

NUCLEAR MAGNETIC RESONANCE STUDIES
OF AQUEOUS AND RELATED SYSTEMS

A thesis submitted for the degree of
Doctor of Philosophy
in the
Faculty of Science
of the
University of Leicester
by

John Davies

1971

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STATEMENT

The experimental work described in this thesis has, unless otherwise acknowledged in the text, been carried out by the author in the Physical Chemistry Laboratory of the Department of Chemistry, Leicester University, during the period between October 1968 and April 1971.

No part of this thesis has been submitted, or is being submitted concurrently for any other degree.

A handwritten signature in black ink, appearing to read "John Davies". The signature is written in a cursive style with a horizontal line underneath the name.

John Davies.

The Physical Chemistry Laboratory.,
The University.,
Leicester.
July, 1971.

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Financial support from the Science Research Council is gratefully acknowledged.

To my parents, without whose
understanding and encouragement,
at all stages in my education,
this thesis would not have been
possible.

SYNOPSIS

In recent years magnetic resonance methods have been used to shed fresh light on the problems associated with ionic solvation and interactions between ions in solution.

This thesis concerns the application of the Nuclear Magnetic Resonance solvent shift technique to both aqueous and non-aqueous electrolyte solutions.

Two methods of determining a set of self consistent 'absolute' ion shifts for aqueous solutions are described, and an attempt is made to establish how such shifts vary with changes in solution temperature.

The resulting shifts for simple ions are discussed in terms of a model that considers the competitive nature of hydrogen bonding to the pure water and bonding between the water and the ion. The shifts of the quaternary ammonium and related ions are discussed in terms of a model based on enclathration of the solute. For these latter ions a possible explanation for anomalous n.m.r. salt shifts, previously reported by Hertz and Spalthoff, is given.

Salt and ion shifts measured in the related solvents, methanol, ethanol and ethylene diol are compared and contrasted with the aqueous results.

Evidence for solvent-shared ion-pairs in methanolic solution is given.

A report of a preliminary investigation concerning

the determination of absolute ion shifts for solutions of electrolytes in liquid ammonia is given.

Problems connected with n.m.r. salt shift referencing, that are inherently associated with investigations of type undertaken, are discussed. The use of a suitably chosen internal reference is suggested. In this context, the use of the proton resonances of a quaternary ammonium cation such as $(\text{CH}_3)_4\text{N}^+$ has proved to be satisfactory for the aqueous solutions.

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"Horse and man we have been made; from the dawn of history and until the doom of history shall overtake us, man and horse we shall remain. And who shall regret it, that has ever tasted the thrill, the pure mad happiness of a good horse's hoofs rattling the turf, 'quadrupetante putrem sonitu quatit ungula campum', as Virgil described it, when horse's and man's pulses quicken and the blood of both rushes imperiously through their veins, rushing forward together in unison, two souls and but one burning desire, the same that animates the hounds in front of them, the same that has come down to them, untainted and unchanged, from age-old ancestry.

And what then is that passion?

None other, assuredly, than the urge of achievement, that drives all men forward in whose hearts the sublime spark of the indomitable is aglow.

And is it not essential for the future of humanity that men and women capable of keeping that precious fire burning shall be enabled to do so, shall keep their identity and shall not lose themselves forever in the colourless mass of mediocrity so beloved of contemporary rulers?"

Henry Wynmalen, M.F.H.

"A man would do nothing, if he waited until he could do it so well that no one would find fault with what he has done."

Cardinal Newman.

N.M.R. SHIFTS

For all the n.m.r. solvent shifts (salt or individual ion), reported in this thesis, positive shifts, designated (+) are taken as being upfield relative to the pure solvent resonance. Consequently, downfield shifts are designated (-).

N.M.R. solvent shifts will normally be quoted in parts per million (p.p.m.), otherwise they will be given in Hertz (Hz.), in which case the spectrometer operating frequency will be stated.

CHAPTER ONE

INTRODUCTION

1.1 The Structure and Properties of Water.

The plight of the Ancient Mariner, who saw ' Water, water, everywhere, Nor any drop to drink, ' was occasioned by the fact that, while water is the most abundant of all compounds, it is also the best solvent and so never occurs pure in nature.

One of the first scientific experiments an individual ever performs is to distil brine and so obtain a sample of pure water, the properties of which can then be verified, namely¹;

"Water is an odourless and tasteless liquid which in small quantities appears to be without colour, though large masses are blue or green. At 760 mm. it melts at 0° and boils at 100° (the thermometric ' fixed points '). Its density is exactly 1g. per c.c. at 4° , since the gram is defined as the weight of 1 c.c. of water at this temperature. In many ways water has unusual and unexpected properties; thus it boils about 162° higher than its analogue hydrogen sulphide, increases in density from 0° to 4° , and possesses abnormally high specific and latent heats.

Water is an exceedingly good solvent, dissolving certain elements (e.g. chlorine, bromine and oxygen), most electrolytes, and many co-valent compounds. It is also the best ionizing solvent, a fact perhaps connected with its high dielectric constant and with the ability of its molecule to ' donate ' and ' share ' electrons."

Having been introduced to some of the anomalous

properties of water, it is not long before students are allowed to loose sight of them. Subsequently water is treated as an 'inert solvent medium' capable of sustaining certain chemical reactions, these reactions, not the solvent being the focus of all attention.

The above approach assumes the solvent-water to be a dielectric continuum, being devoid of any structure. Fundamental work concerned with the study of equilibria, reaction kinetics and the properties of electrolytic solutions has been based on this treatment.

As Ives and Lemmon² state in their review of the structure and properties of water, "Solvents are often treated just as media, of status little more than the reaction vessel".

In view of the role played by water in biological and other systems it is vitally important that more is understood about its structure and the way this is perturbed by dissolved substances.

Of the three states of matter, liquids in general and water in particular are not well understood. In the context of the liquid state, water is anomalous. Amongst its uncharacteristic properties are; a large heat capacity, a temperature of maximum density, a low entropy of fusion and a minimum in the viscosity versus pressure plot. To explain such unusual properties many structural models have been proposed, full details of these can be found in many reviews²⁻⁷ which extensively cover the subject. Brief details of the basic under-

lying principles of such models are given below.

The form of the unassociated water molecule is shown in Figure 1.1a. The molecule consists of approximately tetrahedrally disposed protons and 'lone pair' electrons, the structure being based on sp^3 hybridization of oxygen orbitals. Such a unit has a symmetry (point group C_{2v}) that enables it to associate with other water molecules in a regular way, so forming a basis for larger structural units.

Regular association of water molecules is perfected in ordinary ice - ice Ih. This form of ice is based on a tetrahedrally co-ordinated oxygen atom skeleton, the protons lying on, or at least very near to the O—O bonds. The three dimensional oxygen skeleton contains rather large channels (Figure 1.1b) that thread their way between adjacent layers of hexagonal oxygen rings, thereby giving rise to an 'open' structure. Structural units based on tetrahedral co-ordination are not, however fully consistent with an exclusive dipolar interaction. The net moments of the molecules, lying symmetrically between the OH bonds, neither fully support nor oppose each other. The ice structure is therefore described as a hydrogen bonded aggregate of water molecules.

The hydrogen bond is usually represented as $O^1H \cdots \cdots O^2$ where the dashed line represents the hydrogen bond proper. It is a controversial point as to in what way the hydrogen bond differs from a truly dipolar interaction⁸. Most treatments consider the hydrogen

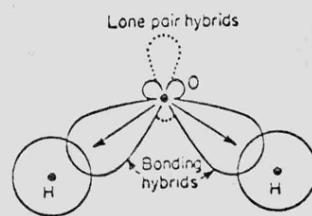


Figure 1.1a. The water molecule.

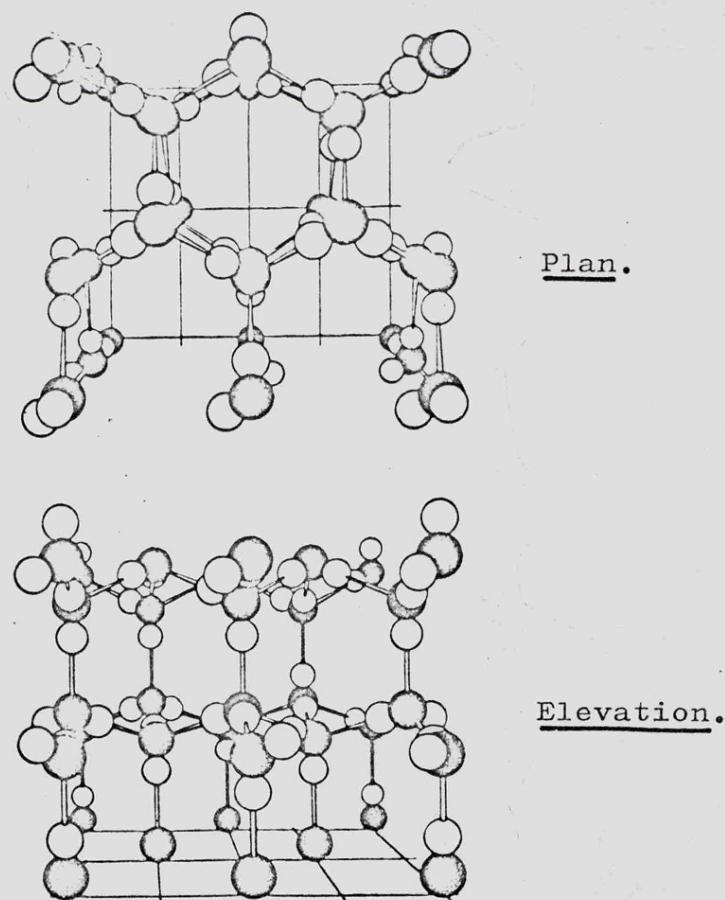


Figure 1.1b. The structure of ice Ih.

(Taken from reference 2.)

bond in terms of the perturbation of the electron distribution of O^2 by the O^1H group.

Figure 1.1b represents an idealised Ih ice structure, defects and dislocations will normally be present. A disordered structure is suggested by the residual entropy of ice, furthermore, the electrical properties of ice show the protons to be mobile. Such effects lead to the conclusion that both proton transfer (ionic) and rotation of water molecules about an $OH....O$ axis (orientational) are intrinsic defects present in ice structures.

X-ray measurements produce radial distribution curves that imply a retention of 'structure' for water in the liquid state, furthermore, studies of this type indicate that a structural contraction occurs when ice melts. Any models which set out to explain the structure of water must accomodate this contraction as well as the increasing density found for $273 < T \leq 277.13K$.

The various models proposed for water structure fall into two main categories:

- (i) Uniform Models.
- (ii) Mixture Models.

Uniform Models.

These postulate that individual water molecules (at any particular instant) behave in much the same way as any others. There is no localised structuring that is in any way unique, these are therefore one state models.

The classic uniform models are due to Bernal and

Fowler⁹ and Pople¹⁰.

Bernal and Fowler's model ascribes to water three preferred molecular arrangements that pass continuously and reversibly into one another as the temperature varies.

Pople proposed that when ice melts no hydrogen bonds break, they merely distort and bend. Further bending of hydrogen bonds takes place as more energy enters the system, resulting in an entropy increase and destruction of long range order.

Mixture Models.

Models of this type envisage an equilibrium between two or more distinct hydrogen bonded species. Such models are usually based upon broken down ice lattices, water clusters or water clathrate cages.

The ice lattice (or interstitial) models stem from the persistence of ice-like features in liquid water, as indicated by x-ray studies¹¹. Various workers^{12,13} have put forward variations on the theme, namely, the placement of monomeric water molecules in the interstitial cavities of ice-like lattices.

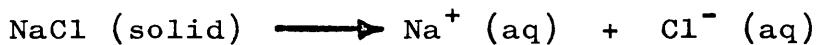
The 'flickering cluster' model of Frank and Wen^{14,15} typifies the second class. The model postulates the co-operative formation and destruction of hydrogen bonded water clusters, the lifetimes of which are in the order of 10^{-11} sec. Nemethy and Scheraga¹⁶ have placed the Frank and Wen model on a semi-quantitative basis.

Clathrate cage models are based on the occurrence of stable clathrate hydrates for non-polar molecules

such as the 'inert gases' or 'hydrocarbons'. Structurally, clathrate cages are based upon the Pentagonal Dodecahedron, this forming the geometrical building unit. The most well known clathrate cage model for water structure is due to Pauling¹⁷.

1.2 The Behaviour of Electrolytic Solutions.

The terms 'hydration', 'aquation' or, more normally 'solvation' are used when discussing the interaction of electrolytes with solvents. The solvent in most general everyday use is water, it is so abundant that it tends to be taken for granted. When writing down equations such as;



there is a tendency to forget that it is aquated rather than free species being represented.

Large energy changes are associated with the dissolution of electrolytes in water. Lattice energies are considerable, and their destruction means that solvation energies must be of the same order of magnitude. The solvation energy is taken to be the energy difference between the gas phase and hydrated species.

If an ideal salt solution is considered, then ion-ion interactions can be neglected, this can be achieved theoretically by considering the solute to be in its standard state, i.e. of unit activity. In the absence of ion-ion interactions the thermodynamic functions of the species in solution will be additive. Unfortunately it is not possible to determine absolute thermodynamic

data for individual ions. It is therefore necessary to make an arbitrary choice for one ion, which is then taken as a reference. By convention the hydrogen ion is taken as zero, therefore:

$$\text{Partial Molar Free Energy, } \Delta G^\ominus(\text{H}^+, \text{aq.}) = 0$$

$$\text{" " Entropy, } \Delta S^\ominus(\text{H}^+, \text{aq.}) = 0$$

$$\text{" " Enthalpy, } \Delta H^\ominus(\text{H}^+, \text{aq.}) = 0$$

A consequence of the arbitrary zero is that only differences between the individual quantities have any real significance.

The classical way of determining the free energy of solvation, ΔG^\ominus , is by use of the Born equation¹⁸.

$$\Delta G^\ominus = - \frac{N(Ze)^2}{2r} \left[1 - \frac{1}{\epsilon} \right]$$

Where ΔG^\ominus is the free energy change associated with the process in which an ion of radius r and charge Z is transferred from the gas phase to a solvent. The equation assumes the solvent to be a continuous medium of dielectric constant ϵ . (N = Avogadro's number and e = electronic charge)

By making use of the fundamental relationship;

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$, other thermodynamic quantities can be derived.

$$\Delta S^\ominus = - \frac{\partial \Delta G^\ominus}{\partial T}$$

$$\Delta H^\ominus = - \frac{N(Ze)^2}{2r} \left[1 - \frac{1}{\epsilon} - \frac{T}{\epsilon^2} - \frac{\partial \epsilon}{\partial T} \right]$$

Such equations require that there should be a linear relationship between the thermodynamic quantities and reciprocal ionic radii. In order to fit calculated free

energies to experimentally derived data, Latimer et al.¹⁹ found it necessary to add increments to ionic radii in order to obtain an 'effective radius'. By using these corrected radii, experimental points were made to fall on the predicted straight line. A rationalization of the use of 'effective radii' is that one should consider the ion and the first hydration shell as an entity, this unit should then be used in applying the Born equation. Such a rationalization cannot, however, be correct in principle. The interaction between the ion and the first hydration shell will, of course, be the most important contribution to the total free energy of hydration. The crux of the problem is that of evaluating the radius of an ion in aqueous solution²⁰, this is a continuing problem and will be referred to in later chapters of this thesis.

Noyes²¹ has used the Born equation to calculate an 'effective dielectric constant' of the solvent for each ion. The calculation was made using the ionic radius and the experimental free energy (corrected for the free energy of hydration of a neutral atom). The results suggested that for closed shell cations:

$$\epsilon_{\text{eff}} = 1 + 1.376r,$$

ϵ_{eff} being independent of the charge of the cation. The relationship, however, does not fit the data for anions, nor non-closed shell cations.

The Born treatment has been extended. Bernal and Fowler⁹ have made an allowance for the structure of the solvent around the ion. The interaction between the ion

and the first layer of water molecules in this treatment is given by;

$$- \frac{Nnze\mu}{(r+r_w)}^2$$

where n is the number of water molecules with dipole moment μ and radius r_w in the layer. The Born equation (solvent dielectric continuum) is taken to be applicable beyond this first hydration shell. This approach introduces yet another variable parameter, n -the solvation number, with which to adjust theoretically derived results.

The failure of the simple electrostatic Born approach for aqueous solutions²², taken together with the failure of Waldens rule for ionic mobilities²³ indicates that water cannot be treated as a dielectrically continuous medium.

Ions in solution perturb water-water interactions, they may intensify or weaken them. Enhancement of such interactions, sometimes referred to as hydrophobic hydration, is taken to be the main reason for the entropy decrease that occurs when non-polar solutes are dissolved in water.^{14,24} Non-polar solutes of this type are said to be 'structure formers'. When electrolytes are dissolved in water, the ions are thought to 'electrostrict' a number of solvent molecules into an effectively frozen hydration layer. Thus, if an ion is removed from solution to the gas phase then the release of 'electrostricted' water molecules should result in a significant increase in entropy. It is found that for

aqueous solutions of potassium chloride, the entropy of evaporation $\Delta S_v^\infty = 217 \text{ J Mol}^{-1} \text{ K}^{-1}$, whereas that for two moles of argon (being of similar size) is $253 \text{ J Mol}^{-1} \text{ K}^{-1}$. The result suggests that the salt solution contains (initially) 'too much' entropy. Such excess entropy is attributed to a degree of disorder ('structure breaking') that is present in solutions of electrolytes beyond the first hydration layer. Observations of this type have given rise to structural models for ionic solutions, details of such models can be found in section 5.2.

1.3 The Nuclear Magnetic Resonance Technique.

The fundamental theoretical and practical details of the nuclear magnetic phenomenon are well documented²⁵⁻²⁷ and will therefore be omitted. The application of the n.m.r. solvent shift technique to the study of electrolytic solutions will be discussed so as to provide a basis for work reported in later chapters.

The n.m.r. technique provides two sets of information;

- (i) The chemical shift - providing information about small changes in magnetic shielding.
- (ii) Nuclear spin relaxation times - providing information concerning the time dependence of molecular motions.

It is point (i) that is the concern of this thesis.

For a given nucleus, the frequency at which it resonates (when placed in an external magnetic field),

is intimately connected with its electronic environment. The hypothetical 'bare' nucleus does not experience any electronic shielding, however, real nuclei are always partially shielded by their associated electron clouds. Such shielding may be direct, or via coupling mechanisms between local and more distant electrons.

Extra nuclear electrons, when placed in a magnetic field, tend to circulate so as to induce a field in opposition to that applied. This phenomenon is generally referred to as 'diamagnetic circulation.' Clearly;

$$H_{\text{effective}} = H_{\text{applied}} - H_{\text{induced}}$$

where H is the conventional symbol for magnetic field. Since any induced field will be directly proportional to that applied, then;

$$H_{\text{induced}} = \sigma H_{\text{applied}}$$

$$\text{i.e., } H_{\text{eff}} = H_{\text{applied}} (1 - \sigma)$$

The constant of proportionality, the shielding (or screening) constant, is given the symbol σ . For an isolated atom the extent of any shielding effects will be constant, however, for a molecular atom, shielding constants will vary with electron denisty changes. For a particular nucleus, i , the shielding constant of which is σ_i , a general relationship can be written;

$$H_i = H (1 - \sigma_i)$$

where H_i = the effective field at the nucleus i ,
and H = the externally applied field.

If the nucleus i exists in two different environments

a, b then the previous equation may be rewritten as;

$$\Delta = H_i^a - H_i^b = H (\sigma_i^b - \sigma_i^a) \text{ milli gauss.}$$

The above situation is shown diagrammatically in Figure 1.2.

The chemical shift, Δ , between the absorbance peaks of Figure 1.2 can be measured in several ways;

- a) directly in milli gauss.
- b) holding the field constant and varying the frequency.

Neither of these are, however, entirely satisfactory.

Since measured shifts are directly proportional to the applied field, H, chemical shifts are normally quoted as a fraction of the applied field or frequency;

$$\text{i.e., } \delta = \frac{H_i^a - H_i^b}{H} = \sigma_i^b - \sigma_i^a ,$$

where δ is expressed in parts per million (p.p.m.).

The chemical shift δ (p.p.m.), being the difference between the shielding constants, is now independent of the spectrometer operating frequency or field.

Absolute chemical shift measurements would, of course, need to be based on the resonance position of a 'bare' unshielded nucleus. Since this primary standard is impracticable it is necessary to select a substance to act as a secondary standard. In normal analytical proton magnetic resonance, the compound most universally selected is tetramethyl silane, $\text{Si}(\text{CH}_3)_4$, or TMS. For aqueous work (TMS is insoluble in water), sodium 4,4 dimethyl -4-silapentane 1-sulphonate, NaDSS, is generally

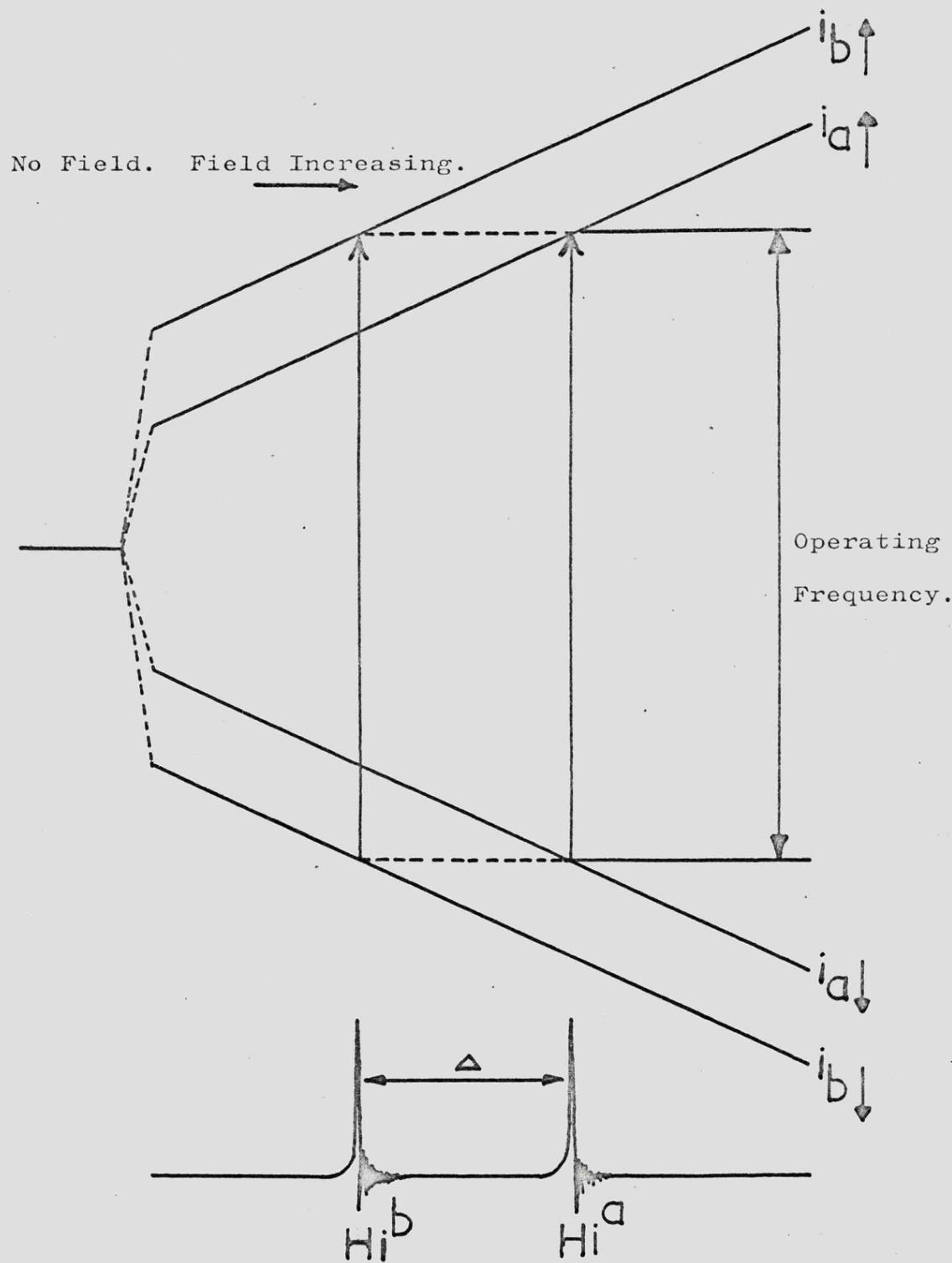


Figure 1.2. The effect of an applied magnetic field on the energy levels of the hydrogen nuclei Hi^a and Hi^b .

used. Such references can be used either internally or externally, however, their use is not as straightforward as would at first appear. Problems associated with referencing procedures are fully discussed in Chapter 3.

1.4 The Study of Electrolytic Solutions by the N.M.R. Solvent Shift Technique.

The chemical shift, being a direct measure of differences in shielding constants, provides a very powerful means of probing the environments of nuclei. The chemical shift is also a very precise measurement, most n.m.r. spectrometers can distinguish lines 0.3 Hz or 0.1 milli gauss apart. At an applied field of 1.5×10^4 gauss or 60 MHz, this represents a resolving power of 1 part in 10^8 , no other spectroscopic technique approaches this precision. The development of superconducting magnets capable of producing fields of around 55,000 gauss, giving operating frequencies for the proton of 220 MHz, is of direct relevance to the study of aqueous salt solutions. Spectrometers which utilise such magnets give increased signal intensities together with a greater spread of chemical shifts, so allowing more positive spectral analyses. A 220 MHz spectrometer has been used for part of the work reported in this thesis, however, lack of machine time precluded extensive utilization.

The local electron density at a nucleus is not the only factor that determines the value of the shielding

constant. Another, frequently very important, contribution arises from the field induced circulation of electrons in neighbouring parts of a molecule. The electron distribution around a given nucleus can also be varied by external forces that perturb the molecule. Such forces must, however, be reasonably strong for present methods to detect any change in shielding (hence the advantages of 220 MHz spectrometers). Examples of such relatively strong perturbations are:

- (i) Interactions which manifest themselves in the formation of hydrogen bonds.
- (ii) The large electrostatic fields in the neighbourhood of ions, which can polarize surrounding dipoles.

It is interactions of this type that are of importance in ion-solvent effects.

In 1955 Shoolery and Alder²⁸ carried out an investigation of the effect of electrolytes on the p.m.r. of water. They noted two main effects;

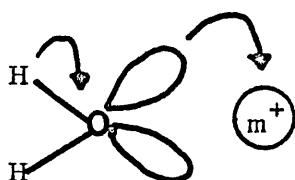
- a) A single shifted resonance for the water protons
- b) Line widths which were the same as for pure water, except for highly concentrated zinc chloride solutions - these being ascribed to solution viscosity effects.²⁵

The measured salt shifts were assumed to arise from three fundamental interactions:

- (i) Protons associated with cations.
- (ii) Protons associated with anions.
- (iii) Protons remote from ions and in nearly the same environment as in pure water.

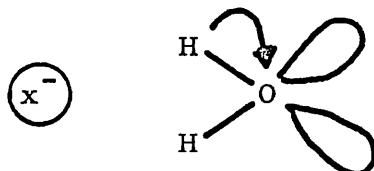
Shoolery and Alder's analyses of the effect of these interactions on the proton shift of the water have been used in most subsequent publications, they are as follows.

Cations:



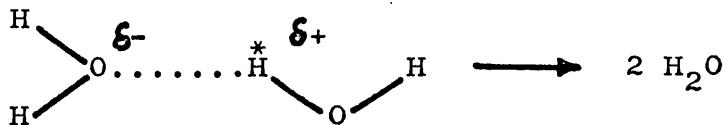
Polarization of the charge distribution as shown makes it less probable to find electrons on the protons. The reduced shielding of the protons gives a n.m.r. shift to lower applied fields.

Anions:



The electrons are repelled from the protons by the charge cloud of the anion, again a reduced shielding occurs resulting in a n.m.r. shift to lower applied fields.

Ions were also assumed to be capable of breaking down the hydrogen bonded structure of the water. When two water molecules are separated, the mutually induced dipoles are removed;



the proton $\overset{*}{\text{H}}$ will have become more shielded in the unassociated form, so giving a n.m.r. shift to higher applied fields. This deduction is supported by the high field shift that occurs when water is heated.²⁹

The observed linear variation of the proton shift with salt concentration was taken to imply that ionic effects were additive;

$$\delta = M (a \delta^+ + b \delta^-)$$

where δ = the salt shift (molal) for the salt $m_a x_b$.

δ^+ , δ^- = the molal ion shifts.

M = salt molality.

The problem of the subdivision of salt shifts immediately arises. Shoolery and Alder arbitrarily gave the perchlorate anion a molal shift of +0.085 p.p.m. (+ = an upfield proton shift). This shift was then used as a reference with which to obtain a self consistent set of individual ion shifts.

Many workers have carried out n.m.r. proton shift measurements on aqueous and related systems since those of Shoolery and Alder, the field is well covered in various reviews.³⁰⁻³²

At normal temperatures the presence of extremely rapid and generally random molecular motions averages local magnetic fields and so gives rise to single, solute-shifted, narrow resonance lines (figure 1.3i). If exchange between various environments can be slowed ($\tau_{1/2} > \text{ca. } 10^{-4} \text{ sec.}$) then it should be possible, at least in principle, to observe separate resonances from solvent

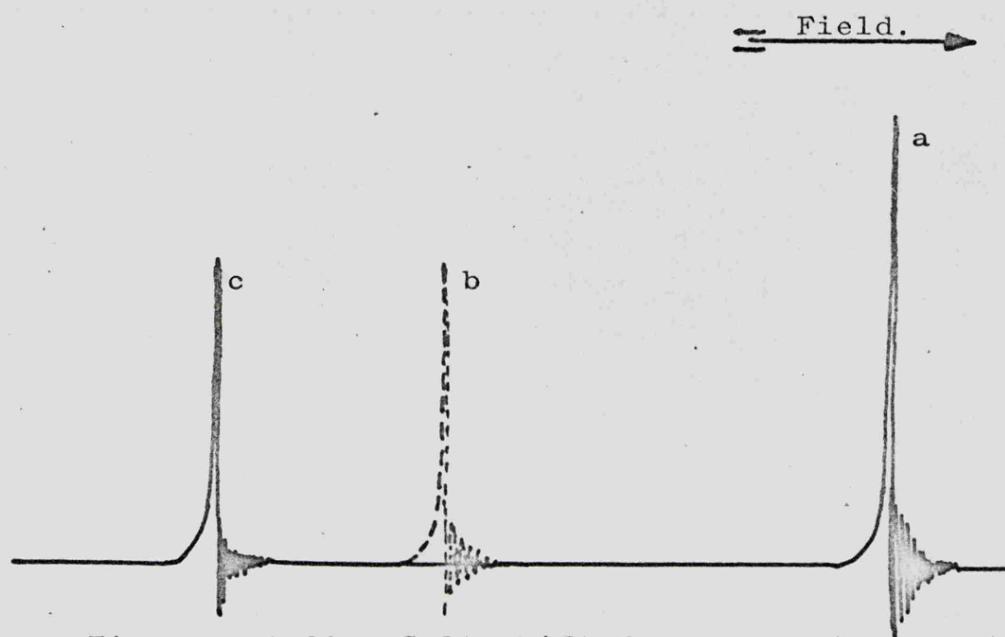


Figure 1.3i. Salt shifted p.m.r. water spectrum.

a, Reference (internal or external).

b, Pure water resonance.

c, Salt shifted water resonance.

