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"INVESTIGATION INTO THE NATURE OF COMPLEXES FORMED BETWEEN ORGANIC ACIDS AND BASES IN APROTIC SOLVENTS"

A Thesis submitted in fulfilment of the
requirements for the degree of Ph.D.,
University of London, 1968.

by

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ABSTRACT

The work described in this thesis consists of an investigation into the nature of the complexes formed between organic acids and bases in aprotic solvents. The physical techniques employed were dielectric constant measurement and nuclear magnetic resonance (n.m.r.) respectively.

The first section of the thesis consists of a summary of the properties of hydrogen-bonded systems and of the theories concerning the nature of the hydrogen bond.

The second section deals firstly with the methods based on dielectric constant determination which have been used for the simultaneous determination of association constant and dipole moment of these complexes. This is followed by an account of the determination of both association constant and dipole moment of several complexes of acetic acid with heterocyclic bases. This work was carried out with the object of establishing:

(i) Whether or not there exists a valid method for the simultaneous determination of association constant and dipole moment from dielectric constants.

(ii) Whether or not the dipole moment change in the components on complex formation can be found with sufficient accuracy to throw light on the nature of the bonding between acid and base.

Computer program~~me~~s were developed to assist the determination of both association constant and dipole moment. This technique is particularly helpful in cases where one of the components of the mixture is strongly self-associated, but should be of general use. The results suggested that little charge transfer accompanied hydrogen bond formation.

The third section consists of an account of the n.m.r. spectra of acetic acid dissolved in benzene, cyclohexane and several heterocyclic bases. The results were consistent with the view that little charge transfer is associated with the hydrogen bonding between acetic acid and those bases.

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"Absolute certainty is a privilege of uneducated minds - and fanatics. It is for scientific folk an unattainable ideal".

C.J. Keyser

ACKNOWLEDGEMENTS

The writer wishes to express thanks to Professor J.W. Smith, Bedford College, for his constant help and encouragement. He also wishes to thank Professor P.B.D. de la Mare, Bedford College, for providing the facilities that made this investigation possible and the Science Research Council for a studentship.

A. GENERAL INTRODUCTION TO HYDROGEN BONDING

(1) Nature of the Hydrogen Bond

The aim of this research was to investigate the nature of the complexes formed by the interaction of organic acids and bases in aprotic solvents. To contribute to this end, the dipole moments of the complexes and association constants of complex formation were determined. Nuclear Magnetic Resonance (n.m.r.) spectra were also determined. This information has served as a basis for discussion of the nature of these complexes.

Many years ago it was recognised [1] that special theories were necessary to explain the behaviour of associated compounds. A particularly tenacious interaction was recognised in molecules with hydrogen-containing functional groups. In 1903 Werner [2] proposed that an ammonium salt has a configuration in which a proton lies between the ammonia molecule and the ion, i.e. $(H_3N\ldots\ldots H)X$. This idea was developed further by Moore and Winmill [3] who proposed a hydrogen-bonded structure of undissociated trimethyl ammonium hydroxide.

In 1920 Latimer and Rodebush [4] recognised the cause of the association of water and also the cause of its peculiar physical and chemical properties. From these beginnings has grown up an immense amount of research into the nature of hydrogen bonding.

Today, this subject presents a challenge to the chemist, in that it can be regarded as the borderland between the fields of strong chemical bonds and those weaker interactions responsible for liquefaction at sufficiently low temperatures. It is difficult to define this interaction in precise terms; indeed, E.B. Wilson, Jnr. [5] once observed that a precise definition usually evokes criticism from two directions. This is particularly pertinent to the case of the hydrogen bond but for the purposes of this thesis a hydrogen bond can be said to exist between a functional group AH and an atom or group of atoms B in the same or a different molecule when there is evidence for bond formation and further there is evidence for an interaction between AH and B specifically involving the hydrogen atom already bonded to A. This definition leads immediately to the question of what groups form hydrogen bonds. Pauling [6] noted that chemists talk about bonds when convenience dictates identifying a group of atoms as an entity. The hydrogen bond A-H...B is usually considered to be a bond in which a hydrogen atom lies between two closely spaced electronegative atoms A and B, e.g. oxygen, nitrogen or fluorine. There are, however, other systems not universally accepted as hydrogen bonding systems, chloroform and pyridine, self association of hydrogen cyanide, in both of which a C-H bond appears to bond to nitrogen. There is evidence for hydrogen bonding of acetylenic C-H bonds, and there is also good evidence for hydrogen bonding between Lewis acids and aromatic hydrocarbons acting as bases.[7] In fact, the phenomenon of hydrogen bonding is more widespread than one would first imagine. The operational definition of a hydrogen bond given earlier permits examination of evidence for hydrogen bonding in systems not generally considered to involve this type of interaction.

(2) Properties of hydrogen-bonded substances

The formation of a hydrogen bond in a solution or in a compound modifies a great many physical and a few chemical properties. These changes are not surprising in light of the fact that hydrogen bonding alters the electronic structure of the functional groups concerned. The most commonly observed physical property modifications are frequency shifts of Infra-Red and Raman bands, altered freezing and boiling points, changed dielectric properties and proton magnetic resonance shifts. Other properties which are affected include liquid and vapour densities, molar volume, viscosity, electronic spectra and thermal conductivity.

These various effects may be classified by briefly considering the changes in the molecule which are responsible for the changes in observed properties. For example, the spectral changes indicate altered electron arrangements and positions of atoms in the neighbourhood of donor groups. Deviations from ideal gas and solution laws are caused principally by the increased molecular weight resulting when one complex unit is formed from two or more simpler units. Electrical properties are abnormal for hydrogen-bonded substances because the dipoles are affected by the positions of the hydrogen atoms, and, in many materials the dipoles are aligned in special orderly arrangements by polymeric complexing. An obvious example of this is water.

(3) Methods of Detection of Hydrogen bonds

(a) Non-Spectroscopic

Hydrogen bonds were first detected through solubility studies [1] and were quickly found by the many other non-spectroscopic techniques available in the first quarter of the twentieth century. Several reviews of hydrogen bonding systems [8,9] and their non-spectral properties exist. Non spectroscopic methods of detection depend on the fact that the engagement of a group in hydrogen bond formation modifies the physical, and to a lesser extent the chemical properties of the group concerned. The methods therefore consists of a comparison of properties displayed by the substance suspected to have a hydrogen-bonded structure with those of similar substances known not to have a hydrogen-bonded structure. Alternatively the actual value of a particular physical property may be compared with a predicted value of that property. This predicted value is the value expected assuming no hydrogen bond formation.

For example, the viscosity of an associated substance is commonly higher than that of similar non associated compounds. This greater viscosity is reasonable in view of the increased size and reduced mobility of molecules of the associated substance. The effect of hydrogen bonding on some physicochemical properties of liquids is summarised in the below table:

TABLE A.1.

Property	Behaviour of intermolecular hydrogen bonded compound relative to non hydrogen bonded compound
Molar Volune	Lower
Density	Higher
Molar Polarisation	Higher
Thermal Conductivity	Higher
Viscosity	Higher
Surface Tension	Higher

To illustrate this table let us consider the effect of hydrogen bonding on the thermal conductivity of a liquid. Palmer [10] has shown that it probably assists the conductivity in two ways; firstly by causing the molecule to orientate itself in the direction of heat flow and secondly by affording an additional method for the transfer of heat energy to take place.

The use of electrical measurements has been fairly important in the study of hydrogen bonding. One of the most important results of hydrogen bonding in liquids such as water, hydrogen cyanide and hydrogen fluoride is the high dielectric constant compared with other compounds with a similar dipole moment. The molecular polarisation of such substances is affected not only by changes in dielectric constant but also by the high densities of these liquids resulting from this association. The effect of hydrogen bonding on dielectric constant or dipole moment is complex. However, the following generalisations are valid:

(a) Dielectric constant, ε, and dipole moment, μ, do not increase together, i.e. high ε does not necessarily mean high μ.

(b) High values of ε are usually found in intermolecularly hydrogen bonded substances in which non cyclic association occurs, e.g. H_2O.

(c) Low values of ε are usually found in intramolecularly hydrogen bonded substances, e.g. salicaldehyde.

(d) The arrangement of atoms within a molecule, and with less confidence of molecules within a polymeric unit can be determined by comparing the measured dipole moment with values calculated by the vectorial addition of bond moments for various arrangements.

(e) Hydrogen bond formation between the components of a mixture can be inferred in the same way as (d).

These topics will be dealt with at greater length later in this thesis.

A second general dielectric method is the measurement of dispersion or loss. This involves the measurement of the dielectric constant over a range of frequencies in the microwave or short radio wave region, where dispersion can be related to molecular properties. In general dispersion phenomena occur when the response of a system lags behind the exciting force. In dielectric substances such a lag indicates that a finite time period accompanies some type of rearrangement within the molecule. This finite period is called the relaxation time, τ , and varies with the form of the rearrangement. Hasted and co-workers [11] found that water-dioxane mixtures had longer relaxation times as the proportion of dioxane increased or the temperature was lowered. Both these trends can be explained by the formation of a hydrogen bonded complex.

TABLE A.2.

Type of Relaxation Process	Relaxation Times
Electronic	10^{-15} sec.
Atomic	10^{-12} to 10^{-14} sec.
Dipole-Molecular Gas	10^{-12} sec.
Dipole-Molecular liquid	10^{-10} to 10^{-11} sec.
Dipole-Molecular viscous liquid	10^{-6} sec.
Dipole-Molecular solids and extremely viscous liquids	10^{-2} to 10^{2} sec.

Table A.2 gives some indication of the lengths of various relaxation processes.

In summary these conclusions are well established. Firstly, hydrogen bonds occur in all three phases of matter and are less common as temperature increases. Secondly, hydrogen bonding may be detected more or less easily by any physico-chemical test method. However, tests applied to solutions and pure liquids which are of the greatest interest suffer from an incomplete theoretical treatment of these states. At present, with the exception of spectral studies, dielectric measurements give the most information about hydrogen bonding though cryoscopic and solubility investigations are very valuable.

(b) Spectroscopic

This section deals with spectroscopic methods of detecting hydrogen bonding in all phases of matter. Any such account must first look at Infra Red (I.R.) Spectroscopy for it was the realisation that the I.R. spectrum provides a criterion for detection of hydrogen bonds [12] which first established I.R. Spectroscopy as an analytical tool in chemistry. The most prominent effect of hydrogen bonding on the vibrational spectrum is the shift of the absorption of the A-H stretching mode and its harmonics to lower frequencies. This was first observed for a number of compounds which form intermolecular hydrogen bonds. A little earlier it had been found [13] that the intensity and frequency of the O-H stretching mode of an alcohol were dependent on concentration and temperature. This behaviour was attributed to molecular association. Soon it was generally realised that the I.R. spectrum provided a criterion for detecting hydrogen bonding. The effect of hydrogen bonding on the A-H stretching mode is complex in that as well as the shift in frequency, there are changes in the half width and integrated absorption coefficient. The half width of the fundamental and its harmonics are both broadened and while the integrated absorption coefficient of the fundamental is increased many-fold, the corresponding coefficients for the harmonics are decreased slightly. All these effects are for the most part equally applicable to Raman spectroscopy. Both these spectroscopic techniques reveal the characteristic vibrational frequencies of a molecule, and for most molecules both are needed before the vibrational pattern can be fully understood. In addition to these two there are other valuable spectroscopic techniques for examining hydrogen-bonding systems. Hydrogen bonding will alter the ultra-violet-visible spectrum of a molecule if the chromophoric portion of the molecule is perturbed by the hydrogen bond. The recognition and interpretation of the effect of hydrogen bonding on electronic transitions has been inhibited by the difficulty of distinguishing it from non hydrogen bonding solvent interactions. Nagakura and Baba[143] were first to recognise the effect hydrogen bonding could have on the visible and ultra-violet (u.v.) spectra. Since then numerous examples have been reported including an interesting recent observation by Nagakura and Kaya[154] who noticed shifts in the characteristic absorption bands of amides in the vacuo u.v. region. These shifts were attributed by the authors to hydrogen bond formation, and in particular the shift to higher frequency to ring dimer formation, and the shift to lower frequency to chain dimer formation.

Since 1950 there has been a rapid development of the use of nuclear magnetic resonance (n.m.r.) spectroscopy for the investigation of molecular structure. The hydrogen bond is one of the specific bonding situations mostsuited to investigation by n.m.r. This will be dealt with later in this thesis. For the moment it will suffice to say that this technique is probably as valuable as I.R. spectroscopy.

(4) Theoretical treatment of the hydrogen bond

Progress towards the development of an all embracing theory of the nature of the hydrogen bond has been somewhat disappointing. Pauling [15] considered that the hydrogen bond must be electrostatic in nature. His model of the hydrogen bond was based on the Valence Bond representation of chemical bonds and cites the Pauli Exclusion Principle as well as a considerable volume of chemical evidence in its support. Pauling argued that a hydrogen atom with only one stable orbital cannot form more than one pure covalent bond as the bond forming power of the outer orbitals was negligibly small. In reply to the suggestion that use might be made of an L [x] orbital to form a second covalent bond he argued [17] that if an A-H bond with little ionic character is formed then the proton is almost completely shielded by its half of the shared electron pair and accordingly has no power to attract an L electron. Further if the A-H bond was sufficiently ionic to

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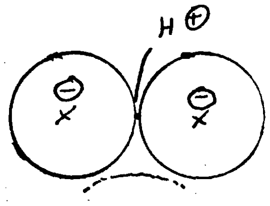
[x] L orbital means one for which the principal quantum number, $n = 2$.

attract an L electron then the proton could use its IS orbital for covalent bond formation and so would not need to call upon the unstable L orbital.

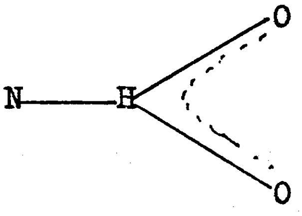
This electrostatic picture of the hydrogen bond serves to explain a great many of its observed properties. For example, the hydrogen is normally a bond by hydrogen between two atoms. The positive hydrogen ion is a bare proton with no occupied electron shell around it. This small action would attract one anion (shown below as a rigid sphere of finite radius) to the equilibrium internuclear distance equal to the anion radius and could then similarly attract a second anion to form a stable complex.

Figure A.1.



A third anion would be prevented from approaching close to the proton by anion-anion contacts. Exceptions to the general rule that the co-ordination number of hydrogen does not exceed two are rare. One interesting example is cited by Albrecht and Corey [18] in which they showedthat the crystal structure of glycine contained what appeared to be a bifurcated hydrogen bond.

Figure A.2.



Secondly, only the more electronegative atoms should form hydrogen bonds, and the strength of the bond should increase with increase in the electronegatuities of the two bonded atoms. It is found that fluorine forms very strong hydrogen bonds, oxygen weaker ones, and nitrogen still weaker ones. Although it has the same electronegativity as nitrogen, chlorine has only a very small hydrogen bond forming power; this may be attributed to its large size relative to nitrogen which causes its electrostatic interactions to be weaker than those of nitrogen.

If, however, only electrostatic forces were involved in hydrogen bonding then one would expect that the dipole moment, μ, of the electron donor B would be the controlling factor in determing the strength of an A-H....B formed with any one A-H. This, however, is not the case. It is now realised that electron delocalisation effects arising from the mutual polarisation of the two molecules, repulsive forces between doubly filled orbitals in the molecules, and dispersion forces of the London/Van der Waals type must be taken into consideration. Sokolov[19] suggested that if only the electrons associated with the A-H bond and the lone pair on B are to be taken into account, then three structures must be combined in describing the state of the linkage:

(1)	A-H B	Pure covalent link
(2)	$A^{(-)}$ $H^{(+)}$ B	Pure ionic link, no charge transfer
(3)	$A^{(-)}$ $H\text{-}B^{(+)}$	Charge transfer, H-B bonding

This work was extended by Coulson and Danielsson[20] using the same basic three structures but alternative empirical relationships. Tsubomara[21] added two further contributing structures:

(4) $A^{(+)} H^{(-)} B$ Pure ionic, no charge transfer
(5) $H^{(-)} A\text{-}B^{(+)}$ Charge transfer, A-B bonding

The complete calculation of the relative weights of these structures is prohibitively difficult. Tsubomara attempted it in the case of the $O_1 - H....O_2$ bond between two water molecules. Taking the $O_1....O_2$ distance to be 2·70 Å he estimated the weights to be:

(1) 70% (2) 8% (3) 1% (4) 19% (5) 1%

Now a distance of 2·70 Å should correspond to a rather weak hydrogen bond and consequently the weights of (3) and (5) should be small but one would not expect the weight of (4) to exceed that of (2). It is likely that using some of the more recently developed approximations to perform similar calculations, one might obtain more sensible results. Further it would be sensible to choose rather different orbitals from those used by Tsubomara.

There has always been considerable doubt regarding the appropriate law to use for the overlap repulsion force. Theory would suggest a force obeying an exponential type relationship e^{-br} between neutral atoms. However, in this case the atoms are not neutral, furthermore the existence of partial covalent bonding expressed by structures 3 and 5 must imply that the simple description of these overlap forces is inadequate.

Ever since London's pioneer work it has been generally agreed that dispersion forces contribute to all intermolecular and interatomic potentials. There are, however, difficulties in any estimate of their magnitude in the case of hydrogen bonding. The most serious of these is that the atoms in question are too close together for the customary analysis of dispersion forces to apply. There is a further difficulty in applying formulae derived for isolated atoms, for we must clearly exclude the electrons utilised in an electron-pair bond. Yet it is these electrons which would be the most highly polarisable and would therefore contribute most to the dispersion energy.

The molecular orbital description of the hydrogen bond has received surprisingly little attention. Pimental [22] discussed the structure of the bifluoride ion in terms of molecular orbitals formed by a linear combination of atomic orbitals. Using only fluorine orbitals directed along the bond (p_A and p_B) and the hydrogen atom IS orbital($\cancel{s}$) three molecular orbitals result. These are shown in Table A.3. (not normalised).

Figure A.3.

A H .... B

p_A s p_B

TABLE A.3.

Molecular Orbitals for Hydrogen Bond Formation

	Symmetrical Hydrogen Bond	Unsymmetrical Hydrogen Bond	No Bond
$_3$antibonding	$(p_A - p_B) - a_3s$	$(p_A - b_3p_B) - a_3s$	$(p_A - a_3s)$
$_2$nonbonding	$(p_A + p_B)$	$(b_2p_A + p_B)$	p_B
$_1$bonding	$(p_A - p_B) + a_1s$	$(p_A - b_1p_B) + a_1s$	$(p_A + a_1s)$

Into these three molecular orbitals have to go four electrons. The ground state would involve both the bonding and non bonding molecular orbitals. This description can be extended to unsymmetrical hydrogen bonds. In each orbital the coefficient b decreases from unity to zero as B is moved away from a symmetrical position. When the distance is sufficiently large no hydrogen bond exists, the pair of electrons in ψ_1 forms the A-H bond, and the other pair is located on the base atom B. It is interesting to compare this picture of an hydrogen bond to the three centre orbitals proposed by Lipscomb and co-workers [23] for the borane B-H-B bridges. The principal difference is that the bifluoride ion case involves four electrons, hence the non bonding orbital must be utilised. Whilst the borane is electron deficient, only the bonding orbital being occupied by an electron pair. Since this implies high charge on the terminal atoms, the bond will be most stable if these atoms are highly electronegative.

Another approach to this problem is to assume an explicit form for the potential function associated with the movement of the hydrogen atom in the hydrogen bond. The most developed such function is due to Lipincott and Schroeder [24,25] and is written as the sum of four terms.

$$V_{A-H....Y} = V_1 + V_2 + V_3 + V_4 \qquad (1)$$

where $$V_1 = D_o \left\{ 1 - \exp\left[\frac{-n(r-r_o)^2}{2r}\right] \right\} \; ;$$

$$V_2 = D_o^x \left[1 - \exp\left[\frac{-n^x(r^x-r_o^x)^2}{2r^x}\right] \right] - D_o^x \; ;$$

$$V_3 = A\,[\exp(-bR)]; \quad V_4 = -\frac{B}{R^m} \; ;$$

In V_1 r = A-H internuclear distance, r_0 = A-H internuclear distance in the absence of the hydrogen bond, D_0 = A-H dissociation energy. In V_2, r^*, r_0^*, D_0^* have the same meaning for the B-H bond. The third and fourth terms represent the Van der Waals' repulsion force and the electrostatic attraction between A and B.

The usefulness of the function, like that of the Morse function for diatomic molecules depends on its applicability to observational data. Unfortunately it does not possess the virtue of simplicity.

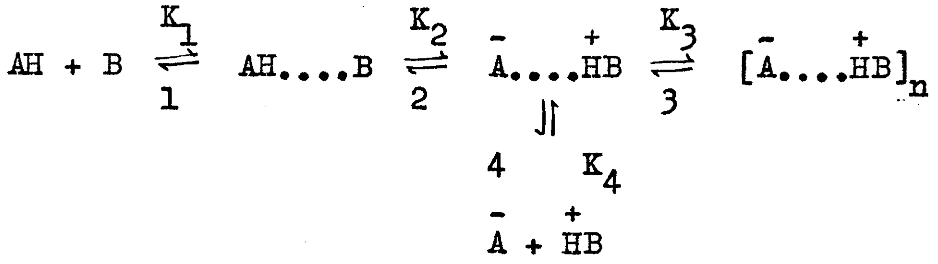
In summary there are two basic reasons for the substantial support enjoyed by the electrostatic model of the hydrogen bond. Firstly it avoids the clash of the hydrogen bond extravalency with our classical theory of the chemical bond. Secondly, it offers the possibility of quantitative calculation of hydrogen bond behaviour. Unfortunately some phenomena are not too amenable to this model. The covalent description has appeal from this stand-point explaining some behaviour not readily explained by the electrostatic model. However, it does have the difficulty of fitting extravalency into our present valence bond understanding of the chemical bond. This difficulty may foreshadow a turn towards the molecular orbital approach.

B. MOLECULAR COMPLEXES. SIMULTANEOUS DETERMINATION OF ASSOCIATION CONSTANT AND DIPOLE MOMENT

(1) Introduction

The formation of complexes between organic acids and bases may be represented as a series of equilibria.

Figure B.1.



$$\begin{array}{ccccccc} \mathrm{AH}+\mathrm{B} & \underset{1}{\overset{K_1}{\rightleftharpoons}} & \mathrm{AH....B} & \underset{2}{\overset{K_2}{\rightleftharpoons}} & \overset{-}{\mathrm{A}}....\overset{+}{\mathrm{HB}} & \underset{3}{\overset{K_3}{\rightleftharpoons}} & [\overset{-}{\mathrm{A}}....\overset{+}{\mathrm{HB}}]_n \\ &&&& 4 \ \updownarrow \ K_4 && \\ &&&& \overset{-}{\mathrm{A}}+\overset{+}{\mathrm{HB}} && \end{array}$$

The extent to which the equilibrium 1 is shifted to the right is very much dependent on the nature of AH and B. In general for a given acid AH, increase in the strength of the base will result in an increase in the tendency towards ion-pair formation rather than existence in the hydrogen-bonded form. The last stage 4 in the equilibrium process can only occur appreciably in media of high dielectric constant. This investigation is concerned only with complex formation in benzene solution and consequently this stage can be ignored. At the same time, however, the position is complicated by the fact that in non-ionising solvents, carboxylic acids tend to associate, principally into dimers.

The association of dipolar molecules may lead to considerable changes in the dielectric polarisation of the medium in which they are contained; consequently dielectric constant measurements provide a good method for detecting the formation of molecular complexes in solution.

Before this work on molecular complexes was started an investigation into the molecular state of acetic acid in benzene solution was carried out.

(2) Previous Work

(a) Acetic Acid

The problem of the structure of carboxylic acids in solution has attracted a considerable amount of attention. It is now generally accepted that at very low concentrations of acid, there exists an equilibrium between dimeric and monomeric species,

$$2M \rightleftharpoons D \quad ; \qquad K_{assn} = \frac{[D]}{[M]^2}$$

At higher concentrations there may well be further association to form polymeric species. Le Fèvre and Vine [26] measured the dielectric constants, refractive indices and densities of dilute solutions of acetic and chlorinated acetic acids in benzene. Their chosen concentration range was from 10^{-3} to 10^{-1} moles per litre. In the upper limit of such a concentration range their assumption that all the acid is present as an equilibrium between monomer and dimer and nothing else is probably incorrect. The authors did not evaluate μ_m or μ_D but instead from the variation of molecular polarisation with concentration showed that the stability of the dimeric form in an aprotic solvent does not increase with increase in acid strength. This was contrary to what had been expected, as it was thought that in a given series the electron withdrawing power of the $-CX_3$ group would operate to promote association. It should be pointed out that owing in part at least to acid association the acid strength measured in water is not necessarily a satisfactory criterion against which to compare the stabilities of acid-base complexes in an aprotic solvent.

Pohl, Hobbs, Gross and Marryot [27-29] in a series of papers studied the association of various carboxylic acids in both benzene and heptane solution. The concentrations used by these authors were lower than those used by Le Fèvre [26] [for example, in the case of acetic acid in benzene solution, the molar fraction range was from $5{\cdot}48 \times 10^{-5}$ to 1418×10^{-5}]. Table B.1. shows the results obtained for acetic acid.

TABLE B.1.

