b) $30^\circ \pm 1^\circ C$
c) $26^\circ \pm 1^\circ C$ d) $25^\circ \pm 1^\circ C$
e) $25^\circ \pm 1^\circ C$ f) $25^\circ \pm 3^\circ C$

Fig. 4.11: Plots of C Λc Vs. 1/ Λc for PyI in acetone at temperatures,

      ○ a) $33° \pm 2°C$

      ● b) $25° \pm 2°C$

      ⊛ c) $26° \pm 3°C$
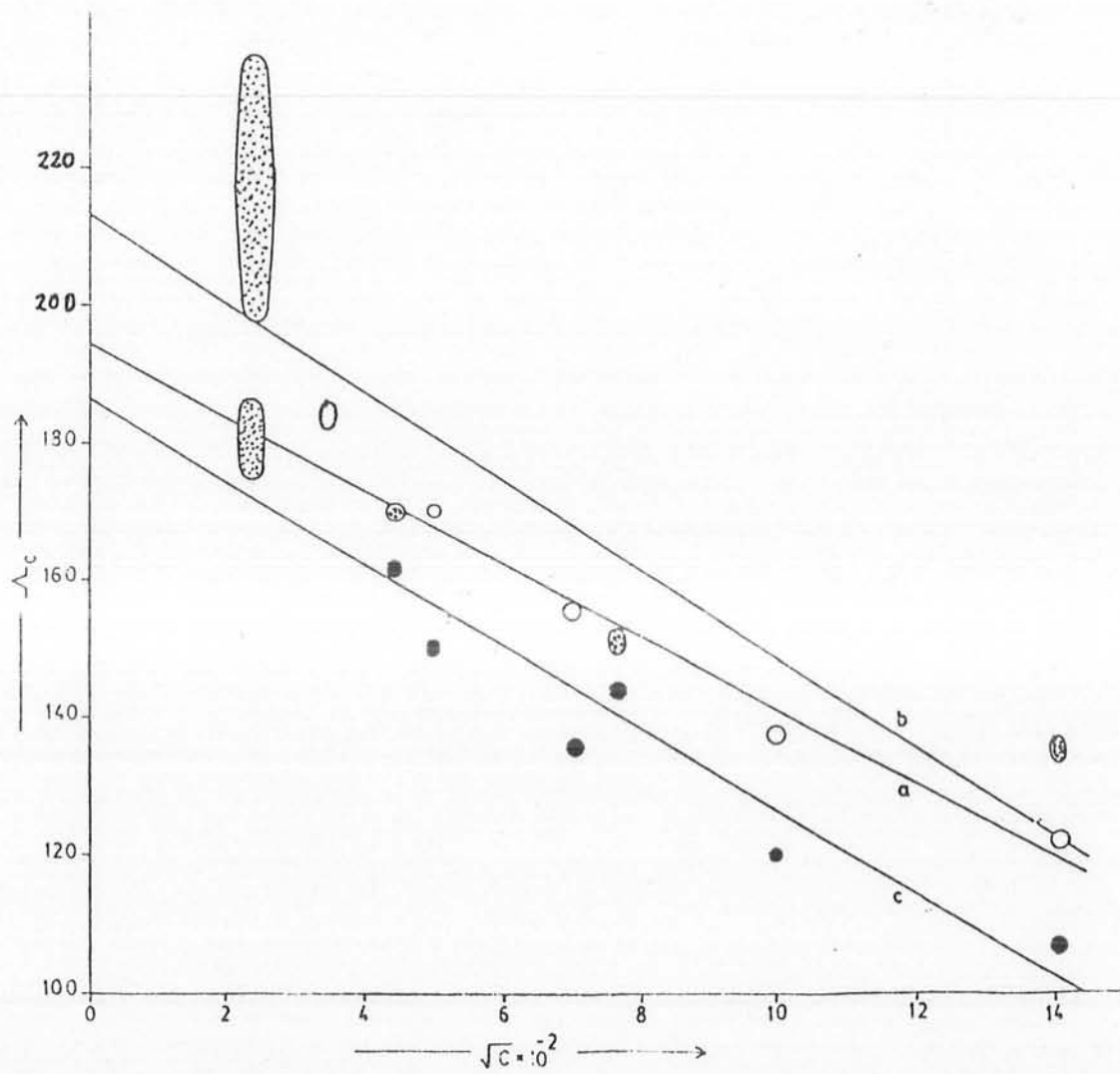
Fig. 4.12: Plots of Λc Vs. $\sqrt{c}$ for PyI in acetonirile at temperatures,