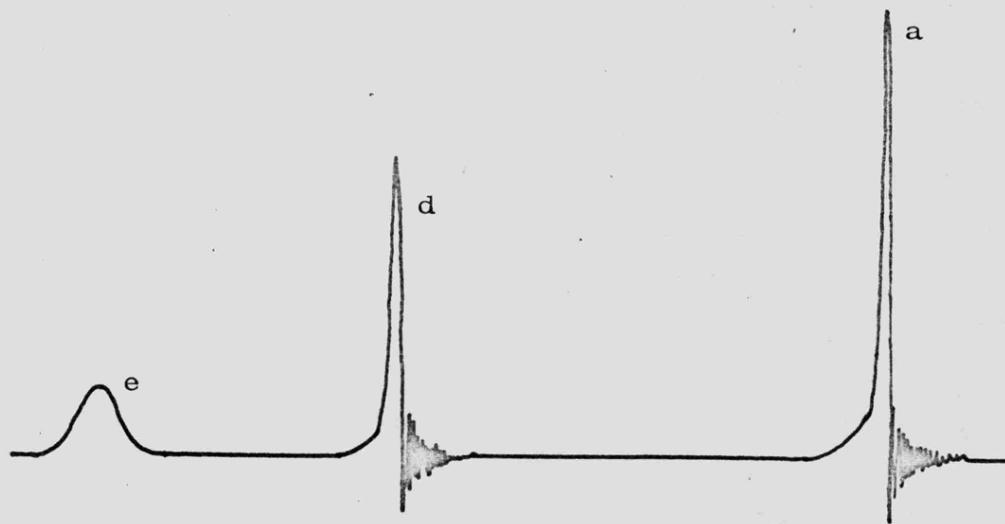


Figure 1.3ii. Low temperature spectrum of a hydroxy solvent.

d, Salt shifted bulk hydroxyl resonance.

e, Cation solvation shell resonance.

molecules bound to ions in primary solvation spheres, (figure 1.3ii). In practice such behaviour has only been observed for highly charged cations at very low solution temperatures, e.g. for Mg^{2+} in methanolic solution at 198K.³³ Cation solvation shell resonances have also been obtained in ethanolic solution³⁴ and for highly concentrated aqueous solutions containing multivalent species.³⁵ Experiments of this type have been used to determine solvation numbers, these have tended to support those derived in the past.

The extraction of information from the single shifted resonances at normal temperatures is more complex. Derivations of individual ion shifts have necessitated the use of somewhat arbitrarily chosen reference shifts. A full discussion of such determinations is set out in Chapter 4 and two alternative methods of deriving the molal shift of the chloride ion are given. Chapter 4 also probes the temperature dependence of ion shifts, a phenomenon which has in the past been mainly overlooked, probably as a consequence of arbitrary assignments.

Ion shifts, once derived, are normally interpreted in terms of polarization and structure making/breaking effects. Particularly important in this respect are the quaternary ammonium cations. The properties of these alkylated ions, in aqueous solution, as interpreted from n.m.r. measurements³⁶ are at variance with those inferred from other methods.³⁷ Chapter 6 gives details of work

concerning the effect of the quaternary ammonium cations on the proton resonance of the solvent, water. The results obtained seem to partially explain the previously reported anomalous results. The shifts measured in the present work indicate a water structure enhancement for solution temperatures below 300K.

CHAPTER TWO

EXPERIMENTAL PROCEDURE

2.1 Spectrometers.

The greater part of the spectra recorded for the work described in this thesis were obtained by the use of a Varian Associates A.60. n.m.r. spectrometer. The operating frequency of this instrument being 60 MHz.

A Varian Associates DA.60 spectrometer, operating at 56.4 MHz, was also utilized, but to a lesser degree.

For some of the measurements made on aqueous solutions of tetra n-butyl ammonium bromide, a Varian Associates 220 MHz spectrometer was employed. This instrument, being the property of the Science Research Council and located at the Petrochemical and Polymer Laboratory of Imperial Chemical Industries Ltd, necessitated the spectra being recorded by ICI staff in accordance with written instructions.

2.2 Recording of Spectra.

Spectra were recorded in the standard way, this being fully described in the spectrometer manufacturers manual.³⁸

The calibration of the chart paper (sweep width) was periodically checked. Calibration was achieved by making use of the known separation of the TMS and chloroform proton resonances. In many cases spectra were individually (and independently) calibrated by means of the 'side band' technique. In this technique an external oscillator places symmetrical sidebands about a chosen central resonance, an accurate frequency counter

is then used to determine the side band separation.

By carrying out such calibration procedures, n.m.r. solvent shifts could be measured to an accuracy of ± 0.3 Hz.

2.3 Temperature Control.

The work described in this thesis is concerned with the accurate measurement of salt shifted hydroxylic proton resonances. The resonant frequency of such protons is, however, markedly temperature dependent.^{39,40} Indeed, this very property is utilized as a means of determining the temperature of the n.m.r. probe.⁴¹ In order to meaningfully compare the shifts of hydroxylic solvent protons, induced by differing solutes, accurate and stable temperature regulation is essential.

The spectrometers previously described were equipped with the Varian Associates V.6040 variable temperature unit, temperatures being controlled by the flow of thermally regulated nitrogen gas around the sample. The system is fully described in the manufacturers manual.⁴² The limits of temperature regulation of the unit are specified as:

Range. 213K to 473K

Temperature regulation at sensor $\pm 1^\circ$

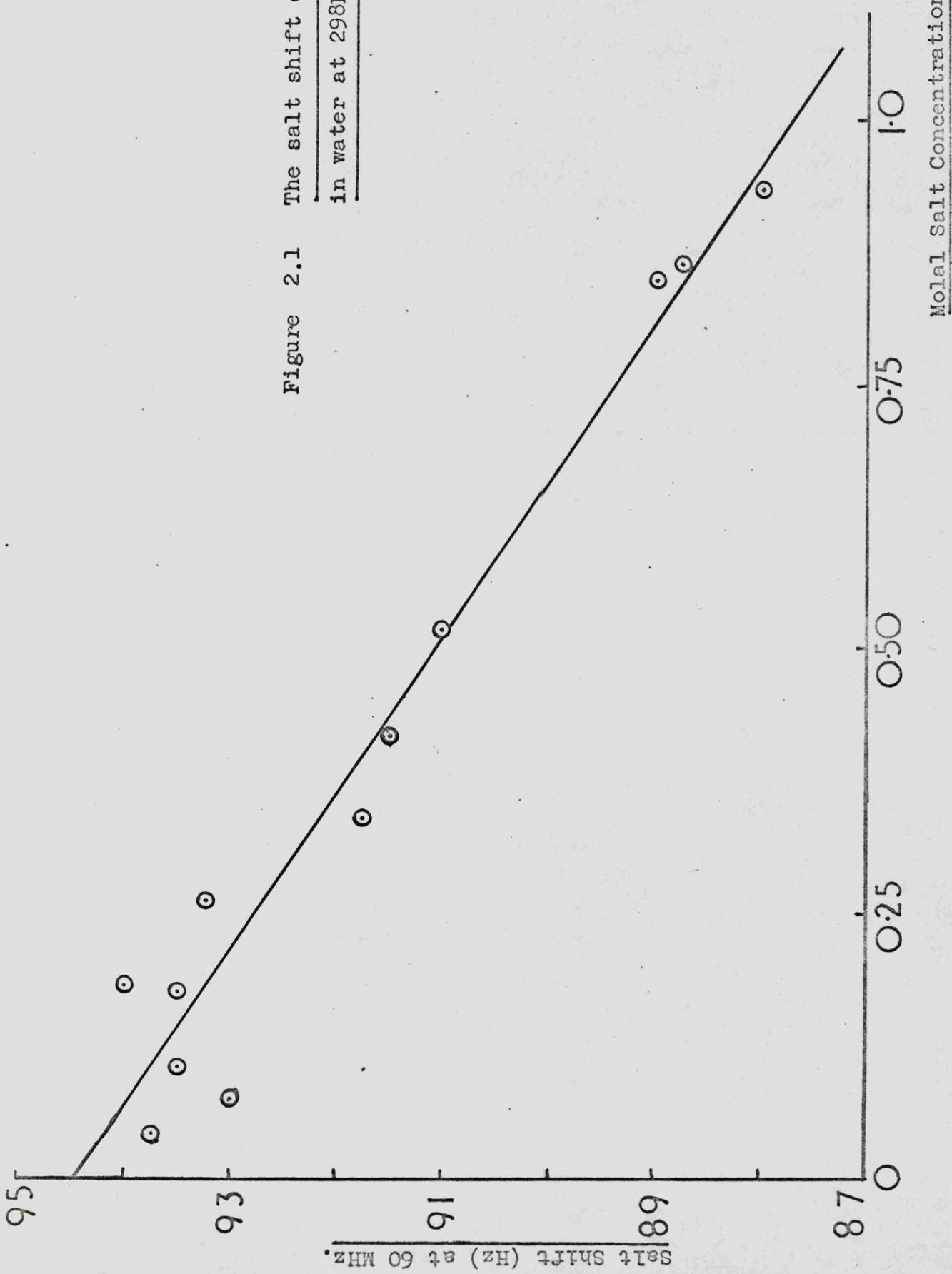
Temperature regulation at sample $\pm 2^\circ$

In preliminary experiments the probe was set at a predetermined temperature using the methanol substitution technique.⁴² A series of aqueous salt shifts were

then measured at this temperature and the results plotted in the form of a salt shift versus concentration graph. Figure 2.1 shows a typical plot resulting from these preliminary experiments. It is noted that the scatter of experimental data is quite marked, and furthermore, cannot be reasonably attributed to either instrumental or concentration errors. The conclusion drawn from these results was that variation of temperature (about a mean) when changing samples was, in all probability, the source of the observed excessive scatter. In order to largely eliminate such errors the following procedure was adopted for all subsequent salt shift determinations.

The solution under investigation was contained in the inner section of a Wilmad co-axial n.m.r. cell,⁴³ the annulus being filled with dry methanol (Figure 2.2a). The methanol used for this purpose was Carl-Fischer Reagent Grade distilled from calcium hydride and containing a trace of concentrated hydrochloric acid. The acid promotes hydroxyl proton exchange at low temperatures and so gives rise to a single narrow hydroxyl resonance under all operating conditions. Each spectrum will therefore possess a temperature 'print', as shown in Figure 2.2b. The hydroxyl proton shift-temperature relationships for both methanol⁴⁰ and water³⁹ are well known, measured salt shifts could therefore be corrected to a common temperature. For the work carried at temperatures in excess of 340K, ethylene glycol replaced the methanol.

Figure 2.1 The salt shift of Et_4NI
in water at 298K.



Molal Salt Concentration.

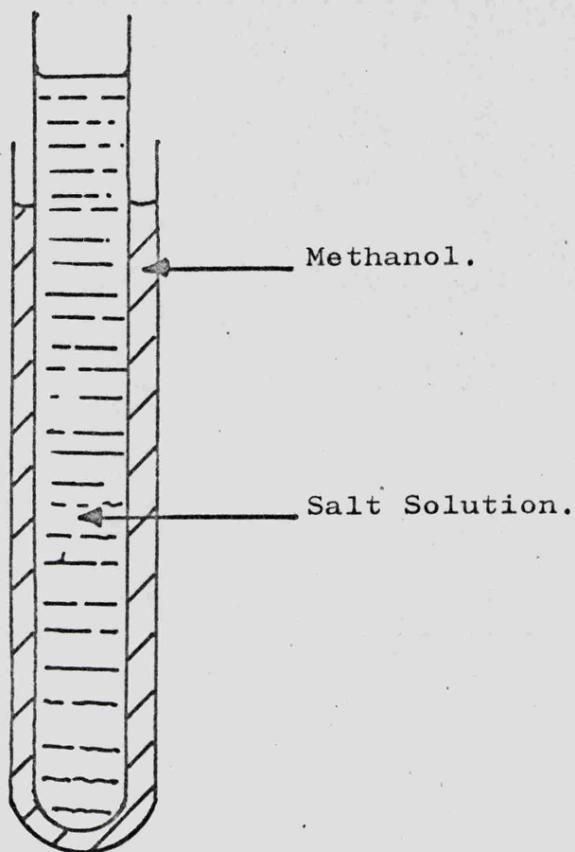


Figure 2.2a. Wilmad Co-Axial N.M.R. Cell.

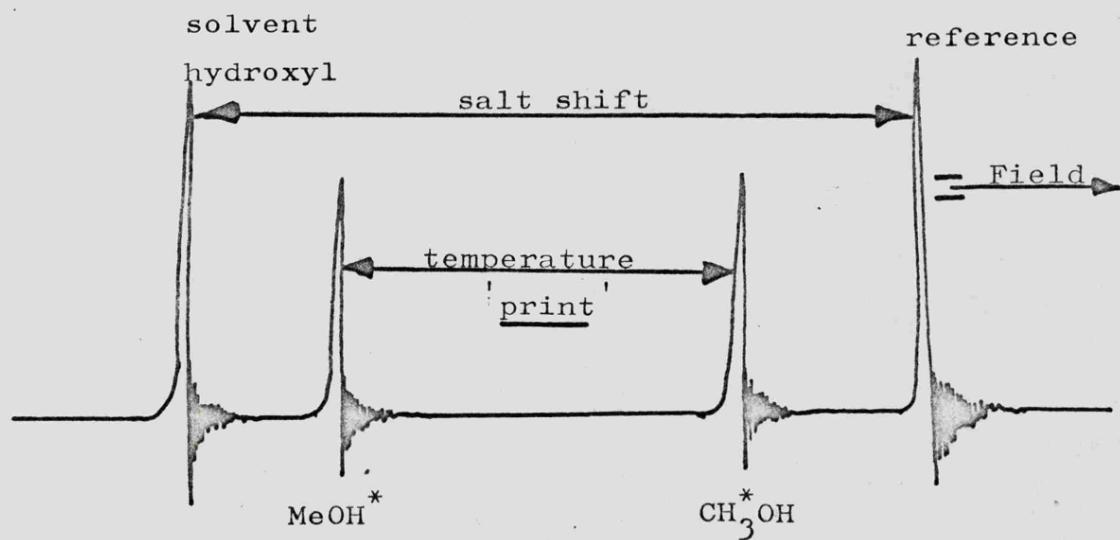


Figure 2.2b. Temperature 'print' n.m.r. spectrum.

An implicit assumption in the above procedure is that the proton shift temperature dependence of pure water and aqueous solutions will be identical, however, there may be slight deviations. For the purpose of the present temperature corrections such deviations have been ignored. This would not seem to be unreasonable as the method has never been applied when a correction in excess of ± 1.0 Hz. would result, in such cases primary temperature adjustments were made. Figure 2.3 shows a salt shift versus concentration plot that has been temperature corrected, it is noted that the experimental scatter is greatly reduced.

2.4 Sample preparation and handling.

(i) Solvents.

Water.

De-ionised water was distilled from alkaline permanganate under an atmosphere of oxygen free nitrogen.

Methanol.

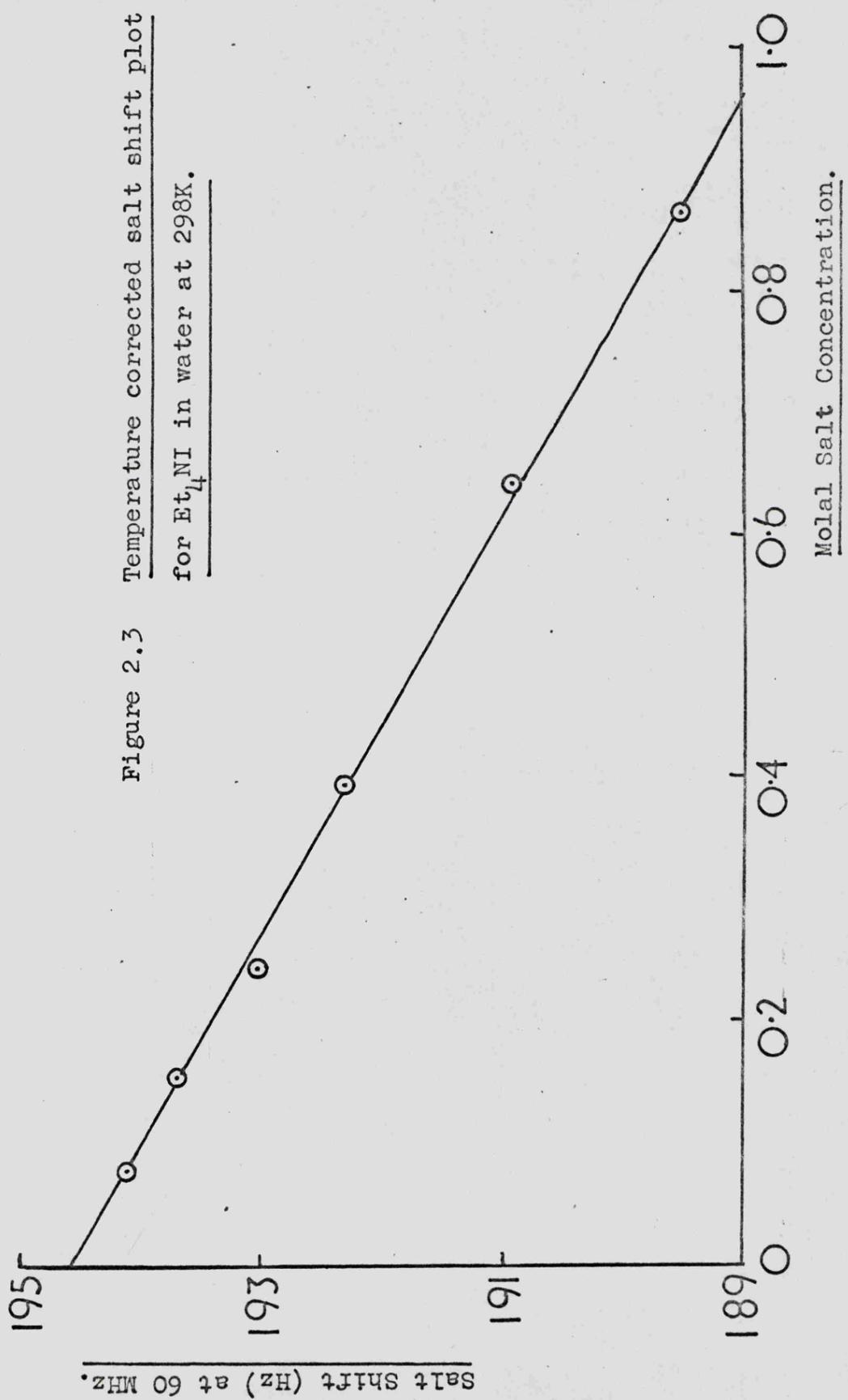
Carl Fischer grade methanol was distilled from calcium hydride and stored over molecular sieves.

Ethanol.

Absolute alcohol was distilled from calcium hydride and stored over molecular sieves.

Ethylene diol.

Reagent grade ethylene diol was distilled from calcium hydride and stored over molecular sieves.



Ammonia.

Anhydrous ammonia was distilled from potassium/liquid ammonia solution as required (a vacuum line operation).

(ii) Salts.

The salts used were of 'analar' or 'reagent' grade and were used, in the majority of cases, without further purification. The main exceptions were the quaternary ammonium and carboxylic acid salts, these being recrystallised from various alcoholic solvents.⁴⁴

Dehydration of the salts (where necessary) was carried out in a vacuum oven for periods of at least twelve hours, at temperatures up to 420K. The dry salts were then stored in a vacuum desicator, over phosphorus pentoxide.

(iii) Solutions.

Solutions were made up gravimetrically. Transfer operations were carried out, where necessary, in a dry box under an atmosphere of nitrogen. Concentrations were checked periodically by standard volumetric techniques.

2.5 Vacuum line operations.

For the investigations carried out concerning ion-pair formation in methanolic solution, and the determination of ion shifts in solutions of liquid ammonia (both reported in Chapter 7), a high vacuum system was employed. Further experimental details concerning the vacuum system can be found in the relevant sections of Chapter 7.

CHAPTER THREE

N.M.R. REFERENCING PROCEDURES

3.1 Introduction.

The n.m.r. technique requires a unique fixed resonant frequency which can be utilised as a reference from which accurate chemical shifts can be measured. In normal analytical work it is usual to employ the narrow methyl resonances of either TMS or NaDSS, these being used internally. Internal references are added in very low concentration and are taken as non-interacting.

The work described in this thesis concerns the shifts of proton resonances of a solvent arising from the presence of a dissolved substance. The use of an internal reference would therefore seem unwise. It could well be that the internal reference would interact with the system being studied, so producing a secondary contribution to the observed salt shift.

An alternative approach is to use an external reference. Such references are contained in either a central capillary tube or in the annulus of a co-axial cell (cf., Figure 2.2a. p.26). The use of external references is, however, not without inherent disadvantages. Bulk magnetic susceptibility corrections must be applied to externally referenced salt shifts before meaningful comparisons can be made. Such corrections arise from the difference in bulk diamagnetic susceptibility between the reference and the sample.

In cylindrically shaped containers, the actual fields experienced by individual nuclei will depend on the magnetic polarization near the surface. The volume

of the sample can be divided into two regions:

- 1) A sphere around any given molecule within the sample large enough to be of macroscopic dimension compared to the size of the sample.
- 2) The remainder of the sample.

The field experienced by a nucleus at the centre of the sphere (as under 1) is made up of three contributions:

- a) The applied field H_0 .
- b) The field due to induced magnetism in the region between the small sphere and the sample boundary.
- c) The field due to induced magnetism in the inner sphere.

It is (b) that gives rise to the bulk susceptibility effect, and this must be allowed for before genuine comparisons of (c) can be made.

Magnetic polarization near the surface can be replaced by an imaginary distribution of magnetic dipoles on the outer surface of the specimen. If α is a numerical factor depending on the geometry of the n.m.r. cell, then this distribution gives a field $-\alpha \chi_v H_0$, where χ_v is the volume susceptibility. The distribution on the sphere gives a field of $\frac{4\pi}{3} \chi_v H_0$. If H_{eff} is the field in the inner sphere, then;

$$H_{eff} = H_0 + \frac{4\pi}{3} \chi_v H_0 - \alpha \chi_v H_0$$

i.e.,

$$H_{\text{eff}} = H_0 \left(1 + \left[\frac{4\pi}{3} - \alpha \right] \chi_v \right)$$

For spherical samples $\alpha = \frac{4\pi}{3}$ and so $H_{\text{eff}} = H_0$, hence no susceptibility correction would be necessary. It is unfortunate that concentric spherical containers are not available, consequently cylindrical cells have to be used. For cylindrical containers having a large length/radius ratio, $\alpha = 2\pi$ and so,

$$H_{\text{eff}} = H_0 \left(1 + \left[\frac{4\pi}{3} - 2\pi \right] \chi_v \right)$$

$$\text{i.e., } H_{\text{eff}} = H_0 \left(1 - \frac{2\pi}{3} \chi_v \right) \dots \dots \dots \text{(i)}$$

(note: χ_v is negative for diamagnetic substances.)

The effect of polarization in the cylinder is therefore equivalent to a contribution of $\frac{2\pi}{3} \chi_v$ to the shielding constant.

The chemical shift is defined as the difference in the shielding constants;

$$\delta = \sigma - \sigma_{\text{ref.}} = \frac{H - H_{\text{ref.}}}{H_{\text{ref.}}} \dots \dots \text{(ii)}$$

Where H and $H_{\text{ref.}}$ are the resonant fields of the sample and the reference. Substitution in (i) from (ii) gives;

$$\text{true } \delta = (\sigma - \frac{2\pi}{3} \chi_v) - (\sigma_{\text{ref.}} - \frac{2\pi}{3} \chi_{v \text{ ref.}})$$

$$\text{hence; } \delta = \frac{H - H_{\text{ref.}}}{H_{\text{ref.}}} + \frac{2\pi}{3} (\chi_{v \text{ ref.}} - \chi_v)$$

$$\text{i.e., } \delta = \underline{\delta_{\text{obs}} + \frac{2\pi}{3} (\chi_{v \text{ ref.}} - \chi_v)} \dots \text{(iii)}$$

Equation (iii) is the basis of the bulk susceptibility correction.

If the salt shifted solvent resonance is measured from a given external reference, then;

$$\delta = \delta_{\text{obs}} + \frac{2\pi}{3} (\chi_{v \text{ ref}} - \chi_{v}^{\text{solution}})$$

Furthermore if the pure solvent resonance from the same external reference is given by;

$$\delta' = \delta'_{\text{obs}} + \frac{2\pi}{3} (\chi_{v \text{ ref}} - \chi_{v}^{\text{solvent}})$$

Then the true salt shift is given by;

$$\Delta = \delta - \delta'$$

$$\text{i.e., } \Delta = \delta_{\text{obs}} - \delta'_{\text{obs}} - \frac{2\pi}{3} (\chi_{v}^{\text{solution}} - \chi_{v}^{\text{solvent}}) \dots \text{ (iv)}$$

The volume susceptibility of the reference ($\chi_{v \text{ ref}}$) has been eliminated. Experimentally it is much more convenient to use mass (specific) susceptibilities as these can be measured on a Gouy balance.⁴⁵ Equation (iv) can be modified to accomodate mass susceptibilities as follows;

$$\chi_{\text{mass}}^{\text{solvent}} = \frac{\chi_{v}^{\text{solvent}}}{d_{\text{solvent}}}$$

$$\chi_{\text{mass}}^{\text{solution}} = \frac{\chi_{v}^{\text{solution}}}{d_{\text{solution}}}$$

(d = density)

Furthermore,

$$\chi_{\text{mass}}^{\text{solution}} = (\text{weight fraction solvent}) \chi_{\text{mass}}^{\text{solvent}} + (\text{weight fraction solute}) \chi_{\text{mass}}^{\text{solute}}$$

If 1 cm³ of solution is considered, then;

$$\chi_m^{\text{soln}} = \frac{\text{wt. solvent}}{\text{wt. soln}} \chi_m^{\text{solv}} + \frac{\text{wt. solute}}{\text{wt. soln}} \chi_m^{\text{solute}}$$

$$\therefore d_{\text{soln}} \chi_m^{\text{soln}} = \text{wt. solvent} \chi_m^{\text{solv}} + \text{wt. solute} \chi_m^{\text{solute}}$$

since, wt. soln = d_{soln} for 1 cm³.

Substituting in equation (iv),

$$\Delta = \delta_{\text{obs}} - \delta'_{\text{obs}} - \frac{2\pi}{3} \left(\text{wt. solv} \chi_m^{\text{solv}} + \text{wt. solute} \chi_m^{\text{solute}} \right) - \chi_m^{\text{solv}} d_{\text{solv}} \quad \left. \right\}$$

But, wt. solv = wt. solution - wt. solute.

$$\therefore \Delta = \delta_{\text{obs}} - \delta'_{\text{obs}} - \frac{2\pi}{3} \left[\chi_m^{\text{solv}} (\text{wt. soln} - d_{\text{solv}}) - (\chi_m^{\text{solv}} - \chi_m^{\text{solute}}) \text{wt. solute} \right]$$

$$\text{However, wt. solute} = \frac{M \cdot W}{1000}$$

where M = molecular weight of the solute,

and W = molarity of the solution.

$$\therefore \Delta = \delta_{\text{obs}} - \frac{2\pi}{3} \left[\chi_m^{\text{solv}} (d_{\text{soln}} - d_{\text{solv}}) - \frac{(\chi_m^{\text{solv}} - \chi_m^{\text{solute}}) M \cdot W}{10^3} \right] \quad \dots \dots \quad (v)$$

The last relationship (v) is the one normally used to correct externally referenced salt shifts for bulk susceptibility effects. In order to facilitate the calculation of such corrected shifts, a computer programme was written. Details of this programme (which is based on equation v) can be found in appendix 1.

3.2 Externally referenced results.

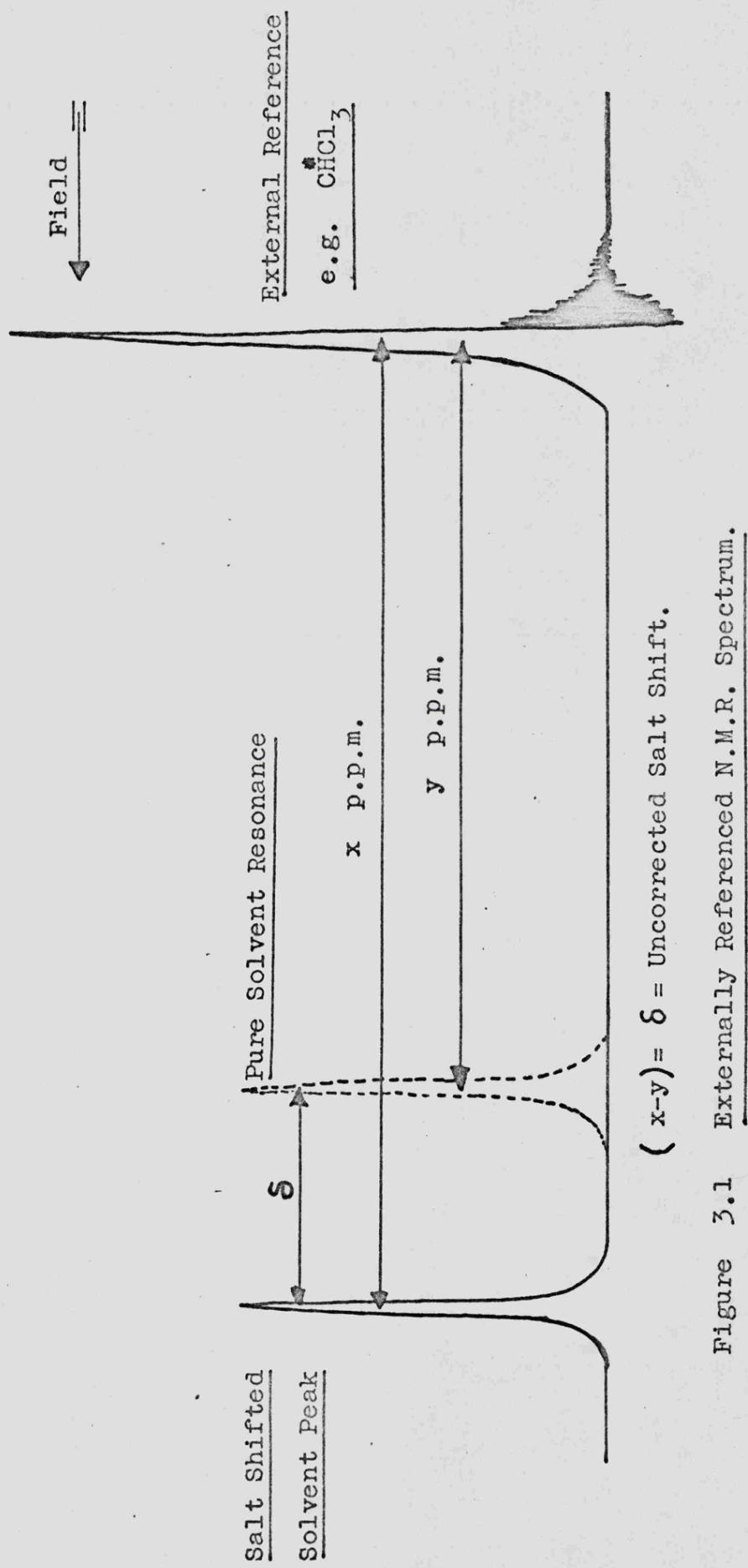
A consideration of equation (v) shows that the following requirements must be met before accurate bulk susceptibility corrections can be made.