Solvent	m	D (Debye Units)	$K_{association}$ (K_d)
Benzene	1·68	0·94	370 l.mole^{-1}
n-Heptane	-	0·92	37,000 l.mole^{-1}

The authors state that the figures for heptane solution are less reliable than those obtained in benzene solution. The high value of K_d meant that it was impossible to obtain even a moderately accurate figure for the moment of the acid monomer in heptane solution. This work was probably the first reliable determination of the moment of the acid monomer. In this connection it is of interest to note that, from measurements of the dielectric constant of acetic acid vapour at various temperatures, Zahn [30] obtained a value of 1·73 Debye Units for the dipole moment of acetic acid monomer. The author assumed that at the temperatures used all the acid is present in the monomeric form. It is also interesting to speculate as to why the dimerisation constant in heptane should be so much greater than in benzene solution. One possible explanation is that a solute-solvent directed interaction between the acid monomer and a benzene molecule stabilises this form in solution. This idea will be discussed at greater length in the section dealing with nuclear magnetic resonance spectroscopy.

Pohl and co-workers found evidence for the suggestion that there is a systematic relationship between K_d and the ionisation constant, K_i, amongst acids in the aliphatic series. This is contrary to the findings of Le Fèvre and Vine,[26] but it should be pointed out that the findings of Le Fèvre and Vine were based on measurements at concentrations much higher than those of Pohl and co-workers, so less reliance should be placed on their findings. The table below summarises the findings of Pohl and co-workers.

TABLE B.2.

Acid	K_d, benzene solution	K_i, aqueous solution
Propionic	390 l.m.$^{-1}$	$1{\cdot}4 \times 10^{-5}$
Acetic	370 l.m.$^{-1}$	$1{\cdot}86 \times 10^{-5}$
Formic	126 l.m.$^{-1}$	$21{\cdot}4 \times 10^{-5}$
Chloroacetic	102 l.m.$^{-1}$	155×10^{-5}

The method of calculation used by the authors to determine both K_d and the dipole moments of acid monomer and dimer from the variation of dielectric constant with concentration is of considerable interest. This method was originated by Pohl, Hobbs and Gross in an earlier paper.[31] The authors postulated that at low acid concentrations an equilibrium would be set up between dimer and monomer.

$$D \rightleftharpoons 2M$$

$$\frac{1}{K_d} = K_{diss} = \frac{C_M^2}{C_D V} \qquad (1)$$

where C_M, C_D are equal to the number of moles of monomer and dimer respectively, per mole of solvent, and V = molar volume of the solvent. The dissociation constant,

K_{diss}, can be expressed in terms of polarisations according to the equation below:

$$K_{dissn} = \frac{(P_2 - \frac{P_D}{2})^2 . 2f_2}{(P_M - P_2)(P_M - \frac{\cancel{P}}{2})^{P_D/2}} \qquad (2)$$

where P_2 = molar polarisation of the solute based on the molecular weight of the monomer at a mole fraction f_2.

P_M = molar polarisation of the monomeric molecules at infinite dilution.

P_D = molar polarisation of the dimeric molecules at infinite dilution.

f_2 = mole fraction of solute based on molecular weight of monomer.

(2) may be re-expressed:

$$K_{dissn} = \frac{2K_o}{(P_M - \frac{P_D}{2})} \qquad (3)$$

where K_o is defined by the above equation. Consequently, we obtain:

$$\frac{2K_o}{(P_M - \frac{P_D}{2})} = \frac{(P_2 - \frac{P_D}{2})^2 . 2f_2}{(P_M - P_2)(P_M - \frac{P_D}{2})}$$

i.e. $$K_o (P_M - P_2) = f_2 (P_2 - \frac{P_D}{2})^2$$

from which they derived the following equation:

$$P_2 = \frac{P_D}{2} + G_M (P_M - \frac{P_D}{2}) \qquad (4)$$

where G_M = fraction of molecules in monomeric state.

If the values of P_M and P_D are known then μ_M, μ_D and K_{dissn} may be calculated. The authors [31] obtained approximate values of P_M and P_D by the method of averages and used these approximate values to calculate K_{dissn} for each solution. It was found that K_{dissn} was very sensitive to the choice of P_M in the very dilute region where $P_2 \rightarrow P_M$ and to the choice of P_D in the more concentrated solutions. Using the method of successive approximations the values of P_M and $\frac{P_D}{2}$ were adjusted to give the most constant value of K_{dissn}. After Table B.2. it was stated that the authors felt that the value of K_{dissn} obtained for acetic acid in heptane solution was only approximate because of the sensitivity of K_{dissn}

to the choice of P_M and P_D. The low value of K_{dissn} means that there is little monomer present even at the lowest acid concentrations, and consequently little margin for error in the choice of P_M.

This analytical treatment of the results has been criticised by Raats and Buckingham ^{32} on the grounds that the approximation might not be valid in the limiting case of zero concentration of acid. Using the experimental results of Pohl, Hobbs and Gross ^{27} they have proposed an alternative treatment which depends on the fitting of the dielectric constant-concentration data to a straight line plot. They have assumed that the experimental data - dielectric constants, ϵ, refractive indices, $_Dn$, and densities, d - vary with concentration of solute according to the equation:

$$\begin{aligned} \epsilon_{12} &= \epsilon_1 + \alpha'_w w_2 + \alpha''_w w_2^2 + \ldots. \\ {}_Dn_{12}^2 &= \epsilon_1 + \beta'_w w_2 + \beta''_w w_2^2 + \ldots. \qquad (1) \\ d_{12} &= d_1 (1 + \gamma'_w w_2 + \gamma''_w w_2^2 + \ldots.) \end{aligned}$$

in which suffix 12 refers to the solution, 1 to the solvent and 2 to the solute. w_2 = weight fraction of solute. In utilising these relationships they effectively assume that the coefficients, α''_w and β''_w are zero. Objections to this method can be raised. Firstly, the assumption that for a non-polar substance the square of the refractive index is equal to the dielectric constant is incorrect. Smith [33] has shown that for a solvent of dielectric constant approximately equal to two, the maximum difference between ε and n^2 is about 0·18 and the resultant maximum error in μ 1%. The authors [32] make no estimation of any possible error introduced by their approximation. Secondly, the authors [32] have attempted to fit experimental data to a straight line plot whilst an inspection of the results shows that the plot of $\Delta\varepsilon/w_2$ against w_2 is not linear. There is undoubtedly some theoretical justification for their procedure and it is perhaps unfair to criticise the authors on this count. There is no good justification for the assumption that if there is no association the coefficients α''_w etc. would be zero. It may be concluded that this method of analysis is superior to that adopted by Pohl, Hobbs and Gross.[31]

In equation (1) the term in w_2 is related to the apparent dipole moment of the monomer solute at infinite dilution whilst the term in w_2^2 is related to the properties of interacting groups containing two molecules and can be interpreted in terms of the mean square dipole moment $\langle M^2_{12} \rangle$ of the dimer. Both $\langle M^2_{12} \rangle$ and K_{dissn} can be related to the coefficients in equation (1). The authors [32] obtained a value of 1·46 D.U. for the moment of the monomer compared with the figure of 1·68 obtained by Pohl, Hobbs and Gross.[27] Assuming that the carboxylic acid dimer is non polar, the authors [32] obtained a value of 454·5 $l.moles^{-1}$ for K_d compared with the figure of 370·1 $l.moles^{-1}$ obtained by Pohl, Hobbs and Gross.[27] Davies and co-workers [34] obtained a value of 130·2 $l.m.^{-1}$ for K_d at 25° C using a distribution method. Buckingham and Raats [32] corrected this value for temperature - Pohl, Hobbs and Gross' measurements were done at 30° C - and substituting this corrected value, obtained a value of 1·39 D.U. for the root mean square dipole moment, $\langle M^2_{12} \rangle^{\frac{1}{2}}$, of acetic acid dimer. It is interesting to note that a further analysis of Pohl, Hobbs and Gross' measurements by the writer utilising a method developed by Bauge and Smith [35] led to yet different values for μ_M / μ_D and K_d. These results together with those of Buckingham and Raats[32] and the original calculation of Pohl, Hobbs and Gross 27 are summarised in the table below:

TABLE B.3.

Method of Analysis	μ_M(D.U.)	μ_D(D.U.)	K_d (l.m.$^{-1}$)
Pohl, Hobbs and Gross[27]	1·68	0·94	370·1
Buckingham and Raats[32]	1·46	0·00/1·39	454·5/116·0 [a]
Bauge and Smith[35] (Jenkins)	1·65	0·97	323·3

[a] Corrected figure of M. Davies, Moelwyn-Hughes and co-workers.[34]

There is some discrepancy between the values of K_d determined using distribution methods and values obtained from dielectric constant measurements. Table B.4. illustrates this phenomenon.

TABLE B.4.

Authors	Temperature ($^{\circ}$ C)	$K_{assn.}$ (l.mole^{-1})	Method
Pohl, Hobbs and Gross[27]	30	370·1	DC
M. Davies, Moelwyn-Hughes and co-workers[34]	25	130·2	D
	35	81	D
Brown and Matheson [36]	25	500	D
M. Davies and Griffiths[37]	25	129·4-138·3	D
Christian, Affsprung and Taylor [38]	15	605	D
	35	125	D

Abbreviations: DC = Dielectric constant measurements
D = Distribution Method.

Both Davies and Griffiths [37] and Christian, Affsprung and Taylor [38] have made allowances for the solubility of water in benzene, association in the aqueous phase and the presence of higher polymeric species. The distribution method is normally criticised on the grounds that no allowance is made for those effects. The relative merits and de-merits of these determinations of K_d can best be discussed along the results of this investigation at a later stage.

There is unfortunately no recorded determination of K_d of acetic acid in benzene using Infra Red Spectroscopy (I.R.). Hobbs and Harris [39] obtained a value of 4000 $l.mole^{-1}$ at 25° C for K_d in carbon tetrachloride using I.R. Spectroscopy, whilst Barrow and Yerger [40] obtained 1000-2650 $l.mole^{-1}$ over an unspecified temperature range. One would expect K_d in carbon tetrachloride to be higher than K_d in benzene as the dielectric constant of the former is lower, and also because association of the acid with the solvent will not occur to the extent to which it does in benzene.

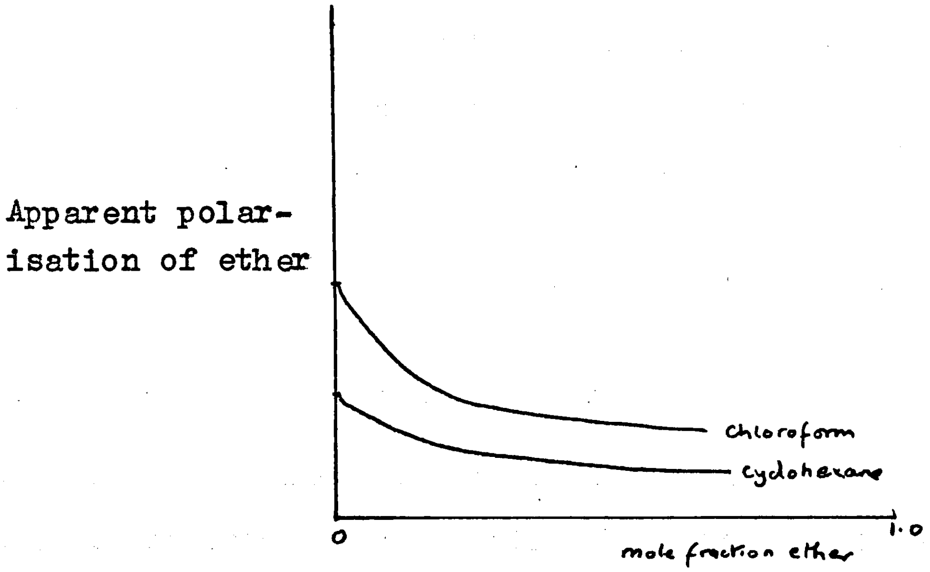
As a result of studies of the dielectric loss in benzene solutions of acetic acid, Constant and Lebrun[41] inferred that at low acid concentrations a monomer-dimer equilibrium was set up, whilst at higher concentrations considerable amountsof higher polymeric species were present. They further considered that there were both cyclic and open chain polymers present.

It is therefore well established that at very low acid concentrations a monomer-dimer equilibrium is set up. What are not so well established are the values of the dipole moment of this monomer and dimer and the dimerisation constant. This investigation attempts to throw further light on these matters using both dielectric constant measurements and nuclear magnetic resonance spectroscopy.

(b) Acid-Base Complexes

Dielectric constant measurements present not only a potential means of detecting the formation of intermolecular complexes in solution but also a way of determining both the dipole moment of the complex formed and the association constant of complex formation. The first reported use of dielectric constant measurements to this end was by Earp and Glasstone.[42,43] From the measurements of dielectric constants and densities of binary systems the authors calculated the total polarisation of each mixture. Then assuming that the polarisation of one component was equal to that in the pure liquid state and remained constant throughout, the polarisation of the other component was evaluated for each solution. A plot of the molar polarisation versus molar fraction of one component was compared with the plot of the molar polarisation versus molar fraction of the same substance in an inert solvent, e.g. cyclohexane. It was found that not only was the polarisation greater in the active solvent but also there was a more rapid increase at high dilution. One such plot is reproduced below.

Figure B.1.



A reasonable explanation for this marked increase in polarisation was that compound formation involved the introduction of a new co-ordinate link joining the two molecules. The authors[42,43] supposed that it was a consequence of the Law of Mass Action that, if a compound was formed between two substances then, if one of these substances is in great excess, then the other exists <u>entirely</u> in the form of compound. Using this conception they derived values of the equilibrium constant of compound formation and the dipole moment of the compound formed.

Hammick, Norris and Sutton [44] criticised this method on several grounds. Firstly, they argued that unless the equilibrium constant for complex formation, K, was infinite then not all A is in the form of complex AB even when it is present at very low concentration.

$$K = \frac{f_{AB}}{f_A . f_B} \quad ; \quad \frac{f_{AB}}{f_A} = Kf_B \quad ; \quad f_B \leqslant 1.$$

where f = mole fraction of species.

Secondly, they pointed out that in the calculation of the total polarisation of a solution, P, Earp and Glasstone[42,43] took the mean molecular weight as $M_A f_A + M_B f_B$ whereas its true value is $\frac{M_A f_A + M_B f_B}{(1 - x)}$, where x is the portion of each of the molar fractions which has been used in complex formation. Lastly, they held that it was extremely doubtful whether the Law of Mass Action could be applied to binary mixtures over the whole range of compositions. They suggested and examined modifications of the method and found that the only dielectric constant method which produced satisfactory results involved measurements on dilute solutions of the two components in a third unreactive solvent. They concluded that in practice it was very difficult to derive an exact measure of both the polarisation and the degree of association from these measurements alone, and that it would be best to use them in conjunction with an independent means of determining the degree of association.

Few and Smith [45] however felt that one of the methods discussed by Hammick, Norris and Sutton [44] was worthy of further consideration. This method involved the determination of the apparent molecular polarisation at infinite dilution of a compound A in an active solvent B, in an inert solvent, S, and in mixtures of B and S. This method had been rejected by Sutton and co-workers [44] on the grounds that with the system diisopropyl ether-chloroform-benzene different results were obtained depending on whether the ether or the chloroform was considered as the solvent at low concentrations. Few and Smith [45] measured the apparent molar polarisation of one component, A, in a series of constant mixtures of the other component, B, and an inert solvent, S. They assumed that the active masses of the two solutes can be represented by their concentrations, and showed that the difference between the limiting value of the molar polarisation of A at infinite dilution in a mixture of B and S, $(P_{A\infty})_{BS}$, and its value in pure solvent, $(P_{A\infty})_S$, is given by the equation below:

$$\frac{\Delta P}{(P_{A\infty})_{BS} - (P_{A\infty})_S} = \frac{M_B V_{BS}}{K\, w_B} + 1 \qquad (1)$$

where K = association constant for complex formation

w_B = weight fraction of B in solvent mixture BS

$\Delta P = P_{AB} - P_A - P_B$

From (1) it follows that a plot of $\frac{1}{(P_{A\infty})_{BS} - (P_{A\infty})_S}$ versus $\frac{M_B V_{BS}}{w_B}$ should be linear with slope $\frac{1}{K\,\Delta P}$ and intercept $\frac{1}{\Delta P}$. Hence it is possible to determine both K and the dipole moment, μ_{AB}, of the complex. This method is particularly suitable for determining the association constants and dipole moments of complexes formed between weak acids and bases, e.g. the work of Cleverdon, Collins and Smith[46] on the ternary systems comprising benzene, pyridine and an alcohol. It is however impossible to apply this method to ternary system containing a carboxylic acid due to the high degree of self association of the latter. If however the association constant for complex formation between the carboxylic acid and organic base was considerably greater than the dimerisation constant of that acid, and if the base was present in great excess. This method should be applicable. Unfortunately in each of the systems studied by the writer it appeared that the complex formation constants were lower than the dimerisation constant of acetic acid.

Most subsequent attempts to determine simultaneously both dipole moment and association constant from dielectric constant measurements have been based on Few and Smith's [45] method. These determinations have recently been criticised by Jumper and Howard [47] on the grounds that changes in the dipole moment of the complexing molecule on complex formation render impossible accurate calculations of the geometry of the complex. The authors [47] further maintain that it is impossible to estimate these changes. This seems a rather restrictive attitude bearing in mind that the prime object is to determine K and μ rather than to provide theoretical justification for the results so obtained.

An interesting alternative method for the simultaneous determination of K and μ is based on a method of determining equilibrium constants due to Rose and Drago.[48] They derived a general equation for evaluating acid-base equilibria from spectroscopic data. It has been adapted for use in determining equilibrium constants from dielectric measurements by Sandall.[49]

For the system,

$$A + B \rightleftharpoons AB; \qquad K = \frac{[AB]}{[A][B]} \qquad (1)$$

Let the initial concentrations of A and B be C_A and C_B moles $1.^{-1}$ The weight fractions of A, B and solvent are W_A, W_B and W_S respectively, where

$$W_A + W_B + W_S = 1 \qquad (2)$$

Suppose that a fraction ΔW_A of A be converted into AB, then the equilibrium concentrations of A, B, AB and S expressed in weight fraction terms are $(W_A - \Delta W_A)$, $(W_B - \Delta W_B)$, $(\Delta W_A + \Delta W_B)$, W_S respectively. The measured difference in dielectric constant between any solution and solvent is given by:

$$\Delta\varepsilon = (W_A - \Delta W_A)\alpha_A + (W_B - \Delta W_B)\alpha_B + (\Delta W_A + \Delta W_B)_{AB} \qquad (3)$$

where α_A and α_B are equal to the slopes of the dielectric constant increment versus weight fraction for solutions of A and B in S. These may be determined by a separate experiment, and for many substances in say, benzene, are well known. α_{AB} is theoretically equal to the equivalent slope for pure complex. This, of course, is unknown, and when determined will lead directly to the dipole moment of the complex. A quantity $\Delta\varepsilon^{*}$, equal to the theoretical change in dielectric constant assuming no complex formation, is also calculated for each solution. This is given by $\Delta\varepsilon^{*} = W_A\alpha_A + W_B\alpha_B$. The difference between $\Delta\varepsilon$ and $\Delta\varepsilon^{*}$ is referred to as $f(\varepsilon)$ and is given by the equation below:

$$f(\varepsilon) = \Delta\varepsilon - \Delta\varepsilon^{*} = (\Delta W_A + \Delta W_B)\alpha_{AB} - \Delta W_A\alpha_A - \Delta W_B\,{}_B$$

$$f(\varepsilon) = xv[(M_A + M_B)\alpha_{AB} - M_A\alpha_A - M_B\alpha_B]$$

$$\text{or } f(\varepsilon) = x\,v\,R \qquad (4)$$

where $R = [(M_A + M_B)\alpha_{AB} - M_A\alpha_A - M_B\alpha_B]$, x = concentration of complex in moles $l.^{-1}$ and v = specific volume of solution.

Now $$K_{assn} = \frac{x}{(C_A - x)(C_B - x)} \qquad (5)$$

Substituting for x, C_A and C_B in (5) we obtain,

$$K_{assn} = \frac{v\ f(\varepsilon)/R}{\frac{W_A}{M_A} - \frac{f(\varepsilon)}{R} \quad \frac{W_B}{M_B} - \frac{f(\varepsilon)}{R}} \qquad (6)$$

The only unknown in (6) is therefore α_{AB} contained in R. If this can be estimated, K_{assn} may be calculated for each solution. The normal procedure involved making several guesses at α_{AB} and calculating K_{assn} for each solution. A plot of K_{assn} for any particular solution against $\frac{1}{R}$ will be linear provided certain conditions are satisfied. The denominator in (6) must be constant and for this to be so then $W_S \gg W_B \gg W_A$. The plots of K versus $\frac{1}{R}$ should then all intersect at one point. The values of K and R corresponding to this point will be the correct ones for that particular system. From R one obtains α_{AB} and hence μ, the dipole moment of the complex.

Unfortunately this method is again unsuitable for ternary systems containing a carboxylic acid which is strongly self associated even in dilute solution.

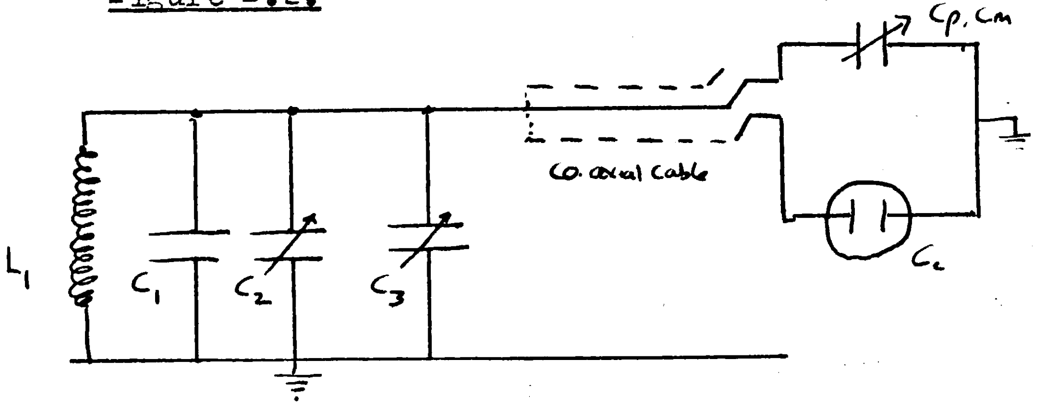
(3) Experimental Details

(a) Apparatus

In order to determine the dipole moment of a compound in solution one needs to measure the dielectric constant ε , refractive index n, specific volume v and weight fraction of solute w_2 of several solutions of that compound in a particular solvent.

In principle, the dielectric constant, or specific permittivity, of a substance is defined by $\varepsilon = C_s/C_o$ where C_s and C_o are respectively the capacities of a condenser when the space between its plates contains the medium under consideration, and when this space is evacuated. To measure these capacities the modified heterodyne beat apparatus of Few, Smith and Witten [50] was used. Basically this apparatus consists of two oscillators X and Y of which X is variable and includes the dielectric cell and precision condensers, and Y is a constant frequency crystal oscillator working at 1 Mc. The signals from the two oscillators of frequency f_X and f_Y are fed to the horizontal and vertical plates of an oscillosocpe. This oscilloscope is a Telequipment S52 instrument with a 5" flat faced single beam Cathode Ray Tube with horizontal and vertical deflection amplifiers. These enable one to observe separately the two input signals. The difference in frequency ($f_X - f_Y$) is shown on the screen. In the original apparatus and still incorporated at present, the two signals were fed into a mixer circuit, whose output of frequency $| f_X - f_Y |$, the beat note was fed to an amplified detector circuit. This beat note is ultimately detected audibly through an earphone for approximate setting of the condensers and visibly through the oscillatory motions of the needle of a microammeter. It had proved possible to obtain a setting giving a frequency difference of 1 $c/_s$ or less using this method. By using the oscilloscope it has been possible to adjust the condensers so as to match the two oscillators exactly. The main reason for switching from use of the microammeter to the oscilloscope was not so much improvement in accuracy of measurement, but rather improvement in experimental technique. Another improvement to the original apparatus has been described previously.[51] This comprised the insertion of a H.W. Sullivan C689 micrometer condenser, C_M. The tuned circuit is shown in Figure B.2.

Figure B.2.