○ a) 34.5° ± 1°C

◐ b) 28° ± 1°C

● c) 25° ± 2°C

Fig. 4.13: Plots of Λc Vs. $\sqrt{c}$ for PyI in D.M.F. at temperatures

a) $33° \pm 1°C$

b) $25° \pm 1°C$
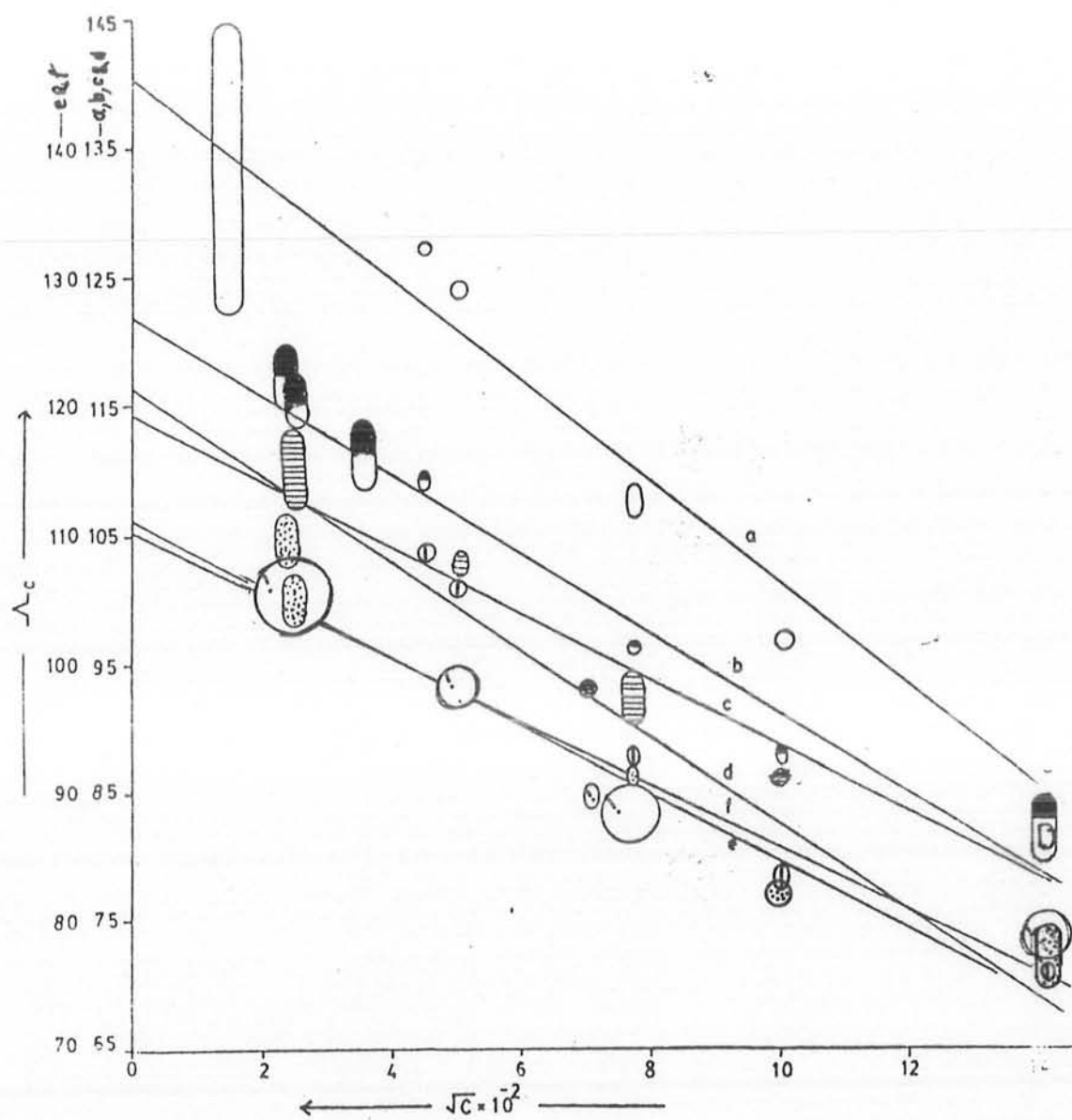
Fig.4.14: Plots of Λ_c Vs. $\sqrt{c}$ for PyI in methanol at temperatures