- a) Precision co-axial cells or capillary tubing. (geometrical condition)
- b) Accurate mass susceptibility data.
- c) Accurate density data. (for both solutions and pure solvents)

Initial work carried out on aqueous salt solutions was performed using chloroform as an external reference, this being contained in a central capillary tube held in place by 'teflon' O rings. The spectra resulting from this procedure are typified by the one shown in Figure 3.1.

The results of these experiments are listed in Table 3.1 and graphically represented in Figure 3.2.

A consideration of these results, together with those of Hindman⁴⁶, shows that susceptibility corrections can be as much as 800% of the experimentally measured salt shift. Consequently such corrections must



$(x-y) = \delta$ = Uncorrected Salt Shift.

Figure 3.1 Externally Referenced N.M.R. Spectrum.

Results at 298K.			
Salt.	Molal uncorrected shift. p.p.m.	Correction p.p.m.	Molal corrected shift. p.p.m.
KCNS	+0.078	+0.020	+0.098
KMnO ₄	+0.250		
K ₃ PO ₄	-0.200		
*KNO ₂	+0.078		
*K ₂ CrO ₄	-0.075		
KNO ₃	+0.088	+0.015	+0.103
*KCNO	+0.033		
(NH ₄) ₃ PO ₄	-0.391		
(NH ₄) ₂ CrO ₄	-0.090		
LiCl	-0.029	+0.049	+0.020
NaCl	+0.031	+0.049	+0.080
KCl	+0.041	+0.037	+0.078
CsCl	+0.008	+0.086	+0.094
RbCl	+0.012	+0.098	+0.110

* Possible to correct these results by extrapolation of available density data.			

Results at 273K.			
LiCl	+0.013	+0.009	+0.022
NaCl	+0.075	+0.035	+0.110
KCl	+0.062	+0.043	+0.105
RbCl	+0.057	+0.039	+0.096
CsCl	+0.016	+0.124	+0.140

TABLE 3.1

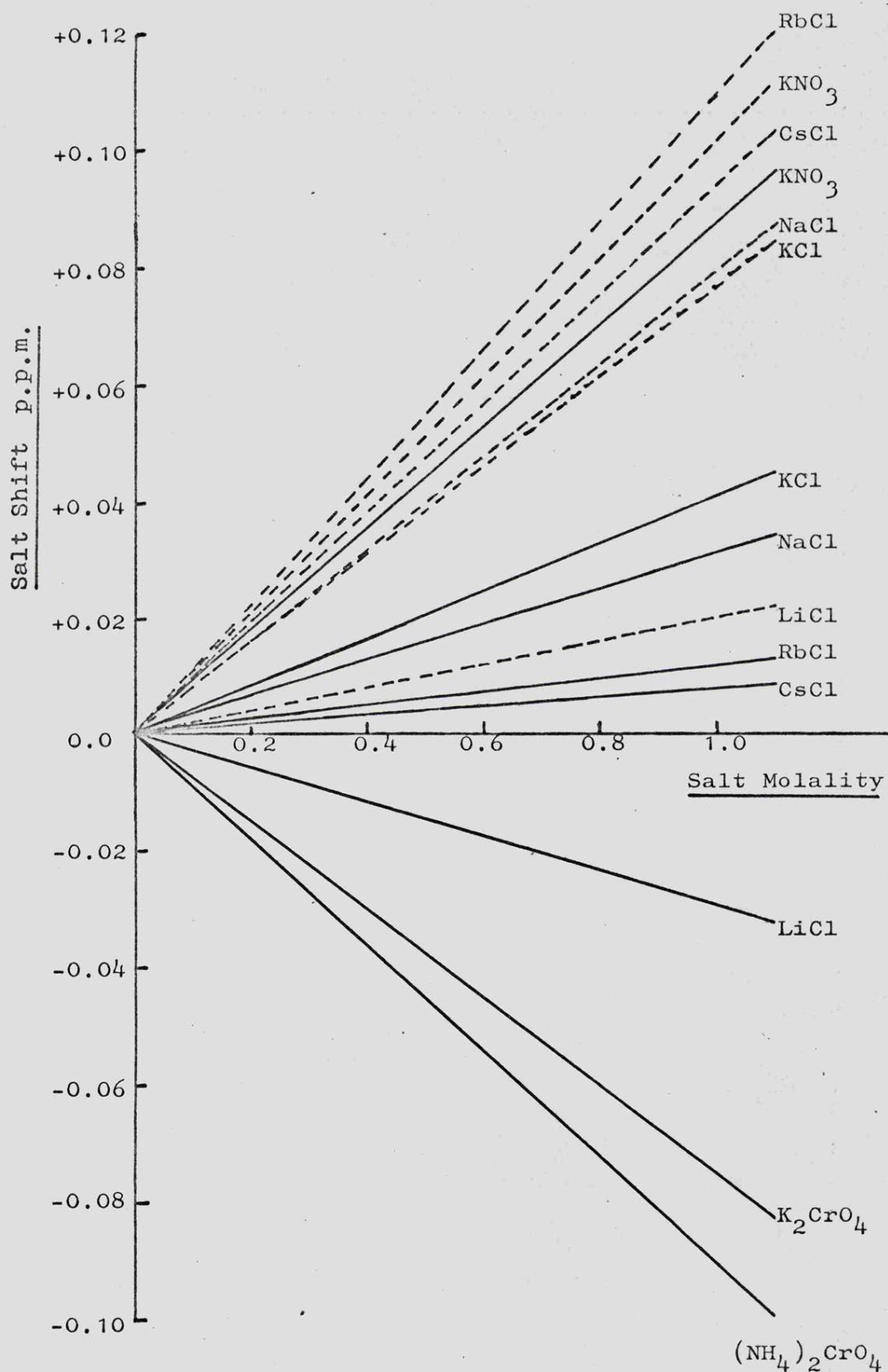


Figure 3.2 Externally referenced aqueous
salt shifts at 298K.
— uncorrected
- - - corrected

be treated with some reserve. Table 3.2 lists the results of various workers⁴⁶⁻⁴⁹ concerning externally referenced n.m.r. salt shifts. The temperatures of these determinations are essentially the same, however, the scatter of the susceptibility corrected results is disturbing.

Fabricand and Goldberg⁴⁷ have discussed the advantages of using either Pauling's theoretical susceptibilities or experimentally measured ones. The conclusion reached was that the theoretical values should be used when performing bulk susceptibility corrections. The choice was based on the observed scatter in additivity of individual ion shifts (i.e. greater when the experimental susceptibilities were used) and also the cation shift dependence on ionic radius. Goto and Isemura⁴⁹ contest this choice of susceptibility, so obtaining a totally different dependence of alkali metal cation shift when plotted versus ionic radius.

Variation of the parameters in the bulk susceptibility correction equation (v) shows that accurate density and mass susceptibility data is required. In particular a 1% variation in density leads to a 7% change in the corrected salt shift.

In view of the magnitude, and contentious nature, of bulk susceptibility corrections the possibility of using a 'non-interacting' internal reference for subsequent determinations was investigated. A further incentive for such an approach lay in the wide range of salts and experimental temperatures to be investigated, for

Table 3.2

SALT	Ref.46 298K	Ref.49 293K	Ref.47 294K		Ref.48 295K	This work. 298K
			Expt. χ	Theo. χ		
LiCl	-0.010	-0.010	+0.019	+0.026	+0.017	+0.020
NaCl	+0.076	+0.090	+0.080	+0.080	+0.086	+0.080
CsCl	+0.053	+0.081	+0.064	+0.102	+0.059	+0.094
NaF	-0.018	-	-0.034	-0.044	-0.036	-
RbI	-	-	+0.106	+0.200	+0.115	-
LiI	-	-	+0.065	+0.124	+0.088	-
NaClO ₄	+0.144	-	-	-	+0.132	-

Externally referenced, bulk susceptibility corrected,
molal salt shifts at the stated temperature.

Positive shifts are upfield.

which a lack of available density data was apparent.

3.3 Internal references.

For an internal reference the terms χ_{vref} and χ_v in the equation;

$$\delta = \delta_{obs} + \frac{2\pi}{3} (\chi_{vref} - \chi_v),$$

are identical. Hence $\delta = \delta_{obs}$, i.e. no bulk susceptibility correction is necessary.

Possible specific interactions between solvent and reference molecules and also salt effects on the internal reference can be sources of error.⁵⁰

It seemed that a suitable internal reference for the present work would be a quaternary ammonium salt, utilizing one of the shielded internal proton resonances.

As it was intended to extensively study the behavior of quaternary ammonium salt solutions, such a reference system would give rise to the added advantage that the quaternary ammonium salts would provide their own reference. An approach similar to this has been used by Clifford and Pethica⁵¹ in a study concerning the properties of aqueous solutions of sodium alkyl sulphates. By using TMS solubilised in the alkyl sulphate micels they were able to show that the separation between the terminal methyl peaks of the alkyl sulphate and the TMS peak did not vary with the concentration of the alkyl sulphate. They consequently used the terminal methyl as a reference.

Hertz and Spalthoff³⁶ have carried work concerned with electrolyte shifts in water, they used 0.3 molal tertiary butyl alcohol as an internal reference. For the work described in this thesis tertiary butyl alcohol (TBA) was rejected in view of the properties of TBA-water mixtures⁵², it may well be that the alcohol would cause detrimental effects in the water structure, even at very low concentrations.

3.4 Tetra methyl ammonium chloride as an internal reference.

A tetra methyl ammonium salt would, if suitable, be an ideal internal reference. The methyl protons of the cation give a sharp narrow resonance peak. The methyl ammonium cation is also relatively compact, its use would avoid complications brought about by the presence of longer chain alkyl ammonium cations. The effects of such long chain ions on water structure is both marked and controversial.^{37,53}

As a prerequisite to the use of any compound as an internal reference, it must be established that the resonant frequency of the reference is independent of any environmental effects of the system being studied.

A series of aqueous solutions of Me_4NCl with varying concentrations (0.015-0.60 molal) were prepared. A trace of NaDSS was added to each, to act as a primary standard, and the constancy of the NaDSS-methyl (of the methyl ammonium) separation checked. The results of

these experiments are given in Table 3.3.

Table 3.3

Molality of Me_4NCl	NaDSS- Me_4NCl separation p.p.m.
0.613	3.186 \pm 0.003
0.357	3.183 \pm 0.003
0.178	3.186 \pm 0.003
0.016	3.183 \pm 0.003
Temperature 298K	
Spectra calibrated by the side band technique.	

The constancy of the separation (Table 3.3), taken together with the analogous results of Clifford and Pethica,⁵¹ indicates that the methyl resonance does not appreciably shift with varying Me_4NCl concentration.

The main assumption made in the above experiment is that the NaDSS and Me_4NCl reference peaks are not equally affected. The fact that the NaDSS was added in differing quantities (i.e. by spatula) to each of the solutions does lend some support to this assumption.

A further condition to be satisfied is that the methyl resonance position (of Me_4NCl) is independent of added salts. In order to probe the added salt effect the Me_4NCl solutions described above were used as the 'solvent', and a series of salt shifts for various alkali metal chlorides (Li, Na, K, Cs) measured in each.

The results of this series of experiments are typified by those of cesium chloride, shown graphically in Figure 3.3.

The shift versus concentration plots are essentially parallel over the complete range of reference concentration, furthermore, the intercepts (ordinate) pass through, within the limits of experimental error, the water- Me_4NCl 'pure solvent' separation. It is concluded, from the parallel nature of the plots in Figure 3.3, that the measured salt shifts are independent of the reference concentration over the range 0.015-0.60 molal. That the intercepts pass close to the water-reference only separation, implies that the reference (Me_4NCl) is not perturbed, at least to any measurable extent, by added salts.

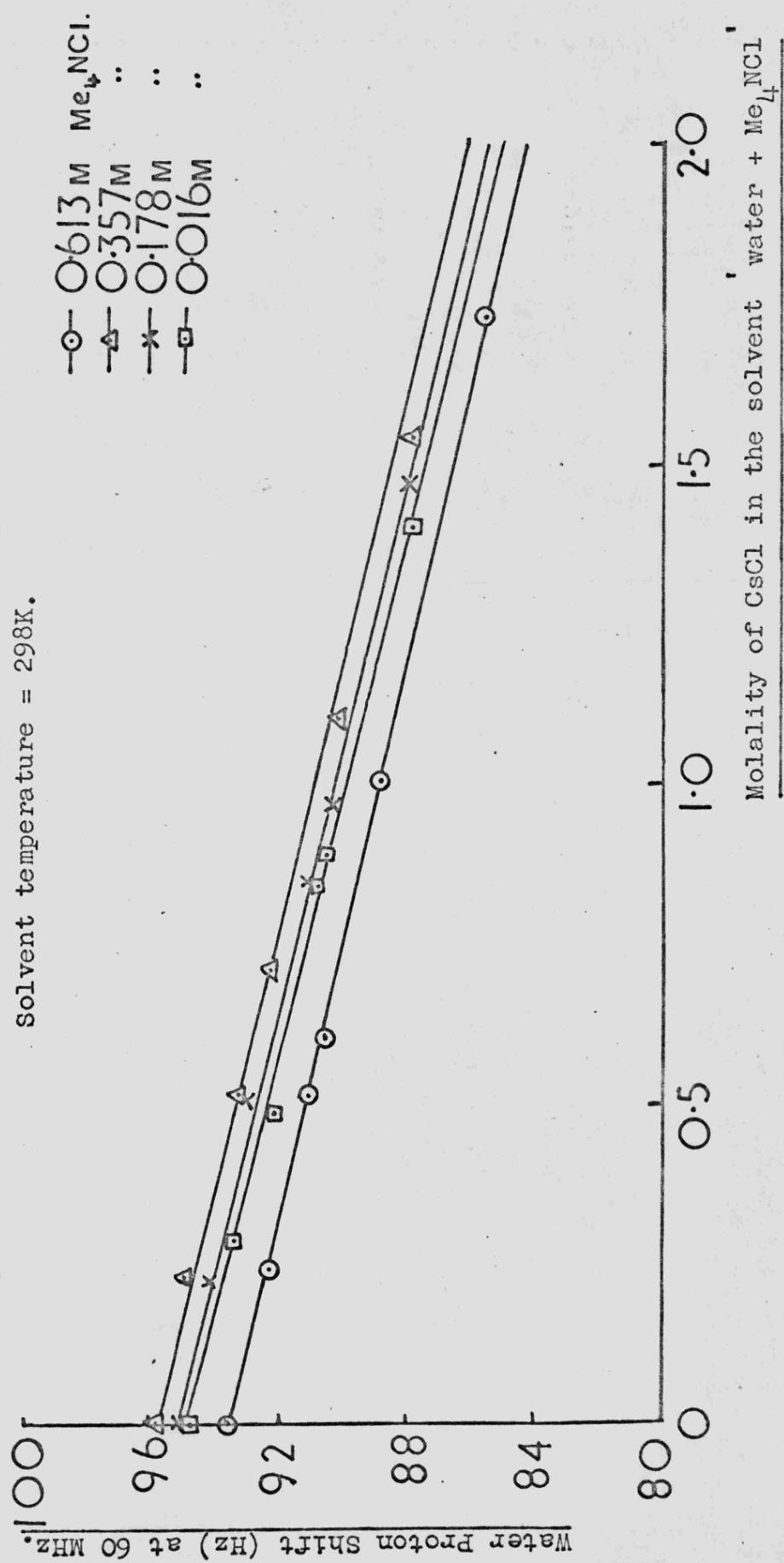
It was concluded that ¹³C methyl ammonium chloride, in low concentration, would be a suitable non-interacting internal reference for use when measuring proton shifts of aqueous electrolytes. The chosen reference concentration was 0.02 molal, it follows that a solution of this strength is taken as the 'solvent water' for all subsequent work on n.m.r. salt shifts.

At this small Me_4NCl concentration the structure of the water is not greatly perturbed, the n.m.r. shift of the water protons being negligible. Figure 3.4 compares the salt shift of Me_4NCl in aqueous solution with that of NaDSS, another commonly used water soluble reference. In both cases the methyl protons of the salt have been

Figure 3.3 The Salt Shift of CsCl in water using

Me_4NCl as an internal reference.

Solvent temperature = 298K.



used as a reference. The salt shift of Me_4NCl is considerably smaller than that of NaDSS, and can therefore be taken as negligible at 0.02 molal.

3.5 Referencing for studies concerning Methanolic, Ethanolic, and Ethylene diol solutions.

Referencing of solutions containing the above mentioned solvents is facilitated by the fact that the methyl or methylene proton resonances of the solvents themselves can provide a suitable non-interacting internal reference. Further details can be found in section 7.2.2.

3.6 Referencing for studies concerning liquid ammonia solutions.

Salt shifts measured in this solvent were externally referenced. The external reference used was the methyl proton resonance of methanol, the use of this reference substance had the additional advantage of providing each spectrum with a 'temperature print' (section 2.3). Further details can be found in section 7.4.

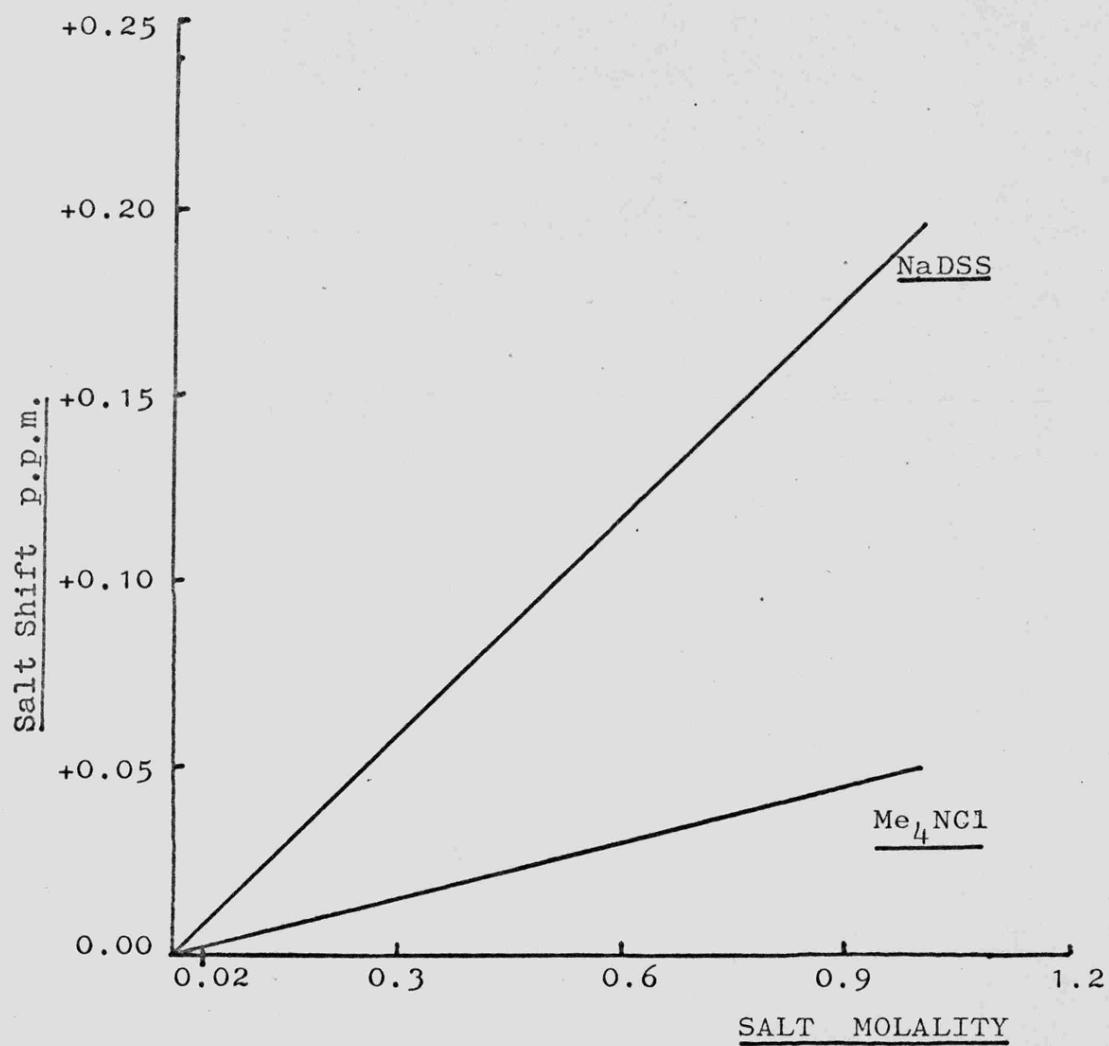


Figure 3.4 Salt shift v molal concentration
at 298K. Aqueous solution.

CHAPTER FOUR

ABSOLUTE PROTON MAGNETIC RESONANCE SHIFTS
FOR CATIONS AND ANIONS IN AQUEOUS SOLUTION

4.1 Introduction.

The directly measured parameter in the n.m.r. experiment, the infinite dilution molal salt shift, must be subdivided into individual ionic contributions before any discussion of specific ion-solvent interactions can be made.

Shoolery and Alder,²⁸ in their paper concerning the effect of electrolytes on the proton resonance of water, arbitrarily assumed that the large singly charged perchlorate anion possessed a molal shift of +0.085 p.p.m. (upfield). This value was subsequently used as a reference ion shift with which to subdivide their measured salt shifts into ionic contributions. No particular justification was given for the chosen perchlorate value.

Hindman⁴⁶ questions Shoolery and Alder's choice, stating; 'It would seem desirable to establish a scale based on a reference ion whose effect on the water structure is known'. Based on a consideration of certain properties of ammonium chloride solutions; e.g. viscosity and molar refraction, Hindman proposed assigning the ammonium ion a zero shift. The ammonium ion by virtue of its tetrahedral shape and hydrogen bonding properties was stated to cause a minimum disturbance to the water structure on dissolution. The whole of the observed upfield shift of ammonium chloride was therefore attributed to the chloride ion.

The resulting ion shifts, derived on this basis,

were then compared with those of Shoolery and Alder²⁸ and good agreement between the two sets of ion shift values noted. In view of the fact that the latter values were measured using an external reference and reported without correction for bulk susceptibility effects, some doubt must be cast on both of these fundamental assignments.

Detailed arguments concerning the meaning of derived ion shifts are usually given in the literature, it would therefore seem desirable to devise a more reliable method of separating cation and anion effects. Given below are details of two independent methods of determining an absolute shift for the chloride ion. The derived chloride shift will be used in later chapters of this thesis to obtain a set of ion shifts which are believed to be close approximations to the true absolute values.

4.2 The 'discontinuity' method.

Butler and Symons⁵⁴ have suggested a method of determining absolute ion shifts in methanol, having as a basis Taube's³³ discovery of separate resonance signals from methanol molecules directly bonded to magnesium cations. In order to apply this method, low temperatures have to be employed, so as to prevent rapid methanol exchange ($\tau_{1/2} < \text{ca } 10^{-4} \text{ sec.}$) between various environments and so allow the detection of resolved cation solvation shells. At 204K the n.m.r. spectrum of methanolic

magnesium perchlorate is similar to that depicted in Figure 4.1a. By neglecting secondary cation effects (assumed negligible) and carrying out calculations involving the weighting of the solvation shell signal with that of the pure solvent hydroxyl resonance, Butler and Symons were able to arrive at a primary cation shift for Mg^{2+} in methanol at 204K. The residual hydroxyl shift (Figure 4.1a), in the absence of secondary cation effects, was set equal to the primary anion shift. At higher temperatures exchange of methanol between the bulk solvent and cation shells results in the resolution of only a single salt shifted hydroxyl resonance (Figure 4.1b), hence the derivation of primary cation shifts by the above method is no longer possible. The low temperature (204K) cation shifts were presented in the form of a plot versus charge/radius ratio (using Paulings ionic radii), the resulting curve is reproduced in Figure 4.2a. It was noted that the curve was continuous, and furthermore, that the shifts of the long chain quaternary ammonium ions tended to the zero values found for non-polar solutes. Butler and Symons made the assumption that the behavior of the large quaternary ammonium ions at 204K was repeated at higher temperatures (tending to zero cation shift with increasing alkyl chain length) and so obtained a set of methanolic cation shifts at 313K. These high temperature cation shifts are shown plotted versus charge/radius ratio in Figure 4.2b, again a continuous curve is evident.

(note: in Figures 4.2a,b. the Ca^{2+} and Sr^{2+} cation shifts

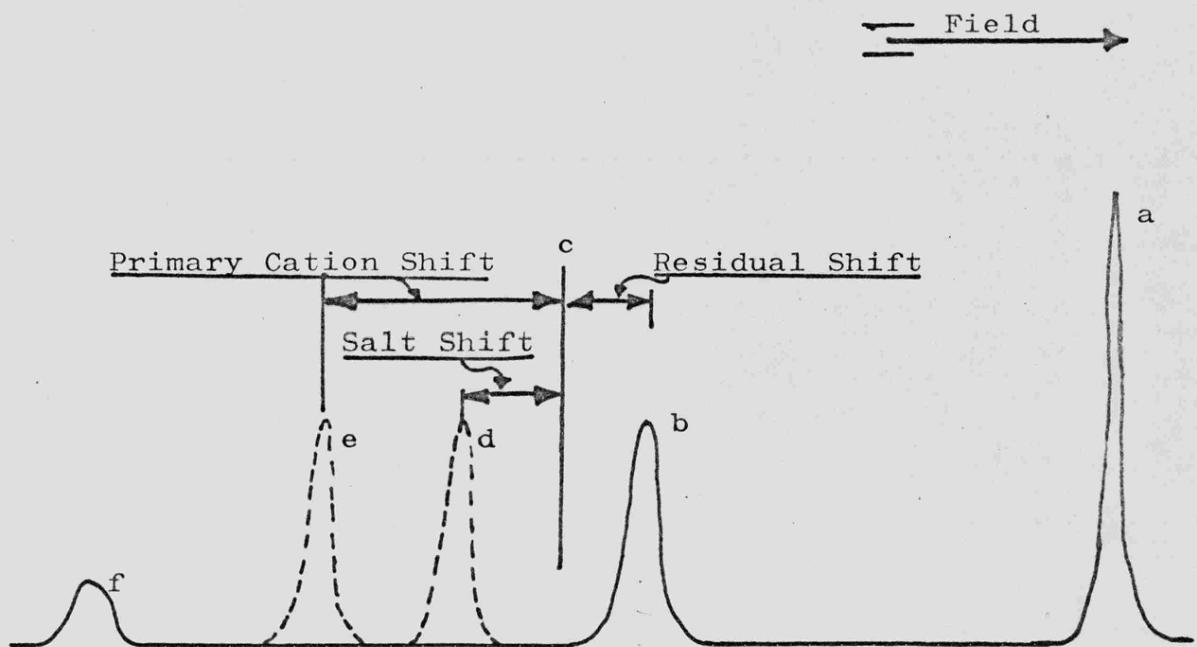


Figure 4.1a Low temperature n.m.r. spectrum of an electrolyte in methanol.

- (a) methyl resonance of methanol.
- (b) residual bulk OH resonance of the solution.
- (d) hypothetical OH after coalescence of cation shell and bulk solvent, b.
- (c) OH of pure methanol.
- (e) hypothetical OH after coalescence of cation shell and pure methanol, c.
- (f) OH of cation solvation shell.

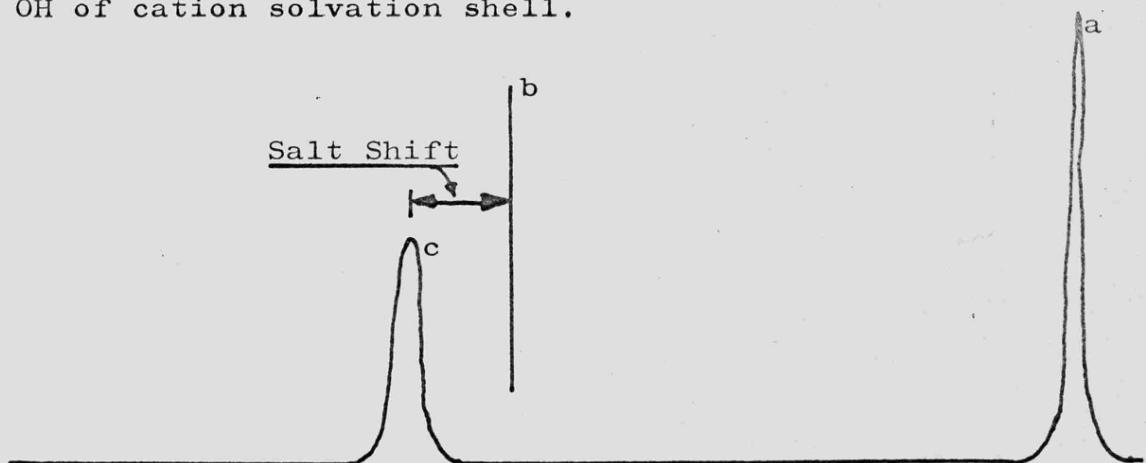


Figure 4.1b High temperature n.m.r. spectrum of an electrolyte in methanol.

- (a) methyl resonance of methanol.
- (b) OH of pure methanol.
- (c) salt shifted OH resonance of methanol.