It consists of the coil L, the packing condensers $C_X = C_1 + C_2 + C_3$, the dielectric cell C_c and the precision condenser C_p and C_m. The switch brings alternatively the precision condensers or the cell into the rest of the circuit. The major precision condenser C_p is a H.W. Sullivan C700 linear air capacitor of about 300 pF capacity. Its scale is divided into seven hundred units and can be read to 0•02 units. The micrometer condenser, C_m, mentioned earlier has a scale of length 2•5 cm. and can be read to 0•0002 cm. Its nominal capacity is 8•5 pF with the minimum at 2•5 cm. where the residual capacity is 5•7 pF. The condenser obeys the linear law of capacity charge over the whole of the range with a maximum deviation of 0•003 cm. or 0•001 pF. As the linearity of C_m is so good, C_p is calibrated in terms of 1 cm. units of C_m. This was done as follows. Starting with $C_p = 0$ and $C_m = 0$, C_2 and C_3 were adjusted so that $f = |f_X - f_Y| = 0$, i.e. 'zero beat'. C_m was then set to 2•5 cm. and C_p adjusted to obtain zero beat. C_p was then read off. C_m was reset to zero and C_2 and C_3 adjusted to obtain zero beat. C_m was then set to 2•5 cm. and C_p re-adjusted and read off. This procedure was repeated over the greater part of the scale of the measuring condenser, which was thereby divided into a series of step numbers, SN, each equal to a 2•5 cm. unit of C_p. The whole procedure was repeated two further times and the mean of these three calibrations used. The advantage of this is that a reading of the micrometer condenser is readily converted to a reading in SN, and hence to a dielectric constant change. The other improvement to the apparatus was the replacementof the original source of H.T., a Clarke's Atlas eliminator connected to the mains by a set of Varta Deac hermetically sealed Nickel-Cadmium accumulators. The main advantages of sealed accumulators are that they do not require maintenance as the electrolyte need not be renewed or replenished. Further to all this several small radio components have been replaced. During a measurement with the cell, C_c, switched in, C_x is adjusted to zero beat. C_p and C_m are then switched in and adjusted to the same zero beat. The frequencies across the tuned circuits are then both equal to 1 Mc. By alternately depressing and releasing the push button switch, the beat notes in each circuit can be compared very exactly. The capacity of the dielectric cell, together with its leads is then equal to the capacity of the standard condenser with its leads. This means, of course, that absolute measurements of ε are impossible, unless the capacity of the leads is accurately known. This is not serious as the readings obtained with solutions in the cell can be compared with the setting for a reference liquid, normally the solvent used.

The actual series of measurements on the ternary solution were done as follows. First with C_m set at 25 cm. the reading for balance of the cell was taken whilst it was full of dry nitrogen, C_{N2}. It was then filled with benzene and the balance reading C_{B2} determined by adjusting C_p whilst C_m was kept at 2·5 cm. These two readings of C_p wereconverted into step numbers, SN_{N2} and SN_{B2} respectively. In this method a linear dependence between dielectric constant and capacity of the cell has been assumed. Strictly this is not so, because of the edge effects. It has been found [52] that if the dielectric constant of nitrogen is taken as equal to unity, then the edge effects may be ignored provided that the unknown dielectric constant lies between 2 and 3·5. This was the case in all my measurements. The difference in step number Δ SN corresponds to the numerical difference in dielectric constant between benzene and nitrogen, and therefore, all step numbers could be converted into changes in dielectric constant. The cell was then filled with a solution of an organic base in benzene, this solution being called mixed solvent or MS. C_m was kept constant and C_p adjusted to zero beat and read off. This reading was also converted into a step number, SN_{ms}, and hence the dielectric constant of the mixed solvent deduced. The mixed solvent was then replaced by the most dilute solution of acid in mixed solvent, C_p was kept constant and C_m adjusted to yield zero beat. The change in C_m was readily converted into a dielectric constant change. This was followed by a stronger solution of acid and so on. Thus the total increase in dielectric constant on mixing various quantities of organic acid in a solution of organic base in benzene can be readily obtained. C_m is divided into 0•0010 units and the fourth place can be easily read off to ± 2. This then gives an error of about 0•00001 in the dielectric constant. As the apparatus can be adjusted to within 1 $^c/s$ and the oscillator frequency is 1 Mc/s, this gives a sensitivity of 1 part in 10^6. This is equivalent to a capacity change (cell = 100 pF) of about 0•0001 pF corresponding to a change of about 0•00001 in the dielectric constant. The condenser arrangement therefore utilises the full sensitivity of the apparatus.

The dielectric cell is of the Sayce-Briscoe type of all glass construction. The cell is held in place in the thermostat with a close fitting metal frame without exerting any strain that might lead to distortion of the cell and hence to variation in capacity. The leads to the heterodyne-beat apparatus comprise two stiff copper wires with their ends immersed in mercury cups.

The specific volumes were measured with a

Warden's specific gravity bottle of nominal capacity 25 ml. During a measurement it was kept in the thermostat for about half-an-hour to ensure thermal equilibrium.

A Hilger Abbé refractometer capable of reading to ± 0·0001 units was used for the measurement of refractive indices. Temperature control was provided by circulating the thermostat~~e~~ liquid through it. This was drawn through the blocks by a rotary pump as pushing it through thecell tended to cause a slight rise of temperature. The refractive indices when required were measured after the dielectric constant measurements because of disturbance from the pumping motor. A small amount of liquid was inserted by pipette into the cell of the refractometer and the refractive index read off when a constant value was obtained.

All solutions were made up by weight. To minimise any errors caused by absorption of moisture, all solutions were made up in a Dry Box through which dry nitrogen was circulated.

All measurements were carried out at 25° C ± 0·01 in a water thermostat. The temperature was regulated with a toluene-mercury regulator and controlled by a thyraton control circuit.

(b) Materials

Anhydrous acetic acid was presented to me by Dr. J.S. Lomas of this laboratory who prepared it by fractional distillation. Pyridine, 4-picoline, 2,6 Lutidene were distilled, dried and stored over potassium hydroxide pellets. Suitable amounts were distilled off when required. Quinoline (GPR grade) was usedwithout further purification. The benzene used was of Analar grade and was purified by re-crystallisation and drying with sodium wire. Suitable amounts were distilled off as required. The product obtained was of a high degree of purity and the refractive indices of different batches showed little variation ($n_D^{25} = 1{\cdot}4972 \pm 0{\cdot}0001$).

TABLE B.5.

Substance	Origin and Quality	m.p.(^{o}C)	b.p.(^{o}C)	Purification
Acetic acid	M.B. R.G.	16·5		Fractional distillation
Pyridine	M.B. R.G.		115·5	Distillation
2,6 Lutidene	B.D.H. L.R.		145·6-145·8	Distillation
4-Picoline	B.D.H. L.R.		143·1	Distillation
Quinoline	H.W.G.P.R.		-	-
Benzene	B.D.H. A.R.		80·1	Recryst./distillation

Abbreviations: M.B. May and Baker; B.D.H. British Drug Houses; H.W. Hopkin and Williams; A.R. Analytical Grade; R.G. Research Grade; L.R. Laboratory Reagent; G.P.R. General Purpose Reagent.

(c) Sources of Error

Non systematic errors due to evaporation, absorption of moisture etc. cannot be estimated. They were minimised by careful handling of the solutions and also by following the strict routine for measurements mentioned earlier.

It is difficult to make a sensible estimate of the systematic errors due to uncertainties in the readings of the condensers, refractometer and balance. This is partly due to the complicated relationship between the measured quantities ε , n etc. and the dipole moment and formation constant of the complex. As well as this, the error varies very much with the individual measurement. For example, throughout this investigation there is a greater error in determining α , the rate of variation of dielectric constant with weight fraction, for the organic base in benzene than for the acid in the mixed solvent. The reason for this was that measurement of the former involved adjustment of C_p to balance the two oscillators and the latter involved adjustment of C_m. Now C_p can be read to an accuracy of ± 0.02 scale division which corresponds to an uncertainty of about ± 0·0001 rather than an uncertainty of ± 0·00001 in the other case. It was necessary to do this as the concentrations of basewere too high to permit measurement using C_m alone.

Everard, Hill and Sutton [53] have shown that in determination of a dipole moment, μ , in solution an exact knowledge of the absolute values of the dielectric constant ε_1, specific volume V_1, and refractive index n_1 of pure solvent is of secondary importance. It is therefore legitimate to ignore small variations in these quantities and to assign them standard values. The major factors controlling the accuracy are the rates of variation of dielectric constant and refractive index with concentration of solute. In fact for the error in μ to exceed 1%, i.e. 0·01 Debye when $\mu = 1$ and M is 200, the error in α $(= \frac{\Delta\varepsilon}{w}, w_2 = 0)$ and γ $(= \frac{\Delta n^2}{w}, w_2 = 0)$ must be greater than 0·01 and 0·0035 respectively. Now changes in refractive index can be measured to ± 0·0001 and as in most cases the refractive index is approximately linear over an appreciable concentration range, an accurate mean value of can be obtained. However, α often varies appreciably with w_2. In these cases special techniques have been necessary to obtain an accurate value of α. It is difficult to make any sensible estimation of the accuracy of α in these instances. That this is so will readily be seen when these methods are discussed in detail.

It is well established [54] that accurate measurement~~s~~ of β $(= \frac{\Delta v}{w_2}, w_2 = 0)$ is unecessary for the determination of a dipole moment in solution. This was borne out by Hill, Everard and Sutton [53] who showed that for the error in μ to exceed 1%, β would have to be wrong in the first decimal place (i.e. it almost suffices to guess it). The specific volumes measured in this investigation were probably accurate to ± 0.0002, consequently the values of β will be well withih the required limits.

(4) Results

(a) Acetic Acid-Benzene System~~s~~.

The dipole moments of the acetic acid monomer and dimer, μ_M and μ_D respectively, have been measured in benzene solution. The dimerisation constant, K_d, has also been determined.

$$2M \overset{K_d}{\rightleftharpoons} D$$

K_d, μ_M and μ_D were calculated using a method developed by Bauge and Smith [35] for the determination of the dipole moments of quaternary ammonium salts. This method was based on that devised by Pohl, Hobbs and Gross [31] to interpret the concentration dependence of the apparent molar polarisation of carboxylic acids in solution. It was assumed that at low concentrations there is an equilibrium between monomeric and dimeric species. Under these circumstances each solute species present produces an increment in the dielectric constant which is proportional to its weight fraction in the solution, i.e.:

$\Delta\varepsilon = \Delta\varepsilon_M + \Delta\varepsilon_D$ ... (1) where $\Delta\varepsilon_M$, $\Delta\varepsilon_D$ are the increments due to monomer and dimer respectively.

This may be re-expressed:

$\Delta\varepsilon = \alpha_M w_M + \alpha_D w_D \ldots$ (2) where α and w have their usual meanings. If the active masses of monomer and dimer can be represented by their concentrations C_M and C_D in moles cc^{-1} then the dimerisation constant K_d is given by the expression:

$$K_d = \frac{C_D}{C_M^2} = \left(\frac{w_D}{2M_m \nu}\right) \Big/ \left(\frac{w_M}{M_m \nu}\right)^2 = \frac{w_D}{w_M^2} M_m \cdot \nu \qquad (3)$$

where M_m = molecular weight of monomer and ν = specific volume of the solution. Now $w_M + w_D = w$, the total weight fraction of solute. For any particular solution $\frac{\Delta\varepsilon}{w} = \alpha$, then

$$\Delta\varepsilon = \alpha(w_M + w_D) = \alpha_M w_M + \alpha_D w_D \qquad (4)$$

hence

$$w_M = \frac{w(\alpha - \alpha_D)}{(\alpha_M - \alpha_D)}$$

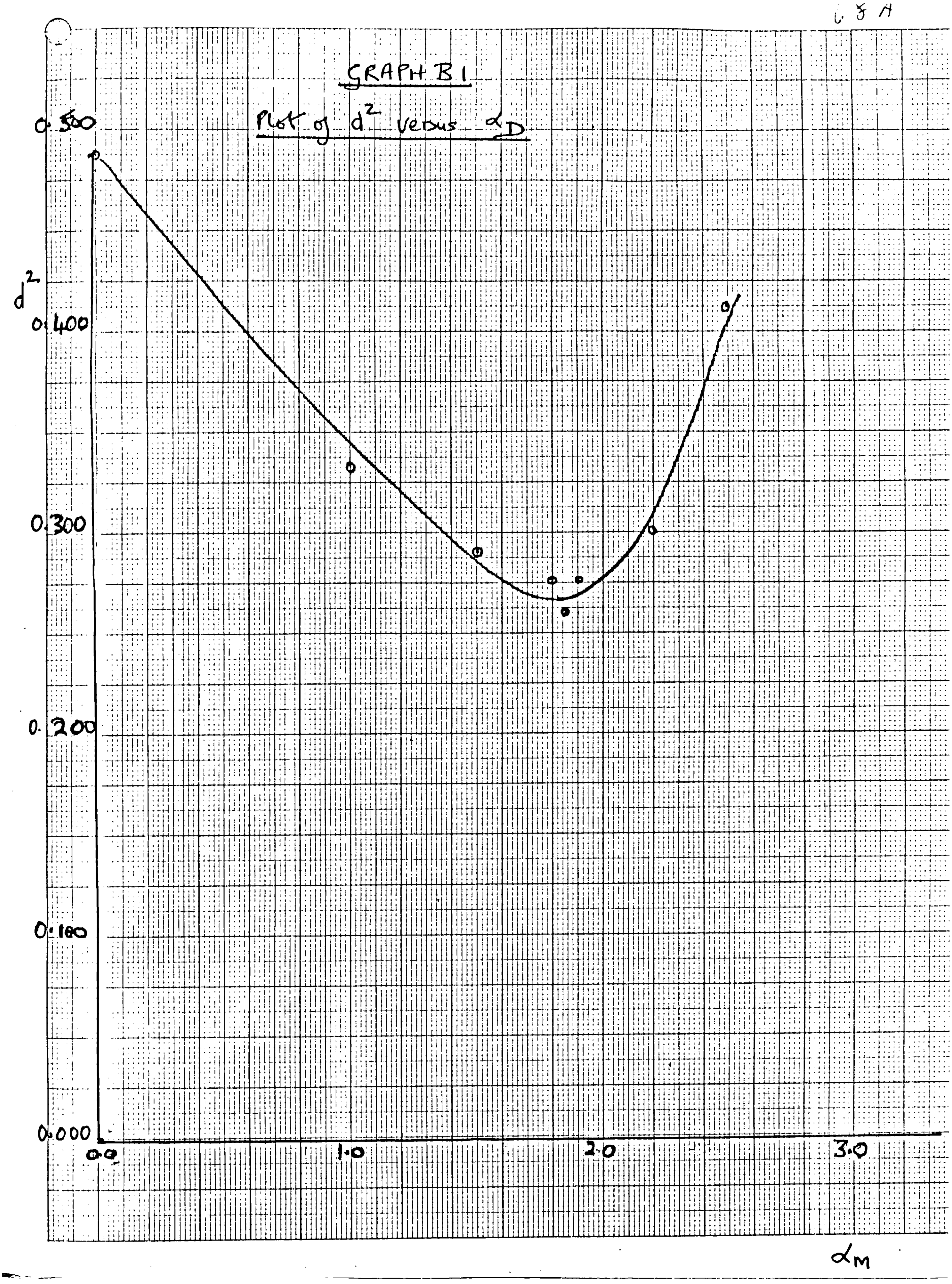
substituting for w_M in (3) we obtain:

$$K_d = \frac{(\alpha_M - \alpha)(\alpha_M - \alpha_D)}{(\alpha - \alpha_D)^2} \; \frac{M_m \cdot \nu}{2w} \qquad (5)$$

For this system $(\alpha_M - \alpha_D)$ and M_m are constant. Thus by putting $K' = \dfrac{2K_d}{(\alpha_M - \alpha_D)M_m}$, it follows that:

$$\alpha = \alpha_M - (\alpha - \alpha_D)^2 \frac{w}{V} K' \qquad (6)$$

If therefore α is plotted against $(\alpha - \alpha_D)^2 \frac{w}{V}$ one should obtain a straight line plot with intercept α_M and slope $- K'$. These two constants are best obtained from the data using the principle of least squares. This method assumes that the fixed values of one independent variable, in this case w, are correct and hence only the dependent variable is subject to error. It also assumes that the line of best fit is the one which makes the sum of the squares of deviations from that line a minimum. A series of values of α_D were chosen and used to evaluate α_M and K. At the same time α is calculated for each solution and the square of the modulus ~~molecules~~ of the difference, d, between this calculated α and the experimental value determined. A plot of the sum~~s~~ of these squares against the chosen value of α_D has a minimum at $\alpha_D = 0{\cdot}185 \pm 0{\cdot}005$ (see Graph B.1.). Inspection of the series of plots of α against $(\alpha - \alpha_D)^2$ w (see Graph B.2.) confirmed that this minimum corresponded to the best straight line.



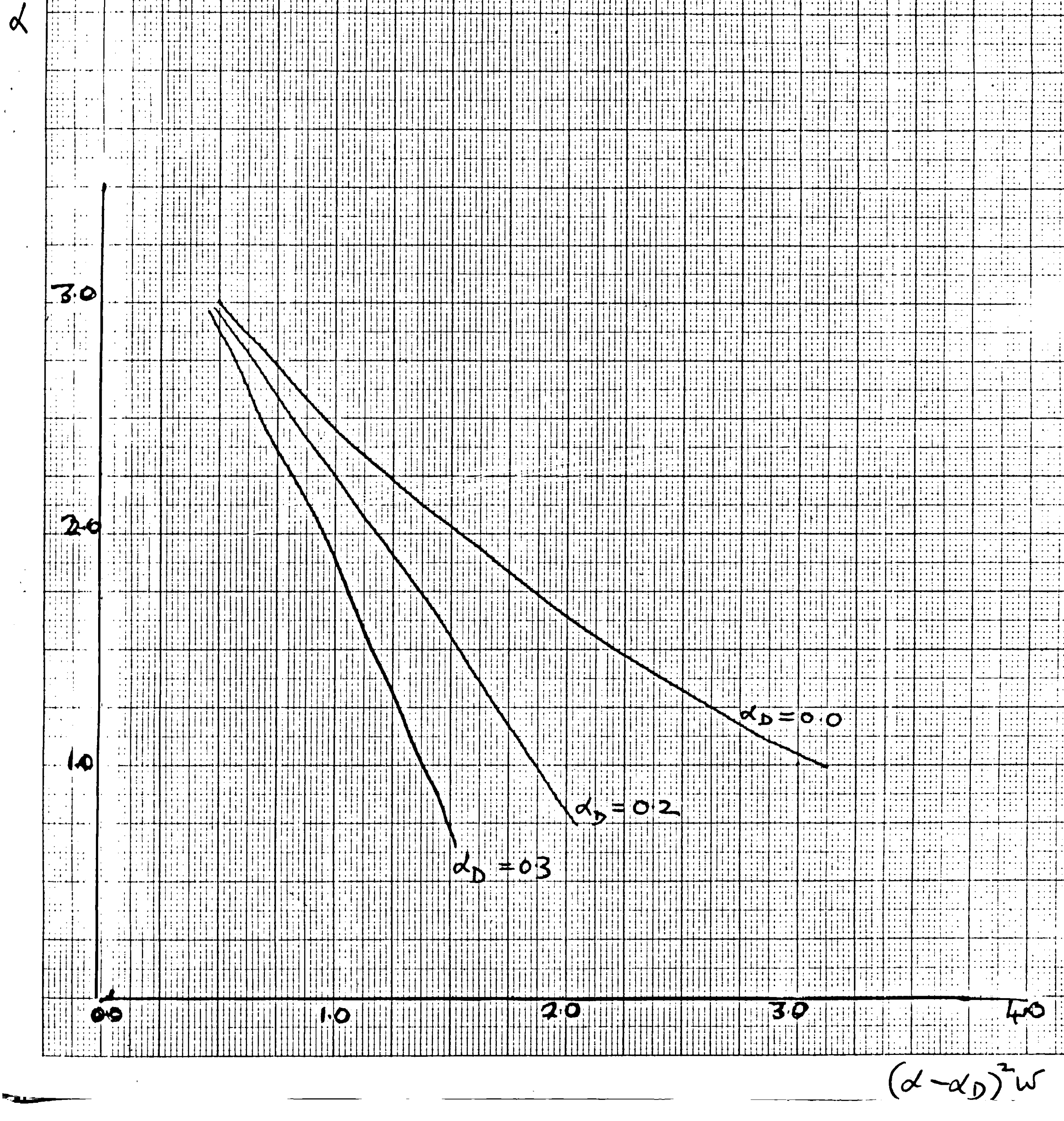
GRAPH B1

Plot of d^2 verus α_D

6.8 B 6

GRAPH B.2

Plot of $(\alpha-\alpha_D)^2 W$ versus α



The values of α_M and K corresponding to α_D = 0·185 are 3·659~~8~~ and 138·9 l.mole^{-1}

TABLE B.6.

ACETIC ACID-BENZENE

$\frac{\Delta\varepsilon}{w} = \alpha$	$\Delta\varepsilon$	w(x 10^3)
3·093	0·00018	0·05819
3·038	0·00019	0·06253
2·949	0·00027	0·09154
2·800	0·00034	0·1214
2·630	0·00043	0·1635
2·484	0·00048	0·1932
2·320	0·00059	0·2543
2·207	0·00070	0·3172
1·830	0·00089	0·4864
1·782	0·00102	0·5724
1·502	0·00156	1·039
1·456	0·00159	1·090
1·412	0·00186	1·317
1·366	0·00211	1·545
1·211	0·00223	1·842
1·156	0·00260	2·249
1·056	0·00302	2·861
0·955	0·00384	4·021

TABLE B.7. (see Graph B.1.)

ACETIC ACID-BENZENE

α D	α M	$-\frac{K'}{V}$ (10^3)	K(l.mole^{-1})	$\sum d^2$
0·000	3·478	0·798	83·3	0·4877
0·100	3·524	0·949	111·4	0·3311
0·150	3·617	1·084	123·8	0·2912
0·180	3·643	1·683	128·5	0·2777
0·185	3·659	1·174	138·9	0·2602
0·190	3·744	1·202	142·0	0·2785
0·220	3·819	1·426	169·5	0·3044
0·250	3·943	1·654	206·5	0·4123

Calculation of the dipole moments of acetic acid monomer and dimer

Halverstadt and Kumler [56] assumed that in dilute solution, the dielectric constant, ε_{12}, and specific volume, V_{12}, of the solution are linear functions of the weight fraction of solute w_2 so that:

$$\varepsilon_{12} = \varepsilon_1 + \alpha w_2 \qquad (1)$$

$$V_{12} = V_1 + \beta w_2 \qquad (2)$$

where ε_1 and V_1 are the dielectric constant and specific volume of pure solvent and α , β constants.

Expressing the Clausius-Mossotti equation in the form:

$$p_{12} = \frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \cdot V_{12} \qquad (3)$$

where p_{12} is the specific polarisation of the solution it follows from (1) and (2) that:

$$p_{2\infty} = \frac{3\alpha V_1}{(\varepsilon_1 + 2)^2} + (V_1 + \beta)\,\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \qquad (4)$$

where $p_{2\infty}$ is the specific polarisation of the solute at infinite dilution. The specific refraction may be calculated from the analogous equation with dielectric constant replaced by the square of the refractive index and α by γ , the limiting value of $\frac{\Delta n^2}{w_2}$.

$$r_{2\infty} = \frac{3\gamma V_1}{(n_1^2 + 2)^2} + (V_1 + \beta)\,\frac{n_1^2 - 1}{n_1^2 + 2} \qquad (5)$$

The corresponding total molar polarisation and refraction are readily obtained from (4) and (5) by multiplying by the molecular weight. Now the total molar polarisation, $P_{2\infty}$, is equal to the sum of the electronic, atomic and

~~orit~~orientation polarisations. The electronic polarisation is equal to the molar refraction extrapolated to infinite wavelength. There is no systematic relationship between this and the atomic polarisation which depends on the individual polarities of the bonds. Consequently, the only allowance made for the atomic polarisation was the use of n_D^2 instead of n_∞^2. The dipole moment, μ, is obtained from the orientation polarisation, ${}_oP_2$, using the equation:

$$\mu = \sqrt{9kT/4\pi N}\ \sqrt{{}_oP_2} = 0{\cdot}2212\ \sqrt{{}_oP_2}$$

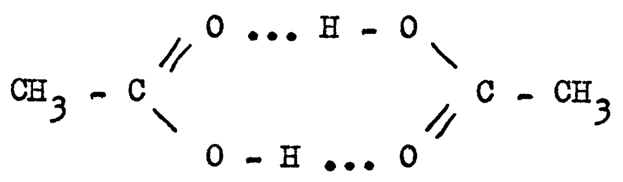
at 25° C. Calculations of the moment of acetic acid monomer and dimer yield 1·505 and 0·832 Debye Units respectively.

Discussion

TABLE B.8.