a) $40° \pm 3°C$: b) $30°\pm1°C$

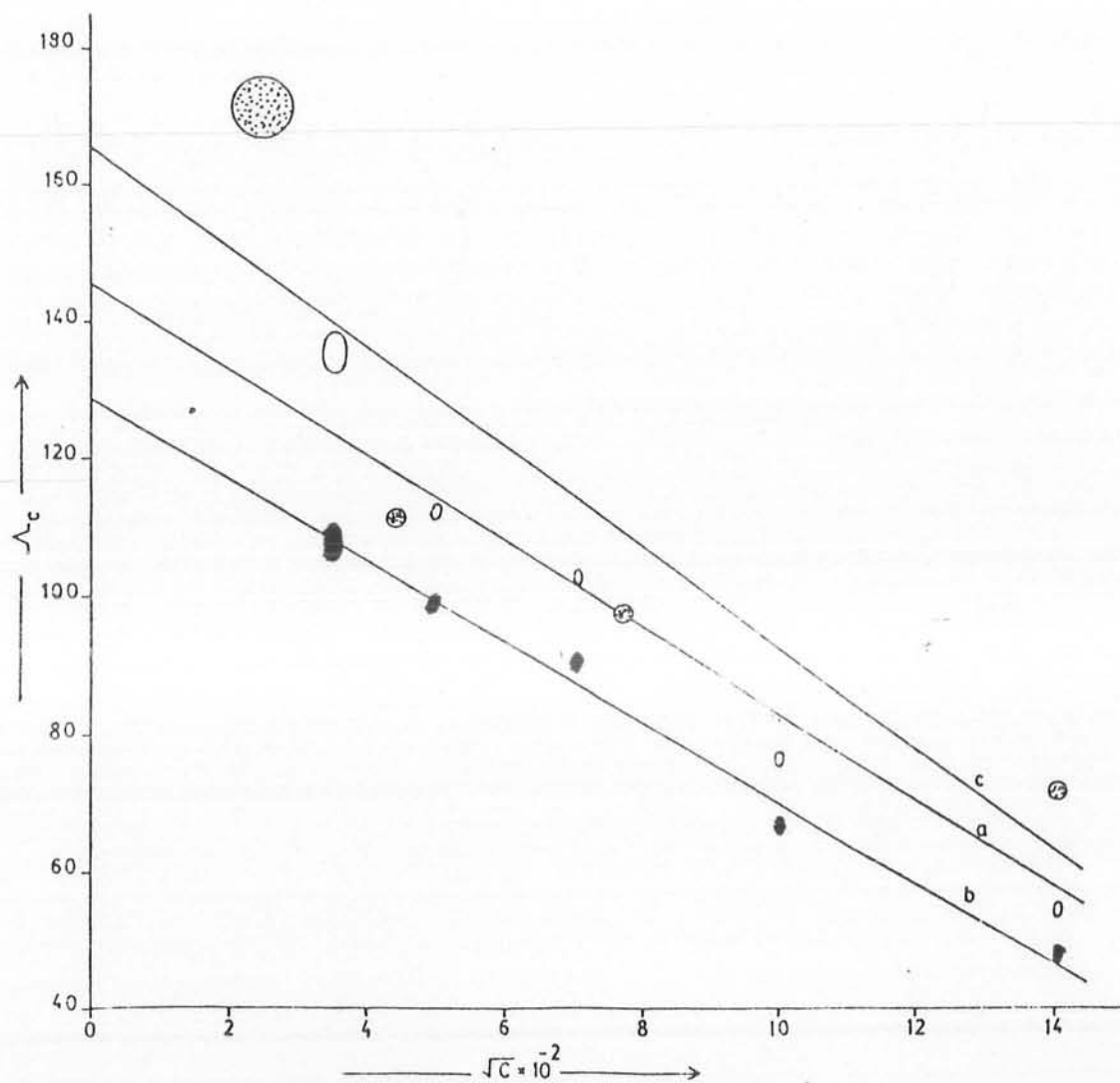c) $26° \pm 1°C$: d) $25°\pm1°C$

e) $25° \pm 1°C$: f) $25°\pm3°C$

Fig. 4.15: Plots of Λ_c Vs. $\sqrt{c}$ for PyI in acetone at temperatures

O a) $33^{\circ} \pm 2^{\circ}C$