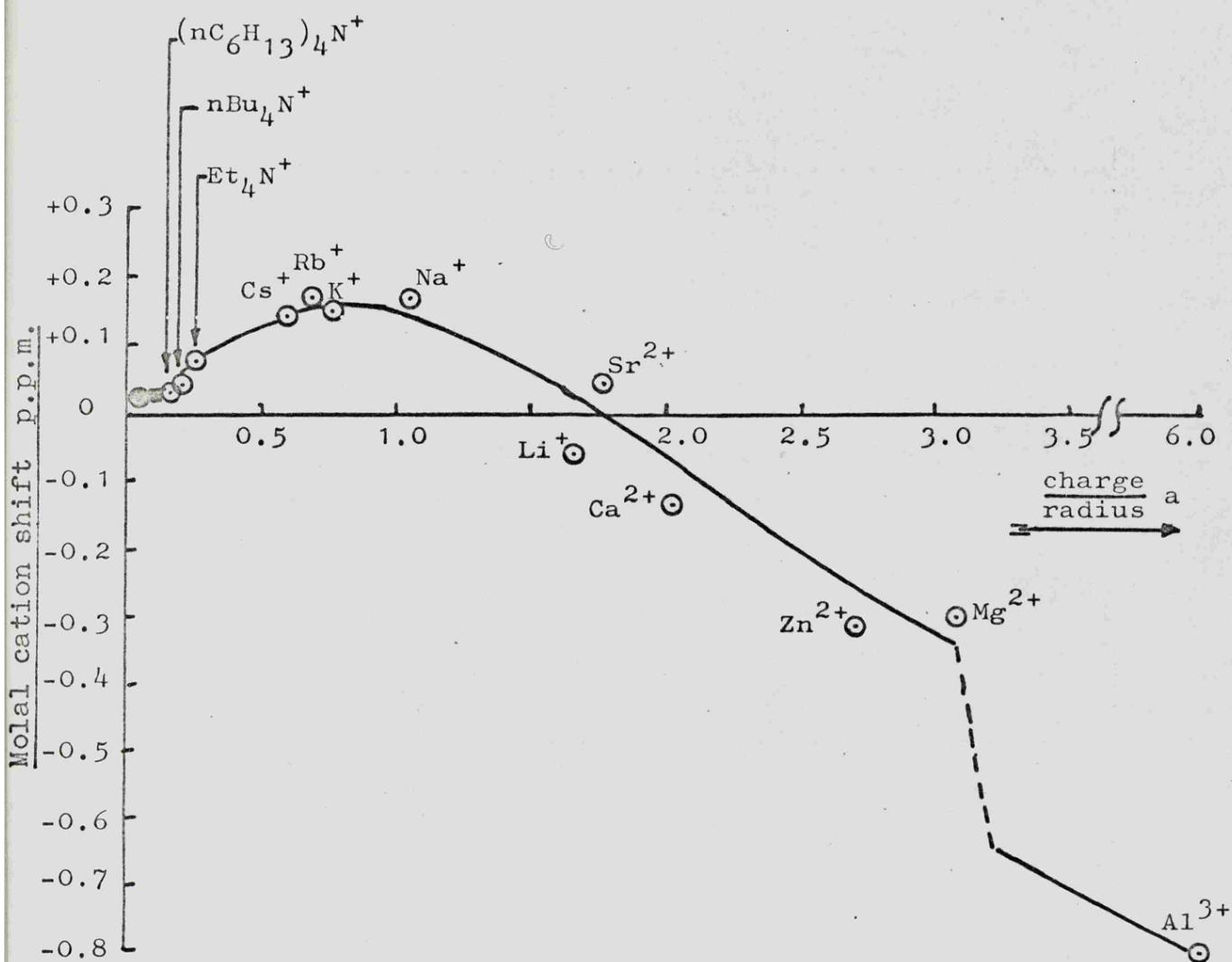


Figure 4.2a Molal methanolic cation shifts versus charge/radius ratio at 204K.

a Pauling ionic radii (p.m x 10^2)

● 2,2- dimethoxy propane

■ di-butyl ether

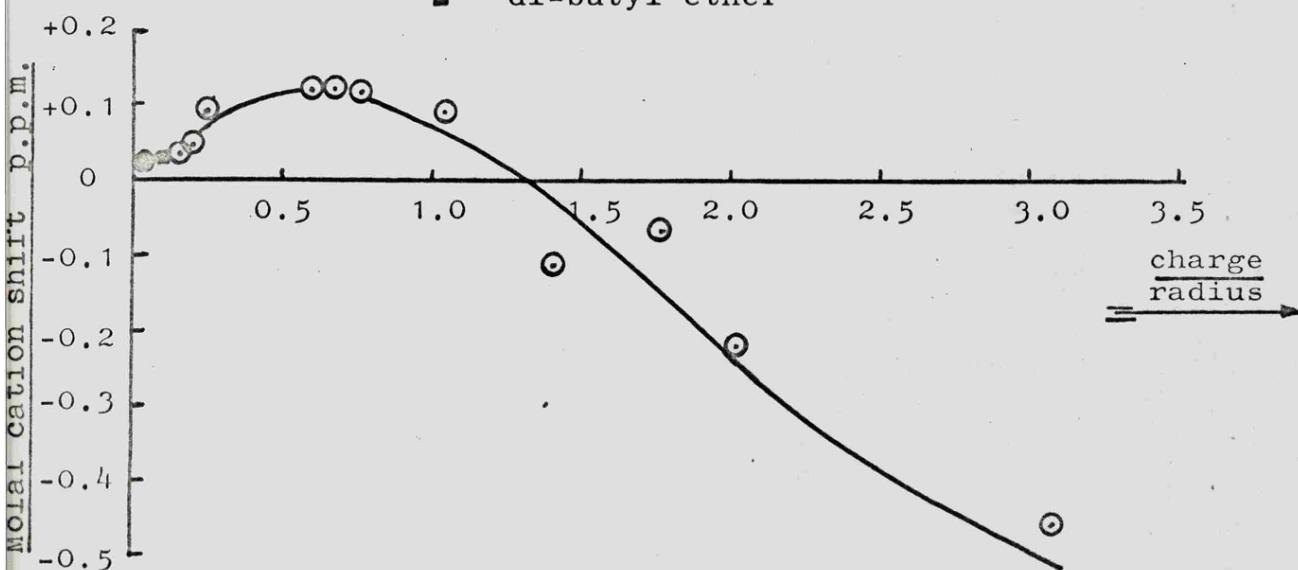


Figure 4.2b Molal methanolic cation shifts versus charge/radius ratio at 313K.

were determined by the present author, in order to give more complete curves.)

As part of the work carried out for this thesis, aqueous salt shifts for the alkali and alkaline earth chlcrides at both 273 and 298K were determined, details of these results are given in table 4.1. In order to establish whether or not the aqueous cation shifts, when plotted versus charge/radius ratio, give similar curves to those apparent in methanol (Figures 4.2a,b) the salt shifts need to be subdivided into ionic contributions. Initially this subdivision was achieved by arbitrarily assigning to the chloride ion a molal shift of 0.00 p.p.m., this value being based solely on considerations of computational convenience. The resulting plot for the 273K results is shown in Figure 4.3a. It is noted, that in contrast to the methanolic case, the curve contains a marked discontinuity between the shifts of the alkali metal and alkaline earth cations. The observed discontinuity could be inherent in the system being studied, alternatively, it could result as a mathematical consequence of the arbitrary choice of δCl^- :-

If a common anion X^- is chosen together with corresponding cations A^{n+} , $B^{(n+y)+}$ and the salt shift for AX_n is P Hz and that for $BX_{(n+y)}$ = R Hz, then assuming X^- to have an arbitrarily chosen ion shift of p Hz the following relationships can be written;

$$\delta_A^{n+} + np = P$$

$$\delta_B^{(n+y)+} + (n+y)p = R$$

Table 4.1

SALT	273K	298K	313K
LiCl	+0.070	+0.047	+0.023
NaCl	+0.120	+0.096	+0.081
KCl	+0.143	+0.111	+0.091
RbCl	+0.121	+0.092	+0.083
CsCl	+0.104	+0.080	+0.064
BaCl ₃	+0.160	+0.095	-
SrCl ₂	+0.133	+0.074	+0.062a
CaCl ₂	+0.110	+0.048	+0.006a
MgCl ₂	-0.005	-0.035	-0.092a
AlCl ₃	-0.445	-0.513	-0.590a

Molal salt shifts at the quoted temperatures.

All shifts in p.p.m.

Positive shifts are upfield.

a... Data taken from reference 35

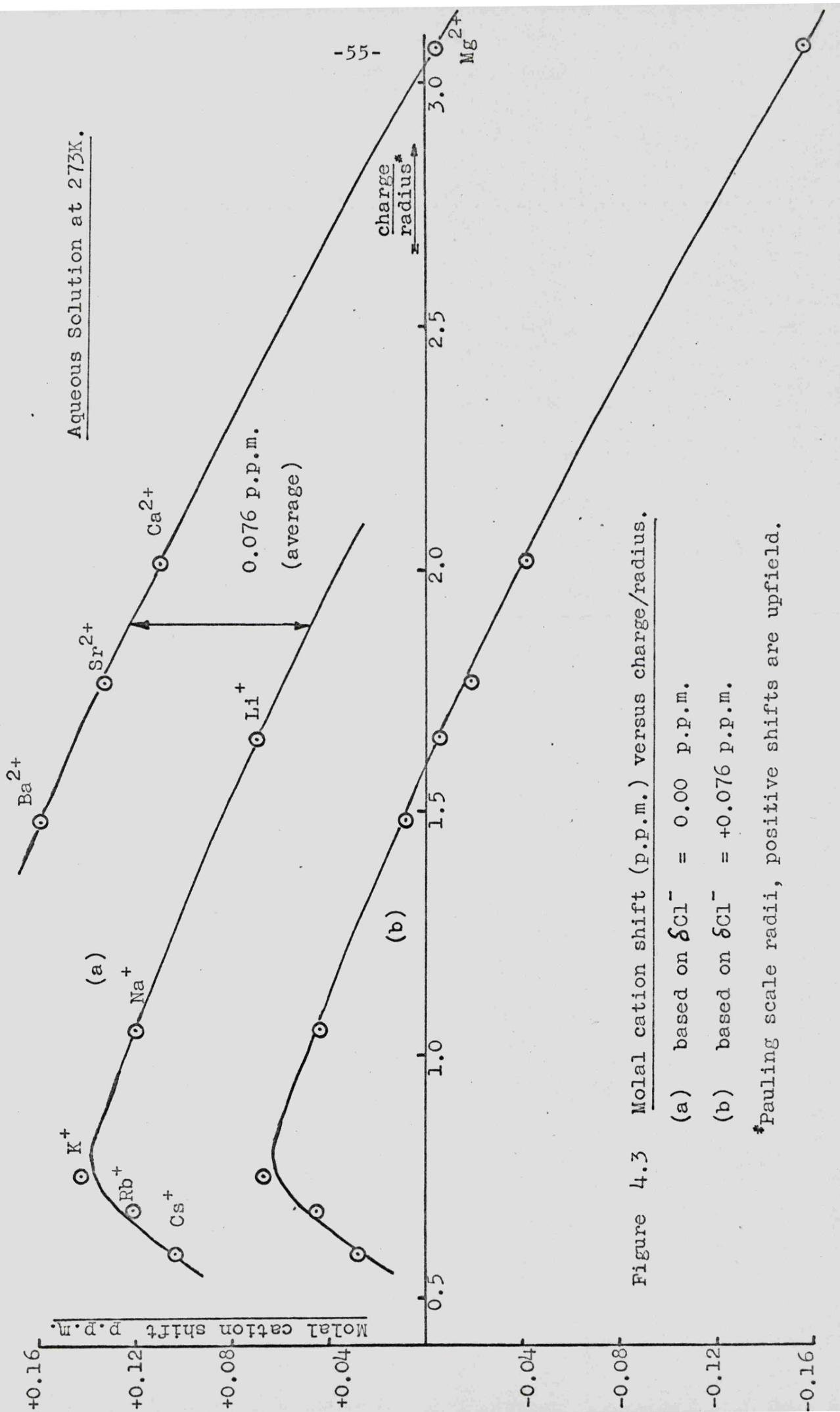


Figure 4.3 Molar cation shift (p.p.m.) versus charge/radius.

(a) based on δCl^- = 0.00 p.p.m.

(b) based on $\delta Cl^- = +0.076$ p.p.m.

*Pauling scale radii, positive shifts are upfield.

therefore $\delta_B^{(n+y)+} - \delta_A^{n+} = (R - P) - y\mu \dots \dots \text{(i)}$

However $(R - P)$ is fixed by experiment, consequently the difference $\delta_B^{(n+y)+} - \delta_A^{n+}$ is a function of μ , the arbitrarily chosen reference ion shift.

The alkali and alkaline earth cations possess closed shell configurations, it would therefore seem not unreasonable to postulate that the cation shift v charge/radius curves should be continuous functions, as found in methanol. It would seem very unlikely that water as a solvent would introduce a large discontinuity, it being in the same class of hydrogen bonding solvents as the alcohols. Elimination of the discontinuity (Figure 4.3a) to produce the continuous curve shown in Figure 4.3b results in a unique value for the reference ion shift, in this case chloride. This 'discontinuity' method has been used to arrive at unique chloride ion shifts for 273, 298 and 313K. Results for the latter temperature are based on the work of Fratiello and Miller³⁵, the reported salt shifts were for 2 molal chloride solutions, consequently the values given in table 4.1 are half the figure stated in their paper.

The curves shown in Figure 4.2a,b were obtained by using Pauling's values of ionic radius.¹⁷ Ionic radius parameters are, however, a vague concept.^{55,56} Pauling's ionic radii (for crystals) were derived in a semi-empirical way, the values being computed so as to produce a set, self consistent with observed inter-atomic distances. Other values have been proposed. Gourary and Adrian⁵⁷

using the electron density maps of Krug, Witte and Wolfel,⁵⁸ arrived at a new set of radii for certain ions possessing rare gas configurations. Blandamer and Symons²⁰ consider these radii to be more appropriate to the properties of ions in solution than those of Pauling. Table 4.2 gives the values of ionic radius and also charge/radius ratios relevant to this work based on both of these scales. In the case of the Gourary and Adrian radii, values for the alkaline earth cations have been derived from published values of inter-ionic distances.⁵⁹ A more complete discussion of the problems concerning ionic radius parameters is given in appendix 2.

Both of the sets of charge/radius ratio given in table 2 have been used in the application of the discontinuity method, the resulting curves are shown in Figures 4.3 - 4.7, the derived chloride ion shifts being listed in Table 4.3. It is noted that the derived chloride shifts depend slightly on the origin of the radius parameter, accordingly the shift values have been averaged, these average values being entered at the foot of the table. The values shown in Table 4.3 must be subject to error, the exact magnitude of which is difficult to estimate with any certainty. A figure of ± 0.02 p.p.m. would appear to be a reasonable estimate after taking into account the accuracy of the measured salt shifts (± 0.005 p.p.m.) and the degree of tolerance available when superimposing the two curves. Figure 4.7 shows the continuous curve that results from the data of

Table 4.2

Ion	Radius p.m.	Radius p.m.	charge radius	charge radius
	Pauling.	G&A.	Pauling.	G&A.
Li ⁺	60.0	94.0	1.666x10 ⁻²	1.064x10 ⁻²
Na ⁺	95.0	117.0	1.053 "	0.855 "
K ⁺	133.0	149.0	0.752 "	0.671 "
Rb ⁺	148.0	163.0	0.675 "	0.613 "
Cs ⁺	169.0	186.0	0.592 "	0.538 "
Ba ²⁺	135.0	152.0	1.481 "	1.316 "
Sr ²⁺	113.0	130.0	1.770 "	1.538 "
Ca ²⁺	99.0	116.0	2.020 "	1.724 "
Mg ²⁺	65.0	82.0	3.076 "	2.439 "
Al ³⁺	50.0	67.0	6.000 "	4.477 "
NH ₄ ⁺	143.0	-	7.00 "	-
Cl ⁻	181.0	164.0	0.552 "	0.609 "
F ⁻	136.0	116.0	0.735 "	0.862 "
Br ⁻	195.0	180.0	0.517 "	0.555 "
I ⁻	216.0	205.0	0.463 "	0.489 "

Table 4.3

	273K	298K	313K (a)
Based on Paulings radii.	+0.076	+0.040	+0.050
Based on G&A radii.	+0.098	+0.080	-
AVERAGE.	+0.087	+0.060	-
Molal chloride ion shifts (p.p.m.) derived by the discontinuity method.			
(a) Data taken from ref. 35.			
Error \pm 0.02 p.p.m.			

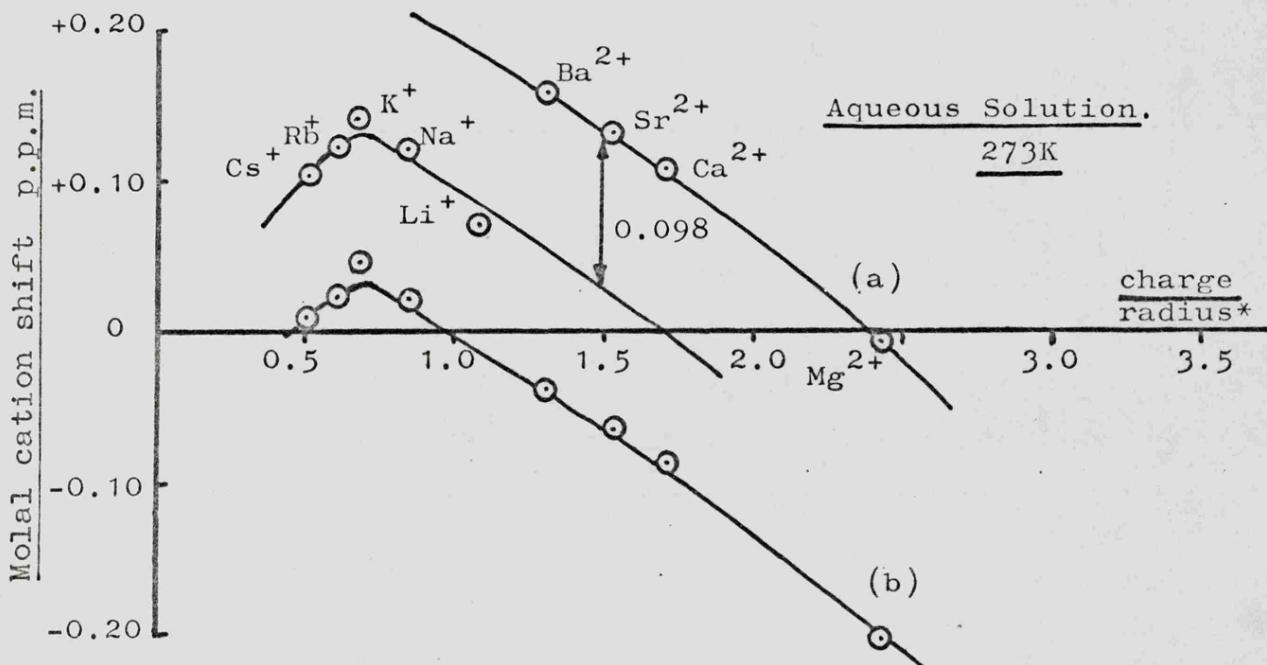


Figure 4.4 Molal cation shift versus charge/radius.

* radii based on Gourary and Adrian scale.

(a) based on $\delta Cl^- = 0.00$ p.p.m.

(b) based on $\delta Cl^- = +0.098$ p.p.m.

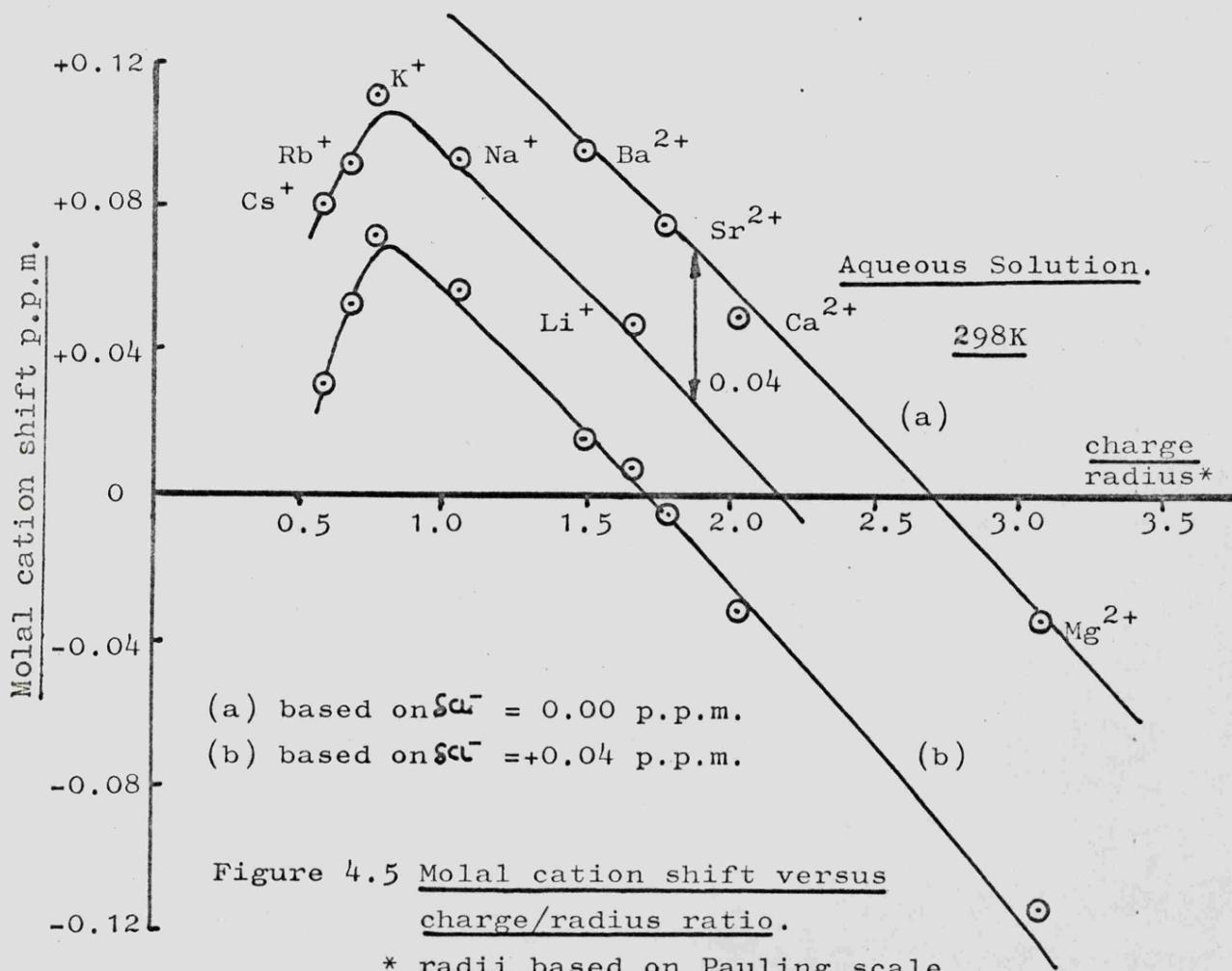


Figure 4.5 Molal cation shift versus
charge/radius ratio.

* radii based on Pauling scale

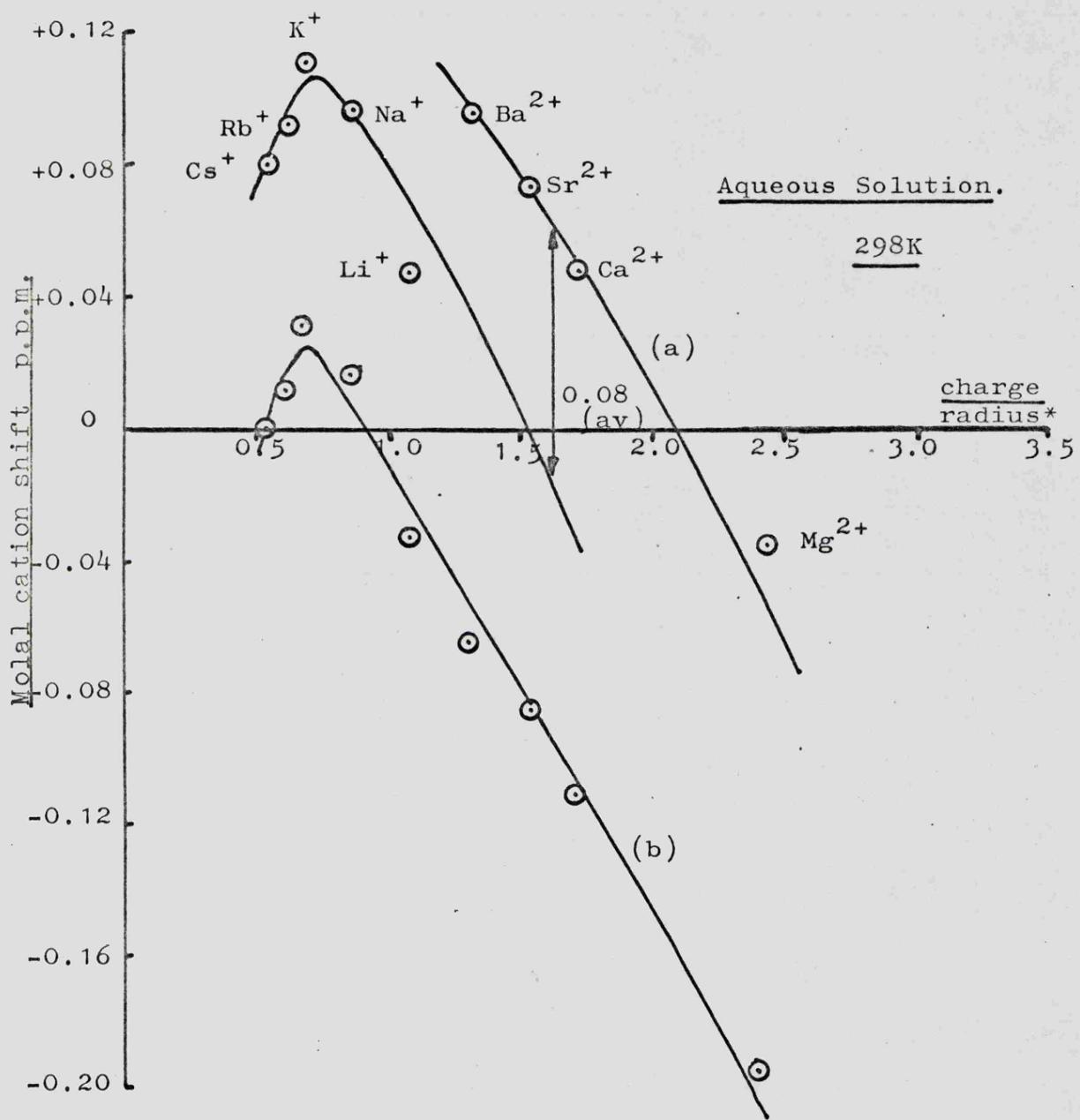


Figure 4.6 Molal cation shift versus charge/radius.

* radii taken from Gourary and Adrian scale

(a) based on $\delta\text{Cl}^- = 0.00$ p.p.m.

(b) based on $\delta\text{Cl}^- = +0.080$ p.p.m.

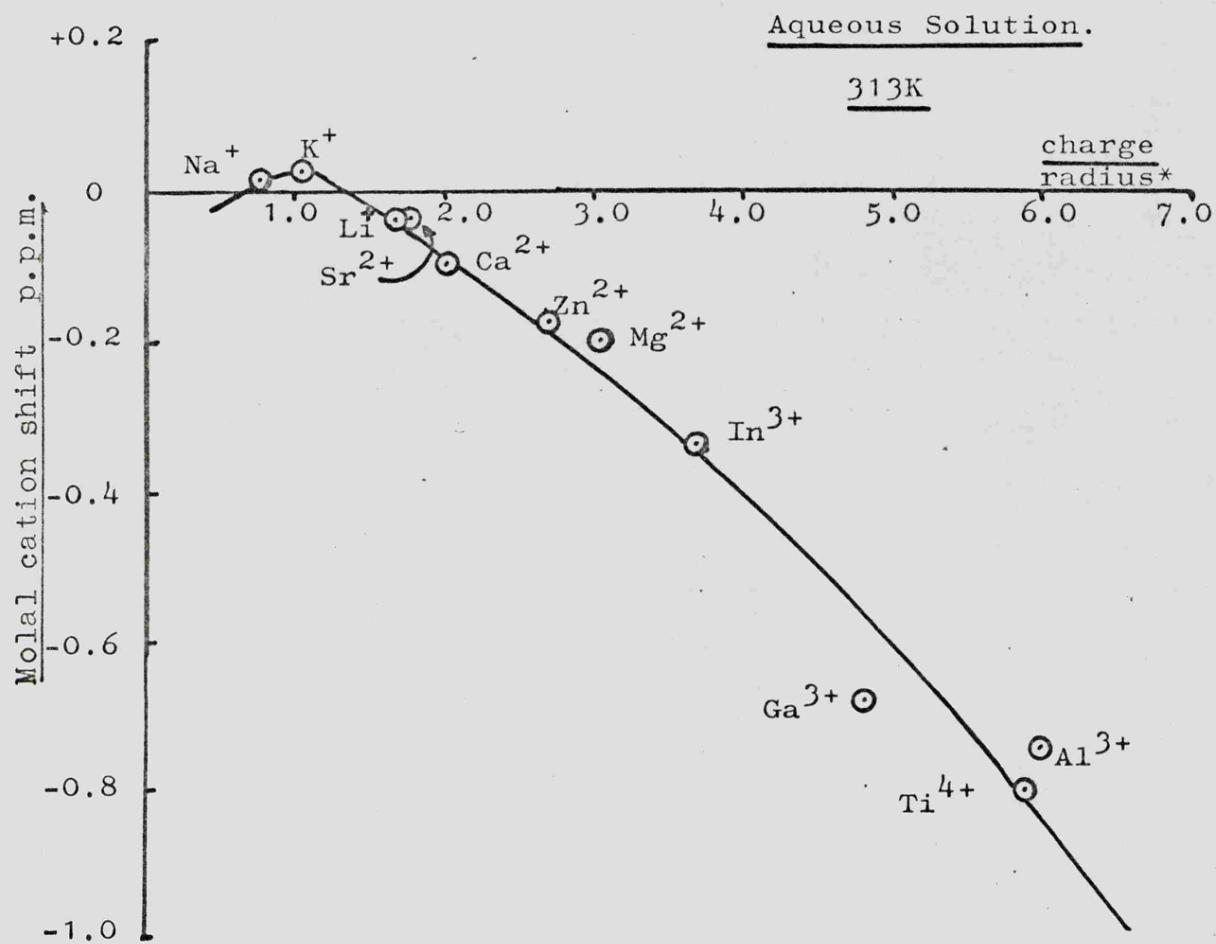


Figure 4.7 Molal cation shift versus charge/radius.

* radii based on the Pauling scale.
shifts based on $\delta\text{Cl}^- = +0.050$ p.p.m.
data taken from ref. 35.

Fratiello and Miller³⁵ when a chloride ion shift value of +0.050 p.p.m. is used as a reference with which to subdivide the published results. It is encouraging to note that the cation shifts for the 3+ and 4+ ions fit so well. The chloride ion shift determined by fitting the curves for the alkali metal and alkaline earth cations has produced a value able to accomodate cations of a higher charge. It would be expected that marked discontinuities (cf., equation 61 p56), for the high charge cations, should result if the chloride value was subject to serious error.

In order to check the validity of the previous values, a second independent method of arriving at the molal chloride ion shift would seem desirable. Given below are details of such a method.

4.3 The low temperature cation solvation shell method.

The method of Butler and Symons⁵⁴ for directly determining methanolic cation shifts at low temperatures cannot be directly applied to aqueous solutions. In aqueous solution the necessary resolved solvation shells can only be observed if premature freezing is prevented by either the use of high salt concentrations or the addition of co-solvents. Various workers have obtained resolved cation solvation shells for aqueous salt solutions using these procedures.⁶⁰ Figure 4.8 shows typical spectra obtained by these low temperature methods.