Investigators	Method of Calculation	μ_M	μ_D
Pohl, Hobbs and Gross[27]	reference 31	1·64	0·94
"	" 32	1·46	1·39
"	" 35	1·65	0·96
Jenkins	" 35	1·50(5)	0·83(2)

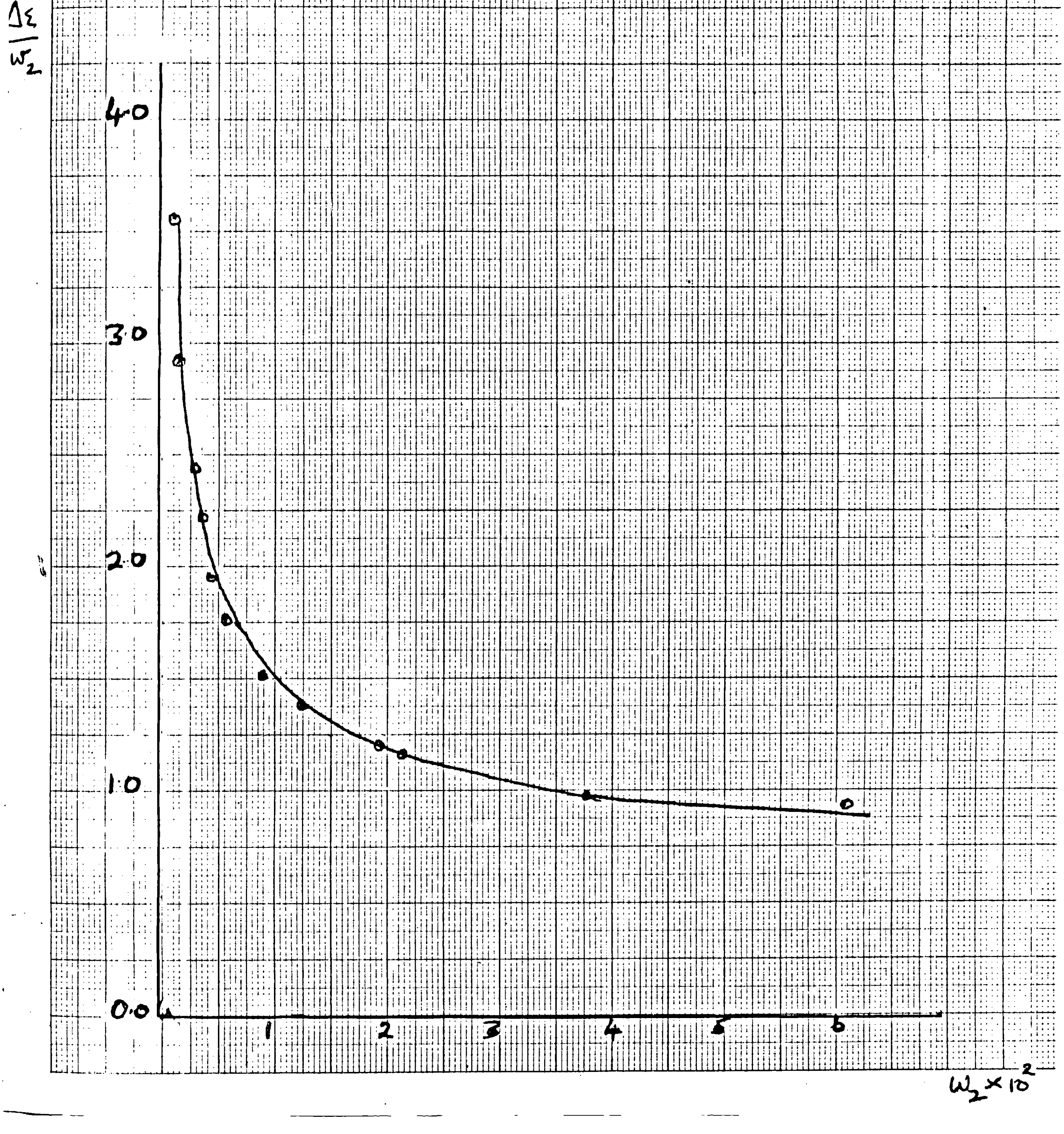
Table B.8. summarises the various calculations of the moments of the acetic acid monomer and dimer. In the three calculations using the experimental results of Pohl, Hobbs and Gross it is readily noticeable that the lower the value of μ_M, the greater the value of μ_D obtained. All three calculations are basically similar in that they attempted to fit to a straight line plot experimental behaviour not adequately described by that straight line relationship. That this is so can be explained by considering the initial premise that at low concentrations there exists in solution only monomeric and dimeric species. This assumes that there is only one dimeric species present, a cyclic dimer. Both these assumptions must be considered doubtful in view of the experimental evidence. Firstly whilst it is quite true that at low concentrations the acetic acid exists largely in either the monomeric or dimeric form. It is also probably true that even at these low concentrations there are some higher polymeric species present. These individual species may have a finite dipole moment and thus contribute to the dielectric constant increment. Buckingham and Raab [32] supposed with some theoretical justification that a plot of $\frac{\Delta\varepsilon}{w}$ versus w should be linear. Inspection of this plot (see Graph B.3.) shows quite clearly that one or both of the initial premises must be incorrect. It has been shown that a cyclic dimer does definitely exist;however its existence does not preclude the possibility of an open chain dimer. An equilibrium could be set up between the two types of dimer present. It is difficult to prove or disprove this premise. However the rather high finite value of the dipole moment of the acetic acid dimer has never been adequately explained. The cyclic dimer has the structure shown below:



Assuming that the dimer is a rigid, planar non ionised ring, then one would expect its moment to be zero. The existence of the large residual polarisation of these dimers could be explained by any or all of the following: (1) Thermal b~~o~~ending of the two halves of the dimer so that a net permanent dipole moment results. This seems to be excluded by the fact that the net carboxyl group moment is nearly at right angles to the

GRAPH B3

Plot of $\frac{\Delta\varepsilon}{w}$ versus W_2 ref Pohl, Hobbs and Gross
J. Chem. Phys. 9, 401 (1941)



line joining the two carboxyl groups and any bending perpendicular to the ring would probably contribute very slightly, if at all to the polarisation. (2) A solvent effect. This seems unlikely since the values of μ_D found are essentially the same in heptane as in benzene. (3) The presence of polar aggregates not considered in the equilibrium calculations. The main objection to this explanation is the constancy of the moment found for the dimeric species of similar carboxylic acids whilst their dimerisation constants vary considerably. (4) Atomic Polarisation. This would arise mainly from chemical bonding and seems to be the most likely explanation. However, the small range of values of μ_D found for different acid dimers should not preclude the possibility of there being an open chain dimer present. Infra-Red Spectroscopy has established the presence of the ring dimer but affords neither proof nor disproof of this hypothesis. Indeed the equilibrium process could be represented as follows:

$$2M \rightleftharpoons D_1 \rightleftharpoons D_2$$

M = free -OH group of monomer

D_1 = open chain dimer containing one free -OH and one hydrogen bonded -OH group

D_2 = cyclic dimer. No free -OH group.

Even at the highest acid concentrations there should be a free -OH stretching frequency. All the I.R. measurements recorded have been done in carbon tetrachloride solution. The dimerisation constant of acetic acid is considerably greater in carbon tetrachloride than in benzene; consequently one would expect the equilibrium process to be shifted well over to the right. Also in benzene there is the possibility of the preferential stabilisation of both the monomer and open chain dimer. This could occur if there was some kind of interaction between the free -OH group and the aromatic π-electrons. There is some evidence for this type of interaction from n.m.r. spectroscopy. The result should be, however, that the mean moment of the dimer should be appreciably greater in benzene than in other solvents.

In summary, the possibility of there being an open chain dimer as well as ring dimer present in solution of acetic acid in benzene should not be discounted.

Hullet, Pegg and Sutton [57] examined the complex formation between a series of phenols and trimethylamine.

The square of the 'excess dipole moment' for the complex, $(\Delta\mu)^2$, was found to be proportional to K, the association constant. The 'excess dipole moment' is the difference between the actual dipole moment and the sum of the dipole moments of the two interacting components. This work was extended by Pimental and McClellan [58] to carboxylic acid dimers. They suggested that the experimental quantity, μ_D, was analagous to $\Delta\mu$ and found a monotonic relationship between $(\Delta\mu)^2$ and K_{assn} for the aliphatic carboxylic acids, with the single exception of chloroacetic acid. Further to this they considered there was a direct relationship between $(\Delta\mu)^{1/2}$ and log K. Whilst this has no more obvious explanation than the relationship between $(\Delta\mu)^2$ and K, it, at any rate, provokes discussion of $\Delta\mu$ in terms of hydrogen bond strengths.

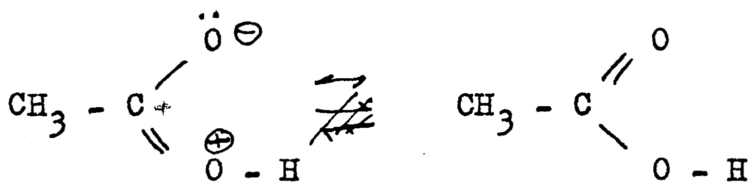
The evidence presented by Pimental and McClellan in support of this claim is somewhat scanty. Indeed use of the commonly accepted value of about 140 rather than 370 for the association constant of acetic acid casts doubt on the whole idea of a definite relationship between K and $\Delta\mu$. It would not seem unreasonable to suggest that any direct relationship between $\Delta\mu$ and K is fortuitous. The evidence quoted by the authors is given below.

TABLE B.9.

Acid	K_d	$\Delta\mu$	$\Delta\mu^2$	$\Delta\mu^{1/2}$	log K
Formic	126	1·06	1·124	1·034	2·1004
Acetic	140/370	0·94	0·884	0·969	2·1461/2·5682
Butyric	428	0·93	0·865	0·964	2·6314
Trimethyl-acetic	690	0·92	0·864	0·959	2·8388
Propionic	392	0·88	0·774	0·938	2·5933
Chloro-acetic	102	1·97	3·881	1·411	2·0086

The moment of the acetic acid monomer is the resultant of the moments of the C - O, C = O and O - H bonds. Approximate values of the bond angles and lengths have been obtained by Karle and Brockway [59] using electron diffraction. These values refer to the molecule in the gaseous phase.

A valence-bond interpretation of the structure involves two possible structures:



The C - O bond distance indicates that the C - O bond has little double bond character. Much double bond character would cause the molecule to exist in two isomeric forms with planar carboxyl groups. One form would have the hydroxyl group cis to the carbonyl group, and the other would have it trans, a structure obtained by rotating the - OH through an angle of 180°. Assuming the following values for the individual bond moments, C = O,2·4 D, C - O 0·74 D, O - H 1·51 D, and C - CH_3 0·4 D, Smyth [60] estimated that the moments be 1·4 D. for the cis, and 3·9 D. for the trans structure. Electron diffraction [61] indicates that the C - O - C plane is about 25° ± 8° out of this cis planar configuration in methyl acetate. Making a similar allowance for non planarity in acetic acid, estimation of the moment of this cis structure yields a value of 1·7 D. The moment can also be calculated in the case of free rotation of the - OH group around the C - O axis. This comes to 2•9 D. All these values are, of course, approximate, but it is clear that the trans structure and that with free rotation have much too high moments to exist alone. M. Davies [62] has calculated that there is a difference of about 7•5 k cal in the interaction energy between the C = O and - O - H groups in the cis and trans carboxyl forms. From this he estimated that at room temperature the relative frequency of occurrence of cis to trans is $3{\cdot}6 \times 10^5{:}1$. Either the cis alone or a mixture of the cis and trans structures with the cis predominant would give the observed moment. The value of 1•505 D.U. obtained in this investigation is intermediate between that calculated by Buckingham and Raabs [32] and that calculated by the writer from the experimental results of Pohl, Hobbs and Gross.[27] All of these values are consistent with such an equilibrium. Comparing the solution values of the monomer with that obtained by Zahn [30] in the gas phase shows that the solution values are consistently lower. The value of the moment in the vapour phase is normally taken to be a pretty accurate indication of the true dipole moment of the isolated molecule, as the measurements are made under such conditions that the substance should exist entirely in the monomeric state. It is generally accepted that the apparent dipole moment of a substance in solution varies with the dielectric constant of the medium. For a molecule in which the resultant dipole lies near to the axis of maximum polarisability the apparent dipole moment will be greater in a medium of lower dielectric constant. Consequently one would expect the value of μ calculated from data obtained at 30° to be slightly higher than that calculated from measurements at 25° C. It is however difficult to explain so great a difference, 1·65 as compared to 1·505, on this basis.

There have been innumerable attempts to derive equations relating the apparent dipole moment in solution with the dielectric constant of the medium. The approaches to this problem fall into four categories. These are: (1) Purely empirical relationships which were derived to explain one or more series of results and which are of limited applicability. (2) Theoretical treatments based on the electrostatic inductive effect of the dipoles on the medium in their vicinity. (3) Theoretical treatments based upon more drastic modifications of the Clausius-Mossotti-Debye theory and (4) Attempts which combine these three approaches. As yet no single theory has been devised which can satisfactorily explain either the variation of the dipole moment of a substance with the dielectric constant of the solvent in which measurement takes place or can interpret the dielectric constant of pure liquids in terms of their dipole moments.

One is forced to conclude by stating that the variation in values of the moments of acetic acid monomer and dimer calculated from the one set of results reflects the inadequacy of the theoretical treatment of the variation of dielectric polarisation with concentration. Every attempt was made by the writer to ensure that his experimental measurements were made under the conditions necessary for application of the theory. The results will be made use of throughout the remainder of the investigation.

(b) Dipole moments of Organic Bases

The dipole moments of pyridine, 4-picoline, 2,6 lutidene and quinoline were determined in benzene solution. Selected literature values are given in the table below.

TABLE B.10.

Base	Dipole Moment (D.U.)	Reference
Pyridine	2•20	Cleverdon, Collins and Smith,[46] JCS, 1956, 4499.
Pyridine	2•21	Cumper, Vogel and Walker,[63] JCS, 3621, 1956.
4-Picoline	2•60	"
2,6-lutidine	1•66	"
Quinoline	2•26	Buckingham, Le Fèvre et alia.[64] JCS, 1405, 1950.
Quinoline	2•20	Le Fèvre and Smith,[65] JCS, 2810, 1932

As it was necessary to have precise values of α, the limiting values of $\frac{\Delta\varepsilon}{w}$ at zero concentration for mixtures of bases with benzene, the dipole moments of these compounds have been determined in benzene solution at 25° C. To evaluate the dipole moment of a simple compound one needs to know in addition to α, the limiting values β and γ of the corresponding slopes of the specific volume and refractive index increments versus weight fraction. With these base all three plots were sensibly linear over a wide concentration range. The Halverstadt-Kumler Equation was used to evaluate the total specific polarisation of the solute base, $p_{2\infty}$, from these paramaters.

$$p_{2\infty} = \frac{3\alpha V_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}(V_1 + \beta)$$

The total molecular polarisation, $P_{2\infty}$, is easily obtained by multiplying $p_{2\infty}$ by the molecular weight of the individual bases. No special allowance was made for atomic polarisation in calculating the dipole moment, μ, from the total molecular polarisation. A summary of the results is given below.

TABLE B.11.

Base	α	β	γ	μ(D)
Pyridine	6·680	-0·126	0·098	2·19
4-Picoline	7·898	-0·079	0·079	2·59
2,6-Lutidine	2·996	-0·044	0·073	1·71
Quinoline	4·322	-0·231	0·279	2·19

For pyridine the values of α, β γ and μ compare favourably with those found by Cleverdon et alia;[46] α = 6·675, β = - 0·133, γ = 0·04, μ = 2·20 D. The values of α, β, γ μ etc. for the other bases also compare favourably with previous work.

(c) Acid-Base Complexes

The dipole moments and association constants have been measured for the complexes formed in benzene solution between acetic acid and the aromatic bases: pyridine, 4-Picoline, 2,6-Lutidine and Quinoline.

Experimentally this involved measuring the dielectric constants of several solutions of acetic acid in constant ratio mixtures of base and solvent. There was always an excess of base present in solution.

It has been pointed out Section B2 that ~~some~~ none of the methods outlined there were particularly suited to the systems investigated by the writer. For example, the method devised by Few and Smith[45] was unsuitable as it made no allowance for the complicating factor of the dimerisation of acetic acid. As has been pointed out, this is so strong as to prohibit the determination of α for the mixture of monomeric acid and complex by any simple extrapolation process. This difficulty could be overcome if the dimerisation constant of acetic acid was small compared with the complex formation constants. That this was probably not the case was inferred from a consideration of the relative values of these constants in other solvents. Barrow and Yerger[40] using I.R. Spectroscopy found that the dimerisation constant of acetic acid lay between 1,000 and 2,650 l.mole^{-1} in carbon tetrachloride and between 100 and 420 l.mole^{-1} in chloroform. Barrow[66] also found that the association constant for acetic acid and pyridine in carbon tetrachloride and chloroform was 220 and 70 l.mole^{-1} respectively. It seemed reasonable to assume that in benzene the dimerisation constant would be greater than the association constant for the acetic acid-pyridine complex. The other organic bases used in this investigation were of a similar nature to pyridine and it was not anticipated that there would be a large variation in the values of the association constants of the various acid-base complexes investigated. Neither Few and Smith [45] nor Sandall [49] made allowance for this.

In a general carboxylic acid-base-inert solvent system the following equilibria are almost certainly set up.

$$(1) \ldots\ldots \quad 2M \rightleftharpoons D \qquad K_1 = \frac{[D]}{[M]^2} \quad \ldots\ldots \quad (3)$$

$$(2) \ldots\ldots \quad M + B \rightleftharpoons C \qquad K_2 = \frac{[C]}{[M][B]} \quad \ldots\ldots \quad (4)$$

where D = acid dimer, M = acid monomer, B = base and C = complex.

Under certain conditions, for example, an excess of acid, there is the possibility of the formation of a 2:1 acid: base complex; also there may be higher polymeric species of acid present. Under the conditions used throughout this investigation, namely low acid concentration and an excess of base, (1) and (2) are the predomina~~t~~nt equilibria.

If the initial concentration of acid is equal to [A], then:

$$[A] = [M] + 2[D] + [C] \qquad (5)$$

If the initial concentration of base, [B], is much greater than [A], then it is a reasonable approximation, bearing in mind that K_1 is much greater than K_2, to say that the equilibrium concentration of B is equal to the initial concentration. Thus as [A] and [B] are both known, K_1 having been previously determined, it should be possible, provided that K_2 were known, to evaluate [M], [C] and [D] for each solution. The measured dielectric constant of each solution, ϵ_{soln}, is related to the equilibrium concentrations of each species present in solution according to the equation:

$$\epsilon_{soln} - \epsilon_{solvent} = w_M \alpha_M + w_D \alpha_D + w_C \alpha_C + w_B \alpha_B \qquad (6)$$

where w_M, w_D, w_C and w_B are the equilibrium concentrations expressed as weight fractions of M, D, C and B respectively. These are related by equation (7):

$$w_M + w_D + w_C + w_B + w_S = 1 \qquad (7)$$

where w_S = weight fraction of solvent.

In (6) α_M, α_D, α_C and α_B are the limiting values of $\frac{\Delta\epsilon}{w}$, as w tends to zero for each species. Of these only α_C has not been previously determined.

If a sensible guess could be made at α_C then it would be possible to calculate $\Delta\varepsilon = \varepsilon_{soln.} - \varepsilon_{solvent}$ for each solution. These calculated values could then be compared with the actual charges in dielectric constant. Thus by trial and error it should be possible to assign values to both K_2 and α_C which would yield calculated values of $\Delta\varepsilon$ closely approximating to, if not equal to, the experimental values. The calculations involved are straightforward if somewhat lengthy. The problem is however well suited to a solution using a computor. Accordingly, programs have been devised to effect these and similar calculations. The computing was carried out on the ATLAS Computor, University of London Institute of Computor Science.

Acetic Acid-Pyridine-Benzene System.

The major difficulty in this method of solution is obviously the assignment of a sensible range of values to K_2 and α_C. In this particular case, remembering that the dimerisation constant of acetic acid in carbon tetrachloride solution is approximately ten times as great as the association constant of acetic acid and pyridine in that solvent, K_2 was assumed to be approximately 10. The choice of a range for α_C seemed to be more straightforward in that it was possible to make use of a previous determination by Mansel Davies and Sob~~y~~zc~~z~~yk [67] of the moment of the acetic acid-pyridine complex in benzene solution. The authors found the effective dipole moment of the complex to be 2•97 ± 0•015 D.U. Whether their measurements were sufficiently accurate to justify their claims to have fixed the dipole moment to within such a narrow range of values is debatable as their experimental values of dielectric constant are quoted to only three places of decimals. However, by putting the moment of the complex equal to 3 D.U. and making use of the approximation developed by Guggenheim [54] and modified by Smith,[55] the writer obtained a value of about 7•5 for α_C. The writer did not attach too much weight to this value for the reason stated above. α_C was allowed to vary between 7•0 and 11•0. It was appreciated that incorrected values of both K_2 and α_C could by chance yield apparently accurate values of $\Delta\varepsilon$ but the writer felt confident that it should be possible to spot such values.

A Program which would calculate $\Delta\varepsilon$ for all possible combinations of α_C and K_2 within any given range of values was written after several unsuccessful attempts. This Program will always be referred to by the suffix A, i.e. 1A refers to its use in this case and 2A, 3A and 4A in succeeding cases. A second somewhat simpler program, labelled B, calculated for one chosen value of K_2 and a range of values of α_C. These programs are written out in full in Appendix 1.

The dielectric constants of several ternary mixtures of acetic acid, pyridine and benzene were measured using the heterodyne beat apparatus described earlier. The results are given in Table B.12. $\Delta\varepsilon$ is a measure of the difference in dielectric constant between the solution and pure solvent.

TABLE B.12.

Concentration of Base B. (moles $l.^{-1}$)	Concentration of Acid A (moles. $l.^{-1}$)	$\Delta\varepsilon$
0·6418	0·0000	0·38551
	0·0024	0·38633
	0·0070	0·39070
	0·0088	0·39223
	0·0141	0·39657
	0·0224	0·40314
	0·0322	0·41114
0·7661	0·0000	0·45966
	0·0120	0·46978
	0·0178	0·47420
	0·0500	0·50018
	0·0820	0·52585
	0·1028	0·54227
	0·1702	0·59531
0·8378	0·0000	0·50200
	0·0077	0·50872
	0·0119	0·51229
	0·0192	0·51775
	0·0262	0·52350
	0·0924	0·57687
	0·1195	0·59873

α_C was assumed to lie in between 7·0 and 11·0, whilst K_2 was assumed to lie between 8·0 and 12·0.

Inspection of the results from Program 1A showed that $\Delta\varepsilon$ for any particular values of B, A and α_C was fairly insensitive to K_2. K_2 then was made equal to 10·00 and Program 1B used to calculate $\Delta\varepsilon$. In addition to this Program 1B printed out the equilibrium concentration of monomer, dimer and complex. Inspection of these results showed the majority of acid to be present in the form of complex, although at the highest acid concentrations there was an appreciable amount of dimer present. In the light of this, the initial premise that the equilibrium concentration of base is equal to the initial concentration was untenable and both Program 1A and 1B were modified to allow for this. This could be done approximately by subtracting the equilibrium concentration of complex from the initial concentration of base. This assumes that only one species of complex, namely 1:1 complex, is present in solution. However, accurate calculation of equilibrium concentration of complex requires an accurate knowledge of the equilibrium concentration of base. That this was so was not realised immediately by the writer. Inspection of the following equations will show that full calculation of the concentration of complex is somewhat lengthy.

$$A = M + 2D + C \tag{1}$$

Let K_1 and K_2 be represented by U and V respectively then:

$$U = \frac{D}{M^2} \tag{2}$$

and
$$V = \frac{C}{M.B_e} \tag{3}$$

where $B_e = B - C$, B being the initial concentration of base and C the equilibrium concentration of complex. Substituting for B_e in (3) leads to:

$$C = \frac{V\ M\ B}{1 + VM} \tag{4}$$

from (2)
$$D = M^2U \tag{5}$$

Substituting for both M and D in (1) yields:

$$A = M + M^2U + \frac{V\ M\ B}{1 + VM} \tag{6}$$

or
$$M^3 + \left(\frac{U + V}{UV}\right) M^2 + \left(\frac{V(B - A) + 1}{UV}\right) M - \frac{A}{UV} = 0 \tag{7}$$

It is possible to reduce the general polynomial $x^3 + ax^2 + bx + c = 0$ to an equation of the form

$x^3 + px + q = 0$ which can be readily solved by the following procedure. Let $x = y - p/3y$. Substituting for x in the polynomial leads to the equation in y:

$$y^3 - p^3/27y^3 + q = 0$$

Multiplying through by y^3, one obtains a quadratic in y^3 which is readily solved

$$y^3 = - q/2 + \sqrt{q^2/4 + p^3/27} \qquad \text{(2 values)}$$

This yields solution for y in the form of cube roots. Substituting these in the formula $x = y - p/3y$ we obtain three pairs of solution for x, paired solutions being equal. Equation (7) therefore may be transformed and then solved for M. A program, D, was devised which incorporated this solution. This is also written out in full in Appendix I. Given the value of M, solution for C and D was a comparatively simple matter. The whole procedure can be avoided by making the original assumption that the equilibrium concentration of base, B_e, equalled the initial concentration, B. In this case the cubic in M reduces to a simple quadratic. It was not felt that the extra accuracy obtained using the full solution for C justified the use of the more complicated program D. Consequently C was calculated assuming B_e = B and B_e was assumed to be equal to the initial concentration, B, minus the ~~conn~~ concentration of complex C. This approximation was then incorporated in both programs A and B. The modified program A was run with α_C allowed to vary between 7 and 11 and K_2 between 8·0 and 12·0. A summary of these results is given below in Table B.13.

TABLE B.13.

Key: Δ = Difference between the calculated increment in dielectric constant and the experimentally observed increment.