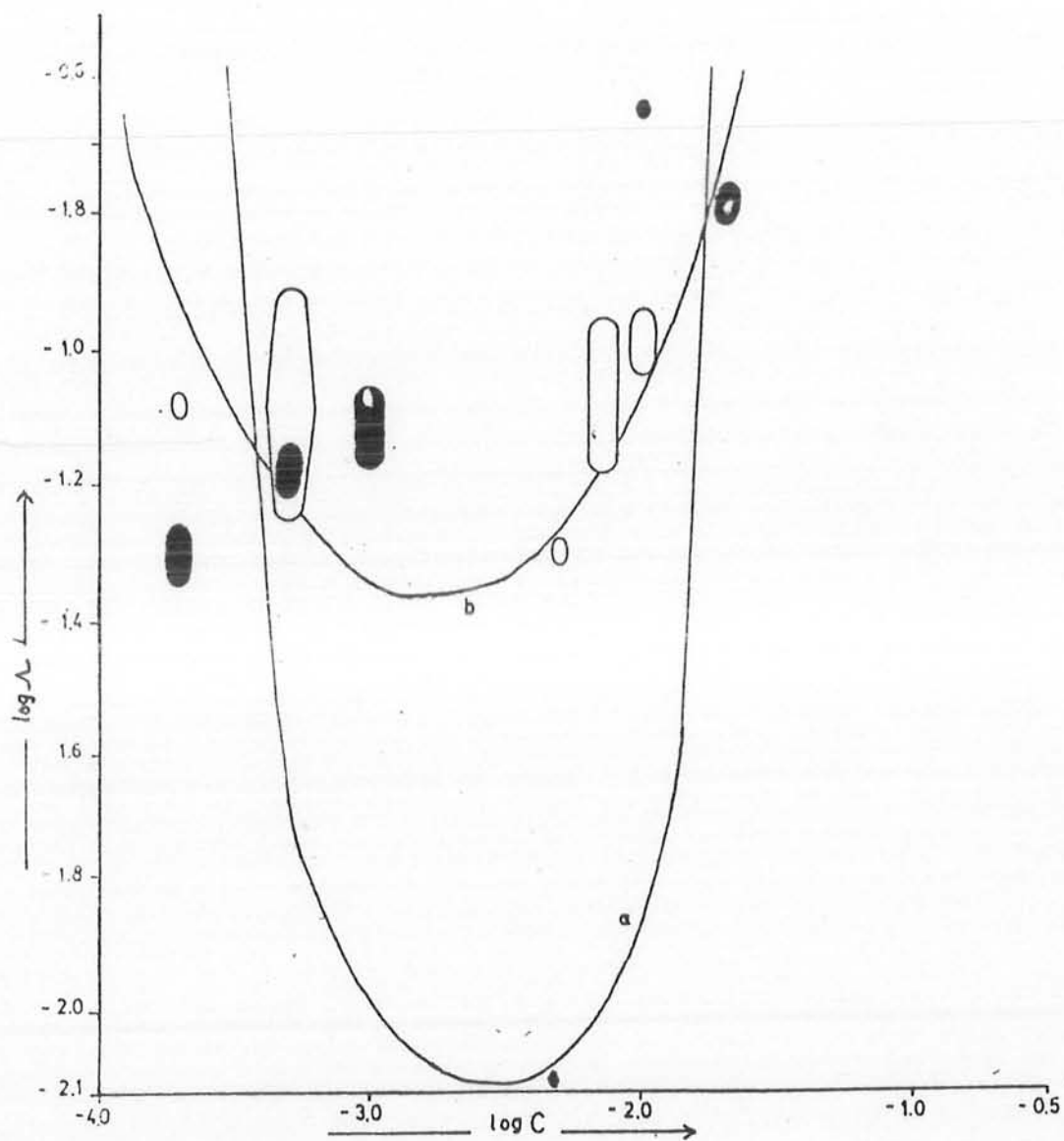● b) $25^{\circ} \pm 2^{\circ}C$

⊚ c) $26^{\circ} \pm 3^{\circ}C$

Fig. 4.16: Log Λ Vs. log C plots for PyI in $CHCl_3$ at temperatures

a) $36.5^{\circ} \pm 1^{\circ}C$

b) $26.5^{\circ} \pm 2^{\circ}C$

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