It should be possible to calculate cation shifts

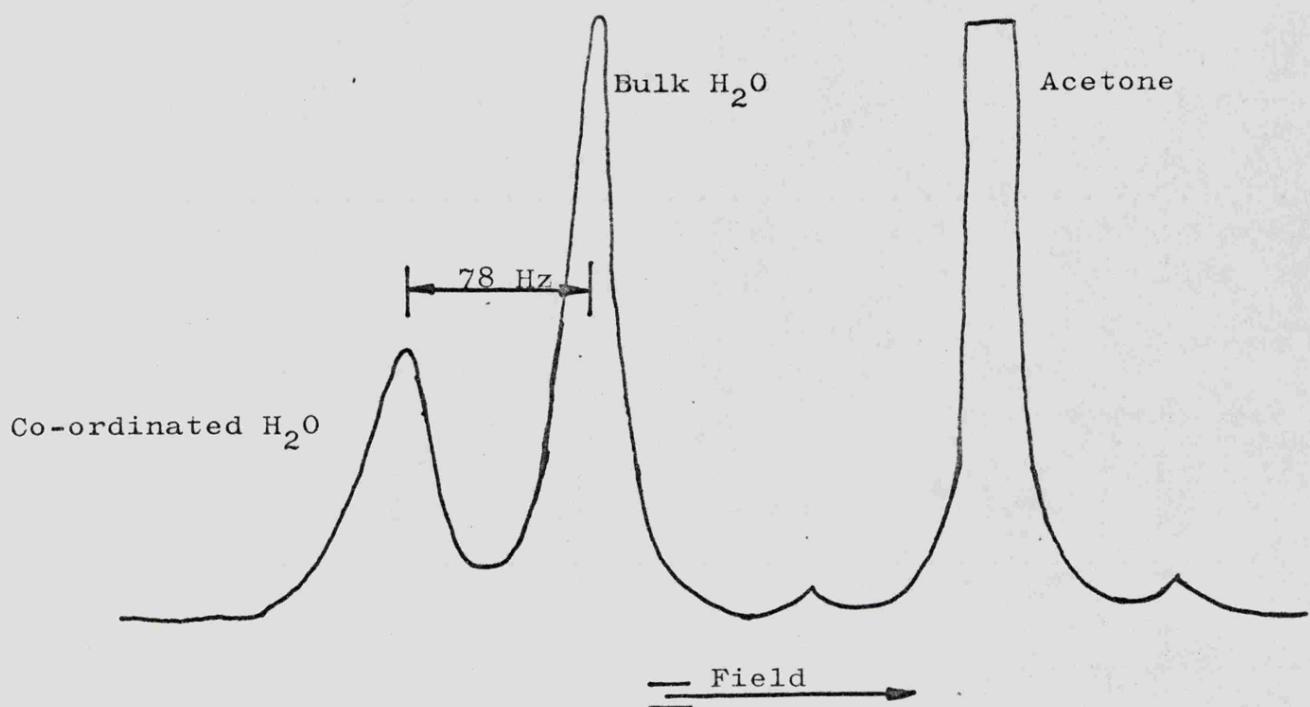


Figure 4.8a The n.m.r. spectrum of 0.50 M $\text{Mg}(\text{ClO}_4)_2$
solution in a 1:2 water to acetone
mixture at 192K.

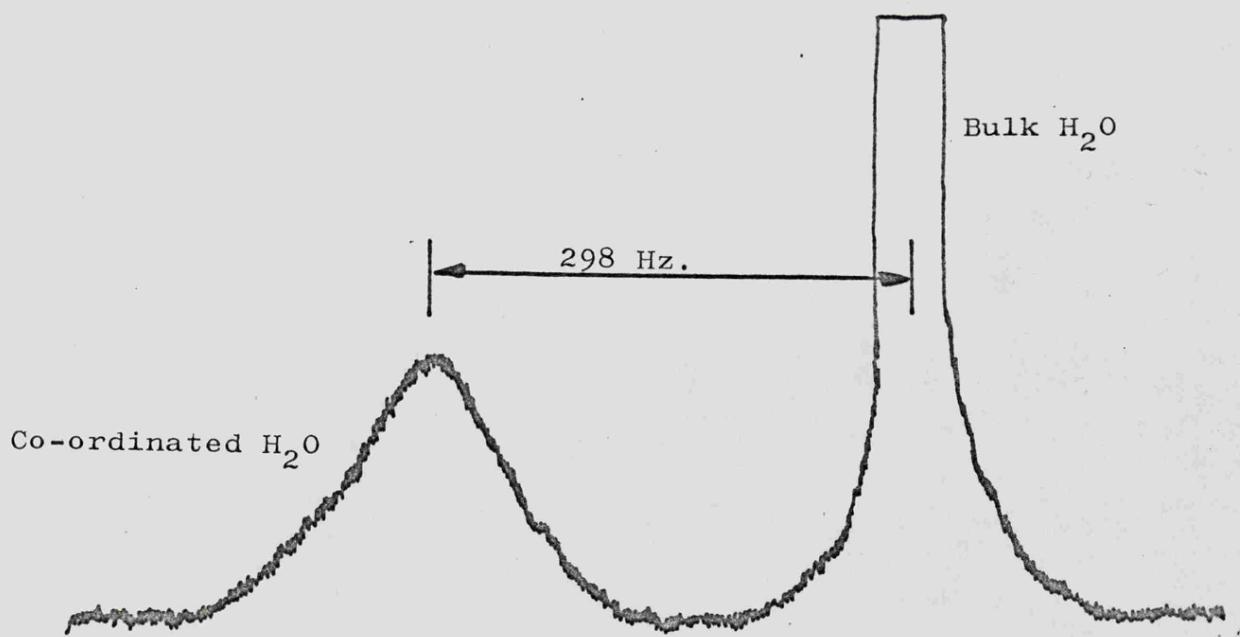


Figure 4.8b The n.m.r. spectrum of 1.29 M $\text{Ga}(\text{ClO}_4)_3$
solution at 211 K.

Data taken from; Fratiello et.al. J.Chem.Phys.,
1968, 48, 3705.

Spectrometer operating frequency: 60 MHz.

from the available literature data⁶⁰ on such solutions, providing certain assumptions concerning the shift of the solvation shell and bulk water signals with increasing salt concentration are made. In this context, work carried out concerning ion association in methanolic solution,⁶¹ and fully reported in Chapter 7 of this thesis, is of direct relevance. It was possible to show, that for methanolic solutions, the cation solvation shell and residual hydroxyl resonance signals shift equivalently with varying salt concentration. The phenomenon is shown diagrammatically in Figure 4.9. If the assumption is now made that such behaviour is also apparent in aqueous solutions, i.e. the separation 'x' in Figure 4.9 remains constant as the salt concentration varies, then molal cation shifts (at the quoted temperatures) can be calculated. A typical example of such a calculation is given below.

For an ideal determination of a molal cation shift, i.e. comparable with that of Butler and Symons⁵⁴, then the position of the pure water resonance in respect to the residual signal (which must include anion effects), cf. 'y' in Figure 4.9, should be estimated. The pure water resonance could then be weighted with that of the cation solvation shell to give a primary cation shift. The magnitude of 'y' compared to 'x' will, however, be very small. Consequently cation shifts derived using the residual signal will not differ greatly from those obtained by making an estimate of 'y' and so using the

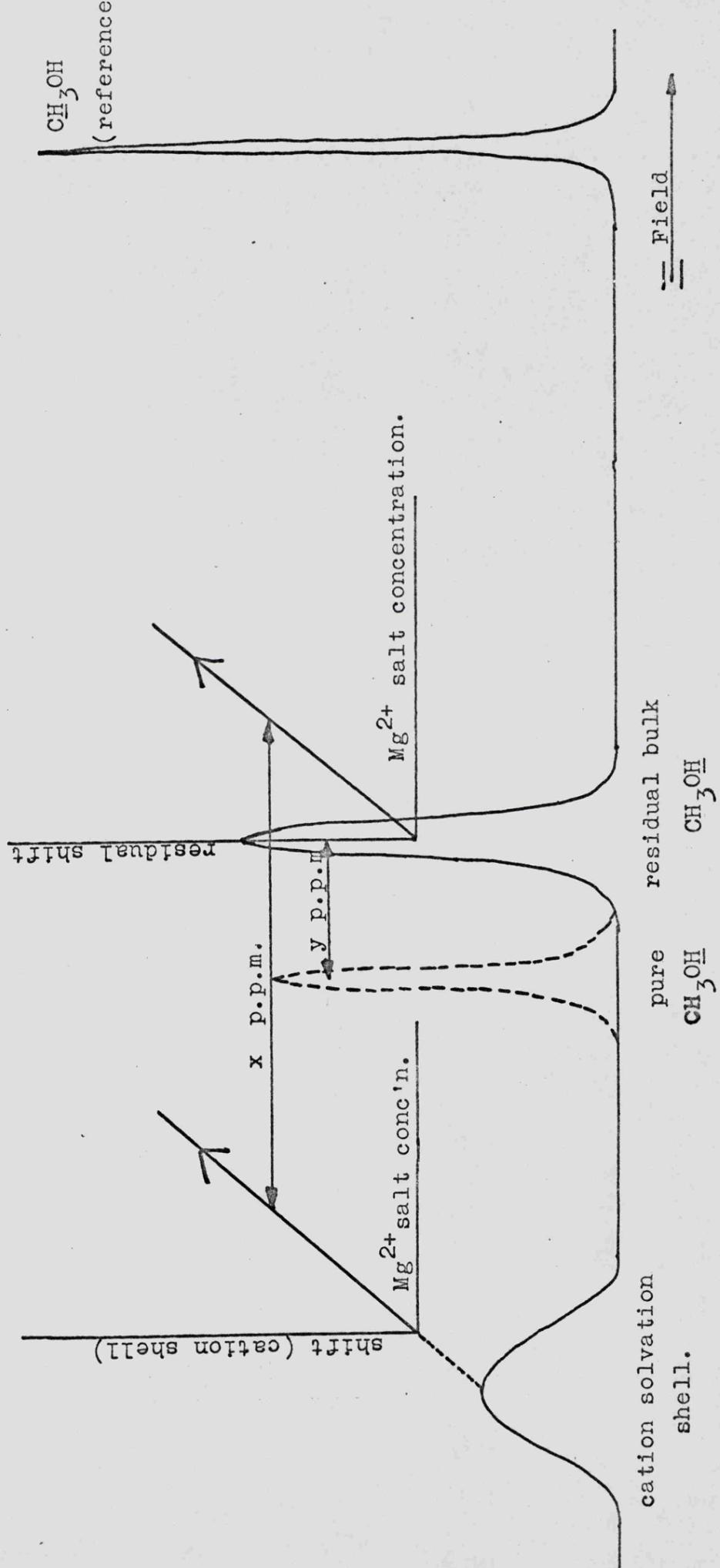
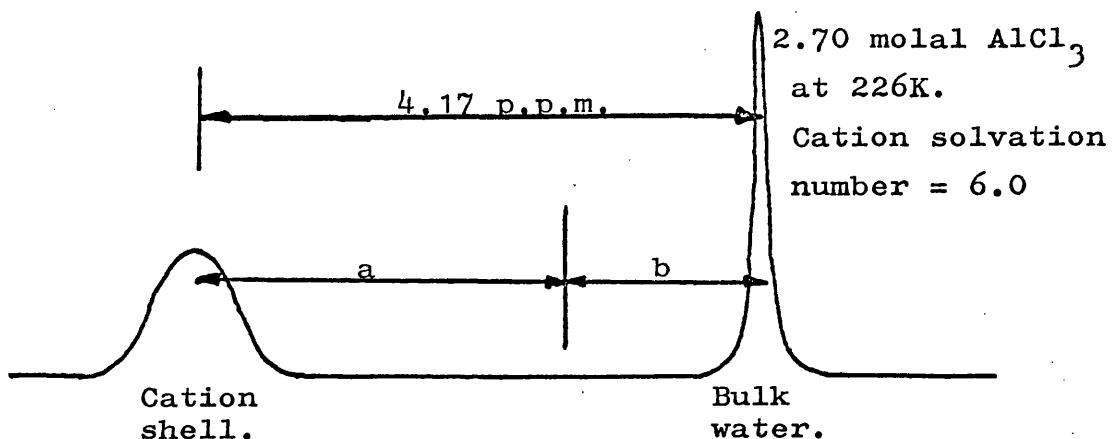


Figure 4.9 A representation of the low temperature n.m.r. spectrum of a methanolic solution of a magnesium salt.

pure water resonance position. Indeed, it is arguable that 'x' is the true infinite dilution separation of the cation shell and pure water resonances in the absence of anion effects. Using data taken from ref. 60:



b = primary cation shift.

(i) Neglecting the 'y' correction;

$$\text{At } 226\text{K} \quad \frac{\text{Area of shell}}{\text{Area of bulk}} = \frac{b}{a} = \frac{N}{55.6 - N}$$

where N is the solvation number.

$$\therefore \frac{b}{a} = \frac{6}{55.6 - 6}$$

$$\text{i.e. } a = 8.28 b$$

$$\text{However, } a + b = 4.17 \text{ p.p.m.}$$

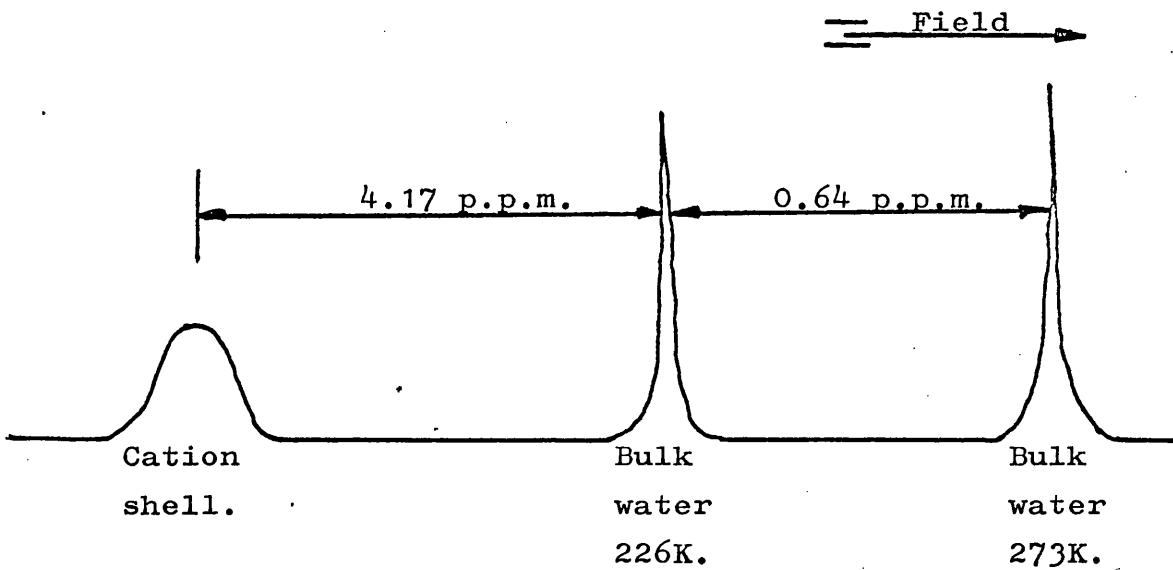
$$\therefore \underline{b = 0.45 \text{ p.p.m.}}$$

The molal cation shift, b , is the value at 226K.

The work of Butler and Symons shows that the position of methanolic cation solvation shells is temperature independent. It is assumed that this is also the

case for aqueous solutions. It does not seem unreasonable that the temperature dependence of the proton resonances of water molecules directly bonded to highly charged cations will, even if present, be small and can therefore be neglected without introducing serious error.

By extrapolating the data of Hindman,³⁹ concerning the temperature dependence of the pure water proton resonance, to lower temperatures (Figure 4.10) then it is possible to determine cation shifts at other temperatures. The upfield shift of the water protons between 226K and 273K is found in this way to be 0.64 p.p.m.

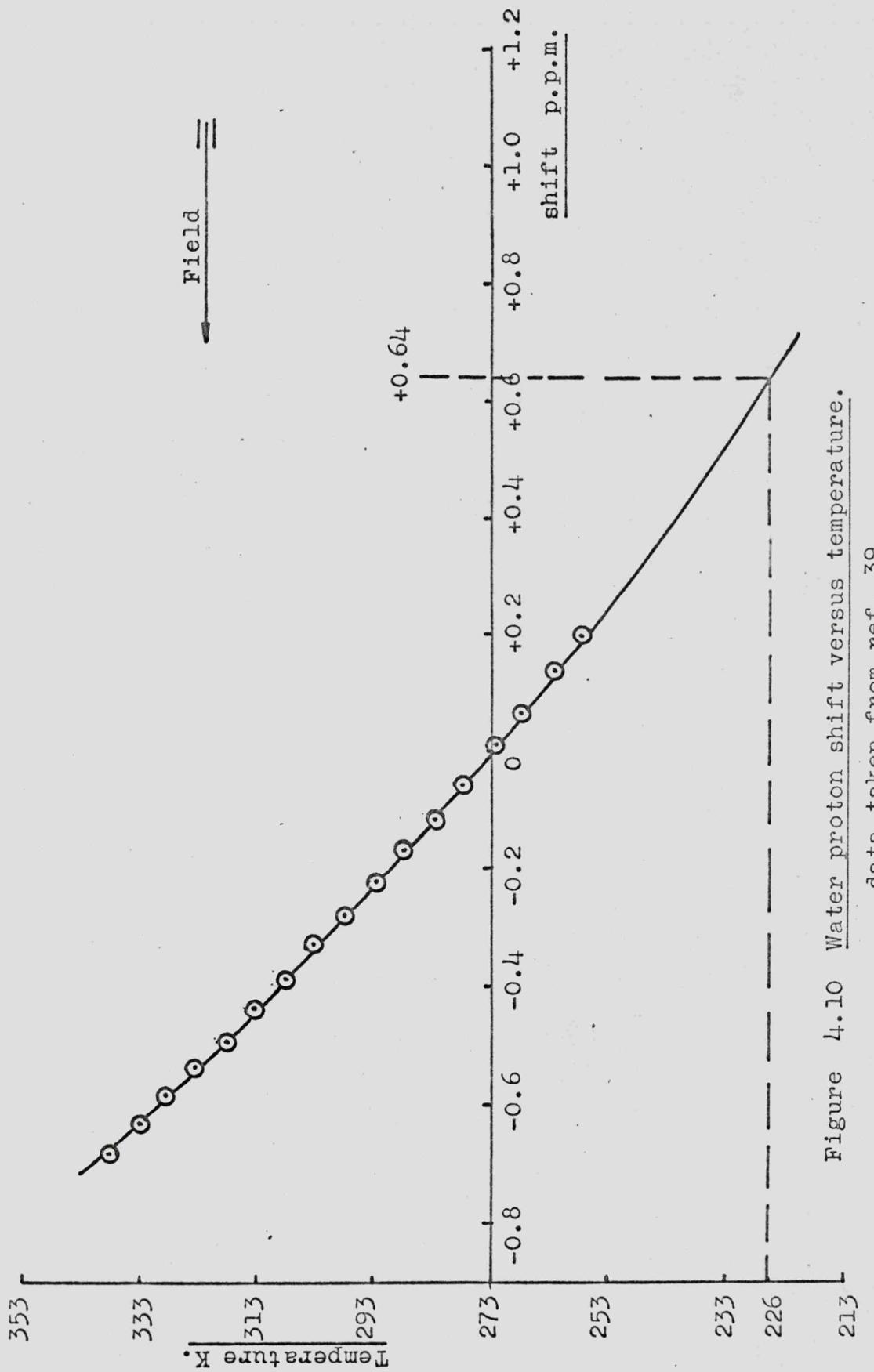


$$\begin{aligned} \text{i.e. } a + b &= 4.17 + 0.64 \\ \text{also } a &= 8.28 b \end{aligned} \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{cf. eqn's page 65.}$$

In this way the molal cation shift of Al^{3+} at 273K is found to be -0.52 p.p.m. (downfield).

(ii) Using the 'y' correction;

The molal chloride ion shift as determined by the discontinuity method can be used to estimate 'y'. The



data taken from ref. 39

value obtained can then be used to modify calculation (i). The molal cation shift for Al^{3+} obtained by this modified method is -0.49 p.p.m. at 273K.

It is apparent that the difference in the Al^{3+} cation shifts, as calculated by both methods (i) and (ii), is small. Extensive calculations based on literature data (ref. 60) have been carried out by the methods given above. Typical average molal cation shifts so obtained are;

$$\delta_{\text{Al}^{3+}} \text{ at } 298\text{K} = -0.54 \text{ p.p.m.}$$

$$\delta_{\text{Mg}^{2+}} \text{ " " } = -0.20 \text{ "}$$

$$\delta_{\text{Al}^{3+}} \text{ " } 273\text{K} = -0.49 \text{ "}$$

$$\delta_{\text{Mg}^{2+}} \text{ " " } = -0.16 \text{ "}$$

These values can now be combined with the measured values for the salt shifts of AlCl_3 and MgCl_2 given in table 4.1 and hence averaged molal chloride ion shifts at both 273 and 298K determined. These values are shown in Table 4.4 together with the δ_{Cl^-} values resulting from the discontinuity method.

Table 4.4

Method	273K	298K	313K
Discontinuity.	+0.09	+0.06	+0.05(a)
Low temperature cation shell.	+0.05	+0.05	+0.04(a)
AVERAGE.	+0.07(0)	+0.05(5)	+0.04(5)
Molal chloride ion shifts at the stated temperature. (p.p.m.) (a) data taken from ref. 35 and 60. Estimated error 0.02 p.p.m.			

4.4 Summary.

The agreement between the chloride ion shift values given in table 4.4, considering the assumptions that have had to be made, is surprisingly good. The overall average results must be subject to error, a value of ± 0.02 p.p.m. would appear to be a reasonable estimate.

Figure 4.11 shows a plot of the average molal chloride ion shift (Table 4.4) versus temperature. The resulting graph is a reasonably good straight line, having a slope of -6×10^{-4} p.p.m.K $^{-1}$. This value compares favorably with that found for the chloride ion in methanolic solution, -7×10^{-4} p.p.m.K $^{-1}$. It would seem appropriate that molal anion shifts should have similar temperature dependences in the two related solvents. A more complete discussion of temperature effects on ion shifts can be found in Chapter 5.

The average molal chloride ion shifts listed in table 4.4 are taken to be close approximations to the true absolute ones at the stated temperatures. Accordingly these values will be used in later chapters of this thesis as a basis for subdividing measured salt shifts into ionic contributions.

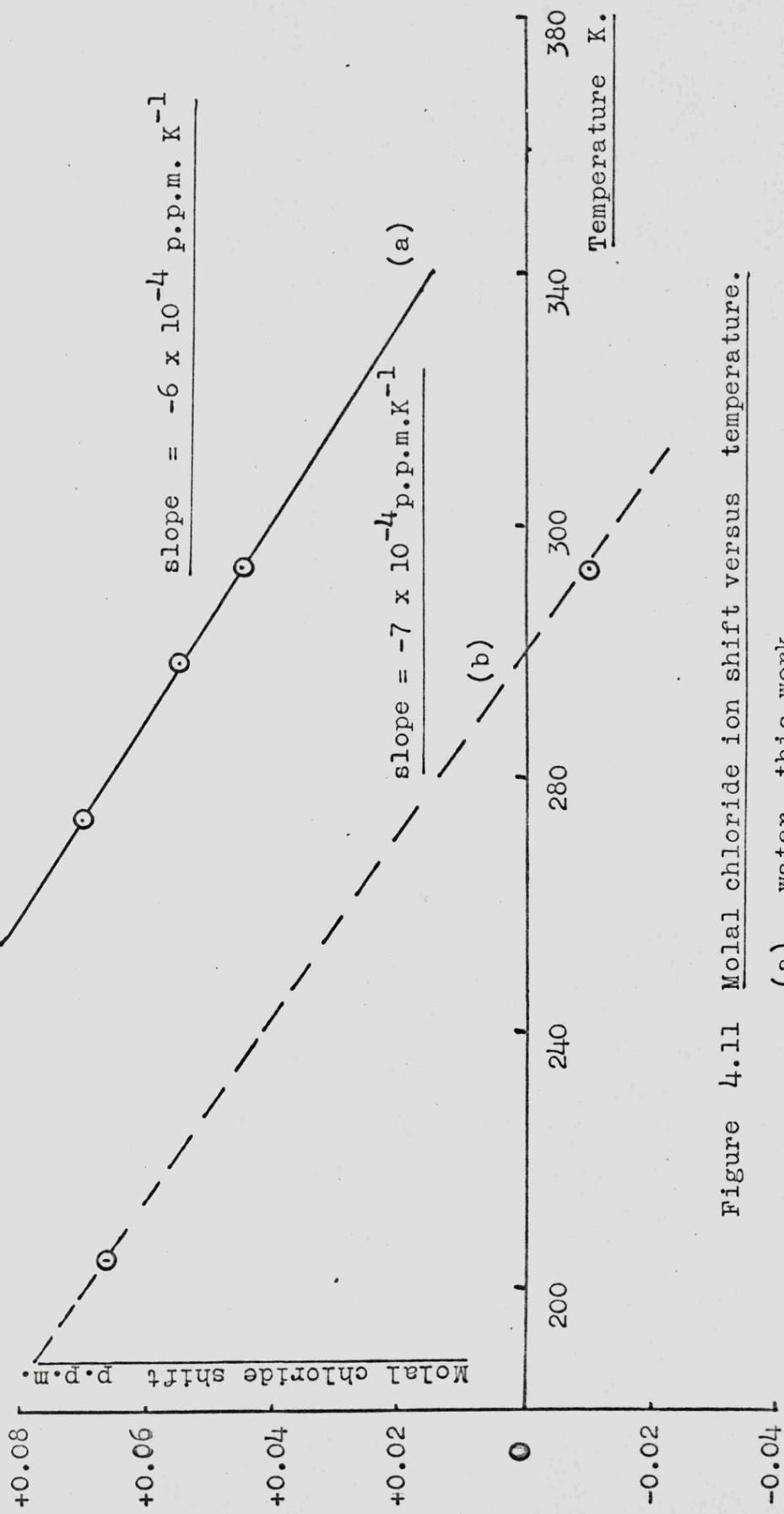


Figure 4.11 Molal chloride ion shift versus temperature.

(a) water, this work
(b) methanol, data taken from ref. 54

CHAPTER FIVE

THE SOLVATION OF SIMPLE IONS IN AQUEOUS SOLUTION

5.1 Introduction.

This chapter concerns the study of ion-solvent interactions by the n.m.r. technique. The discussion will be limited to closed shell cations and simple anions; quaternary ammonium cations and anions containing alkyl chains will be discussed in chapter six.

When studying ion-solvent interactions it is of vital importance that, for any system investigated, ion-ion interactions are precluded. It follows as a direct consequence of this constraint that there is a need to make a distinction between dilute and concentrated salt solutions. The latter are those solutions containing, on average, ions separated by only a few solvent molecules. Indeed, in the limit contact or solvent shared ion pairs may be present. For any given system, the precise concentration at which ion-ion interactions become significant is debatable, the character of the solvent and the properties of the ions involved being important factors.^{61,62}

In the n.m.r. salt shift technique, the experimental procedure adopted to overcome the intervention of such unwanted ion-ion interactions is to measure the molal salt shift at infinite dilution. This parameter being the limiting slope of the salt shift versus concentration plot as the salt concentration tends to zero. The onset of ion pairing effects, at high salt concentrations, is normally assumed to be the cause of the curvature observed in many salt shift plots.²⁸ Figure 5.1 shows an example

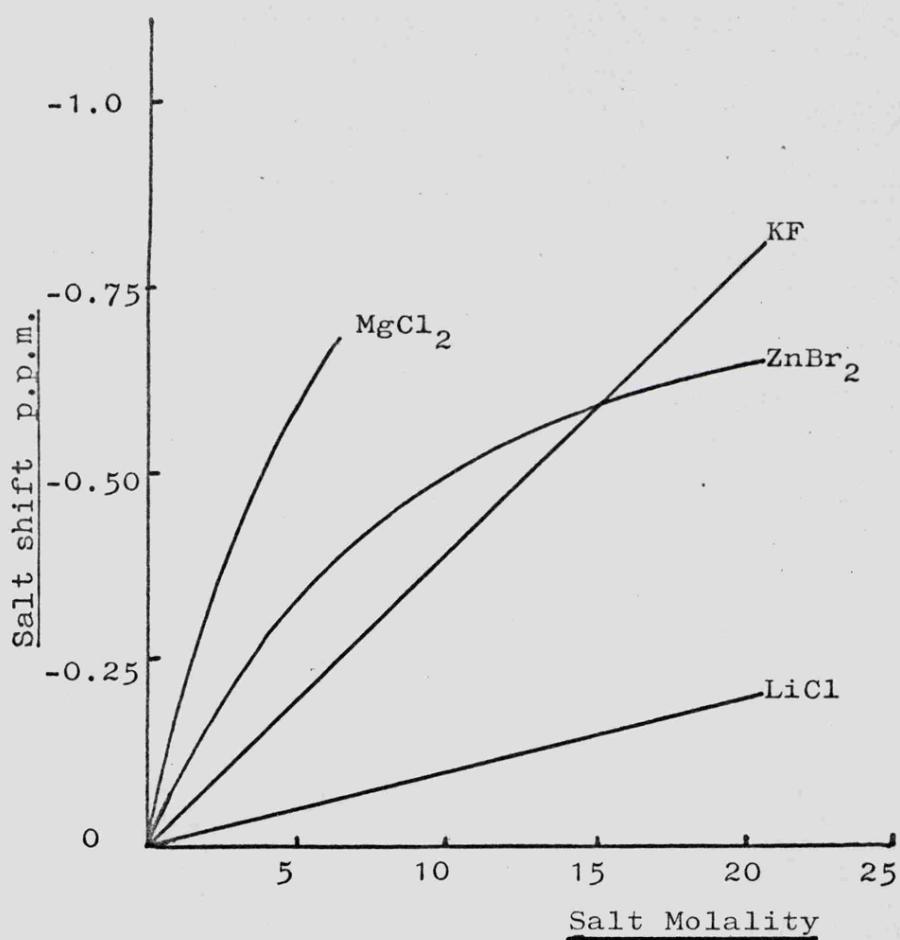


Figure 5.1 Salt shift plots showing ion pairing effects.

data taken from ref. 28
-ve. = downfield shift.

of this type of behaviour, the authors explain the downward curvature found for zinc bromide in terms of ion pair formation.

In the present work salt concentrations used have not normally exceeded 1.5 molal, this upper limit being somewhat arbitrarily chosen as a result of the desire to study ion-solvent interactions only. In most cases studied the observed salt shift plots were linear, having intercepts passing through the origin, hence facilitating measurement of the infinite dilution parameter.

Tables 5.1 and 5.2 give full details of molal salt shifts relevant to this chapter. The molal shifts for the alkali metal chlorides are reported at various temperatures in the range 273 to 353K. Salt shifts have been divided into ionic contributions by making use of the chloride ion shift values derived in Chapter 4. The resulting ion shifts are given in Tables 5.3 and 5.4, all the values quoted having been calculated so as to give maximum consistency between the salts studied. For temperatures in excess of 313K, the ion shifts are based on primary chloride shifts obtained by extrapolation of the temperature dependence plot, Figure 4.11.

5.2 Models for ionic solutions.

A model of an ionic solution is required before any meaningful discussion of the results given under section 5.1 can be undertaken. In this way, possible interactions responsible for determining the magnitude

Table 5.1

Salt	273K	298K	313K	333K	353K
LiCl	+0.070	+0.047	+0.023	+0.012	-0.015
NaCl	+0.120	+0.096	+0.081	+0.063	+0.031
KCl	+0.143	+0.111	+0.091	+0.077	+0.050
RbCl	+0.121	+0.092	+0.083	+0.068	+0.050
CsCl	+0.104	+0.080	+0.064	+0.050	+0.038
BaCl ₂	+0.160	+0.095	-	-	-
SrCl ₂	+0.133	+0.074	-	-	-
CaCl ₂	+0.110	+0.048	-	-	-
MgCl ₂	-0.005	-0.035	-	-	-
AlCl ₃	-0.445	-0.513	-	-	-
NH ₄ Cl	+0.081	+0.051	-	-	-

Molal salt shifts at the quoted temperatures.

All shifts are in p.p.m.

Positive shifts are upfield.