B	A	Δ		Δ	
		K_2 = 8·00		K_2 = 12·00	
(moles $l.^{-1}$)	(moles $l.^{-1}$)	α_C=7·00	α_C=11·00	α_C=7·00	α_C=11·00
0·6418	0·0024	-0·00074	0·00050	-0·00071	0·00062
	0·0070	-0·00261	0·00091	-0·00246	0·00136
	0·0088	-0·00399	0·00109	-0·00318	0·00159
	0·0141	-0·00560	0·00120	-0·00518	0·00233
	0·0224	-0·00905	0·00129	-0·00823	0·00339
	0·0322	-0·01364	0·00056	-0·01228	0·00398
0·7661	0·0120	-0·00492	0·00122	-0·00464	0·00199
	0·0178	-0·00696	0·00190	-0·00647	0·00322
	0·0500	-0·02134	0·00083	-0·01913	0·00630
	0·0820	-0·03724	0·00393	-0·03294	0·00645
	0·1028	-0·04814	-0·00832	-0·04240	-0·00539
	0·1702	-0·08465	-0·02934	-0·07427	-0·00194

TABLE B.13 - Continued

B (moles l.$^{-1}$)	A (moles l.$^{-1}$)	Δ K_2 = 8·00		Δ K_2 = 12·00	
		α_C=7·00	α_C=11·0	α_C=7·00	α_C=11·00
0·8378	0·0077	-0·00282	0·00126	-0·00269	0·00166
	0·0119	-0·00457	0·00164	-0·00432	0·00234
	0·0192	-0·00699	0·00275	-0·00648	0·00410
	0·0263	-0·00992	0·00309	-0·00911	0·00518
	0·0924	-0·04134	-0·00308	-0·03654	-0·00847
	0·1195	-0·05566	-0·00878	-0·04899	-0·00713

This summary affords evidence that both α_C and K_2 lie between the specified ranges. K_2 was put equal to 10·0 and Program B used to calculate the equilibrium concentration of complex, monomer and dimer. Table B.14. shows these concentrations expressed in terms of molar fractions of the total acid concentration. It also shows the same information obtained by putting K_2 = 12·00 in Program B.

TABLE B.14.

K_1 = 138•9 K_2 = 10•00

B ml^{-1}	A ml^{-1}	molar fraction of A present as		
		monomer	dimer	complex
0•6418	0•0024	0•132	0•009	0•859
	0•0070	0•130	0•034	0•836
	0•0088	0•129	0•042	0•829
	0•0141	0•126	0•063	0•817
	0•0224	0•122	0•083	0•795
	0•0322	0•118	0•125	0•757
0•7661	0•0120	0•111	0•042	0•847
	0•0178	0•109	0•059	0•832
	0•0500	0•100	0•137	0•763
	0•0820	0•093	0•196	0•711
	0•1028	0•089	0•227	0•684
	0•1702	0•080	0•305	0•615
0•8375	0•0077	0•103	0•023	0•874
	0•0199	0•102	0•0354	0•863
	0•0192	0•101	0•054	0•845
	0•0263	0•099	0•071	0•830
	0•0924	0•086	0•191	0•723
	0•1195	0•083	0•226	0•691
	K_1 = 138.9	K_2 = 12.00		
0•6418	0•0024	0•113	0•008	0•879
	0•0070	0•111	0•026	0•863
	0•0088	0•111	0•030	0•859
	0•0141	0•109	0•047	0•844

TABLE B.14. - Continued

B ml^{-1}	A ml^{-1}	molar fraction of A present as:		
		monomer	dimer	complex
0·6418	0·0224	0·107	0·072	0·821
	0·0322	0·104	0·096	0·800
0·7661	0·0120	0·095	0·030	0·875
	0·0178	0·094	0·044	0·862
	0·0500	0·086	0·104	0·810
	0·0820	0·083	0·156	0·761
	0·1028	0·080	0·183	0·737
	0·1702	0·073	0·254	0·673
0·8375	0·0077	0·089	0·018	0·893
	0·0119	0·088	0·025	0·887
	0·0192	0·087	0·041	0·872
	0·0263	0·085	0·054	0·861
	0·0924	0·077	0·150	0·773
	0·1195	0·074	0·182	0·744

Several points emerge from a study of this table. For any given acid concentration, the higher the base concentration the greater is the proportion of acid present in the form of complex. At constant base concentration, as the concentration of acid is lowered, then the proportion of acid present as complex and monomer increases whilst there is a corresponding decrease in the proportion of dimer. The converse is also true. Such effects are to be expected from a consideration of the Law of Mass Action.

After a considered study of these results the writer was unable to assign a definite value to α within any sensible degree of accuracy. It was felt that K_2 was adequately defined as 10 ± 2 l.mole^{-1}.

The dielectric constant incre~~a~~ment, $\Delta\varepsilon$, is related to the weight fractions of the various species in solution according to the equation:

$$\Delta\varepsilon = \alpha_M w_M + \alpha_D w_D + \alpha_B w_B + \alpha_C w_C \qquad (1)$$

where the terms α and w have the usual significance. Every quantity in this equation with the exception of α_C is readily determinable or readily calculated. (1), therefore, can be re-arranged in the general form of a straight line equation.

$$y = b + mx \qquad (2)$$

where y represents $\Delta\epsilon$, b represents $(\alpha_M w_M + \alpha_D w_D + \alpha_B w_B)$, m represents α_C and x represents w_C.

Now the term $(\alpha_M w_M + \alpha_D w_D + \alpha_B w_B)$ represented by b is not, strictly speaking, a constant as its value varies from solution to solution. However, its value along with the values of $\Delta\epsilon$ and w_C can be estimated for each individual solution. Consequently one can set up 18 linear equations in α_C. Solution of these 18 equations using the method of averages yielded the most probable value of α_C. This calculated value of α_C will of course depend on the chosen value of K_2. K_2 was first put equal to 10 and substituted in a new Program C which calculated y, b and x for each solution. The value of α_C obtained in this way, 10·74 was then substituted in the Halverstadt-Kumler equation in order to determine the dipole moment of the acetic acid-pyridine complex. Use of the Halverstadt-Kumler equation requires a knowledge not only of α but also of β and γ for the complex. It was impossible to determine these last two quantities directly. There was no need to determine γ as the molecular refraction of the complex was assumed to be equal, or at any rate, very nearly equal to the sum of the molar refractions of the constituent acid and base. β for acetic acid, - 0·122, is very nearly equal to β for pyridine, - 0·126. The molecular weight of pyridine is not very different to that of acetic acid, so it is a reasonable approximation to represent the complex as a 50% by weight solution of acid in base and that β_c = - 0·124. Again this assumes, possibly incorrectly, that the specific volumes are additive. In any case the dipole moment, μ, determined in this way is relatively insensitive to the value of β used (see Section 3c).

Calculation of the dipole moment of the Acetic Acid-Pyridine Complex

$$\alpha_C = 10{\cdot}74, \quad \alpha_C = -\,0{\cdot}124$$

The total specific polarisation, $P_{2\infty}$, is given by the Halverstadt-Kumler equation viz.

$$P_{2\infty} = \frac{3\alpha V_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\,(V_1 + \beta) \qquad (1)$$

V_1, ε_1 are the specific volume and dielectric constant of pure complex.

$$p_{2\infty} = \frac{3 \times 10{\cdot}74 \times 1{\cdot}1444}{(4{\cdot}2741)^2} + \frac{1{\cdot}2741}{4{\cdot}2741}(1{\cdot}1444 - 0{\cdot}124)$$

i.e. $p_{2\infty} = 2{\cdot}3226$

The total molar polarisation, $P_{2\infty}$, is given by the equation:

$$P_{2\infty} = M.p_{2\infty} \qquad (2)$$

M = molecular weight of complex

i.e. $P_{2\infty} = 323{\cdot}20$

Now $$P_{2\infty} = {}_AP_{2\infty} + {}_EP_{2\infty} + {}_OP_{2\infty} \qquad (3)$$

where ${}_AP_{2\infty}$ = atom polarisation, ${}_EP_{2\infty}$ = electronic polarisation which is assumed to be equal to the molar refraction of the complex, and ${}_OP_{2\infty}$ = orientation polarisation. By assuming that ${}_EP_{2\infty}$ is equal to the molar refraction, R_D, one is tacitly making a small allowance for atom polarisation. No further allowance was made in this case.

i.e. $${}_OP_{2\infty} = P_{2\infty} - R_D \qquad (4)$$

or $${}_OP_{2\infty} = 284{\cdot}82$$

The dipole moment, μ, is related to the orientation polarisation by the equation:

$$\mu = \sqrt{\frac{9k}{4\pi N}} \sqrt{{}_0P_2 \cdot T} \qquad (5)$$

k = Boltzmann's Constant, N = Avogadro's Number, T = absolute temperature.

At 25° C this equation simplifies to:

$$\mu = 0{\cdot}2212 \sqrt{{}_0P_2} \quad \text{, i.e.} \quad \mu = 0{\cdot}2212\sqrt{284{\cdot}20} = 3{\cdot}73 \text{ D}$$

Putting K_2 equal to 8 and 12 yielded values of α_C equal to 11·40 and 10·34 respectively. The corresponding dipole moments are 3·84 and 3·66 D. Details of these calculations of α_C, together with those in the first case are all given in Table B.15. which follows shortly.

In summary, therefore, the probable dipole moment of the acetic acid-pyridine complex is 3·73 ± 0·12 D. and the association constant is equal to 10 ± 2 $l.mole^{-1}$.

TABLE B.15.

Results from Program C. $K_1 = 138{\cdot}9$, $K_2 = 10{\cdot}00$, $\alpha_C = 10{\cdot}74$

$B(\text{m l.}^{-1})$	$A(\text{m.l.}^{-1})$	y	b	x
0·6418	0·0024	0·38683	0·38384	0·00032
	0·0070	0·39010	0·38171	0·00092
	0·0088	0·39223	0·38090	0·00115
	0·0141	0·39657	0·37859	0·00180
	0·0224	0·40314	0·37516	0·00277
	0·0322	0·41114	0·37136	0·00385
0·7661	0·0120	0·46978	0·45379	0·00161
	0·0178	0·47420	0·45116	0·00234
	0·0500	0·50018	0·43801	0·00602
	0·0820	0·52585	0·42668	0·00920
	0·1028	0·54247	0·41999	0·01109
	0·1702	0·59531	0·40083	0·01652
0·8375	0·0077	0·50872	0·49856	0·00106
	0·0119	0·51229	0·49654	0·00162
	0·0192	0·51775	0·49315	0·00256
	0·0263	0·52350	0·48998	0·00344
	0·0924	0·57687	0·46455	0·01054
	0·1195	0·59873	0·45563	0·01304

y = experimental value of dielectric constant change

b = $(\alpha_M w_M + \alpha_D w_D + \alpha_B w_B)$

x ~~$= \rho'$~~ = wt. fraction of complex in solution

TABLE B.15. - Continued

$K_1 = 138{\cdot}9,\ K_2 = 8{\cdot}00,\ \alpha_C = 11{\cdot}40$

$B(m\ l.^{-1})$	$A(m.l.^{-1})$	y(ε exp)	b(ε calc ~~eou~~)	x(~~%~~ wt.fr.)
0•6418	0•0024	0•38683	0•38390	0•00031
	0•0070	0•39070	0•38192	0•00088
	0•0888	0•39223	0•38117	0•00110
	0•0141	0•39657	0•37907	0•00170
	0•0224	0•40314	0•37600	0•00259
	0•03220	0•41114	0•37266	0•00355
0•7661	0•01200	0•46978	0•45413	0•00153
	0•01780	0•47420	0•45172	0•00222
	0•0500	0•50018	0•44002	0•00554
	0•0820	0•52585	0•43030	0•00833
	0•1028	0•54247	0•42466	0•00955
	0•1702	0•59531	0•40878	0•01455
0•8375	0•0077	0•50872	0•49875	0•00102
	0•0119	0•51229	0•49686	0•00155
	0•0192	0•51775	0•49373	0•00243
	0•0263	0•52350	0•49083	0•00325
	0•0924	0•57687	0•46857	0•00957
	0•1195	0•59873	0•46103	0•01172

TABLE B.15. - Continued

$K_1 = 138\cdot9$, $K_2 = 12\cdot00$, $\alpha_C = 10\cdot34$

$B(m.l.^{-1})$	$A(m.l.^{-1})$	y(Σ exp)	b(Σ calc ~~cou~~)	x(ø wt.fr.)
0•6418	0•0024	0•38683	0•38380	0•00033
	0•0070	0•39070	0•38157	0•00095
	0•0088	0•39223	0•38071	0•00119
	0•0141	0•39657	0•37825	0•00188
	0•0224	0•40314	0•37456	0•00291
	0•03220	0•41114	0•37042	0•00406
0•7661	0•0120	0•46978	0•45355	0•00166
	0•0178	0•47420	0•45077	0•00242
	0•0500	0•50018	0•43655	0•00636
	0•0820	0•52585	0•42397	0•00985
	0•1028	0•54247	0•41643	0•01195
	0•1702	0•59531	0•39448	0•01808
0•8375	0•0077	0•50872	0•49843	0•00109
	0•0119	0•51229	0•49633	0•00166
	0•0192	0•51775	0•49276	0•00264
	0•0263	0•52350	0•48939	0•00357
	0•0924	0•57687	0•46155	0•01125
	0•1195	0•59873	0•45153	0•01403

Structure of the Acetic Acid-Pyridine Complex

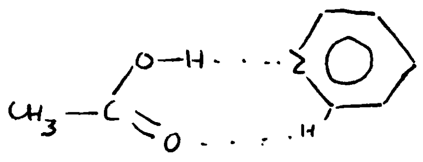
There are three possible spatial configurations for the groups of atoms in this complex. It will be remembered that the acetic acid molecule can be envisaged as existing in three isomeric forms. Similarly one can envisage the acetic acid-pyridine complex existing in three isomeric forms. The independent existence of either the cis or the trans forms is dependent on there being restricted rotation of the attendant groups around the C - O bond. A simple σ bond between two atoms involves an electron distribution which is cylindrically symmetrical about the axis of the bond. Consequently it exerts ~~the~~ no restriction upon the rotation of the attached groups such as is encountered when a π -bond is present. The dipole moment of a molecule containing only σ ~~groups~~ bonds should vary continuously with the relative disposition of the groups with respect to each other, and if all such dispositions are equally probable, the average moment observed should be simply related to the group moments of the attached groups. The C - O bond distance in acetic acid indicates that the bond has little double bond character. However the theoretical dipole moment of the acetic acid monomer in which there is free rotation of the hydroxyl group about the C - O axis is 2·8 D. considerably higher than the value of 1·505 D. obtained by the writer. This value of 1·505 D. has been explained as being consistent with there being an equilibrium between the postulated cis and trans isomers. It is possible to calculate the theoretical dipole moments of both the cis and trans isomeric forms of the acetic acid-pyridine complex, and also of the isomer in which rotation of the hydroxyl-pyridine bond is not restricted. In doing these calculations it was assumed that the approach of a polar base, i.e. pyridine, causes no change in the moment of the - OH group and that a linear - OH .. N bond is formed. Hydrogen bonding normally causes certain modifications to the electron densities of the interacting molecules or groups of atoms. For example, the O - H bond in acetic acid will be lengthened through the attraction of the electron in the approaching pyridine molecule. Also there will be a polarisation of the groupings linked to the basic centre in such a sense that electrons are displaced towards it. Consequently the dipole moments of the interacting molecules may be changed by hydrogen bonding. It is impossible to make allowances for such complications in calculating these theoretical moments.

Using the values assigned by Smyth [60] to the individual bond moments in acetic acid and the value of the dipole moment of pyridine found by the writer, the moments of the cis and trans structures were calculated to be 2·06 and 6·09 D. respectively. If the hydroxylpyridine grouping is assumed to rotate freely about the C - O axis, then the moment is calculated to be 4·54 D. Calculation of the moments of the cis and trans forms involves only a s~~a~~imple vector addition of the various group and bond moments. The dipole moment of the structure with free rotation, μ_f, can be calculated simply using the equation:

$$\mu_f^2 = \tfrac{1}{2}[\mu_c^2 + \mu_t^2]$$

where the suffixes c and t refer to cis and trans respectively.

Steric considerations would seem to favour the cis isomer because of the possibility of a stabilising interaction between the carbonyl group and the ring protons of the pyridine, but too much emphasis should not be placed on this possibility because of the relatively large separation of the ring proton and the carbonyl group.



It is generally accepted that if the dipole moment of a complex is greater than the vector sum of the constituent molecules then the association process has been accompanied by significant charge migration. The estimated moment of the cis complex is 2.06 D. and the measured moment of the complex 3.73 D. It would be wrong to immediately suggest that the complex must be in the cis form and that significant charge migration has taken place. There are two good reasons for this. Firstly it should be remembered that the estimation of the moments of the cis and trans configurations was of necessity very approximate and secondly, and more significant, it is extremely unlikely that the association of a weak acid and weak base would be accompanied by significant charge migration. A less clearly significant measure of the interaction but one which is easy to estimate, is the difference between the moment of the complex and the scalar sum of the moments of the acid and base. In this particular instance the sum of the moments is 3·70, a figure almost identical to that measured experimentally for the complex. This is further evidence of little or no charge migration. As previously mentioned Davies [62] has shown that a cis carboxyl group is favoured thermodynamically to a trans group. All this evidence points to the complex having a spatial configuration more nearly approximating to that of the cis than the trans form. It seems unlikely that there would be complete free rotation of the bulky O - H .... N grouping around the C - O bond.

Acetic Acid- 4-picoline-benzene system

This system was treated experimentally in exactly the same way as the acetic acid-pyridine system. The calculations of the dipole moment and association constant of the complex formed also followed a similar pattern. However, the assignment of a range of values to both α_C and K_2 was somewhat more difficult. 4-Picoline is a stronger base than pyridine, i.e. 4-picoline has a greater pKa than pyridine, 6·0 compared to 5·2. Basic strength in aqueous solution is not necessarily a good criterion for a measure of basic strength in benzene solution. Socrates [68] measured the chemical shifts of the hydroxyl proton resonance of a series of 1:1 phenol + base complexes in carbon tetrachloride solution and found a linear correlation between this measured chemical shift and the dissociation constant of the organic base in aqueous solution. Hence it seemed reasonable to assume that there would be a stronger interaction between acetic acid and 4-picoline than between acetic acid and pyridine. K_2 was assumed to lie somewhere between 15 and 30. In the same way, though with considerably less justification, as 4-picoline had a higher dipole moment than pyridine, it was assumed that α_C would be greater. It was assigned a value between 12 and 16.

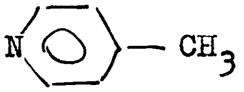
Inspection of the results from Program 2A indicated that K_2 most probably lay between 20 and 25. That this is the case was inferred from the fact that the differences between observed and calculated changes in the dielectric constant were smaller over this part of the chosen range of K_2. Program 2C enabled the writer to calculate the values of α_c which minimised the differences between observed and calculated values of ε for any particular K_2. The results are given in the table below.

TABLE B.16.

K_2	α_C
15	15·30
20	14·47
25	14·00
30	13·71

To calculate the dipole moment of the complex one needs to know in addition to α, the values of β and γ. It was impossible to determine these directly, consequently the molar refraction of the complex was assumed to be equal to the sum of the molar refractions of the constituent acid and base. As in the case of the acetic acid-pyridine complex β_C was estimated from a knowledge of the values of β for acetic acid and 4-Picoline as individual solutes. β_C, therefore, was equal to - 0·096. α_C was made equal to 14·50 ± 0·80 and the moment of the complex was calculated as 4·54 ± 0·12 D. The association constant, K_2, for the complex is 22 ± 5 $l.mole^{-1}$.

Structure of the Acetic Acid-4 Picoline Complex

The same considerations that were applicable to the acetic acid-pyridine system apply in this case. The independent existence of cis and trans forms depend on there being restricted rotation of the attendant groups about the C - O bond. It is extremely unlikely that there is free rotation of such a bulky group as O - H -  about the C - O axis. Approximate calculations of the moments of the cis, trans and free rotation forms give values of 2·37, 6·46 and 4·86 D. respectively. Again the experimental value is closest to that for the free rotation form. 4-Picoline is a slightly stronger base than pyridine, consequently one would expect there to be more charge displacement on hydrogen bonding with acetic acid. Scalar addition of the moments of acetic acid and 4-Picoline gives a value of 4·09 D., much closer to the experimental figure than that of the cis form. Steric considerations favour the cis form, or rather a form more closely approximating to the cis than the trans forms.

In summary, therefore, the probable dipole moment and association constant are 4·54 ± 0·12 D. and

22 ± 5 $l.mole^{-1}$ respectively.

Acetic Acid-2,6-Lutid~~e~~ine-Benzene System

Again this system was treated experimentally in exactly the same way as the two previous systems. The whole problem of calculation of both dipole moment and association constant again centred around the choice of a suitable range of values for both α_C and K_2. 2,6-Lutidene is a stronger base than either pyridine or 4-Picoline. On the other hand the two methyl groups might be expected to sterically hinder any interaction between 2,6-Lutidene and acetic acid. Construction of a molecular model indicated that this hindrance could be quite severe, consequently it was felt that K_2 would be lower in this case than in either of the two previous systems. K_2 was therefore allowed to vary between 1 and 6. The choice of α_C was easier in that it was possible to estimate α_C from a knowledge of the dipole moments of the constituent acid and base. α_C was therefore allowed to vary between 10·0 and 14·0. Inspection of the results from Program 3A indicated that K_2 was probably about4-5. The results of Program 3B in which K_2 was made equal to 4·5 are listed in Table B.17.

TABLE B.17.

ACETIC ACID-2,6-LUTID~~E~~iNE-BENZENE

B ml^{-1}	A ml^{-1}	molar fraction of A present as		
		monomer	dimer	complex
0·2660	0·0060	0·358	0·213	0·428
	0·0119	0·310	0·318	0·371
	0·0177	0·280	0·385	0·335
	0·0265	0·248	0·454	0·297
	0·0333	0·231	0·493	0·276
	0·0641	0·183	0·597	0·219
	0·0046	0·298	0·113	0·589
0·4396	0·0076	0·280	0·166	0·554
	0·0104	0·266	0·206	0·528
	0·0275	0·216	0·356	0·427
	0·0327	0·206	0·386	0·408
	0·0798	0·156	0·536	0·308
0·8945	0·0051	0·188	0·051	0·760
	0·0120	0·178	0·105	0·717
	0·0169	0·171	0·138	0·690
	0·0225	0·165	0·171	0·664
	0·0292	0·158	0·203	0·638
	0·0322	0·156	0·211	0·627

These show the same general features as the equivalent results from the two other systems. K_2 was made equal to 4•0, 4•5 and 5•0 and α_C calculated in each case using Program 3C. The results are listed below:

K_2	α_C	μ (D)
4•0	13•66	4•61
4•5	12•78	4•46
5•0	12•13	4•34

It will be seen that the greater spread in values of α_C was not reflected in a corresponding spread in values of dipole moment.

Approximate calculation of the dipole moments of both cis and trans structures yielded 1•66 and 5•56 D. respectively. Consideration of a molecular model of this complex indicated that the cis structure might be favoured due to the possibility of a stabilising interaction between the carbonyl group and the methyl groups. Any such interaction must obviously be very weak. Further inspection of the molecular model indicated that it was unlikely that there could be free rotation of the attendant groups about the C - O axis. The observed dipole moment, 4·45 ± 0·15 D., is considerably greater than either the scalar sum of the moments of the constituent component or the theoretical moment of the cis complex. This suggests that either there is a considerable amount of charge transfer or else the geometry of the complex more closely approximates to the trans structure rather than to the sterically favoured cis structure. Whilst 2,6-Lutidine is a stronger base in water than pyridine, it seems improbable that there should be a significant difference in the amount of charge transfer as compared with the acid-pyridine complex. It is much more likely that the complex has a structure in which the bulky O - H - Base group was neither cis nor trans to the carbonyl group. Theoretically it should be possible to determine the spatial distribution of all these groups about the C - O axis. It will be remembered that Jumper and Howard [47] felt that as it was impossible to estimate the charges in dipole moment experienced by the constituent molecules on complex formation, and that it was very dangerous to attempt to calculate the exact geometry of the complex from a knowledge of its dipole moment. This generalisation is applicable to all the systems studied in this investigation, as the dipole moment of the complex is very sensitive to the relative disposition of the various groups.

In summary, there the dipole moment of the complex was found to be 4•45 ± 0•15 D. and the association constant for complex formation 4•5 ± 0•5 $l.mole^{-1}$.

Acetic Acid-Quinoline-Benzene System

This system was treated in the same way, both experimentally and mathematically, as the three previous systems. The same basic facts, namely the values of the pKa of the base, possibilities of any steric interactions, and dipole moments of both acid and base, guided the writer in his choice of ranges of values for both K_2 and α_C. Quinoline has a lower pKa, 4•9, than all the other bases used so far. Its dipole moment, 2•19 D., is identical with that of pyridine. Inspection of a molecular model indicates no particular steric inhibition of complex formation. On the face of it, therefore, one would expect both the association constant and the dipole moment to be very similar to, though possibly slightly lower than, those of the acetic acid-pyridine complex. Inspection of the results from Program 4A in which K_2 was allowed to vary between 5•0 and 10•0 indicated that either K_2 or α_C is considerably higher than one might anticipate. K_2 was therefore allowed to vary between 15 and 25. The results from this second run of Program 4A indicated that K_2 probably had a value of about 20. Table B.18. constains the results of a run of Program 4B in which K_2 was made equal to 20.

K_2 was successively made equal to 18•0, 20•0 and 22•0 and Program 4C used to calculate α_C in each instance.

TABLE B.19.

K_2	α_C	μ (D)
18•0	10•57	4•27
20•0	10•44	4•24
22•0	10•36	4•23

The dipole moments were calculated from α_C in the usual way.

It will be noticed that the value of the dipole moment of the complex 4•25 ± 0•02 D. is considerably higher than the dipole moment of the acetic acid-pyridine complex, 3•73 ± 0.12 D. The pKa of Quinoline, 4•9, is lower than that of pyridine, 5•2, but obviously there is a stronger interaction between acetic acid and quinoline than between

TABLE B.18.