Table 5.2

Salt	273K	298K	Salt	273K	298K
LiBr	+0.077	+0.065	Na ₂ CrO ₄	+0.120	+0.085
KF	+0.015	-0.008	Na ₂ SO ₃	+0.033	-0.021
NaF	0.00	-0.021	Na ₂ SO ₄	+0.113	+0.060
NaBr	+0.163	+0.128	Na ₂ HPO ₃	-0.020	-0.061
NaI	+0.216	+0.175	Na ₃ PO ₄	-0.075	-0.255
NaCNO	+0.130	+0.091	MgSO ₄	-0.125	-0.172
NaClO ₄	+0.165	+0.140	HCO ₂ Na	+0.040	+0.017
NaNO ₃	+0.097	+0.081	CH ₃ CO ₂ Na	+0.011	-0.013
NaIO ₃	+0.116	+0.085	CH ₂ ClCO ₂ Na	+0.046	+0.033
NaBrO ₃	+0.138	+0.102	CF ₃ CO ₂ Na	+0.077	+0.035
NaNO ₂	+0.060	+0.043	CH ₃ SO ₃ Na	+0.110	+0.090
NaCN	+0.120	+0.113			
NaSCN	+0.193	+0.143			
NaBF ₄	+0.138	+0.123			

Molal salt shifts at the quoted temperatures.

All shifts are in p.p.m.

Positive shifts are upfield.

Table 5.3

Ion	273K	298K	313K	333K	353K
Cl ⁻	+0.070	+0.055	+0.045	+0.032	+0.019
Li ⁺	0.00	-0.008	-0.022	-0.020	-0.034
Na ⁺	+0.050	+0.041	+0.036	+0.031	+0.012
K ⁺	+0.073	+0.050	+0.046	+0.045	+0.031
Rb ⁺	+0.051	+0.037	+0.038	+0.036	+0.031
Cs ⁺	+0.034	+0.025	+0.019	+0.018	+0.019
Ba ²⁺	+0.020	-0.015	-	-	-
Sr ²⁺	-0.007	-0.036	-	-	-
Ca ²⁺	-0.030	-0.062	-	-	-
Mg ²⁺	-0.145	-0.153	-	-	-
Al ³⁺	-0.655	-0.678	-	-	-
NH ₄ ⁺	+0.011	-0.004	-	-	-

Molal ion shifts at the quoted temperature.

All shifts in p.p.m.

Positive shifts are upfield.

Table 5.4

Ion	273K	298K	313K	Ion	273K	298K
Cl ⁻	+0.070	+0.055	+0.045	BF ₄ ⁻	+0.080	+0.082
F ⁻	-0.054	-0.063	-0.086	CrO ₄ ²⁻	+0.020	+0.003
Br ⁻	+0.113	+0.087	+0.084	SO ₃ ²⁻	-0.067	-0.103
I ⁻	+0.166	+0.134	+0.129	SO ₄ ²⁻	+0.013	-0.022
CNO ⁻	+0.080	+0.050	-	HPO ₃ ²⁻	-0.126	-0.143
ClO ₄ ⁻	+0.115	+0.099	-	PO ₄ ³⁻	-0.255	-0.378
NO ₃ ⁻	+0.047	+0.040	-	HCO ₂ ⁻	-0.010	-0.024
IO ₃ ⁻	+0.066	+0.044	-	CH ₃ CO ₂ ⁻	-0.039	-0.054
BrO ₃ ⁻	+0.088	+0.061	-	CH ₂ ClCO ₂ ⁻	-0.004	-0.008
NO ₂ ⁻	+0.010	+0.002	-	CF ₃ CO ₂ ⁻	+0.027	-0.006
CN ⁻	+0.070	+0.072	-	CH ₃ SO ₃ ⁻	+0.060	+0.049
SCN ⁻	+0.143	+0.102	-			

Molal ion shifts at the quoted temperature.

All shifts in p.p.m.

Positive shifts are upfield.

and the direction of n.m.r. solvent shifts can be located.

One of the most widely used models for an aqueous solution containing simple ions, is that due to Frank and Wen.^{14,30,37} The intense electric field, ca. 10^8 Vm^{-1} , at a distance of 0.6 nm. from the ion centre, aligns nearest neighbour water molecules such that the dipolar axis passes close to or through the centre of the ion. The layers of water molecules so formed are said to be 'electrostricted' and are considered to be effectively immobilised by the direct ion-dipole interaction.⁶³ In order to explain such phenomena as the observed 'excess entropy' for aqueous solutions of potassium chloride,³⁷ the layers of water molecules beyond the electrostricted ones are considered to possess a degree of disorder. Beyond this second region there will be 'structurally normal' bulk water, undisturbed by the presence of the ion. The Frank and Wen model is represented diagrammatically in Figure 5.2. It may be significant that n.m.r. studies⁶⁰ of concentrated aqueous electrolytes at low temperatures (ca. 226K) have detected separate resonances from water molecules directly bonded to cations. These studies have yielded hydration numbers in the range 4-6, indicative of primary hydration shells. Although it is unwise to conclude that at lower concentrations and higher temperatures (where rapid exchange of water molecules between differing environments prevents the resolution of separate solvation shell signals) these shells are still present,³¹ but having considerably

- (A) Region of electrostricted water molecules.
- (B) Region of structure breaking.
- (C) Structurally 'normal' bulk water.

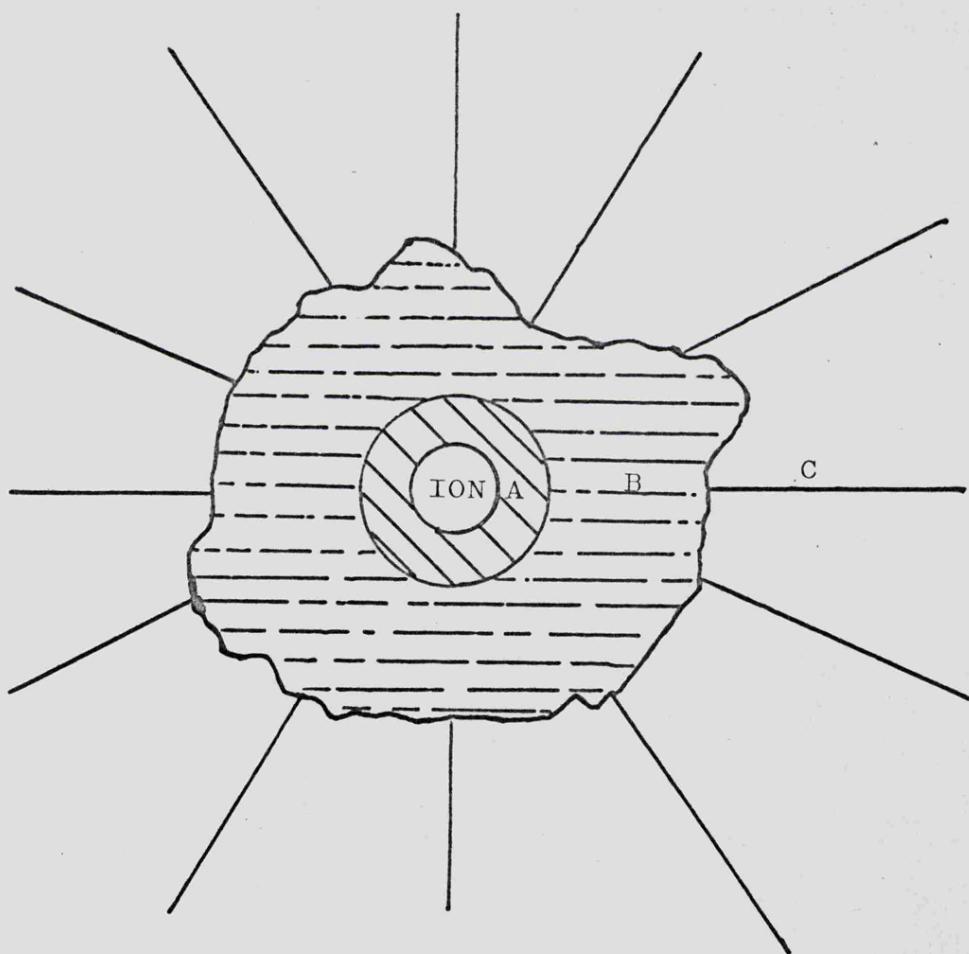


Figure 5.2 The Frank and Wen model for the solvation of a small ion.

reduced lifetimes, the low temperature evidence does lend some support. A further point to note, is that solvation shell resonances have only been observed for di- and tri-valent cations and never for mono-valent ones or, indeed, anions. The Frank and Wen model is looked upon as an essentially instantaneous view of the ion-water interaction.

Bergqvist and Forslind⁴⁸ in their paper concerning n.m.r. studies of the properties of aqueous alkali halides do not subscribe to the above view, following the ideas of Gurney⁶⁴ and Samoilov¹² they prefer to regard the dissolved ion as integrated into the water lattice. The ion is assumed to be located by ordinary chemical bonds, of variable duration and strength.

Engel and Hertz,⁶⁵ when interpreting the results of a n.m.r. relaxation time study, concur with this view. Any structure breaking effects are taken as extending up to the surface of the ion involved.

5.3 Interpretation of n.m.r. salt shifts in aqueous solution.

Whichever of the two models outlined in section 5.2 is adopted, the rationalization of n.m.r. ion shifts usually involves the use of both the 'structure breaking/making' and 'polarization' effects of an ion. These two interactions provide mechanisms by which both up and downfield water proton shifts can be produced. (see also Chapter 1) In this way any observed proton shift

can be readily accommodated by a suitable combination of these competing effects. Hindman⁴⁶ has analysed his data, concerning n.m.r. salt shifts in aqueous solutions of 1-1 electrolytes, by treating the ion-water complex as a molecular species. It would be useful at this point to briefly summarise Hindman's quantitative approach.

The observed ion shift δ , is made up as follows;

$$\delta = \delta_{bb} + \delta_{st} + \delta_p + \delta_{non}$$

where,

δ_{bb} = A high field shift due to the breaking of water-water hydrogen bonds during the re-orientation of water molecules by the ion.

δ_{st} = A high field shift due to the disorganized layer between the hydration shell and the normal water (the B region of the Frank and Wen model).

δ_p = A low field shift due to polarization of the water protons in the neighbourhood of the ion.

δ_{non} = A low field shift due to a non-electrostatic interaction between the ion and the oxygen of a co-ordinated water molecule.

Hindman suggests methods for quantitatively evaluating the shifts attributable to these individual factors.

In interpreting the ion shifts presented in this thesis a qualitative approach will be followed. The approach differs from many others^{28,46,66} in that the observed shifts can be adequately explained without the

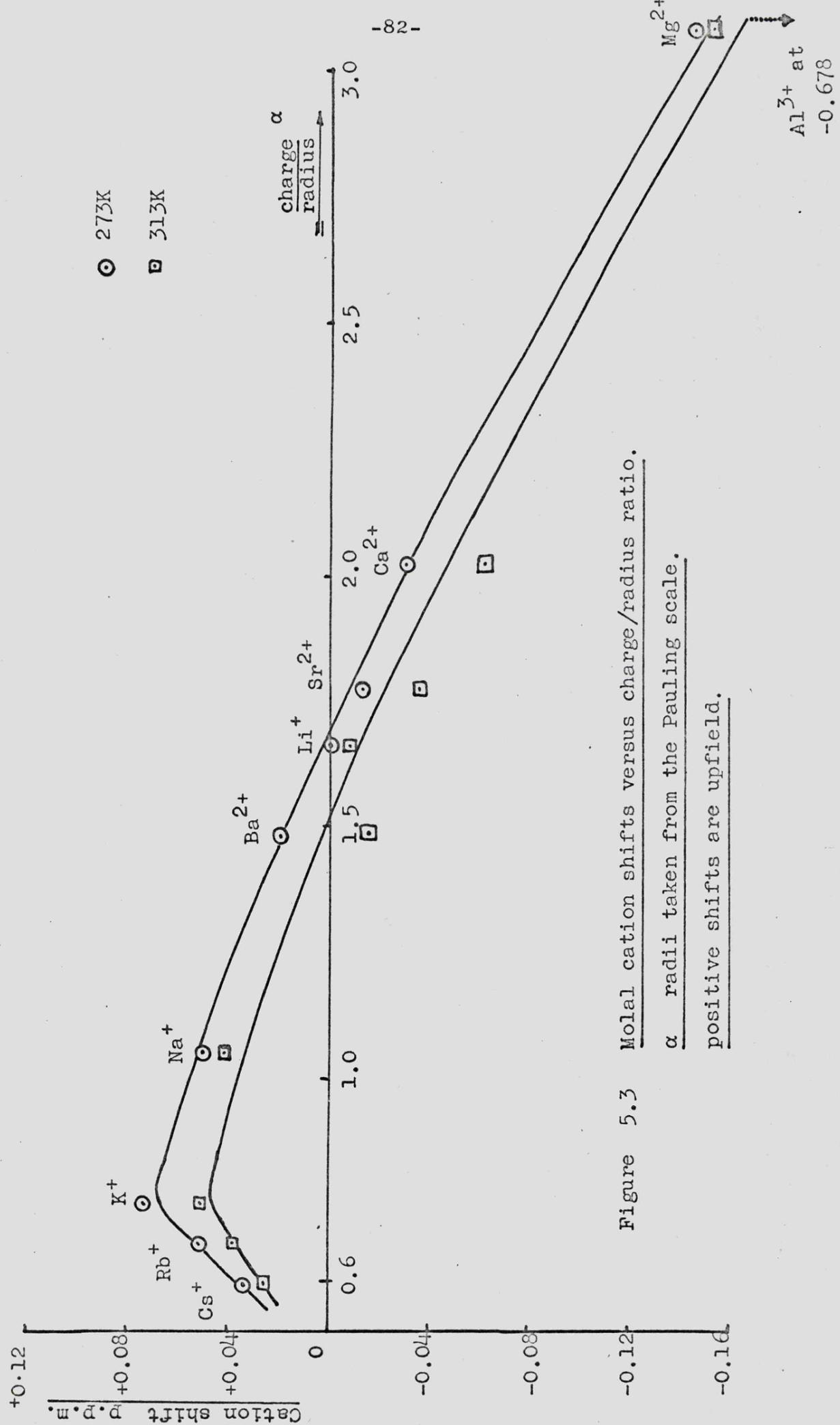
need to invoke longer-range structure making or breaking. It is not the wish to imply that such effects are not present, indeed the alkyl ammonium cations discussed in Chapter 6 are found to be an exception, but simply to suggest that the results for the simple ions give no compelling reason for invoking such effects. Malinowski and co-workers⁶⁷⁻⁷⁰ have used a similar approach, treating water molecules in the intermediate 'B' region (Figure 5.2) as part of the bulk solvent.

In order to facilitate discussion of the derived ion shifts (Tables 5.3 and 5.4), cations and anions will be treated in separate sections.

5.4 Cation shifts.

As a first step towards correlating the cation shifts, those for the alkali and alkaline earth metals are shown plotted versus charge/radius ratio in Figure 5.3. Figure 5.4 shows a similar plot for the alkali metal cations only, at various solution temperatures in the range 273 to 353K. At all the temperatures studied there is an observed shift to higher applied fields through the series $\text{Al}^{3+} \longrightarrow \text{Mg}^{2+} \longrightarrow \text{K}^+$. From K^+ to Cs^+ a fall to lower applied fields becomes evident, however, the overall shift relative to pure water is still upfield.

It is the electric field at, or near, the surface of an ion that must be responsible, at least to a considerable extent, for orientating a neighbouring water dipole.



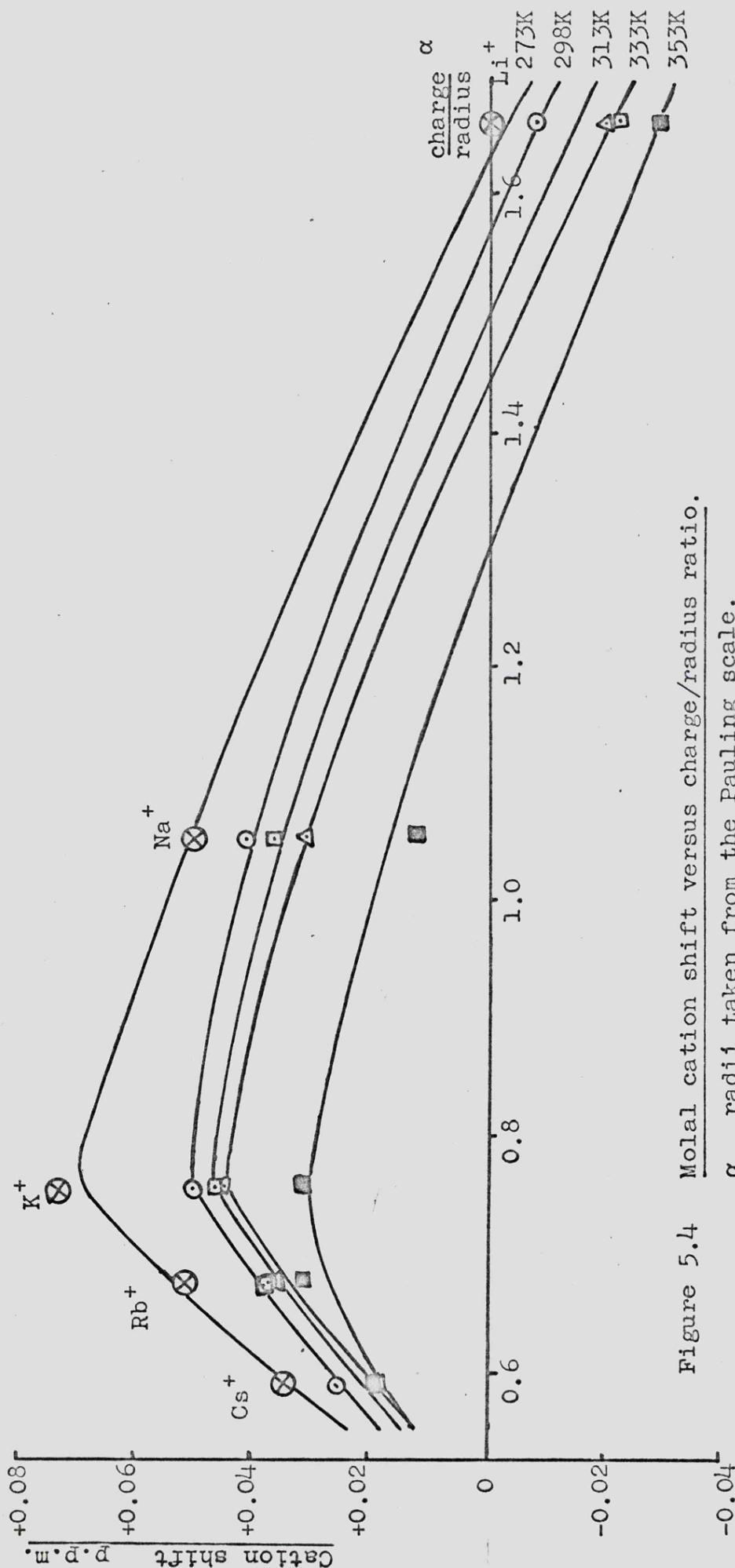
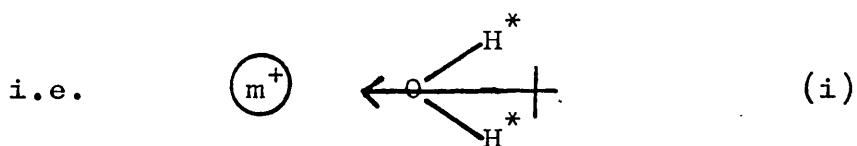


Figure 5.4 Molal cation shift versus charge/radius ratio.

α radii taken from the Pauling scale.

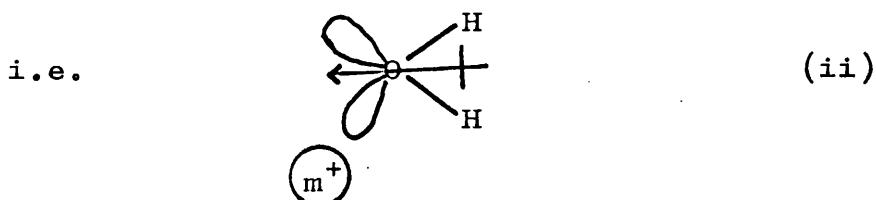
positive shifts are upfield.



(\leftarrow represents the molecular dipole moment of the nearest neighbour water molecules.)

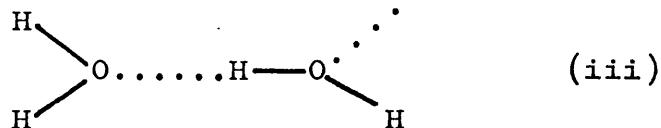
The precise manner in which a particular nearest neighbour water dipole is bound to a cation is still unknown.³⁷

Based on the assumption that the interaction is mainly dipolar, Bernal and Fowler⁹ concluded that water molecules would bind in a co-planar fashion (i). Verwey⁷¹ prefers univalent cations to be attached to the region of negative charge of the oxygen lone pair electrons.



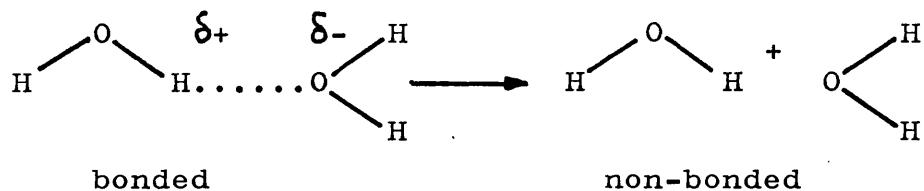
X-ray evidence^{72,73} favours the dipolar (i) rather than the Verwey (ii) configuration, for the purposes of the present discussion the former will be adopted.

The cation m^+ (i) will have polarized the protons H^* so causing a considerable alteration in their magnetic shielding, the position of their resonant frequency must consequently change. The observation of solvation shell resonances downfield of the bulk solvent signal⁶⁰ (cf. Figure 4.1a) must be indicative of the cation-water unit (i) having a large downfield shift relative to the hydrogen bonded situation (iii).



The shift of electron density, resulting in the observed de-shielding, is assumed to have occurred by the dipolar mechanism outlined in section 1.4. This type of interaction alone would seem, at first sight, to be incapable of accounting for the observed shifts to higher fields found for certain cations. It is in this context that the concept of the 'structure breaking' effects of ions has been invoked.⁴⁶

When two hydrogen bonded water molecules are separated mutually induced dipoles are removed, consequently the electron density at the proton is increased.^{28,74} A shift of the resonant field to higher values occurs as a result of the increased shielding relative to the former hydrogen bonded situation.



Evidence for this hypothesis is usually taken to be the upfield shift for the transition water (liq) \rightarrow steam.²⁵ Muller and Reiter⁷⁵ have suggested that the chemical shift of associated species depends quite strongly on the degree of excitation of the hydrogen bond vibrational stretching mode. These workers state that this mode can

be excited by thermal means and their calculations give temperature dependent chemical shifts similar to those found experimentally, even though they assume no dissociation of hydrogen bonded species occurs. Hindman⁴⁶ using temperature dependence data, estimated the magnitude (on a shift per mole of hydrogen bonds broken) of his structure breaking term, δ_{st} (see p.80). In view of Muller and Reiter's evidence, this quantitative approach would seem subject to doubt. The concept of long range structure breaking, however, need not be invoked to explain shifts to higher fields. Butler and Symons⁵⁴ have suggested a mechanism for accomodating cation shifts in methanolic solution, the aqueous shifts reported in Table 5.3 and depicted in Figures 5.3 and 5.4 can be understood in a similar manner. For the particular cations discussed, it is assumed that, in the main, only short range interactions contribute to the observed n.m.r. solvent shift.

Referring to Figure 5.5(i); the cation has, in general, replaced a water molecule and so altered the acidity of the proton H^* . If the gas phase value (Figure 5.5(ii)) is taken as a basic reference, then in both situations (a) and (b) the acidity of the H^* protons has increased relative to this value. The overall direction of the cation shift (W) will depend on the relative strengths of these two interactions. If the interaction (b) exceeds that of (a) then $Z > X$ and so an overall downfield cation shift (W) will result.

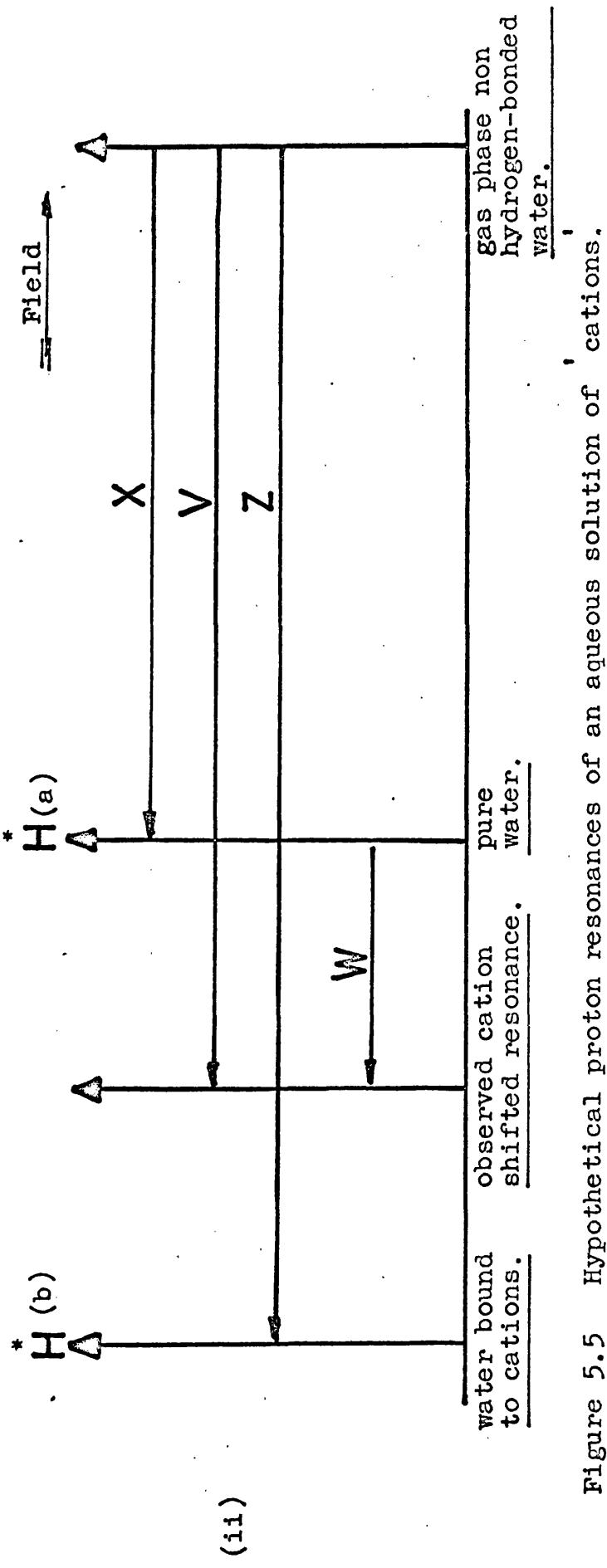
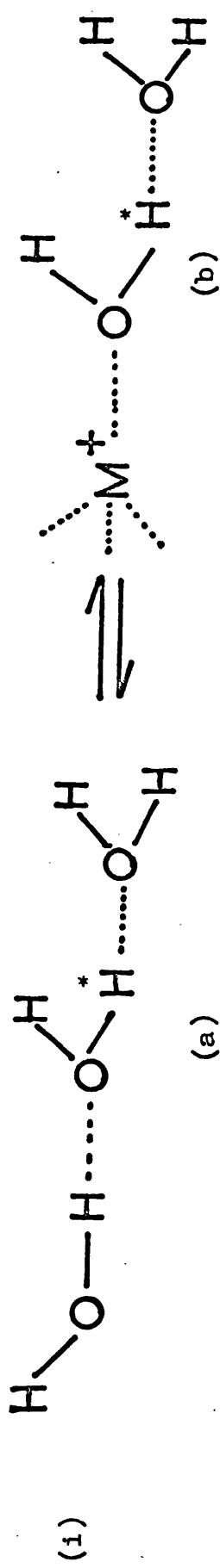


Figure 5.5 Hypothetical proton resonances of an aqueous solution of cations.

This is found to be the case for the highly charged cations Sr^{2+} Al^{3+} as shown in Figure 5.3. As the surface charge density of the cation decreases (right to left in Figure 5.3) then interaction (b) will weaken relative to that of (a), thus the cation shift (δ) moves to higher applied fields. The results for the lithium ion at 273K seem to indicate that a balance has been reached, giving the observed cation shift of 0.00 p.p.m. Such behaviour would, however, appear to be markedly temperature dependent. For the alkali metals, the cation shifts (Figure 5.4) tend to lower applied fields as the temperature rises. In the particular case of Li^+ the cation shift once again becomes downfield overall. The shifts for the cations Ba^{2+} through to K^+ become slightly positive (upfield), the conclusion is drawn that the interaction of the protons H^* with the cation (b) has become weaker than that with water itself (a). A maximum upfield cation shift is noted near to K^+ , this being followed by a downfield trend to Rb^+ and Cs^+ .

To explain the trend to lower applied fields found for these large alkali metal cations, Gotto and Isemura⁴⁹ suggested the formation of clathrate cages around ions such as Rb^+ and Cs^+ . Behaviour of this type would, however, not seem to agree with the extra mobility of water molecules in the vicinity of large mono-valent ions suggested by spin relaxation and self diffusion measurements.⁷⁶ Viscosity evidence⁷⁷ has led to the suggestion that Rb^+ and Cs^+ are 'structure breakers', however, if

structure breaking is associated with an upfield shift it would appear difficult to reconcile the shifts of these ions with that of Na^+ , an ion that is taken (on the same basis) as a 'structure maker'.

It could well be that the ions Rb^+ , Cs^+ have reached such a size that they are no longer able to compete with the water-water hydrogen bonding, the dipolar contribution being largely lost. Such an effect can be considered as a progressive decrease in the hydration number for the mono-valent cations, when their radius exceeds a certain critical value, found at or near that of potassium. On this basis, the cation shifts beyond the critical radius would be expected to tend to return to zero, the water molecules existing in an environment resembling the normal unperturbed one.