ACETIC ACID-QUINOLINE-BENZENE. $K_2 = 20{\cdot}0$

B ml^{-1}	A ml^{-1}	molar fraction of A present as		
		monomer	dimer	complex
0•4734	0•0046	0•102	0•013	0•885
	0•0076	0•100	0•021	0•879
	0•0120	0•099	0•033	0•868
	0•0141	0•0986	0•038	0•863
	0•0179	0•098	0•047	0•855
	0•0267	0•096	0•068	0•837
0•5365	0•0051	0•084	0•012	0•906
	0•0094	0•084	0•019	0•898
	0•0116	0•084	0•022	0•894
	0•0135	0•083	0•025	0•891
	0•0195	0•080	0•057	0•862
0•6281	0•0061	0•074	0•098	0•918
	0•0100	0•073	0•014	0•913
	0•0124	0•073	0•018	0•910
	0•0152	0•072	0•022	0•906
	0•0199	0•072	0•028	0•900
	0•0297	0•071	0•041	0•888

acetic acid and pyridine. Approximate calculations of the moments of the cis and trans forms of the complex yielded 2·06 and 6·09 D. respectively. The moment of the complex in which there is free rotation about the C - O bond is 4·54 D. In this case, as with the other acid-base complexes, the correlation between the experimentally observed moment and the theoretical moment of the structure assuming free rotation is probably fortuitous. Inspection of a molecular model of the complex confirms this.

If the dipole moment of a complex is greater than the vector sum of the constituent molecules then the association process is considered to have been accompanied by charge migration. There is a considerable difference between the measured moment and the calculated moment of the cis complex. There is also a considerable difference between the measured moment and the scalar sum of the moments of the constituent molecules. Both these observations together with the larger than expected association constant either point to there being some significant amount of charge migration or else to there being a different type of interaction to that observed in the three previous systems. Alternatively, one can postulate the existence in solution of a different molecular species, e.g. a 2:1 acid:base complex. Again, as there is a considerable excess of base present, this is unlikely. The relatively high value of K_2 remains somewhat of a mystery.

In summary, the dipole moment was found to be $4{\cdot}25 \pm 0{\cdot}02$ D. and the association constant 20 ± 2 $l.mole^{-1}$.

C. NUCLEAR MAGNETIC RESONANCE STUDIES

(1) Introduction and Previous Work

The use of Nuclear Magnetic Resonance (n.m.r.) in this investigation has been made possible through the kind offices of Dr. A.G. Davies of University College, London.

The possibility of applying n.m.r. measurements to studies of hydrogen bonding became apparent following the observation of Arnold and Packard [69] that the chemical shift of the proton signal of the ethanol - OH group was temperature dependent. An interpretation of this was put forward by Liddel and Ramsay.[70] The existence of a temperature dependence of the resonance signal can be understood if there are alternative molecular states where energy separation is of the order of kT. Since ethanol forms hydrogen bonds involving the hydrogen in the - OH group, this hydrogen should experience a different magnetic shielding in the associated and unassociated states. If the correlation time relating to the lifetimes of the two states is sufficiently small (less than a millisecond) the hydrogen resonance will be observed at the frequency corresponding to the average shielding for the two states. Since changes in temperature will alter the populations of the associated and unassociated states, the resonance frequency will be temperature dependent. Solvent dilution, as it also causes dissociation of the hydrogen bonds, will have an effect equivalent to that of raising the temperature. Such temperature- and dilution-dependent signals are quite general for hydrogen-bonded systems. In applying n.m.r. to investigations of molecular interaction one is interested in the chemical shift of the proton in both the associated and unassociated states. The difference between these two shifts may be termed the hydrogen bond shift.

Studies of the hydrogen bonding of carboxylic acids and general acid-base complexes using n.m.r. are still few in number. The first study of the hydrogen bonding of acetic acid was made by Huggins, Pimental and Shoolery.[71] These authors measured the hydrogen bond shift for phenol, several substituted phenols and acetic acid in carbon tetrachloride solution and also for acetic acid in acetone solution. The proton resonance behaviour could be correlated with the known hydrogen bonding properties of these compounds. Unfortunately in the case of acetic acid in carbon tetrachloride solution the limit of detectability of the proton resonance is at a concentration at which dimer is the predominant species. In acetone solution, however, the competition of the solvent as a hydrogen bonding base causes dissociation of the acetic acid dimers at a higher concentration. These systems can be treated mathematically as follows. The observed chemical shift, δ, is assumed to be the weighted mean of δ_M and δ_D, the assumed characteristic values of the chemical shifts in pure monomer and dimer. If there is only monomer and dimer present in solution then,

$$\delta = \frac{m}{x}\delta_M + \frac{x - m}{x}\delta_D$$

(1) .... $\delta = \delta_D - \frac{m}{x}\Delta_D$ where $\Delta_D = \delta_M - \delta_D$,

or the 'hydrogen bond shift', m = number of moles of monomer, x = total number of moles of solute.

If the equilibrium constant, K, (monomer $\rightleftharpoons$ dimer) is defined in mole fraction terms, then,

$$K = \frac{X_D}{X_M^2} = \frac{(x - m)(2s + x + m)}{4m^2} \qquad (2)$$

where X_D, X_M are the mole fractions of dimer and monomer respectively, and s = number of moles of solvent present. In the limit as X approaches zero, $\delta \rightarrow \delta_M$

$$\left(\frac{\partial \delta}{\partial X}\right)_{X \to 0} = 2K\,\Delta_D \qquad (3)$$

The authors [71] maintained that if a plot of δ versus X is extrapolated to zero concentration, the value of so obtained should be equal to δ_M. This sort of extrapolation was, however, particularly dangerous as the lower limit of X at which experimental observations were made was X = 0·01. There is, of course, no hard and fast rule as to the limiting lowest value of X above which it is dangerous to extrapolate data to zero concentrations. In the particular case discussed by the authors,[71] the dimerisation of phenol in carbon tetrachloride, the necessary conditions which should be satisfied before such an extrapolation is attempted, were probably satisfied. That is to say that the solutions were sufficiently dilute to ensure the presence of only monomer and dimer. This was probably not the case with acetic acid in carbon tetrachloride solution. The first systematic study of hydrogen bonding in acetic acid using n.m.r. was carried out by Reeves and Schneider [72] who measured the position of the - OH proton resonance at various dilutions in several non-interacting solvents of widely differing dielectric constants. They noticed that in benzene contrary to the behaviour of other hydrogen bonded liquids the proton resonance of the - OH group moves first to low field and finally in very dilute solutions moves to high field relative to its position for pure acetic acid. This behaviour underlines the dangers inherent in extrapolation of hydrogen bond shifts to infinite dilution. These unusual dilution shifts are consistent with the presence in concentrated solutions of polymers, the individual hydrogen bonds of which are on the average weaker than those of the dimer. These break up on dilution to form the dimer. In extremely dilute solution or in solvents of high dielectric constant dissociation of the dimer occurs. The dielectric properties of acetic acid solutions are consistent with polymer formation in concentrated solution and pure acetic acid.

Davis and Pitzer [73] studied the n.m.r. spectra of several carboxylic acids in benzene solution in an attempt to obtain more specific information about the equilibria involved and the nature of the monomeric and polymeric species. They started from the premise that the carboxylic acids usually associated to form a cyclic dimer in solution similar to that observed in the vapour phase. In dilute solution the monomer-cyclic dimer equilibrium is the most important. It had been shown previously [71] that such a system could be studied advantageously using n.m.r., and further that the observed shift of the hydroxyl proton was given by the expression,

$$\delta = \frac{m}{x}\delta_M + \frac{x - m}{x}\delta_D$$

and that at infinite dilution the slope of the plot of δ versus mole fraction, X, is given by,

$$\left(\frac{\partial \delta}{\partial X}\right)_{X \rightarrow 0} = 2K\,\Delta_D$$

where the symbols δ, δ_M, δ_D, m, x, X, K and Δ_D have the same meaning as previously. Using values of K determined independently, [37] δ_M and δ_D were determined at various temperatures. The authors recognised that due to the relatively high association constants of carboxylic acids in benzene solution it was impossible to obtain measurements of δ at sufficiently low concentrations to be able to extrapolate the data to infinite dilution. It is thus impossible to obtain an accurate value of K from n.m.r. measurements alone.

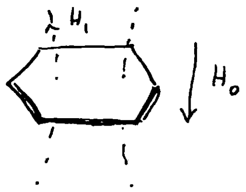
However Parmigiani, Perotti and Riganti [74] reported a determination of the dissociation constant of acetic acid dimers in carbon tetrachloride solution using n.m.r. measurements. The validity of this result ($K_{dissn.} = 1{\cdot}01 \times 10^{2}$ l.mole^{-1}) must be doubtful. At the lowest concentrations on which measurements were made, mole fraction acid $\sim$ 0•001, the acetic acid must largely be still in the dimeric form, as carbon tetrachloride will not promote the dissociation of acid dimers to anything like the same extent as benzene. The authors [74] had to extrapolate to zero concentration a plot of average chemical shift against total concentration of acid. The dangers of this procedure cannot be overemphasised as in this situation the physical property, chemical shift, is particularly sensitive to the change in concentration and traces of moisture, and there is no guarantee that there is a regular linear relationship between the two. More recently Muller and Rose [75] published a paper dealing with the n.m.r. dilution shifts of acetic acid in acetic anhydride, acetone and 1,4 dioxane. They pointed out that the inconsistent pattern of results obtained by previous investigators could be explained by the suggestion that the solvents employed were not rigorously dried. They went on to show that for solutions of acetic acid in these solvents the dilution curve is nearly linear down to fairly low concentrations (mole fraction solute 0·01 ~~0·091~~) and consequently could readily be extrapolated to infinite dilution. The authors [75] did not establish quantitatively how much water still remained in their samples but there can be little doubt that every precaution was in fact taken to exclude moisture from them. Any comparison of results obtained for acetic acid in donor solvents such as acetone with results obtained in aprotic solvents such as carbon tetrachloride is dangerous, as in the former one has to contend with the added complication of solvent-solute interactions.

Conti and Franconi [76] reported that down to the very lowest acid concentrations the predominant equilibrium in solutions of carboxylic acids in aprotic solvents is that between open chain dimer and cyclic dimers. Exactly what the authors [76] mean~~t~~s by open chain dimer is obscure. It is extremely likely that the cru~~t~~cial effect of dilution of a carboxylic acid is the replacement of a chain polymer by a discrete ring dimer.

Using n.m.r. Berkeley and Hanna [77,78] have studied the complexes formed between chloroform and several nitrogenous bases. The authors were interested in the dilution shifts of proton donors in various acceptors or bases. They felt that a distinction should be drawn between an observed dilution shift and a quantity which can be calculated from this, the hydrogen bond shift of pure 1:1 complex, Δ_{AB}. This quantity, Δ_{AB}, is equal to the difference between Δ_{AD}, the shift in pure complex and δ_D, the shift in pure donor. This nomenclature is, of course, only relevant to binary systems with the acceptors the second component. The authors [77,78] have shown that at infinite dilution of the proton donor in an acceptor solvent, the limiting slope and the intercept (limiting shift) of a plot of donor concentration versus shift of the donated proton is sufficient to determine the equilibrium constant for hydrogen bond formation. This method again depends on being able to extrapolate with sufficient certainty to infinite dilution.

The proton resonance shift accompanying hydrogen bond formation is normally towards lower field. This implies a shift towards the resonance of a "bare proton" and could be interpreted as a lowering in the electron density around the proton. This does not seem very sensible and in fact a convincing argument to the contrary can be framed. That an increase in electron density goes hand in hand with a decrease in magnetic shielding means that the dependence of magnetic shielding on the electron distribution is very different from the dependence of the energy on this distribution. Pople, Bernstein and Schneider [79] take as a starting premise the electrostatic model of the hydrogen bond. The chemical shift of the proton in an isolated AH molecule is determined by the intramolecular electronic circulations. There are two probable causes of the hydrogen bond shift. Firstly, the proton in AH will experience a magnetic field due directly to the currents induced in the acceptor molecule B and if this has a non zero average over all directions, there will be a net contribution to the proton chemical shift. Secondly, the presence of B will disturb the electronic structure of the A - H bond and consequently modify its magnetic susceptibility. Both these two effects would be expected to lead to a reduction in screening.

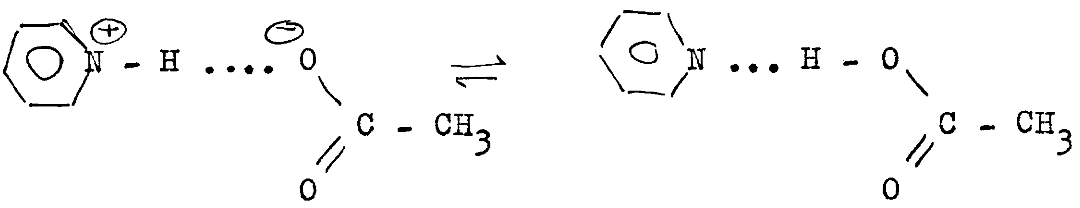
The situation where a polar molecule appears to hydrogen bond to an aromatic solvent molecule is of some interest. Reeves and Schneider [80] and Schneider [7] have demonstrated directed molecular interaction between polar solute molecules and benzene solvents molecules using the n.m.r. technique. The π -electron system in benzene represents a relatively exposed region of electronic charge on each side of the plane of the aromatic ring and consequently if a second molecular species interacts with benzene, this interaction will primarily be through the π-electrons and in the resulting complex the interacting molecules will have a preferred mutual orientation. This results in the proton resonance of the solute shifting to higher applied field. Schneider [7] interpreted the interaction between polar alkyl-x and vinyl-x solutes and benzene as a dipole-induced dipole interaction, the magnitude of which appeared to depend on the magnitude of the molecular dipole moment of the solute as well as on its molecular volume. An example of this type of behaviour is provided by a study of the proton resonance of dilute solutions of chloroform in benzene. If chloroform is dissolved in cyclohexane there are no specific interactions with the solvent other than weak Van der Waals forces and dipole interactions. Cyclohexane can be regarded as effectively an inert medium and accordingly the proton resonance frequency of chloroform in cyclohexane can be accorded the value zero. In benzene, however, the proton of the chloroform molecule becomes directed normally to the molecular plane of the solvent molecule and because of the so-called 'ring current' effect, its resonance is shifted to higher field. If the 'ring current' effect were absent one would have expected this hydrogen bonding interaction to result in a small shift of the chloroform resonance to lower field. In aromatic molecules there are interatomic currents which flow around closed conjugated loops. The secondary magnetic field, H_1, due to these currents is in the opposite direction to the primary applied field H_0, consequently a proto~~m~~n situated above or below the plane of the ring will resonate at a higher applied field.



Addition of more solvent brings more solute molecules into close contact with benzene molecules causing an increased shift of the resonance signal to higher field. This effect forms part of the phenomenon known as the ring current effect.

Recently Musher [81] has claimed that the local diamagnetic anisotropy accounts for anisotropic magnetic susceptibility and for proton chemical shifts both in benzene and in cyclohexane and that ring currents are a fiction. There is no doubt that Musher's model gives a good empirical correlation between structure and diamagnetic anisotropy in polynuclear benzenoid aromatic compounds. It would seen unwise, however, to discard the ring current model as it continues to provide the only satisfactory explanation of the large diamagnetic shift of protons immediately above an aromatic ring.

There appear to be no recorded measurements on the complexes formed between organic acids and heterocyclic bases in benzene solution. Toyoda [82] and coworkers made n.m.r. studies of mixtures of acetic acid, phenol and water with pyridine. The acetic acid-pyridine binary mixture is of some interest. The authors found that the lowest resonance field of the - OH proton occurred at a composition of 50 mole per cent of pyridine and that the separation between ortho and para protons decreased as the concentration of pyridine decreased. This, the authors suggest, is evidence for the existence of a double minimum potential for the proton of the following type.



This assumption is not consistent with the evidence from Infra-Red Spectroscopy. Barrow [66] measured the equilibrium constants for the reaction of pyridine and acetic acid in carbon tetrachloride and chloroform and found them to be 200 $1.cm.^{-1}$ and 70 $1.cm.^{-1}$ respectively. The author [66] felt that the I.R. Spectra of these systems were consistent with the reaction product being a simple hydrogen bonded complex in which the proton remains covalently bonded to the acid whilst the base is associated to the acidic hydrogen through an essentially electrostatic attraction. There is no doubt that the solvent used affects the degree of association but whether it affects the nature of product formed is more doubtful. This matter will be taken up later.

Brügel [83] reported the n.m.r. spectra of 154 pyridine derivatives. The writer has used this source for details of the actual proton magnetic resonance spectra of 4-Picoline, 2,6-Lutidene and pyridine itself. Schaefer [84] reported the n.m.r. spectra of Quinoline.

(2) Experimental Work and Discussion

(a) Acetic Acid-Benzene and Acetic Acid-Cyclohexane Systems

The n.m.r. spectra of a series of solutions of acetic acid in benzene and cyclohexane have been measured. The n.m.r. spectrum of acetic acid consists of one peak due to the hydroxyl proton and a second peak due to the protons of the methyl group. There is no spin-spin coupling between these protons. The separation of the - OH and - CH_3 protons in pure acetic acid is 593 ± 3 c/s. Throughout this investigation the $-CH_3$ resonance peak has been used as an internal reference.

All the n.m.r. spectra were measured on a Perkin Elmer R.10 60 Mc/s Spectrometer. The solutions were all made up by weight and care was taken to avoid undue exposure to the atmosphere. In both of these cases repeated measurements were made on both pure acid and several solutions of that acid in the particular solvent. The results given in Table C.1. represent in the case of pure acid a mean value of several separate determinations and in the case of the solutions are composite of several separate runs.

The acetic acid-benzene system will be considered first. Inspection of the results reveals that there is a maximum separation of the - OH and - CH_3 protons at a mole fraction of acid of about 0·08. This separation, $\triangle$, decreases rapidly with decrease in concentration below that point. This is in sharp contrast to the relative insensitivity of $\triangle$ to concentration at concentration greater than mole fraction acid about 0·1. This type of behaviour is similar to that reported previously [73] and should be contrasted with that displayed by acetic acid in cyclohexane solution (Table C.2.).

In this instance, the rapid decrease in $\triangle$ on dilution of solutions of low concentration does not take place. This is indicative of the fact that cyclohexane is a much poorer disassociating solvent than benzene. The reasons for this are twofold. Firstly, cyclohexane has a slightly lower dielectric constant than benzene and secondly, and perhaps more significantly,

TABLE C.1.

ACETIC ACID-BENZENE

Mole fraction acid (x_A)	Δ(c/s) ± 3 c/s
0·0145	577
0·0194	593
0·0216	601
0·0314	618
0·0568	648
0·0751	658
0·0825	662
0·1041	657
0·1223	653
0·2469	636
0·3421	632
0·4017	624
0·5016	620
0·6287	618
0·7413	614
0·8125	613
0·9146	607
0·9621	602
1·0000	593

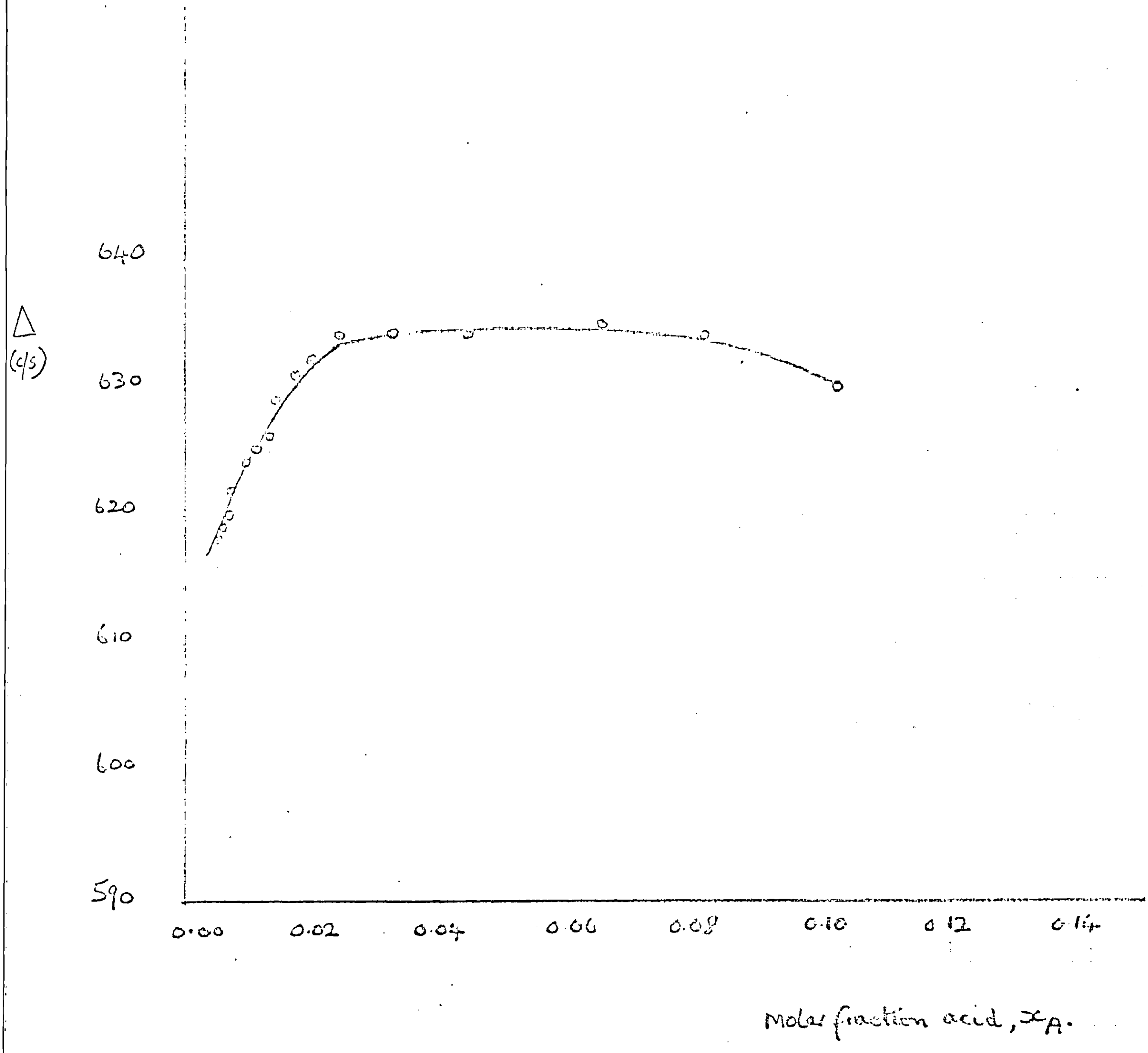
TABLE C.2.

ACETIC ACID-CYCLOHEXANE

Mole fraction acid (x_A)	Δ(c/s) ± 3 c/s
0·0052	618
0·0063	619
0·0071	620
0·0076	622
0·0099	624
0·0115	625
0·0134	626
0·0145	629
0·0172	631
0·0198	632
0·0239	634
0·0316	634
0·0439	634
0·0654	635
0·0807	634
0·1190	630
0·1468	628
0·3686	624
0·5214	622
0·6813	619
1·0000	593

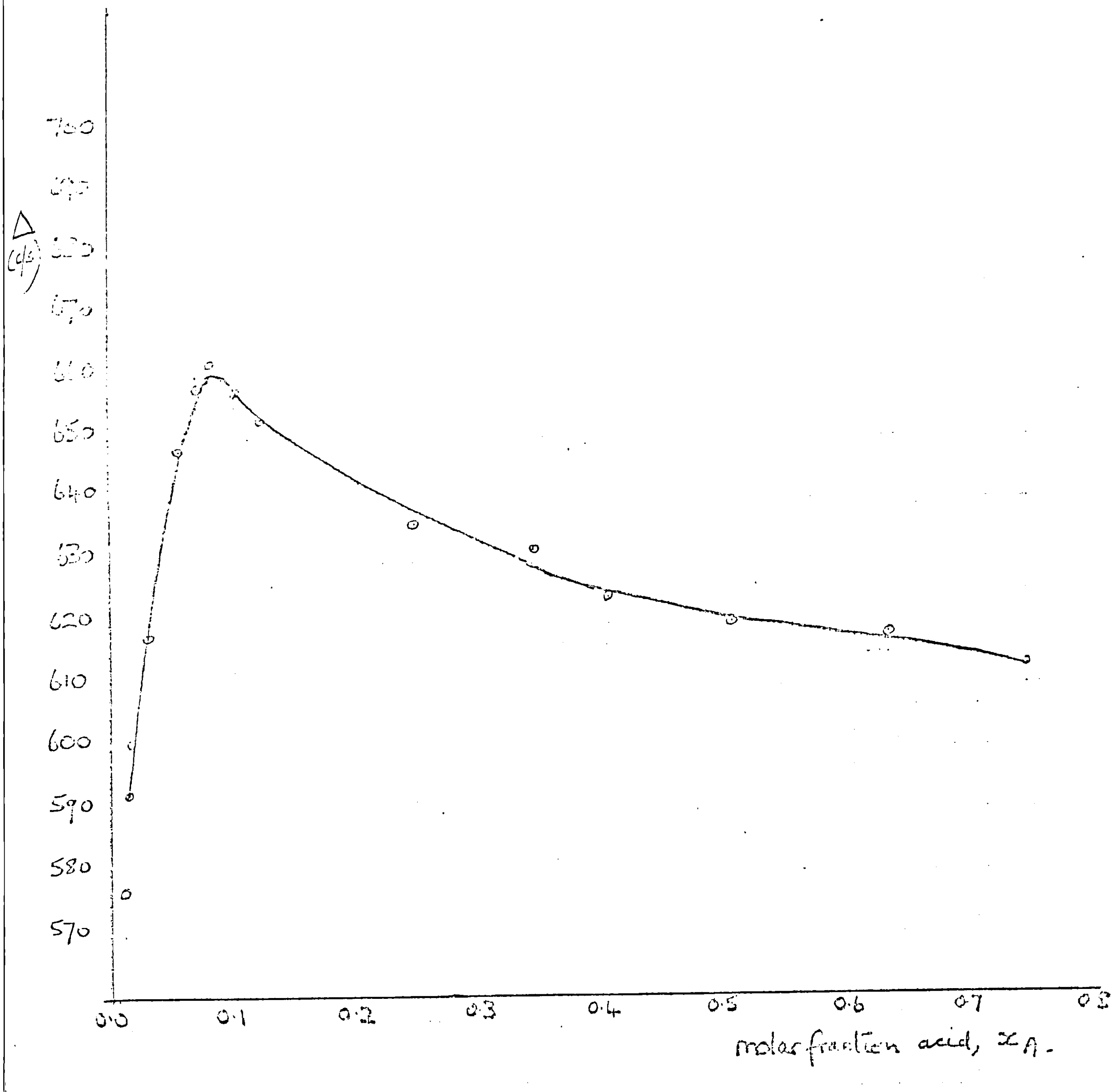
GRAPH C2

ACETIC ACID - CYCLOHEXANE



GRAPH C1

ACETIC ACID – BENZENE



there is probably a specific interaction between the polar acetic acid and the benzene solvent molecule. This type of interaction was first observed by Reeves and Schneider [80] who noted that the chemical shift between the proton in chloroform and an external reference was smaller in benzene than in cyclohexane. This high field shift was explained by assuming a molecular complex to be formed between chloroform and benzene in which the molecular axis of symmetry of the chloroform molecule is parallel with the six-fold symmetry axis of the solvent molecule. The authors [80] felt that the assumption that the chloroform proton lies on the six-fold symmetry axis unjustified, though quite probable. If such a specific action were possible between the acetic acid monomer and benzene then the monomer would be preferentially stabilised with respect to the dimer and consequently $K_{assn.}$ will be much smaller in benzene than in cyclohexane. This, in fact, is the case. Further evidence in favour of such an interaction is the fact that the - OH resonance peak in benzene is much broader than the-OH resonance peak in cyclohexane at similar concentrations. In benzene solution this broadening became noticeable at concentrations as high as mole fraction acid of 0·03 whilst in cyclohexane solution the - OH resonance peaks were sharp right down to the lowest acid concentrations.

In I.R. spectroscopy it is possible to observe vibrational bands for both associated (dimeric) and non associated (monomeric) states simultaneously. This is not possible in n.m.r. spectroscopy as the correlation time is sufficiently small relative to the lifetimes of the two states for the - OH proton resonance to be observed only at the frequency corresponding to the average shielding of the two states. Since only one sharp signal is observed the lifetime of the hydrogen bonded state must be considerably shorter than the reciprocal of the hydrogen bond shift, i.e. less than 10^{-3} seconds. In principle the physical conditions could be altered so that the hydrogen bonded dimer has an average lifetime of the order of 10^{-3} seconds, thereby permitting measurement of the chemical shift (relative to the $-CH_3$ protons) of both monomeric and dimeric hydroxyl protons. It is conceivable that in benzene solution the lifetime of the monomeric species is increased by its preferential solvation by benzene molecules.

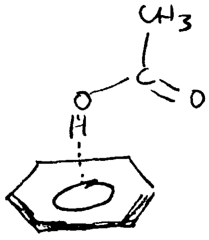
Another approach to the problem is to consider what effect, if any, this specific interaction between a benzene solvent molecule and an acetic acid monomer molecule would have on the characteristic relaxation times of acetic acid. The line width of peaks is related to both T_1 and T_2, the spin-lattice and spin-spin relaxation times respectively. These times are often referred to as the longitudinal and transverse relaxation times. It is well known that the n.m.r. line widths in liquids and gases are much smaller than for the same molecules in the solid state. That this is so is the result of the averaging effect caused by rapid variation of the perturbing environment on the mobile phases. In a solution any factor which tends to slow this variation of local environment may also increase the line width. Thus an increase in the lifetime of the monomeric species could affect the line width by altering T_1 and T_2.

The whole question of the nature of this interaction between solute molecules and benzene is of particular interest. A recent paper by Ronayne and Williams [85] modifies some of the ideas expressed in the past as to the nature of this interaction. The authors, quite reasonably, suggest that any mechanism which purports to explain benzene-induced solvent shifts should consider the following points. Firstly, the nature of the interaction; secondly, the stoichiometry of the interaction; thirdly, the thermodynamic stability of the collision complex and finally its time averaged stereochemical nature. There is considerable evidence[7,86,87,88] that the benzene-molecule acts as an electron donor to an electron deficient region in the solute molecule. This donation induces a transient dipole in the benzene molecule and the interaction may be regarded as of the dipole-induced dipole type. It is widely assumed that the stoichiometry of the collision complex is always 1:1. In fact, as the authors point out there is scant evidence for this assumption. If the interaction can be represented as an equilibrium,

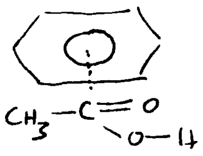
$$\text{Benzene} + \text{Solute} \rightleftharpoons \text{Collision Complex}$$

then the solvent shift ought to be temperature dependent. It has been shown [89] that the proton resonance peaks of aromatic solutes in benzene move to high field as the temperature is lowered. This shift is indicative of the fact that complex formation is favoured at lower temperature.

The stereochemistry of these complexes is assumed to be such as to enable the region of high π -electron density of the benzene molecule to interact with the electron deficient site. The authors [85] went on to point out that as it is generally accepted that benzene will act as an electron donor to an electron deficient site, then there is no real reason why the collision complex need always ben analysed as a 1:1 complex, but rather it would seem sensible to expect an association at each electron deficient site in a polyfunctional molecule. In general, therefore, the benzene molecules will be oriented by the electron deficient site of a local dipole. In the particular case of the acetic acid-benzene interaction a benzene molecule can be considered as solvating the carboxyl group. Whether or not this solvation is effected by the hydroxyl group alone interacting with the π -electron cloud or whether the benzene molecule interacts with the carboxyl group as a whole is an open question. Two types of possible interaction are visualised.



(1)



(2)

In both solvents the general relationship between $\triangle$ and the concentration of acid may be explained by assuming that on dilution the disordered polymeric chains in pure acetic acid are broken up and replaced by the highly ordered dimeric molecules. The hydroxyl proton in acetic acid dimer is less well shielded and consequently the average resonance frequency is lower than in pure acid. At acid concentrations lower than mole fraction equal to 0·1 dissociation of the dimer increases and consequently the average hydroxyl resonance frequency increases. The polar monomer is favoured relative to the dimer in a solvent of high dielectric constant. Benzene has a slightly higher dielectric constant than cyclohexane even so at the lowest concentration at which it proved possible to make measurements, there had been little upfield movement of the hydroxyl resonance frequency. These trends can be seen in Graphs C.1. and C.2.

Pitzer and Davis[73] recognised that it was impossible to obtain an accurate value of $K_{assn.}$ for a carboxylic acid in benzene from n.m.r. data alone. The writer concurs with this. Using the predetermined value of $K_{assn.} = 138{\cdot}9$ l.mole^{-1} attempts have been made to calculate the values of δ_M and δ_D the absolute chemical shifts of monomer and dimer. [All chemical shifts were measured relative to the methyl protons]. Depending on which pair of measurements were used, however, varying values of δ_M and δ_D were obtained. This indicated either that the experimental results were inaccurate or else that the theory of there being only monomer and dimer present in solution inadequate. Indeed the validity of this assumption at concentrations greater than 1% had always been doubtful. This, of course, is borne out by the molecular polarisation measurements.

(b) Acetic Acid-Pyridine-Benzene System

As previously mentioned Toyoda [82] and co-workers reported the n.m.r. spectra of the acetic acid-pyridine binary system. There appeared to be no published work dealing with the ternary system. The writer decided to repeat Toyoda's work in the light of the fact that his conclusions differed from those reached from a consideration of the Infra-Red spectra of these systems.[66] The n.m.r. spectra were measured for a series of binary mixtures of acetic acid and pyridine. A plot of Δ, the separation in c/s between the - OH and - CH_3 proton resonance signals, against x, mole fraction of acid, is shown in Graph C.3.

The n.m.r. spectrum of pyridine was reported by Brügel.[84] The ~~e~~ τ values of the α, β and γ protons were 1·50, 3·015 and 2·65 respectively. The spectrum, a molecule of the type AB_2X_2 with the α protons identified with X_2, and the β and γ protons identified with B_2 and A respectively, is rather complicated. Spin-spin coupling with the nitrogen nucleus is eliminated by quadrupole relaxation.

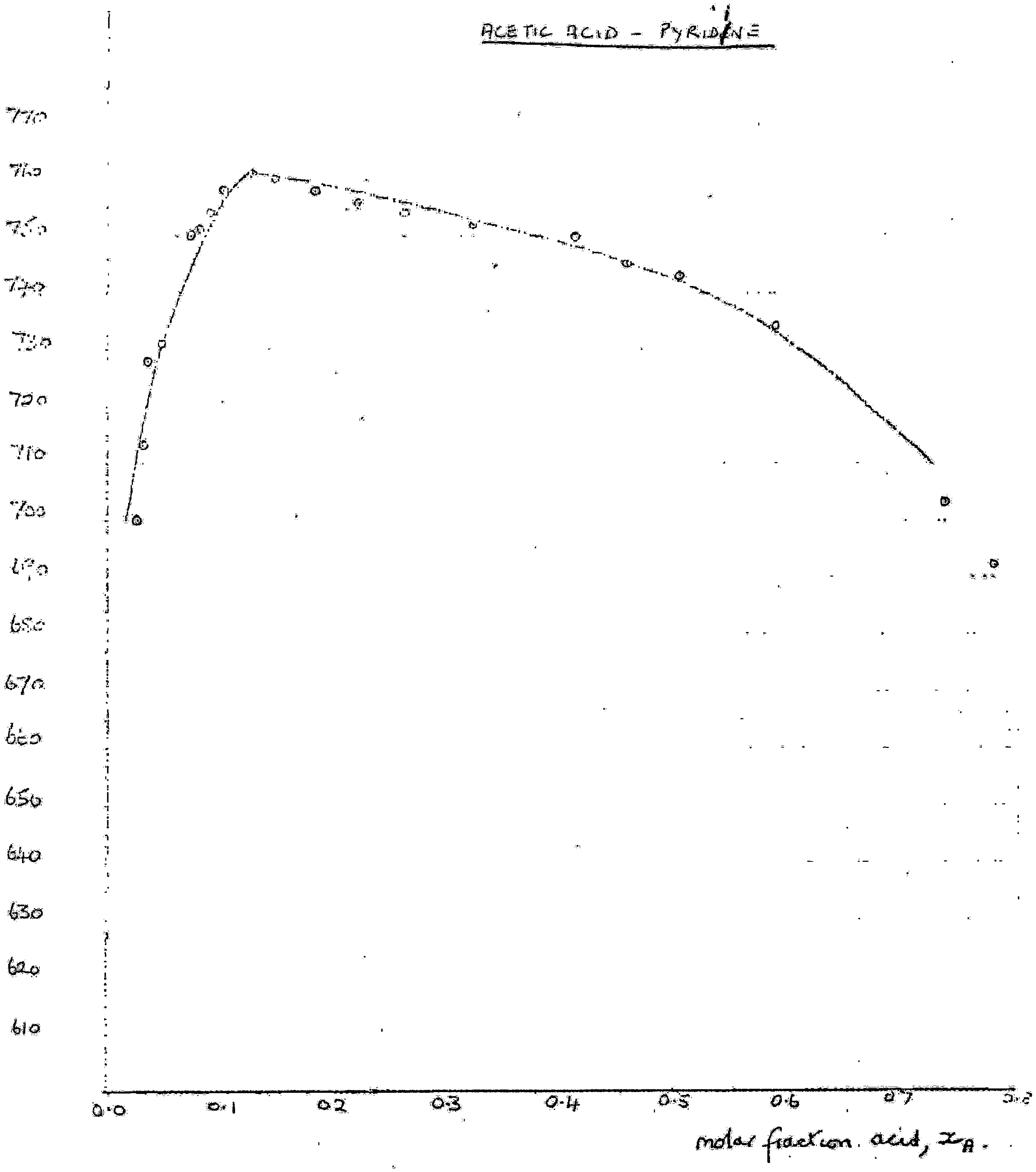
Addition of a very small quantity of acid has

TABLE C.3.

ACETIC ACID-PYRIDINE SYSTEM

Molar fraction (x_A)	Δ (c/s) ± 3
1·0000	593
0·9185	636
0·8487	648
0·8083	683
0.7785	692
0·7374	703
0·5845	734
0.5016	743
0·4562	745
0·4131	750
0·3195	752
0.2597	754
0.2192	756
0·1816	758
0·1483	760
0·1276	761
0·1049	758
0·0913	754
0·0808	751
0·0725	750
0·0448	731
0·0340	728
0·0303	713
0·0274	700

GRAPH C3


ACETIC ACID – PYRIDINE
770
760
750
740
730
720
710
700
690
680
670
660
650
640
630
620
610
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
molar fraction acid, x_A.

no noticeable effect on either the positions or intensities of the lines of the pyridine spectrum. With the addition of increasing amounts of acid there is a definite compression of the spectrum as the β and γ proton resonances move sharply to low field. There is, at the same time, a slight downfield movement of the α proton resonance. It is normal to regard the bonding orbitals of the nitrogen atom in pyridine as being in a sp^2 hybrid state. The atom will contribute one 2p atomic orbital to the conjugated aromatic ring system of pyridine, and one of its electrons can be regarded as being contributed to the aromatic sextet. No change in the state of hybridisation is necessary before bond formation using the lone pair can take place. In the extreme case of protonation to form the pyridinium ion one can envisage the adoption by the nitrogen atom of a formal positive charge. If, however, there is only a weak interaction between the lone pair and a proton then only partial charge transfer occurs with the result that the nitrogen atom carries only a slight excess of positive charge. This would cause a polarisation of the aromatic molecular orbital towards the reacting centre with the result that it will be the β and γ positions that will be denuded of charge density. Consequently their shielding constants will be lowered and their resonance frequencies will shift to lower field.

Addition of pyridine to acetic acid causes a change in the separation of the - OH and - CH_3 proton resonances. As can be seen from Graph C.3. and Table C.3. there is a maximum separation at a mole fraction of acid of about 0·1. This is in sharp contrast to the behaviour recorded by Toyoda. Now the pyridinium ion will be stabilised by resonance to a lesser extent than pyridine. This is shown by the weakness of pyridine as a base. N.m.r. is unable to prove or disprove the existence of both the above species in solution as the exchange time between the two may be short compared to the characteristic time of measurement. This would result in the coalescence of the two signals into a single ϕ - H - N peak which in fact is what is observed. Such a single peak would also be observed if there were only one species in solution. At high acid concentrations there will be at least two species present in solution, namely, free acid and associated acid. There is still only one characteristic hydroxyl proton resonance peak. This suggests that the frequency of making and breaking of hydrogen bonds is much greater than the frequency of measurement.

Barrow [66] suggested that the mixing together of acetic acid and pyridine should result in the formation of a simple hydrogen bonded complex. In theory it should be possible to determine $K_{assn.}$ from the n.m.r. measurements alone. It was not possible however to obtain meaningful measurements of the position of the OH - N peak at concentrations lower than a molar fraction of 0·025. Hence it was not possible to extrapolate the curve of Δ versus acid concentration to zero concentration. At low acid concentrations, as in the case of the acetic acid-benzene system, considerable broadening of the - O - H - N - peak occurred.

Sobyczk and Syrkin [90] suggested that in addition to the - O - H ... N hydrogen bonding, a weak interaction occurs between the carbonyl group of the acid and the protons of the pyridine. N.m.r. suggests that this is not so, as it is the α protons which are least affected by addition of acid. However, n.m.r. is unable to prove or disprove the existence of a species with an acid-base ratio of 2:1. Infra-red evidence suggests that this is not formed.

Some work has been done on ternary mixtures of acetic acid, pyridine and benzene. From this two phenomena present themselves. Firstly broadening of the - OH - N peak occurs at much lower acid concentration than in the binary acid-base mixtures. Secondly, dilution of a constant ratio acid:base mixture with benzene causes a decrease in the separation of the - OH and - CH_3 proton resonance signals. This is explained on the basis that dilution with an inert solvent causes a breaking up of hydrogen bonds in the system resulting in the formation of more acid monomer. Free - OH in monomer has a smaller chemical shift, compared to the - CH_3 protons, than associated - OH in dimer. Consequently there will be an upfield shift of the average - OH resonance frequency and accompanying decrease in Δ. In the ternary system there are at least three competing equilibrium processes. These are as follows:

Acid Monomer + Acid Monomer $\rightleftharpoons$ Acid Dimer ($\rightleftharpoons$ Polymer)

Acid Monomer + Pyridine $\rightleftharpoons$ Acid-Base Complex

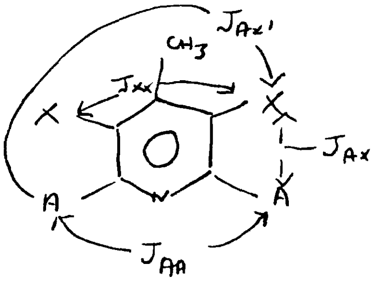
Acid Monomer + Benzene $\rightleftharpoons$ Acid-Benzene 'complex'

The existence of only one characteristic - OH proton resonance, taken together with the known weakness of pyridine as a base in water, tend to suggest that the acetic acid-pyridine complex is a simple hydrogen bonded complex. A definite interaction between the carbonyl group of the acid and the α proton of pyridine has been shown previously to be possible, but in view of the large separation of the two groups little importance should be attached to such a possibility.

In summary, therefore, the acetic acid-pyridine complex is most likely a simple hydrogen-bonded complex.

(c) Acetic Acid-4-Picoline-Benzene System

There is no reported work dealing with the n.m.r. spectra of either binary mixtures of acetic acid and 4-picoline or of ternary mixtures of acid, base and benzene. The writer thought that the effect of acetic acid on the n.m.r. spectrum of a heterocyclic base would be better appreciated by examination of the n.m.r. spectra of this particular system. 4-Picoline has a simple A_2X_2 type spectrum with two different AX spin-coupling constants. The general theory of this type of spectrum indicates that it should consist of two groups of lines each comprising twelve transitions and which are identical in position and intensities with respect to their respective centres. Venkateswarlu [91] reported that the observed spectrum consisted of a group of lines of multiplicity four at low field, with a further group more complicated by coupling with the - CH_3 protons at higher field. Wu and Dailey [92] reported that the n.m.r. spectrum of 4-picoline consisted of four symmetrically placed lines for each set of ring protons. The writer found, however, that the set of lines at high field was complicated probably due to coupling with the - CH_3 protons. The CH_3 proton resonance signal was to the high field of both α and β resonance signals and also appeared to be complicated by splitting.



4-Picoline

The spectra of several solutions of 4-picoline in cyclohexane were also measured. The separation of both α and β proton resonances from the 4-methyl proton resonance position varied with concentration. In fact, the more dilute the solution, the lower was the separation. In addition to this all the proton resonance signals shifted to low field on dilution.

TABLE C.4.

4-PICOLINE-CYCLOHEXANE

mole fraction base	$\Delta(4\text{-CH}_3\text{-}\alpha) \pm$ 4 c/s	$\Delta(4\text{-CH}_3\text{-}\beta) \pm$ 4 c/s
1·0000	785.0	597.6
0·4699	766·8	586·8
0·3069	765·0	584·4
0·1931	748·8	572·4
0·1426	747·8	570·0

These measurements were made in order to determine whether or not the apparent splitting of the - CH_3 proton resonance signal is due to intramolecular coupling with the β ring protons or to an intermolecular coupling with protons on another 4 -picoline molecule. It was thought that if the latter were the case, the splitting should disappear on dilution with an inert solvent. It was important to use a solvent whose only interaction with the 4-picoline molecule would be of the Van der Waals type. In fact the splitting did disappear on dilution, suggesting that it was due to an intermolecular interaction. This might have been expected as the - CH_3 proton and the β ring protons are sufficiently distant from one another for spin-spin splitting not normally to be expected to occur. However the fine structure of the β proton resonance due, it was thought, to splitting with the - CH_3 proton resonance did not disappear on dilution. The shift to low field of all the proton resonance signals on dilution is in line with the findings of Murrel and Gil [93] who studied the n.m.r. spectra of pyridine and several methyl pyridines and found that the position of all signals was sensitive to the nature of the solvent used. In particular they found that the signals were at higher field position in benzene or in the pure liquid than in carbon tetrachloride solution. This is obviously not a simple dielectric constant effect, as the dielectric constant of benzene is very little different from that of carbon tetrachloride but can be explained in terms of specific associations with benzene, or in the case of pure liquid, self association.

The spectra of several binary mixtures of 4-picoline and acetic acid were measured. These are summarised in Table C.5. and graph C.5. The plot of the difference in frequency between the hydroxyl and

TABLE C.5.

4-PICOLINE-ACETIC ACID

x_A	$\Delta \pm 3$ c/s
0·0653	696
0·0784	700
0·0824	708
0·1413	725
0·1749	738
0·2014	744
0·2217	749
0·2540	755
0·2702	757
0·2981	758
0·3096	760
0·3958	762
0·4363	760
0·4593	757
0·6299	744
0·7909	715
0·8362	683
1·0000	593

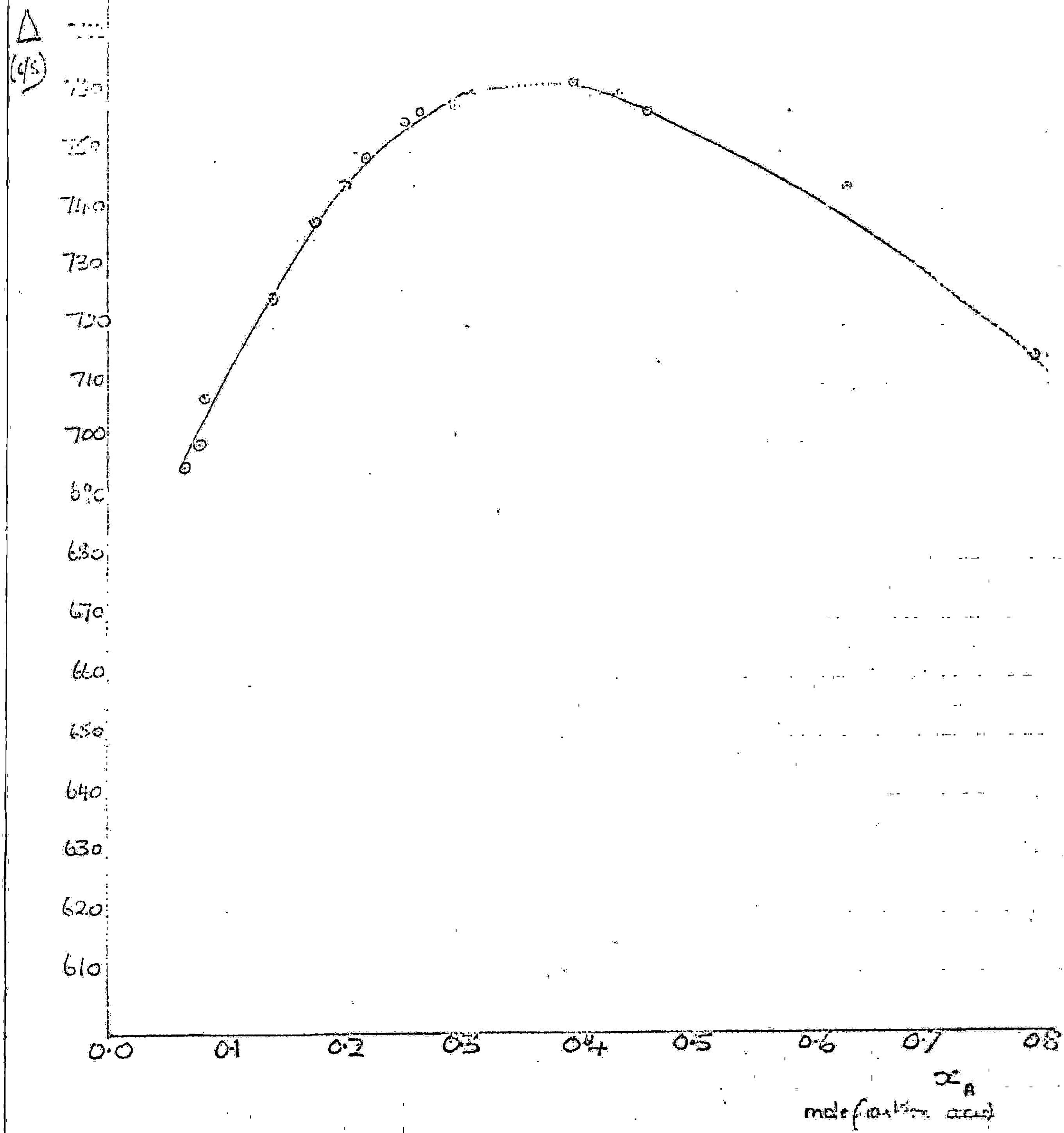
x_A = molar fraction acid

c/s = cycles per second

Δ = difference in $-OH$ and $4-CH_3$ proton resonance.