Useful information can be gained by probing the effects of temperature variation on such parameters as n.m.r. cation shifts. The shifts for the alkali metal cations are shown plotted versus temperature in Figure 5.6. It appears that over the range 273 to 353K two distinct classes exist;

$$\text{Li}^+, \text{Na}^+, \text{K}^+; \quad \frac{dW}{dT} = -5.6 \times 10^{-4} \text{ p.p.m. K}^{-1}$$

$$\text{Rb}^+, \text{Cs}^+; \quad \frac{dW}{dT} = -1.5 \times 10^{-4} \text{ p.p.m. K}^{-1}$$

It may be significant that the change of slope occurs at the position of the maximum in the cation shift versus charge/radius plots. The temperature coefficient of pure water is found to be $+9.56 \times 10^{-3}$ p.p.m. K^{-1} .^{39,67}

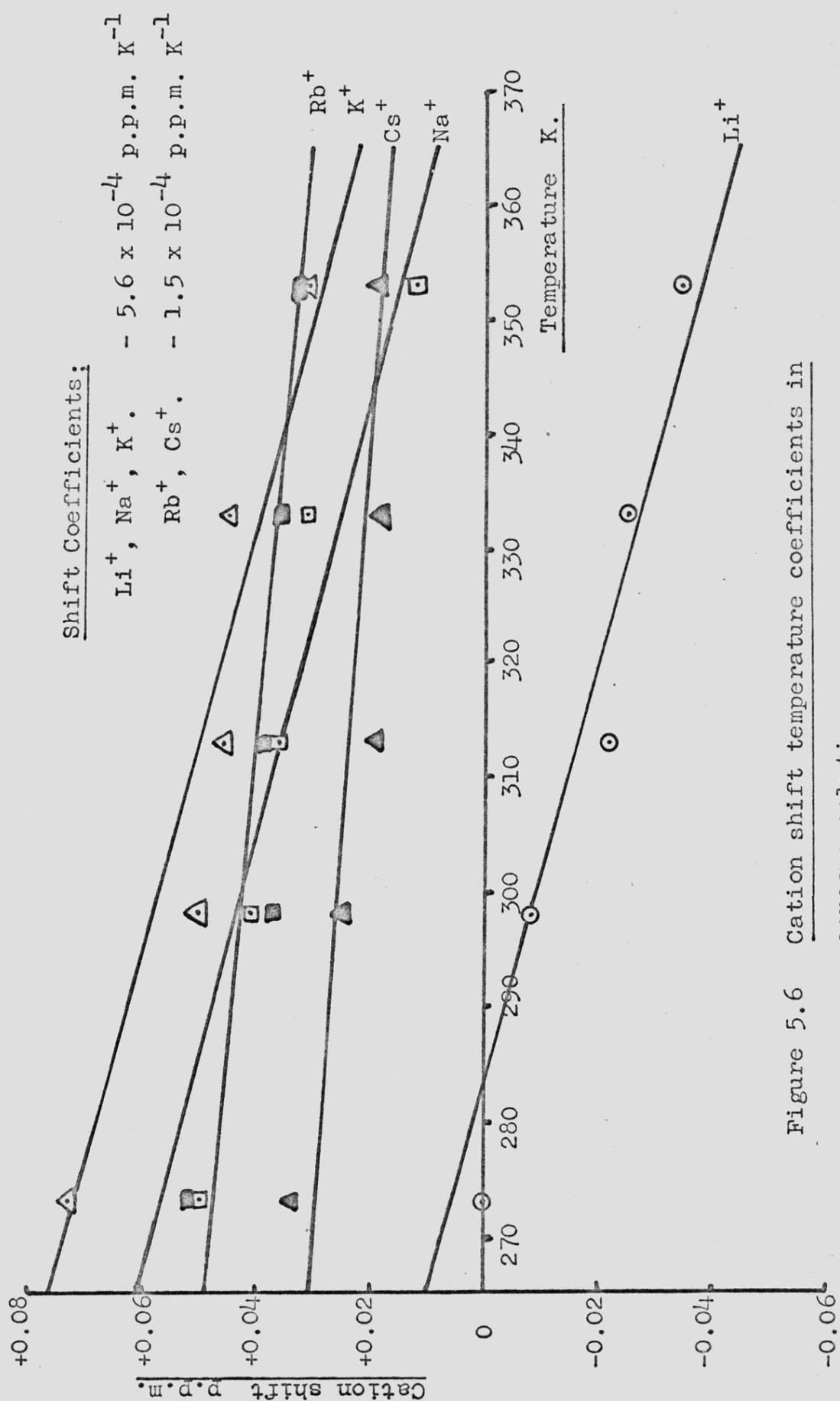


Figure 5.6 Cation shift temperature coefficients in aqueous solution.

Using the notation given in Figure 5.5 these temperature coefficients imply that;

$$\frac{dW}{dT} \ll \frac{dX}{dT}$$

Furthermore W is the weighted mean of X and Z, hence,

if $\frac{dX}{dT} \gg \frac{dZ}{dT}$ then the observed behaviour will be reproduced, i.e. the temperature coefficient of pure water is of greater magnitude and of opposite sign to that of the cation shift, $\frac{dW}{dT}$. The direct cation-water interaction (Figure 5.5(i)b) would therefore seem to be largely insensitive to temperature, indeed, in the limit $\frac{dZ}{dT} = 0$. Butler and Symons⁵⁴ have shown this to be the case for the magnesium cation solvation shell resonance in methanolic solution. Malinowski⁶⁷⁻⁷⁰ has taken the hydrated cation as an independent unit (i.e. assuming $\frac{dZ}{dT} = 0$) and so has derived total effective hydration numbers for the unit 'cation + anion'. By applying a method similar to Malinowski's, to the cation shifts derived in the present work, it should be possible to derive unique cation hydration numbers and so test the postulate, made earlier, of a marked decrease in the solvation numbers for Rb^+ and Cs^+ compared to the smaller cations.

The cation shift, V, (relative to the 'gas phase') can be expressed as the weighted mean;

$$V = R.X + Q.Z$$

where, R = Mole fraction of 'normal' water.

Q = " " " water bound to cations.

However, for 1 mole of cations,

$$R = \frac{55.51 - n}{55.51} \text{ and } Q = \frac{n}{55.51}$$

where n = the hydration number of the cation.

$$\therefore V = \frac{n}{55.51} (z - x) + x$$

The cation shift 'W' is, however, measured relative to pure water at the given temperature.

$$\therefore W = V - x$$

$$\text{hence, } W = \frac{n}{55.51} (z - x)$$

This last expression is now differentiated w.r.t. temperature and the term $\frac{dZ}{dT}$ equated to zero.

$$\therefore \frac{dW}{dT} = \frac{-n}{55.51} \cdot \frac{dX}{dT}$$

$$\text{i.e. } n = -55.51 \frac{\left(\frac{dW}{dT}\right)}{\left(\frac{dX}{dT}\right)}$$

Using; $\frac{dX}{dT} = +9.56 \times 10^{-3}$ p.p.m. K^{-1} . 39,67

$\frac{dW}{dT} = -5.6 \times 10^{-4}$ p.p.m. K^{-1} for Li^+ , Na^+ , K^+ .

$\frac{dW}{dT} = -1.5 \times 10^{-4}$ p.p.m. K^{-1} for Rb^+ and Cs^+ .

two sets of cation hydration numbers, n , are obtained.

For Li^+ , Na^+ and K^+ , $n = 3.3 \pm 0.6$

and for Rb^+ and Cs^+ , $n = 0.9 \pm 0.6$

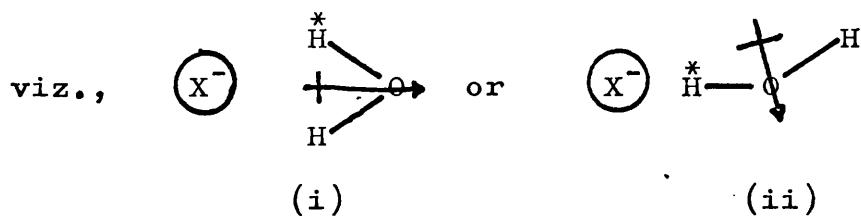
These hydration numbers can only be taken as

approximate in view of the errors involved in the temperature coefficient plot, Figure 5.6. The values do, however, show a significant drop in hydration number from K^+ to Cs^+ . Moreover, the values found for the smaller cations (Li^+ , Na^+ , K^+) are in reasonable agreement with those derived using other techniques,^{46,78,79} numbers in the range 3 to 6 usually being quoted.

5.5 Anion shifts.

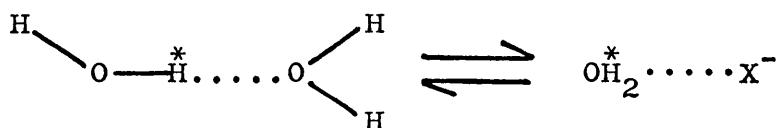
The anion shifts listed in Table 5.4 can be interpreted in a similar manner to that proposed for cations, the basic assumption being made that local effects will tend to outweigh longer range ones.

When an anion is bonded to a water proton, the interaction will presumably be of a direct nature;



In both the dipolar (i) and angular (ii) orientations the proton H^* is intimately associated with the charge cloud of the anion. Comparing this with the cation interaction (Figure 5.5(i)b), where any effects of the field of the ion have to be transmitted through the $O-H$ bond, it would seem likely that any shielding of H^* by the anion would be greatly magnified. At this stage in the discussion, no prediction can be made as to

which orientation of the water molecules associated with the anion, will be preferred. Whichever of them, dipolar or angular, is favoured, the anion shift is assumed to result from the difference in magnetic shielding arising from the competing bonding situations;



Three main factors are thought to be responsible for this difference in shielding, namely;

- a) The number of water molecules intimately associated with each anion, i.e. the anion solvation number.
- b) The relative basicities of the anion and water.
- c) The magnetic anisotropy and local fields associated with the anion and its effect on bonded protons.

Figures 5.7 and 5.8 show plots of various anion shifts versus H-X bond dissociation energies, the values of which are given in Table 5.5.

Table 5.5

Molecule	Dissociation energy.	Molecule	Dissociation energy.
HF	134.6	HO	101.5
HCl	103.2	HC	81.0
HBr	87.5	HS	85.0
HI	71.4	HN	93.0

Bond Dissociation Energies, Kcal.Mole⁻¹ at 298K
Data taken from ref.79

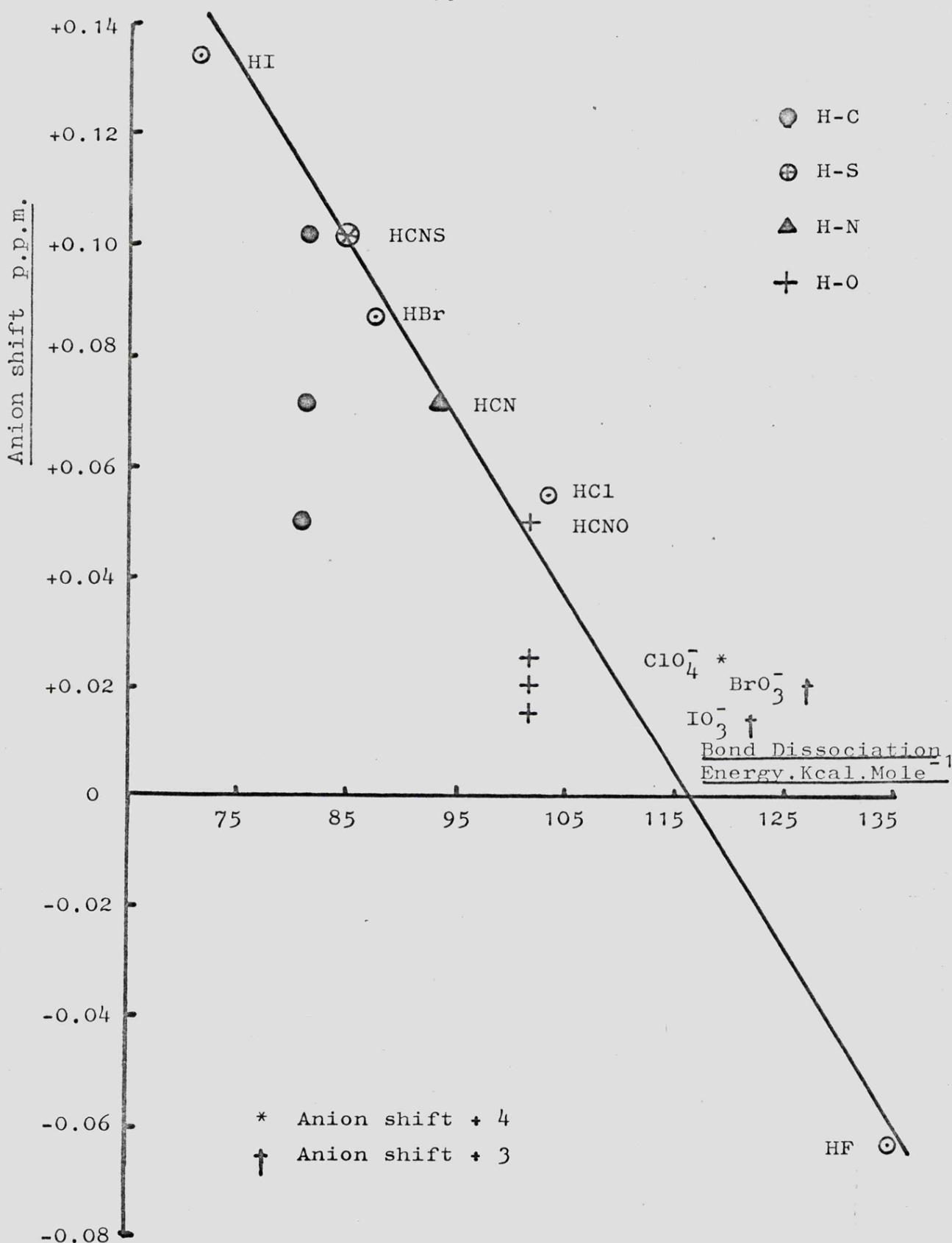


Figure 5.7 Molal anion shifts at 298K plotted against the bond dissociation energy for the H-X bond.

Anion shift p.p.m.

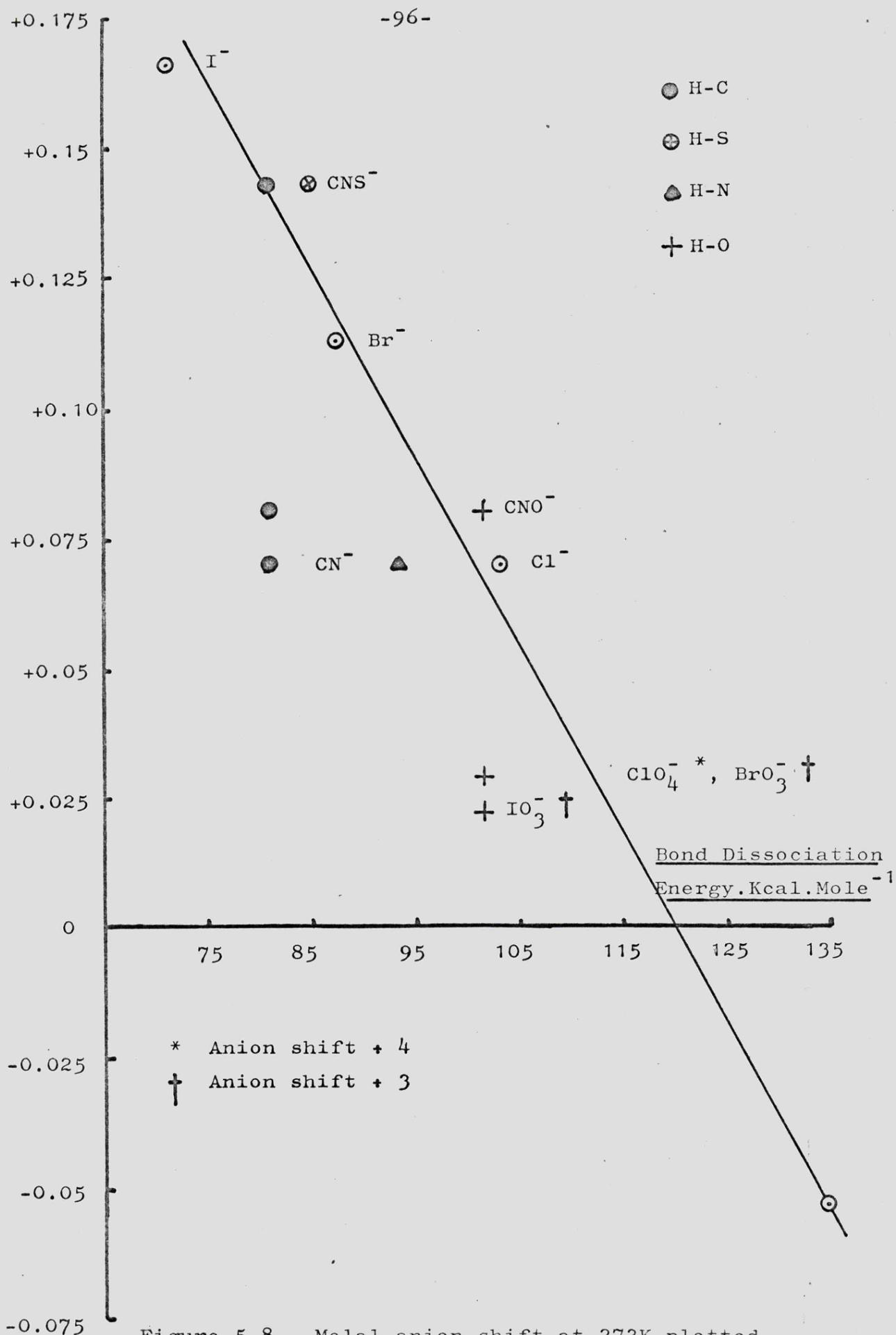


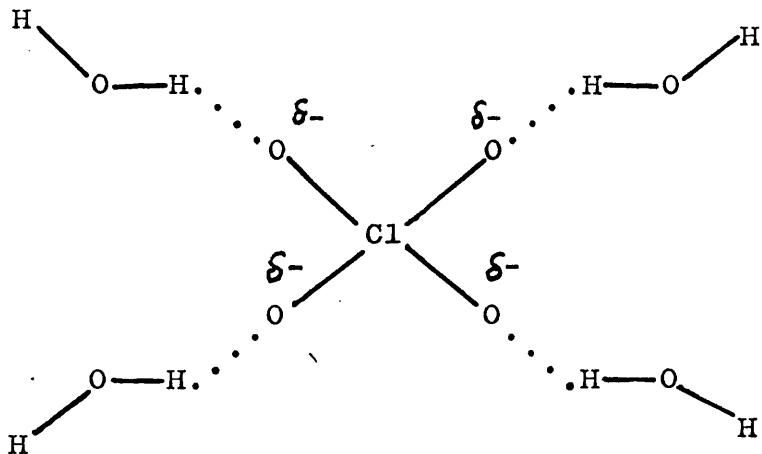
Figure 5.8 Molal anion shift at 273K plotted versus the bond dissociation energy for the H-X bond.

If the assumption that only short range interactions tend to govern the anion shift is correct, then the bond strength parameter (more correctly, the bond dissociation energy) for ions such as the halides would be expected to be a measure of the relative intensity of such interactions. A linear relationship is found for the halides at both 273 and 298K, and furthermore, ions such as CN^- , CNO^- , CNS^- also correlate via the H to O, S and N bond dissociation energies. These latter ions could presumably interact at either end, and, although it would be unwise to place too much emphasis on such an empirical correlation, it could be that the main interaction with these ions is not via the carbon atom. The observed linearity of Figures 5.7 and 5.8 would seem to suggest two possible bonding situations;

- (i) A fluctuating interaction with one water molecule at any instant. This type of anion-water interaction approaches the H-X situation instantaneously, having an interaction time long enough for n.m.r. to detect an effect.
- (ii) An interaction in which the anion is associated with several water molecules. This, however, would require a constant 'solvation number' in order to reproduce the observed linear relationship, as only in this case would each of the ions shown interact with the water protons in direct proportion to the H-X bond energy.

It has been suggested elsewhere⁸⁰ that the perchlorate anion has a solvation number of four. If this is the

case and, furthermore, if the interaction is of the type;



then it would not seem unreasonable that, if $\frac{\delta_{\text{ClO}_4^-}}{4}$ is the observed anion shift,

$$\frac{\delta_{\text{ClO}_4^-}}{4} \propto \text{bond dissociation energy H-O.}$$

It is noted that on this basis the perchlorate anion does correlate with other anions shown in the bond dissociation plots. It is of interest to note that the halate ions IO_3^- and BrO_3^- also seem to correlate in this way, if a hydration number of three is assumed. This bond strength/anion shift evidence does seem to lend some support to the postulate of the overriding importance of short range interactions in the context of such shifts.

For the particular case of the halide ions, which possess spherical symmetry, a correlation between the charge/radius ratio and the anion shift would be expected if either of the two short range effects, (i), (ii), described above were operative. This is indeed found to be so and the observed relationship is shown in Figure 5.9.

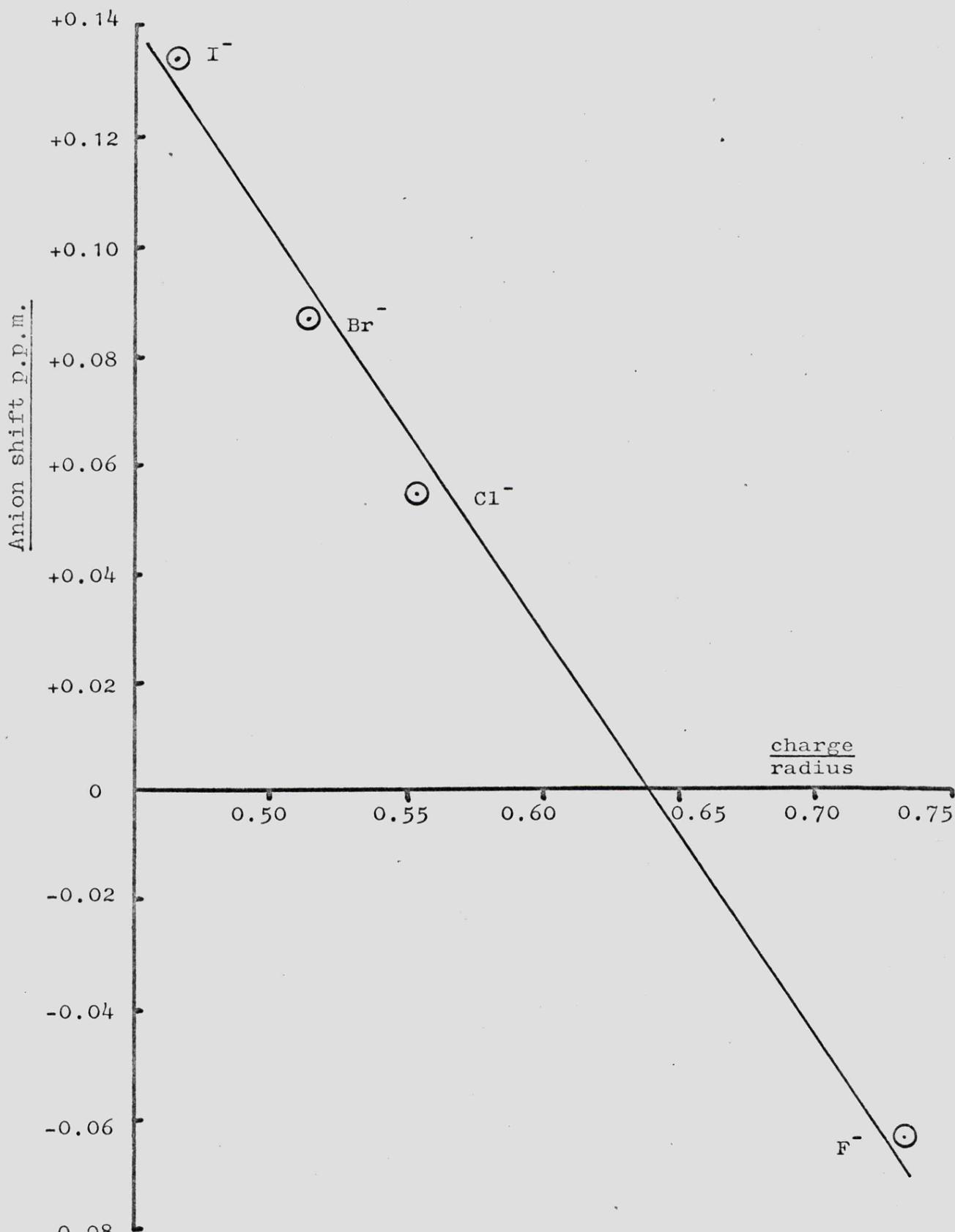
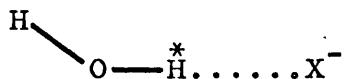


Figure 5.9
Molal halide ion shift at 298K
plotted against charge/radius
ratio. (Pauling radii)

For the halide ions, the charge/radius ratio parameter should be a direct measure of the polarizability of the charge cloud of the anion. It follows therefore, that for an interaction of the type;



the screening of $\overset{*}{\text{H}}$ would be dependent on such polarizability. Fluoride being a small ion and consequently not very polarizable, results in less shielding of $\overset{*}{\text{H}}$ than that afforded by a neighbouring water molecule. Hence a downfield ion shift is observed. Iodide, on the other hand, is large and polarizable, the preceding situation is reversed and an upfield shift is observed. Unfortunately, in view of uncertainties in the size and charge distribution of the complex anions, the charge/radius approach must be limited to the halides.

It is possible, using an approach similar to that given for cations (section 5.4), to test the hypothesis of a constant hydration number for the halide ions. The temperature dependence of the halide ions is shown in Figure 5.10, it is noted that within experimental error the coefficients are constant, having a value of -7.25×10^{-4} p.p.m. K^{-1} . By utilising the previously derived equation,

$$\text{viz. } n = -55.51 \left(\frac{dW}{dT} \right) \cdot \left(\frac{dT}{dX} \right) ,$$

the hydration number for the halides would appear to be constant and of a value, 4.3 ± 0.6 . Such evidence tends to favour the concept of a constant hydration number (ii)

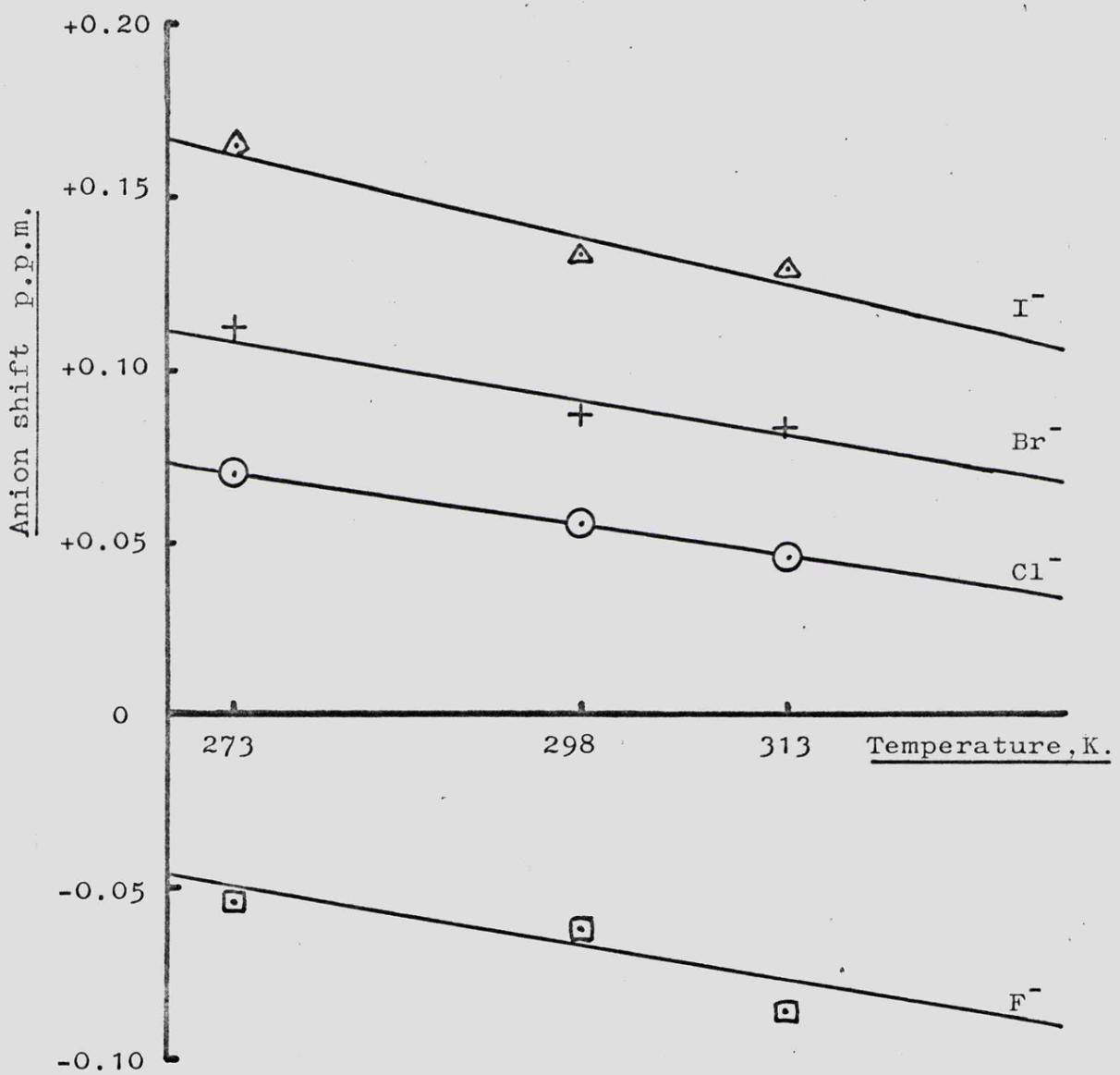


Figure 5.10 Molal halide ion shift plotted against temperature.

Average temperature coefficient
 $= -7.25 \times 10^{-4}$ p.p.m. K⁻¹.

as opposed to the fluctuating single interaction (i).

In order to test the basicity factor, anion shifts have been compared with the pKa values of their conjugate acids in Figure 5.11. The pKa values are shown in Table 5.6.

Table 5.6

Ion	298K	273K	Ion	298K	273K
F^-	-3.62	3.30	HCO_2^-	3.75	3.79
Cl^-	-6.1	-7.3	$CF_3CO_2^-$	0.230	-
Br^-	-9.0	-	$CH_2ClCO_2^-$	2.87	2.85
I^-	-9.5	-	ClO_4^-	-9.9	-
CNO^-	3.71	3.73	BF_4^-	-	-
CNS^-	-3.59	-	$CH_3CH_2CO_2^-$	4.87	-
CN^-	9.21	9.91	$CH_3(CH_2)_2CO_2^-$	4.80	-
NO_2^-	3.29	3.49	CrO_4^{2-}	1.52	-
NO_3^-	-1.37	-1.65	HPO_3^{2-}	6.2	-
SO_3^{2-}	7.2	-	IO_3^-	0.77	0.58
SO_4^{2-}	1.94	-			
$CH_3CO_2^-$	4.756	4.781			
PO_4^{3-}	12.4	-			
BrO_3^-	-	-			

pKa values for the conjugate acids of the anions shown.

Data taken from R.P.Bell, 'The Proton in Chemistry', (Methuen, London, 1959.)