GRAPH 6E

ACETIC ACID – γ-PICOLINE



4 -methyl proton resonances versus the mole fraction of acid present shows a maximum at molar fraction about 0·1 in the case of acetic acid and pyridine.

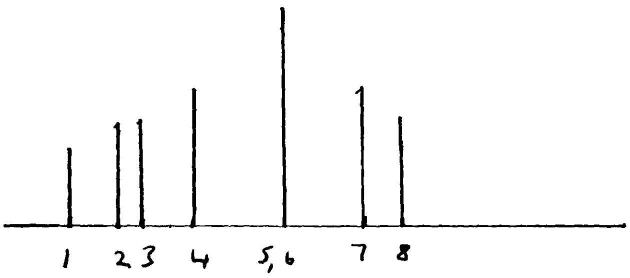
In general when a non-aromatic substance is dissolved in an aromatic solvent, dilution of the solute by the solvent causes the proton resonance signal to shift to higher field. In the particular cases considered in this investigation, the situation is somewhat more complicated. Initial dilution causes a shift to low field, whilst further dilution causes a reversal of this trend. It is an oversimplification to consider this problem as purely one of dissolving acetic acid, a non-aromatic solute, in an aromatic solvent. The position of the resonance signal from the O - H - N proton is an indication of the type of environment ~~in~~ which this proton finds itself in. In benzene as solvent the shift to low field was interpreted as a breaking up of the polymeric acetic acid molecules yielding discrete cyclic dimers; further dilution caused the breaking up of the discrete dimers yielding monomeric acetic acid with accompanying shift of the resonance peak to high field. The chemical shift is a maximum when the concentration of dimer is a maximum. This will occur at different acid concentrations in different physical environments, i.e. in different solvents. What is more remarkable is that the magnitude of this separation is fairly constant.

TABLE C.7.

Solvent	Maximum Chemical Shift of OH - N proton (c/s)
Benzene	662
Pyridine	761
4-Picoline	762
2,6 Lutidene	748
Quinoline	760

(d) Acetic Acid-2,6-Lutid~~e~~ine-Benzene System

There are no investigations of the nuclear magnetic resonance spectra of either the Acetic acid-2,6 Lutidene binary mixture or the acid-base-benzene ternary mixture reported in the literature. 2,6 Lutidene is an example of the AB_2 class of n.m.r. spectra, a detailed examination of which was first reported by Bernstein et alia.[94] The label AB_2 refers to the three ring protons of 2,6 Lutidene and means that there are two different types of proton, the coupling constants between which are of the same order of magnitude as the chemical shift between them. 2,6 Lutidene has a relatively simple spectrum since the coupling constants between the methyl group protons and the ring protons are relatively small because of the great separation (four bond lengths). Further, the possible spin coupling between the N nucleus and the methyl protons is eliminated by quadrupole relaxation. The theoretically calculated spectrum of 2,6 Lutidiene consists of nine lines. The ninth line is not normally observed because of its low intensity.



N.M.R. Spectrum 2,6-Lutid~~e~~ine

The n.m.r. spectra of several binary mixtures of acetic acid and 2,6 Lutidene, and of several ternary mixtures of acid, base and benzene were determined. In the former, interest was centred on (1) the separation of the hydroxyl and methyl proton resonance and (2) the effect, if any, of the addition of acid on the proton resonance spectrum of the base.

A plot of the separation of the hydroxyl and methyl proton resonances versus molar fraction of acid in the binary mixture is shown in Graph C.8. The maximum separation occurs at molar fraction acid 0.5. It will be remembered that Toyoda and co-workers [82] found a maximum at molar fraction 0·5 in the case of the acetic acid-pyridine binary mixture. The authors [82] took this as evidence for there being a double minimum potential energy for the $- O - H - N$ proton of the type

$$N \ldots H - O \rightleftharpoons N - \overset{\oplus}{H} \ldots . \overset{\ominus}{O}$$

In the case of the acetic acid-2,6-Lutidene system the position of this maximum is again indicative of the composition of the mixture containing the maximum concentration of dimer. It will be remembered that the association constant for complex formation for acetic

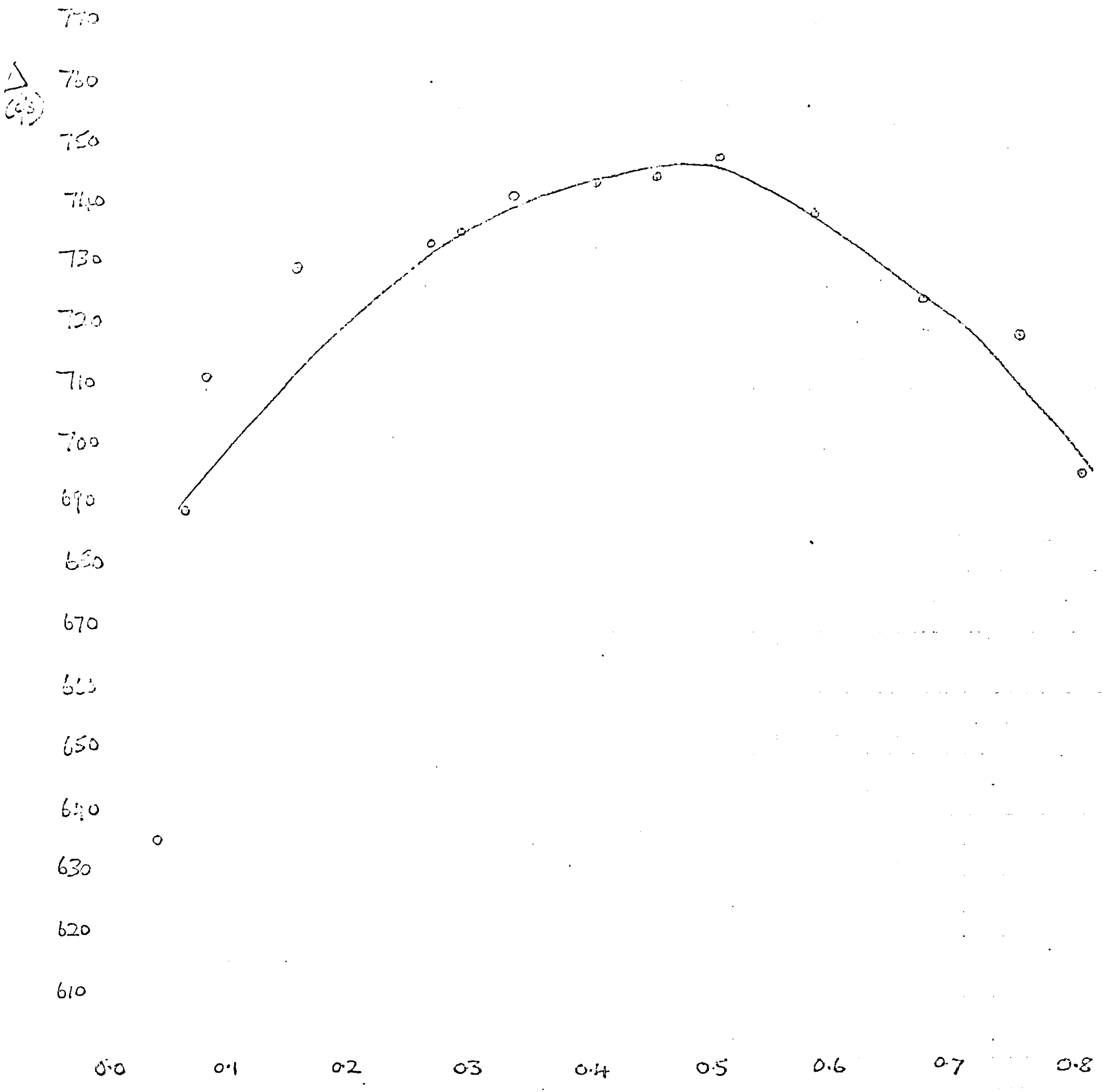
TABLE C.8.

ACETIC ACID-2,6 LUTIDENE

~~Under~~ Molar fraction (x_A)	Δ (c/s) ± 3
1·0000	593
0·9178	656
0·8032	696
0·7504	719
0·6735	725
0·5781	739
0·5031	748
0.4488	745
0·4021	744
0·3367	742
0.2884	736
0·2649	734
0·1540	730
0·0808	712
0·0642	690
0·0414	636

GRAPH 4.8

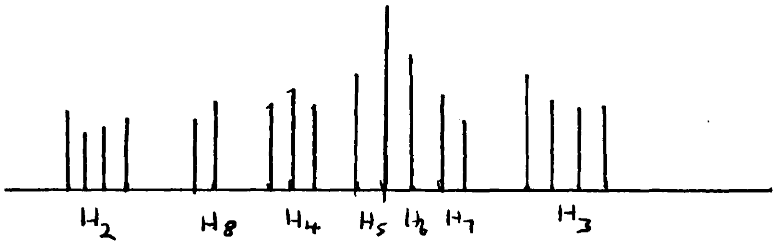
ACETIC ACID - 2,6-LUTIDINE



acid and 2,6 Lutidene in benzene solution has been found to be about 5. The dimerisation constant of acetic acid in benzene has been found to be about 140. It seems reasonable to suggest therefore that the dimerisation process will be favoured in 2,6 Lutidene as compared to the other heterocyclic bases used in this investigation. This is borne out by the low value of the acid-base association constant in benzene.

(e) Acetic Acid-Quinoline-Benzene

Again, as with acetic acid and 2,6 Lutidene there is no work reported in the literature dealing with the nuclear magnetic resonance spectra of either the binary or tertiary systems. The n.m.r. spectrum of Quinoline has been reported by Schaefer.[84] A diagramatic representation is in the diagram below:



N.M.R. Spectrum Quinoline

The quartets ~~and~~ at the lowest and highest fields are identified as the BX part of an ABX grouping expected for protons 2,3 and 4. The quartet expected for H_4 is located in the region indicated in the figure.

N.M.R. spectra of several binary mixtures of acetic and quinoline were determined. A plot of the separation of the hydroxyl and methyl protons versus molar fraction of acid present is shown in Graph C.9. In this case the maximum occurs at molar fraction of acid 0·3.

GRAPH C9

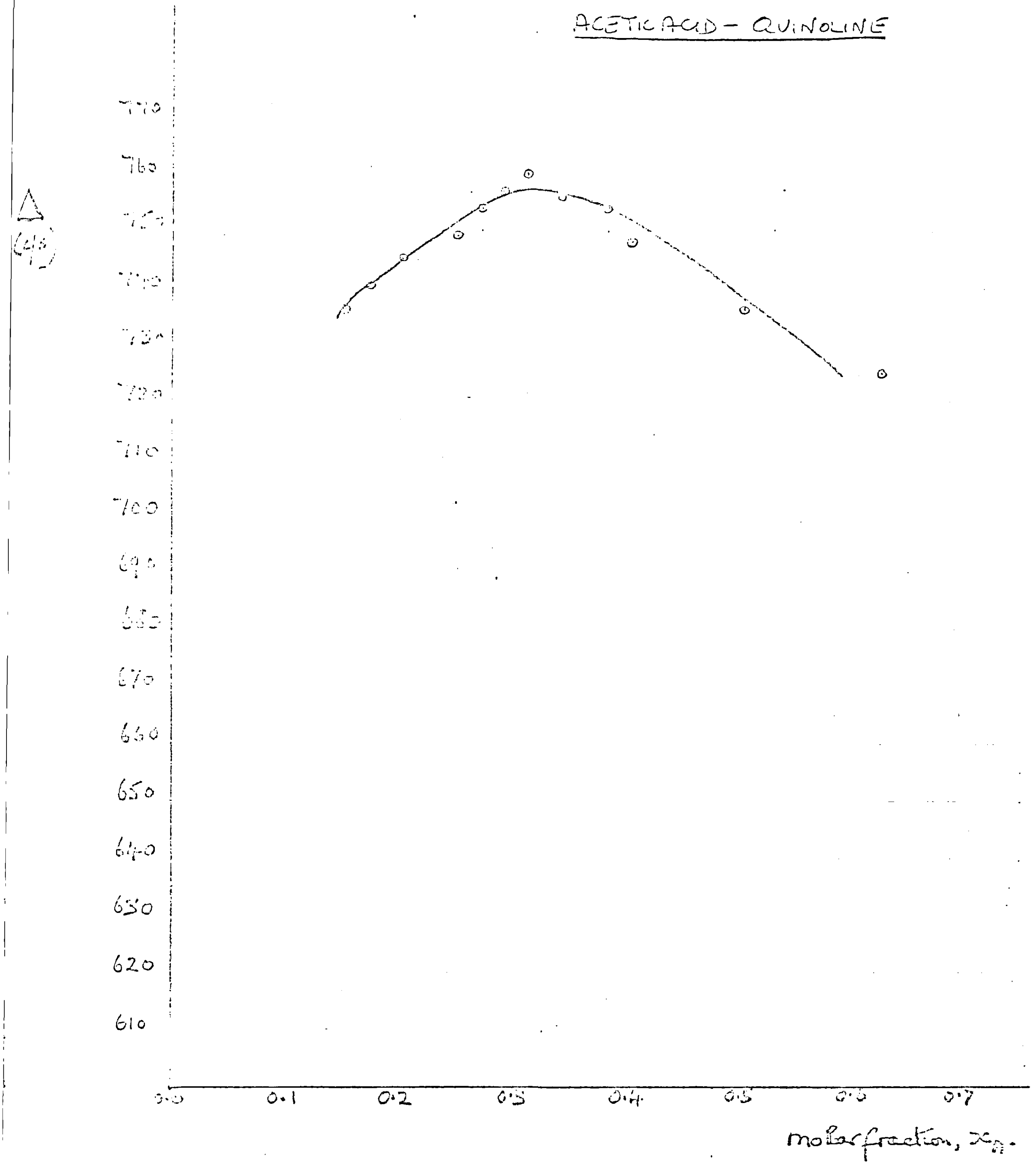

ACETIC ACID - QUINOLINE
Δ (49)
770
760
750
740
730
720
710
700
690
680
670
660
650
640
630
620
610
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
molar fraction, x_A.

TABLE C.9.

ACETIC ACID-QUINOLINE

molar fraction (x_A)	Δ (± 3) c/s
1·0000	593
0·9716	622
0·8305	673
0·6261	725
0·5063	736
0·4085	748
0·3802	754
0·3412	757
0·3155	760
0·2925	757
0·2738	754
0·2563	749
0·2049	746
0·1716	740
0·1524	736

D CONCLUSIONS

The aim of this research was to investigate the nature of the complexes formed between organic acids and bases in aprotic solvents. To do this, both the dipole moments and nuclear magnetic resonance spectra of these complexes were determined. Several investigators [49,67,90] have used the technique of dipole moment measurement to investigate systems similar to those studied here. Similarly n.m.r. spectroscopy has been used to study this type of system. However, the two techniques have never before been used simultaneously.

Earlier in this thesis it was stated that none of the methods used by earlier investigators to measure simultaneously both dipole moment and association constant of an acid-base complex in solution, were suitable for the systems studied by the writer. An appreciation of the method devised by the writer to solve this problem is thus necessary. The experimental techniques were similar to those used by previous investigators.[46] The calculation of both dipole moment and association constant was rendered simple through the successful development of simple computor programs. It was thought possible to spot those values of K_2 and $_C$ which fortuitously yielded seemingly accurate values of the dielectric constant increment. This proved to be the case in this investigation due mainly to a prior knowledge of the approximate dipole moments of the complexes. Without this knowledge the problem would have been more acute particularly in cases where K_2 is very low. Further use of this method is needed before its success or otherwise is determined.

The formation of complexes between organic acids and bases in benzene can be represented as a series of equilibria:

$$AH + B \overset{(1)}{\rightleftharpoons} AH \ldots B \overset{(2)}{\rightleftharpoons} \overset{-}{A} \ldots\ldots \overset{+}{HB}$$

The extent to which this equilibrium is shifted to the right is very much dependent on the nature of AH and B. Acetic acid is a relatively weak acid in aqueous solution and an even weaker one in benzene solution. All the nitrogenous bases used were fairly weak (pKas in aqueous solution varied from 4·9 to 6·7).

The strength of a base in a given solvent is measured by the extent of the reaction,

$$B + SH^{+} \rightleftharpoons BH^{+} + S$$

in which B is the base and S the solvent. It seemed reasonable to suppose that for a given series of chemically similar bases, i.e. the bases used in this work, the relative order of base strength would not vary from solvent to solvent. Indeed by measuring base strengths in acetic acid solution through titration against perchloric acid, Hall [95] has shown that, as in water, pyridine is a stronger base than quinoline.

TABLE D.1.

Base	pKa	K_2 (l.mole^{-1})
Quinoline	4·9	20 ± 2
Pyridine	5·2	10 ± 2
4-Picoline	6·0	25 ± 3
2,6-Lutid~~o~~ine	6·7	4·5 ± 0·5

It is difficult, therefore, to explain the anomalous order of values of K_2 listed in Table D.1. One would expect K_2 for the acid-2,6-Lutid~~o~~ine complex to be relatively low due to the anticipated blocking effect of the two bulky methyl groups. Also one might have expected the relatively bulky quinoline molecule to hinder complex formation. Any such effect, if present at all, is obviously overshadowed by some other phenomenon which results in quinoline being a much better complexing molecule than pyridine or 4-Picoline.

N.M.R. spectroscopy was used in this investigation in order to help to explain the nature of the complexes formed between acetic acid and heterocyclic bases in benzene solution and also to shed further light on the molecular state of acetic acid dissolved in aprotic solvents. Considering the second case first, n.m.r. supports the contention that at low concentration in benzene solution there exists an equilibrium between monomer and dimer. It is unable to prove or disprove the existence of both cyclic dimers and open chain polymers. It does, however, afford fairly conclusive evidence of the existence of an interaction between the acid monomer and the π- electron cloud of the benzene solvent molecule.

Addition of acetic acid caused very little change to either the relative positions or intensities of the ring proton resonance peaks of the heterocyclic bases. This is consistent with the view that only very small charge displacements are associated with hydrogen bonding in these complexes.

There is certainly no simple relationship between the pKa of the base in water and the molar fraction of acid giving the maximum separation of - OH and - CH_3 proton resonances. Nor indeed does there seem to be any correlation between the position of this maximum and the association constant K_2.

In summary, therefore, there appears to be little doubt that these complexes are simple hydrogen bonded complexes. The values of the association constants found by the writer may not be absolute ones, but it is their relative order which is perplexing. The use of n.m.r. has perhaps not been as successful as one would have hoped in elucidating the problem. This was due mainly to the relative insensitivity of the technique to very low concentrations of hydroxyl proton.

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APPENDIX 2

COMPUTER PROGRAMS USED IN THIS INVESTIGATION

1. Program A

```
Computing 4000 instructions

Output

0 Line Printer 2000 lines

Store 35/45 Blocks

Compiler Exchlf

Title

Acid base equilibria


Chapter 0

V -> 500

F -> 10

G -> 10

A -> 500

B -> 10

E -> 1000

Z -> 500

H -> 100

N = 1 (1) 4

Read (FN)
```

```
Repeat
T = 1 (1) 3
Read (GT)
Repeat
Read (U)
K = 1 (1) 3
Read (BK)
L = 1 (1) 6
Read (AL)
Read (H)
I = 0
V(I) =
10) Y = B(K)V(I) + 1
Z' = 8UA(L)
W = * (* SQRT (YY + Z') - Y/* (4U)
C = WB(K)V(I)
D = * (A(L) - C - W)/2
W' = F(1)W
D' = F(2)D
B' = F(3)B(K)
C' = F(4)C
P = 0
Z(P) =
```

```
20) E = G(1)W' + G(2)D' + G(3)B' + Z(P)C' - G(3) F(3) C
E' = E - H
H' = F'F'
Newline
Caption
Help
Print (Z(P), 2, 2)
Print (E, 5, 5)
Print (F', 5, 5)
Print (H', 8, 8)
Z (P + 1) = Z (P) + 0·5
P =P + 1
Jump 20, Z(P) <
Print (L, 1, 0)
Print (A (L), 5, 5)
Print (V (I), 2, 2)
V (I + 1) = V (I) + 1·0
I = I + 1
Jump 10, V (I)
Repeat
Repeat
End

Close
```

2. Program B

```
Computing 4000 Instructions

Output

0 Line Printer 2000 lines

Store 35/45 Blocks

Compiler Exchlf

Title Acid Base Equilibria


Chapter 0

F -> 10

G -> 10

A -> 500

B -> 10

Z -> 500

H -> 100

N = 1 (1) 4

Read (FN)

Repeat

Read (U)

Read (V)

K = 1 (1) 3

Read (BK)

L = 1 (1) 6

Read (AL)
```

```
Read (H)

Y = B (K) V + 1

X = 8 UA (L)

W = * (* SQRT (YY + X) - Y/* (4U)

C = WB(K) V

D = * (A (L) - C - W/2

W' = F (1) W

D' = F(2) D

B' = F (3) B (K)

C' = F (4) C

P = 0

Z (P) =

20) E = G(1)W' + G(2)D' + G(3)B' + Z(P)C' - G(3)F (3) C

F' = E - H

H' = F'F'

Newline

Caption

Help

Print (Z (P), 2, 2)

Print (E, 5, 5)

Print (F', 5, 5)

Print (H', 8, 8)

Z (P + 1) = Z(P) ~~to~~ + 0.2

P = P + 1
```

```
Jump 20, Z(P)< ~~14.2~~
Print (L, 1, 0)
Print (A (L), 5, 5)
Print (C, 5, 5)
Print (D, 5, 5)
Print (M, 5, 5)
Print (C', 5, 5)
Repeat
Repeat
End

Close
```

3. Program C

```
Computing 1000 Instructions
Output
0 Line Printer 300 lines
Store 35/45 Blocks
Compiler Exchlf
Title
Acid Base Equilibria

Chapter 0
F -> 10
G -> 10
```

```
A -> 500
B -> 10
H -> 100
N = 1 (1) 4
Read (FN)
Repeat
Read (U)
Read (V)
K = 1 (1) 3
Read (BK)
L = 1 (1) 6
Read (AL)
Read (H)
Y = B (K) V + 1
X = 8UA (L)
W = * (* SQRT (YY + X) - Y)/* (4U)
C = WB (K) V
D = * (A (L) - C - W)/2
W' = F (1) W
D' = F (2) D
B' = F (3) B (K)
C' = F (4) C
E = G (1) W' + G (2) D' + G (3) B' - G (3) F (3) C
```

```
Newline
Caption
Help
Print (E, 5, 5)
Print (C', 5, 5)
Print (A (L), 5, 5)
Print (H, 5, 5)
Repeat
Repeat ~~End~~
End
Close
```

4. <u>Program D</u>

```
Computing 4000 Instructions
Output
0 Line Printer 2000 Lines
Store 30/45 Blocks
Compiler Exchlf
Title
Acid Base Equilibria
Chapter 0
V -> 2000
F -> 2000
G -> 1000
A -> 2000
```

```
B -> 2000
E -> 4000
Z -> 5000
H -> 2000
N = 1 (1) 4
Read (FN)
Repeat
T = 1 (L) 3
Read (GT)
Repeat
Read (U)
K = 1 (1) 3
Read (BK)
L = 1 (1) 6
Read (AL)
Read (H)
I = 0
V (I) =
10) Y' = VI * (B (K) - A(L) + * (1 - U - VI)/* (UVI)
Z' = * (U + VI)*(3VI * (B(K) - A(L)) + 3)/* (WUVI)
A' = * SQRT (Y'Y'/4 + Z'Z'Z'/9)
V' = - 0.5 Y' + * SQRT (A')
U' = * EXP (0.33333 * LOG (E'))
Y = U' - Y'/*(3U')
```

```
W = Y - x (U + VI)/x (3UVI)
Jumpdown 40, W < 0
Jumpdown 41, W > A(L)
C = VIWB(K)/x (1 + VIW)
D = x(A(L) - C - W)/2
W' = F (1) W
D' = F (2) D
C' = F (3) C
B' = F (4) B (K) - F (4) C
P = 0
Z (P) =
20) E = G (1) W + G (2) D' + G (3) B' + 2 (P) C'
F' = E - H
H' = F'F'
Jump 50
40) W = 66666.66666
Return
41) W = 99999.99999
50) Newline
Caption
Help
Print (Z (P), 2, 2)
Print (E, 5, 5)
Print (F', 5, 5)
Print (H', 8, 8)
```

```
Z (P + 1) = Z (P) + 0·5
P = P + 1
Jump 20, Z (P) < ~~14·2~~
Print (L, 1, 0)
Print (A (L), 5, 5)
Print (V (I), 2, 2)
V (I + 1) = V(I) + 2·0
I = I + 1
Jump 10, V (I)
Repeat
Repeat
End
Close
```