The observed correlation is quite good apart from a few notable exceptions. The cyanide ion is found to have an abnormal upfield shift, it could be that this is caused by the effects of local fields associated specifically

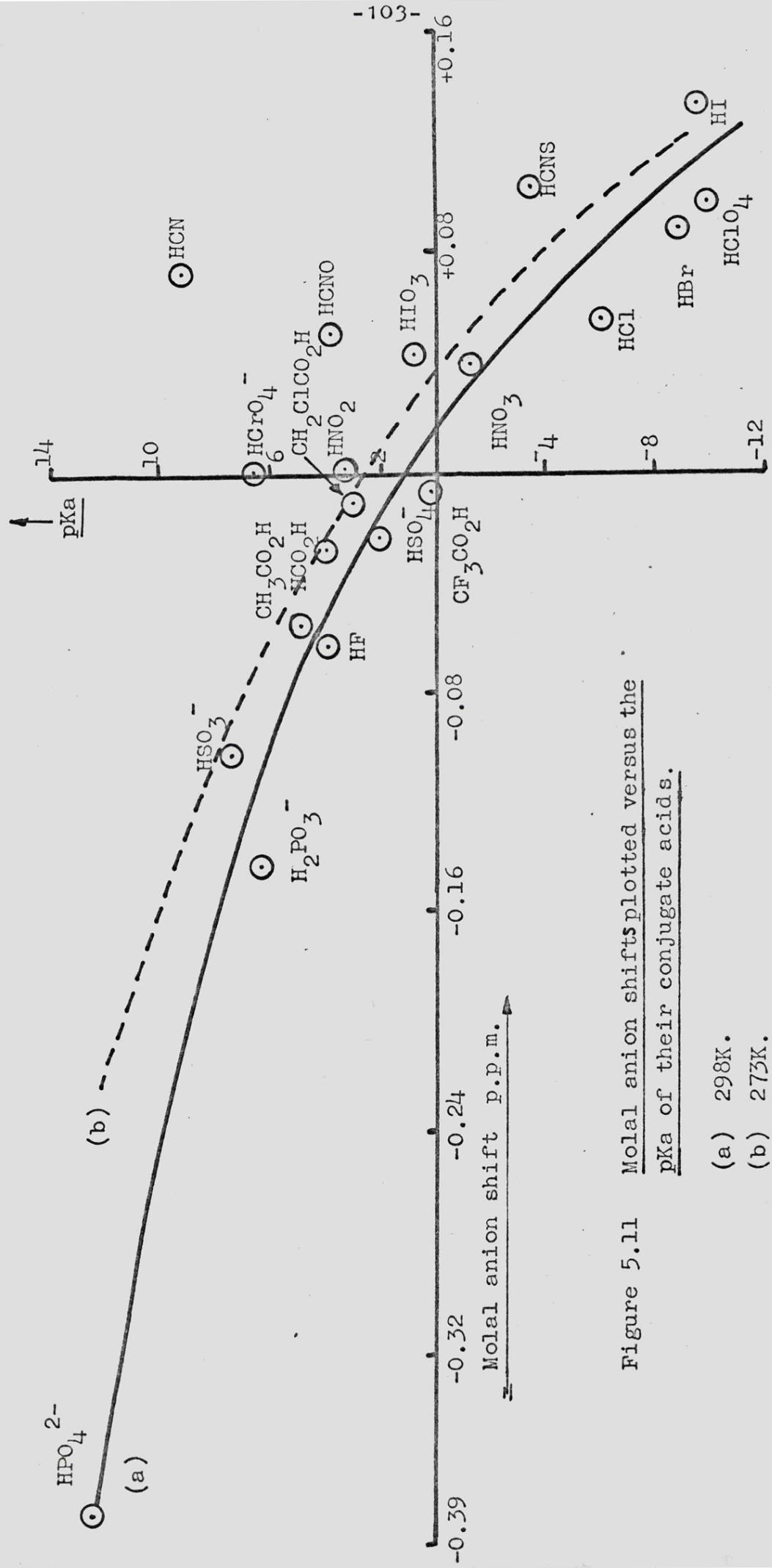


Figure 5.11 Molal anion shifts plotted versus the pKa of their conjugate acids.

(a) 298K.
(b) 273K.

with the $\text{H} \dots \text{CN}^-$ interaction. The cyanide ion was also found to be abnormal, in the same sense, in methanolic solution.⁵⁴ In the methanol work the authors plotted the anion shift against the liquid phase shift of the conjugate acid, a curve resulted that adequately accommodated the cyanide ion. A similar plot for the present aqueous results is shown in Figure 5.12, the cyanide ion is found to be less well accommodated. This would seem to suggest that the concept of specific magnetic interactions applying to both hydrogen bonded and fully protonated cyanide is a poor approximation for aqueous solution. Nevertheless it is probable that CN^- , CNO^- and CNS^- fall of the pK_a plot as a result of asymmetric solvation, hydrogen bonding being preferred along their axes.

The anomalous result for the chromate ion on the pK_a plot is of some interest. This ion is a remarkably strong base compared with sulphate, despite the fact that their electronic configurations are similar. This difference has been interpreted in terms of the greater electronic polarizability of chromate.⁸¹ This difference is clearly not reflected in the n.m.r. shifts, the shift value for chromate being more positive rather than more negative than that for sulphate. It is tentatively suggested that this is a consequence of a special magnetic effect, characteristic of chromate, and comparable with that of cyanide. It is known that, like permanganate, chromate has a small temperature independent paramagnetism

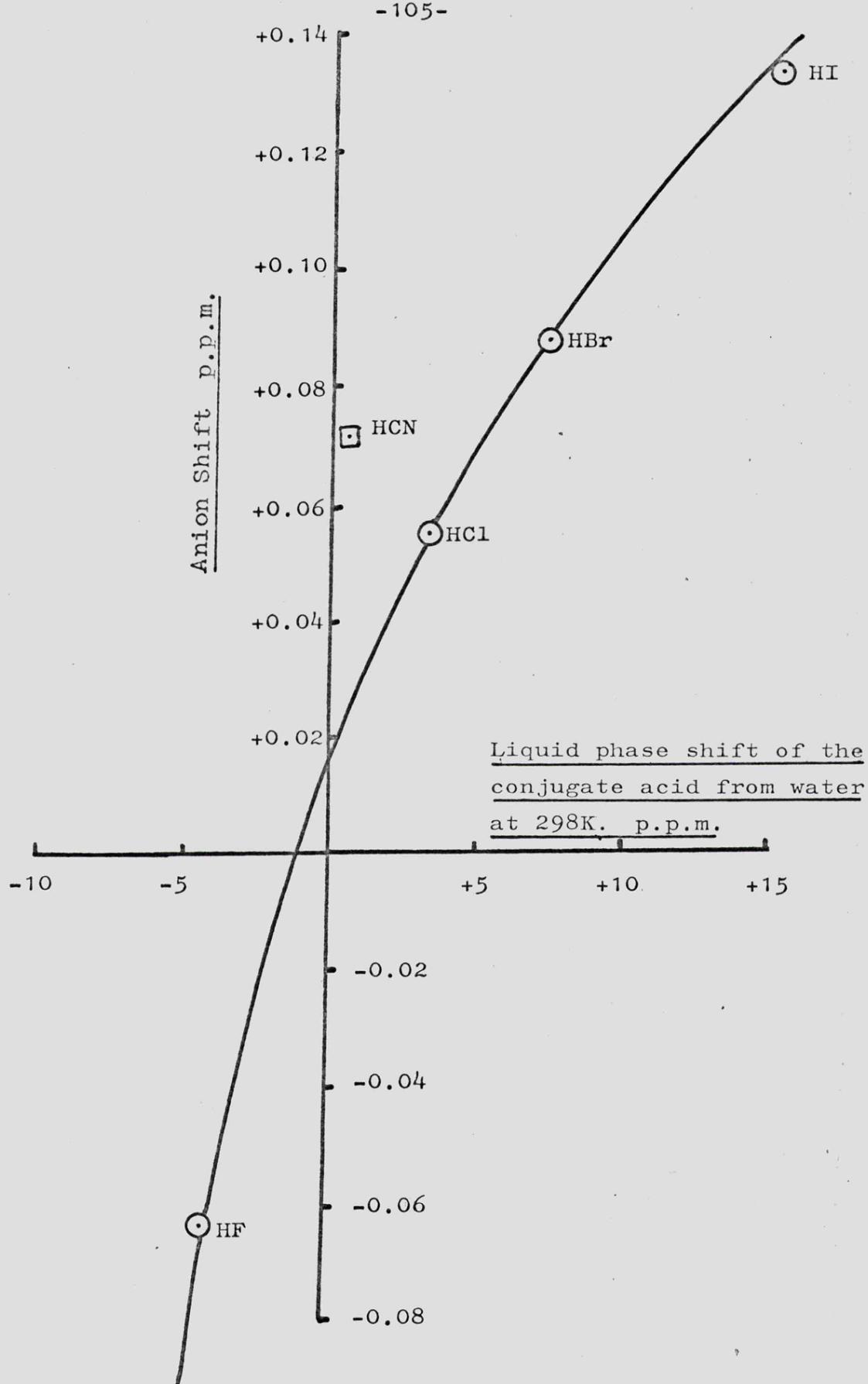


Figure 5.12 Molal anion shifts at 298K plotted against the liquid phase shift of the conjugate acid from water.

and it could well be that hydrogen bonded protons can feel this, an increased shielding could thereby result.

It is interesting to note that, in both Figures 5.11 and 5.12, the curves pass close to the origin. This means that the anion shifts change sign in unison with both pK_a and the liquid phase shift of the conjugate acids, suggesting that the absolute shifts derived in this thesis are of the correct magnitude.

5.6 Summary.

It would seem that the n.m.r. shifts for simple ions can be adequately explained without the need to invoke longer range structure making or breaking.

Although the possibility of longer range effects is not discounted, it does seem remote for simple ions. The results to be discussed in Chapter six suggest that for ions that contain non-polar alkyl chains this is no longer the case, special structuring effects being present.

The orientation of the water molecules in the primary hydration shell cannot be determined with any certainty. For cations it has been taken as dipolar, whereas the anion basicity effect would suggest an angular configuration for the negative species. Further evidence to support this latter configuration will be presented in Chapter seven, when ion shifts in the related solvents methanol, ethanol and ethylene diol are discussed.

CHAPTER SIX

THE INTERACTIONS OF IONS CONTAINING ALKYL GROUPS IN AN AQUEOUS MEDIUM

6.1 Introduction.

Much has been written concerning the unusual properties of aqueous solutions of quaternary ammonium salts.^{14,37,82,83}

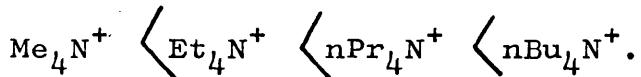
The similarity between the properties of these cations and those of non-polar solutes, when dissolved in water, is taken to be of great significance. Non-polar solutes are thought to exert a 'structure making' influence on the water. There are many sources of evidence for this type of behaviour, entropies of hydration,²⁴ partial molar heat capacities,²⁴ and partial molar volumes⁸⁴ being amongst the most informative.

The partial molar heat capacity of tetra n-butyl ammonium bromide in water at 293.15K is large and positive, this being the behaviour expected of a non-polar rather than an ionic solute. If, for the series $R_4N^+Br^-$ (where R= methyl to n-amyl), the increase in the partial molar volume of water per added methylene group is determined, then a similar dependence to that found for the n-alkanes becomes apparent.

The similarities outlined above lead to models for aqueous solutions of quaternary ammonium salts that are based on predominately hydrophobic interactions between the non-polar alkyl groups of the cations and the water. Hydrophobic interactions lead to a stabilisation of the water lattice around the non-polar groups, an overall enhancement of the water structure resulting.

Frank and Evans²⁴ have used the term 'iceberg

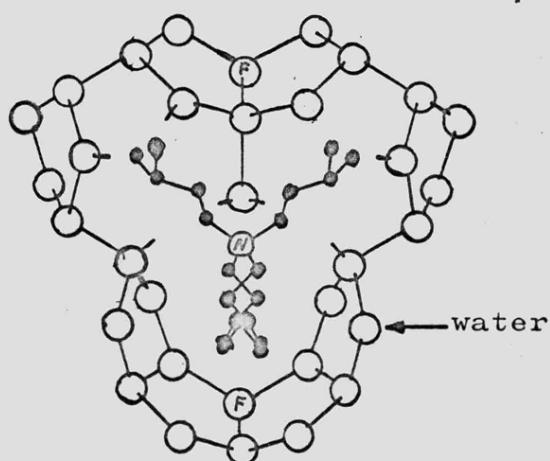
forming tendency' in this context. Water is taken to be capable of forming frozen patches, or microscopic icebergs, around such non-polar groups. The extent of the structure enhancement is thought to increase as the alkyl chain lengthens, following the order;



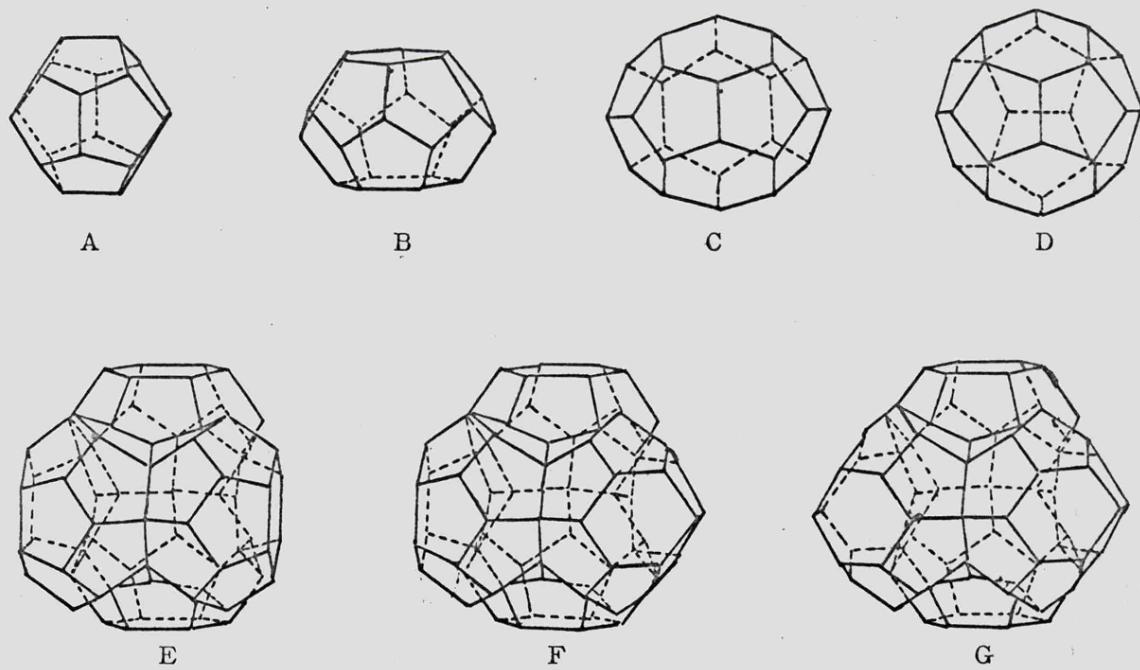
A comparison is often drawn between the clathrate hydrates,⁸⁵ formed by certain of the quaternary ammonium salts, and their behaviour in solution.^{37,86-88} The structures of the clathrate hydrates are formally based on pentagonal dodecahedra of water molecules, the structure found for the hydrate, $(\text{iC}_5\text{H}_{11})_4\text{N}^+\text{F}^-\cdot 38\text{ H}_2\text{O}$, being shown in Figure 6.1. Liquid water at low temperatures is thought to be able to form sufficiently large cavities to accommodate the alkyl chains of dissolved quaternary ammonium ions, hence tending to approach the configuration of the clathrate hydrates.⁸⁹

The 'clathrate cage'/'iceberg' models, based on predominately hydrophobic interactions, are widely but by no means universally accepted.^{53,90,91}

Wirth⁵³ has pointed out that the increase in the partial molar volume of water, that occurs when quaternary ammonium salts are added, can be predicted if ion association (including micelle formation) takes place. Such increases in partial molar volumes have normally been interpreted in terms of structure making, however, from Wirth's point of view the effect of the salt is that of a normal electrolyte, specialised structuring of the water not taking place.



The orientation of a tetraisoamylammonium cation in a
clathrate cage. $(i\text{-C}_5\text{H}_{11})_4\text{N}^+\text{F}^- \cdot 38\text{H}_2\text{O}$.



A, Pentagonal Dodecahedron; B, Tetraakaidecahedron;
C, Pentakaidecahedron; D, Hexakaidecahedron
E-G, Composite units formed by A to D.

Figure 6.1 The pentagonal dodecahedron and the polyhedra
that are commonly found in conjunction with
the clathrate hydrates.

It should be noted at this point, that there is a distinction between the structure forming properties of the alkyl ammonium ions and the so called 'electrostrictive' structure formers. The bulky alkyl ammonium ions are unable to take part in any specific ion-water interactions, lacking readily available sites. Any interactions between these latter ions and water will therefore be of the van der Waals type, being weak in comparison to the more normal dipolar type found for ions such as Li^+ , F^- etc.

6.2 N.M.R. Studies.

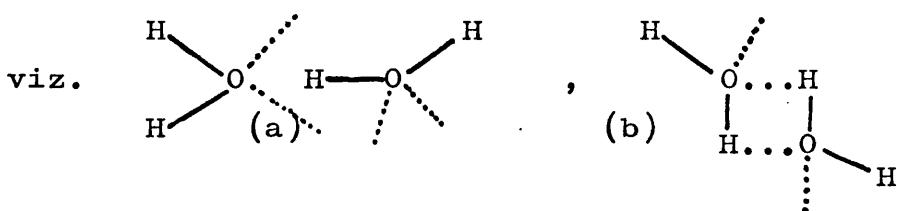
The n.m.r. solvent shift technique has proved to be a valuable tool when studying the modification of water-water interactions that arise from the presence of dissolved salts. The use of the technique for the study of quaternary ammonium, and the related alkyl sulphate and carboxylic acid, salt solutions should provide valuable additional information. In particular, any structure enhancement would be expected to manifest itself in the form of a downfield ion shift. It is indeed unfortunate that one of the first, and most often quoted, n.m.r. studies³⁶ produced conflicting evidence.

Hertz and Spalthoff³⁶ reported that (at 298K) increasing the length of the alkyl chain of a quaternary ammonium ion causes the water proton resonance to shift upfield. As upfield shifts are normally interpreted in terms of 'structure breaking', it would seem that this

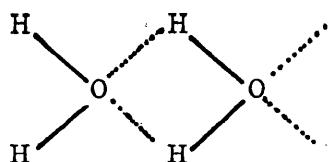
n.m.r. result is at variance with the behaviour that would have been predicted from the 'clathrate cage' / 'iceberg' models, namely, a shift to lower applied fields. The explanation of this anomalous n.m.r. result has produced several alternative theories.^{51,91}

Clifford and Pethica⁵¹ suggest that the effect of hydrocarbon chains on water is to increase the co-valent character of the hydrogen bonding. A shift to higher applied fields is said to result from either a reduction in the electrostatic field at the protons in water molecules adjacent to the alkyl chain due to neighbouring water dipoles or by an increase in the number of partially co-valent hydrogen bonds formed, or by a combination of both effects. On this basis the chemical shift of the water protons is considered as being mainly due to the increased co-valent character of the water hydrogen bonding, as originally postulated in Nemethy and Sheraga's theory concerning the effect of dissolved hydrocarbon chains on the thermodynamic properties of water.¹⁶

Wicke⁹¹ simply postulates that adjacent water groups must be joined by linkages having stronger screening of the protons, so producing the observed upfield shifts. This, it is claimed, rules out 'ice-like structures' (having tetrahedral hydrogen bonds), instead water molecules adjacent to non-polar groups have linkages involving non tetrahedral hydrogen bonding.

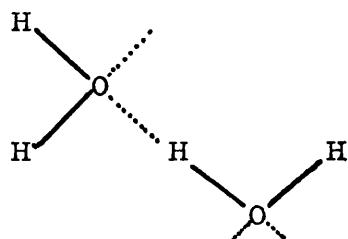


(c)



Wicke states that type (c) is improbable, basing this conclusion on steric factors. Types (a) and (b) have the bridging protons more deeply enveloped in the lone pair electron cloud of the oxygen than would be found in the tetrahedral ice I structure.

viz.



In an attempt to shed some more light on the n.m.r. salt shifts of the quaternary ammonium and related ions, an extensive study has been undertaken. The effect of temperature variation over the range 273 to 353K has also been investigated.

6.3 Results.

For the results reported in this section, the methyl protons of the alkyl ammonium cations have been used as an internal reference, the salt thereby providing its own non-interacting reference. The secondary reference NaDSS was used to establish the validity of this choice, it was found that for all concentrations of added salts, the separation between the two methyl peaks ($\text{NaDSS} - [\text{CH}_3(\text{CH}_2)_x]_4 \text{N}^+$) was constant. A similar approach

has been used by Clifford and Pethica⁵¹ when referencing the salt shifts of aqueous solutions of sodium alkyl sulphates. (see also section 3.3)

In the results reported for the sodium salts of the carboxylic acids, once again terminal methyl protons have provided a suitable internal reference.

Table 6.1 lists the salt shifts relevant to this chapter. The cation shifts are shown in Table 6.2, these have been derived by utilizing the temperature dependent halide ion shifts derived in Chapter four. The values shown have been computed so as to give maximum consistency between the salts studied.

6.4 The behaviour of quaternary ammonium ions in methanol.

As a first step towards interpreting the results of the aqueous study, the behaviour of these ions in methanol will be briefly outlined.

Butler and Symons⁵⁴ have studied the methanolic system using the n.m.r. technique. Figure 6.2 shows their measured cation shifts plotted versus charge/radius ratio.* There is a noticeable trend towards zero shift for the large quaternary ammonium cations (e.g. nHex₄N⁺). Such trends are taken to imply that the large cations, having no peripheral bonding sites, leave the solvent relatively undisturbed. This interpretation is supported by recent work⁹² concerning the solvent isotope effect (ΔH CH₃OH \rightarrow CH₃OD ; ΔH H₂O \rightarrow D₂O) for ions such as Cs⁺

* a full discussion of the radii of quaternary ammonium ions is given in appendix 2.

Table 6.1

Salt	Molal salt shift p.p.m.					
	273K	285.5K	298K	313K	333K	353K
NH_4Cl	+0.081	-	+0.051	-	-	-
Me_4NCl	+0.053	-	+0.050	-	-	-
Me_4NBr	+0.091	+0.083	+0.080	+0.073	+0.061	+0.050
Et_4NCl	+0.043	-	+0.038	-	-	-
Et_4NBr	+0.075	+0.077	+0.071	+0.078	+0.073	+0.067
Et_4NI	+0.126	-	+0.108	-	-	-
nPr_4NBr	+0.057	+0.064	+0.072	+0.077	+0.085	+0.097
nBu_4NBr	+0.042	+0.060	+0.073	+0.103	+0.115	+0.121
OctMe_3NBr	+0.108	+0.125	+0.137	+0.133	+0.130	+0.123
HCO_2Na	+0.040	-	+0.015	-	+0.004	-
$\text{CH}_3\text{CO}_2\text{Na}$	+0.011	-	-0.013	-	-0.011	-
$\text{CH}_3\text{CH}_2\text{CO}_2\text{Na}$	-0.007	-	-0.011	-	-0.024	-
nPrCO_2Na	-0.003	-	-0.013	-	-0.018	-
$\text{isoPrCO}_2\text{Na}$	-0.003	-	-0.010	-	-0.010	-
$\text{nHeptCO}_2\text{Na}$	-0.005	-	-0.003	-	-0.005	-
$\text{CH}_2\text{ClCO}_2\text{Na}$	+0.046	-	+0.033	-	-	-
$\text{CF}_3\text{CO}_2\text{Na}$	+0.077	-	+0.035	-	-	-
$\text{CH}_3\text{SO}_3\text{Na}$	+0.110	-	+0.090	-	-	-

Table 6.2

Ion	Molal ion shift p.p.m.					
	273K	285.5K	298K	313K	333K	353K
NH_4^+	+0.011	-	-0.004	-	-	-
Me_4N^+	-0.017	-0.017	-0.008	-0.009	-0.007	-0.005
Et_4N^+	-0.033	-0.023	-0.023	-0.004	+0.005	+0.012
nPr_4N^+	-0.052	-0.036	-0.020	-0.005	+0.017	+0.042
nBu_4N^+	-0.067	-0.040	-0.019	+0.021	+0.047	+0.066
OctMe_3N^+	-0.001	+0.025	+0.045	+0.051	+0.062	+0.078
HCO_2^-	-0.017	-	-0.028	-0.032	-	-
CH_3CO_2^-	-0.046	-	-0.056	-0.047	-	-
$\text{CH}_3\text{CH}_2\text{CO}_2^-$	-0.063	-	-0.054	-0.060	-	-
nPrCO_2^-	-0.060	-	-0.056	-0.054	-	-
isoPrCO_2^-	-0.060	-	-0.053	-0.046	-	-
nHeptCO_2^-	-0.062	-	-0.046	-0.041	-	-
$\text{CH}_2\text{ClCO}_2^-$	-0.011	-	-0.010	-	-	-
CF_3CO_2^-	+0.020	-	-0.008	-	-	-
CH_3SO_3^-	+0.053	-	+0.047	-	-	-

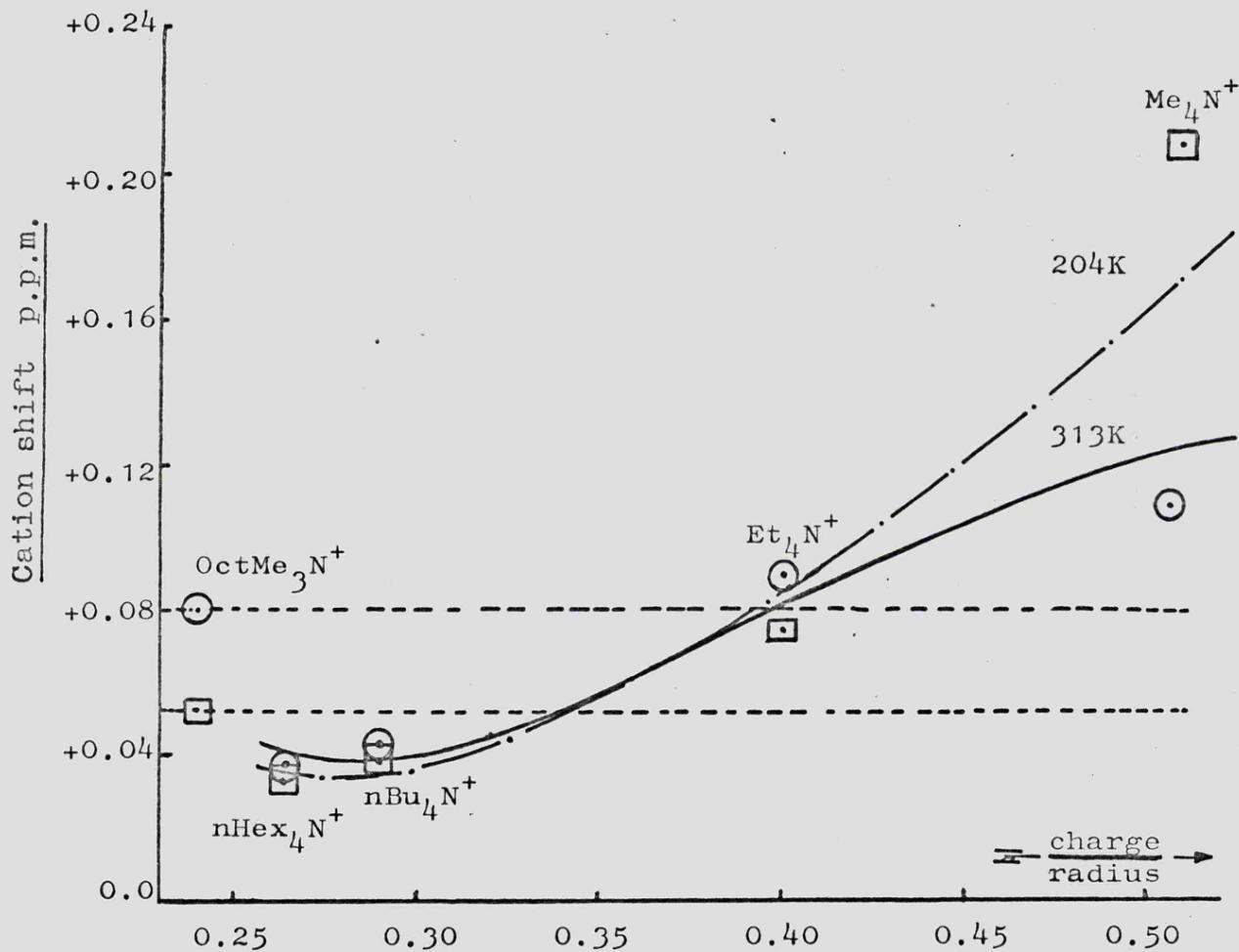


Figure 6.2 Molal ion shifts (methanolic solution)
plotted against charge/radius ratio.

Me_4N^+ - nHex_4N^+ , Data from ref. 54.

OctMe_3N^+ ,

This work, dashed line
represents uncertainty
of the radius parameter.

and $(C_5H_{11})_4N^+$. It is interesting to note that the shift of the asymmetric ion, octyl trimethyl ammonium, does show a slight upfield shift relative to n butyl ammonium. Such behaviour will be referred to, in the context of aqueous solution, in section 6 of this chapter.

6.5 Comparison of the present results for aqueous solutions of quaternary ammonium bromides with those reported by Hertz and Spalthoff.

The normally accepted behaviour of quaternary ammonium ions in water would be expected to produce entirely different n.m.r. results to those exhibited in methanolic solution. The 'clathrate cage'/'iceberg' effect should result in an observed downfield shift and, furthermore, the shifts should move to lower applied fields as the length of the alkyl chain of the ions increases. The shifts of these ions would be expected to resemble the downfield ones reported for aqueous solutions of tertiary butyl alcohol.⁸⁹

The often quoted results of Hertz and Spalthoff,³⁶ however, appear to be contrary to any theory proposing a structure forming interaction which increases in intensity as the alkyl chain of the cation lengthens. Table 6.3 lists the results of Hertz and Spalthoff for the bromides at 298K together with those obtained in the present work. Marked discrepancies (which are outside the limits of quoted experimental errors) are apparent, for all ions with the possible exception of n propyl ammonium.

Table 6.3

Salt shifts at 298K, p.p.m.		
Salt	Hertz & Spalthoff. ref. 36.	This work.
Me ₃ NBr	+0.044 ± 0.005	+0.080 ± 0.005
Et ₄ NBr	+0.043 "	+0.071 "
nPr ₄ NBr	+0.080 "	+0.072 "
nBu ₄ NBr	+0.095 "	+0.073 "

It is tentatively suggested that two factors are, in the main, responsible for these discrepancies;

- i) In the former work 0.3 molal tertiary butyl alcohol solution was used as 'solvent', the tertiary butyl protons being used as an internal reference.
- ii) In order to determine the molal salt shift, Hertz and Spalthoff used quaternary ammonium bromide concentrations of up to 6 molal, employing approximately eight experimental points over the total range.

It is well known that tertiary butyl alcohol imparts a downfield shift to water protons at 298K.⁸⁹ The simple monohydric alcohols in general, when present in small quantities, cause an enhancement of the water structure. The effect is especially marked for t butyl alcohol,^{86,93-96}

probably because of the compact shape of the molecule.

The underlying downfield trend due to the presence of n butyl alcohol, could partially account for the smaller salt shift values found for the tetra methyl and ethyl ammonium bromides by Hertz and Spalthoff. It is also possible that antagonistic interactions between the quaternary ammonium ions and the alcohol could also adversely affect the results.

The salt shift of tetra n butyl ammonium bromide is found to be less than that quoted by Hertz and Spalthoff. Clearly an alternative explanation has to be found for this discrepancy. Figures 6.3 and 6.4* show plots of the salt shift versus concentration found for $n\text{Bu}_4\text{NBr}$ at 273 and 298K (measured at 60 MHz). There is an evident inflexion in the curves, occurring at approximately 0.5 molal. Such behaviour results in a smaller infinite dilution salt shift (+0.042 p.p.m.) than that evident at higher concentrations (+0.103 p.p.m.). In order to confirm this unusual result, the tetra n butyl ammonium bromide salt shift has also been measured at 220 MHz, at this frequency more accurate n.m.r. shifts for small salt concentrations can be obtained. Figure 6.5 shows the results of this 220 MHz study, the limiting salt shift at infinite dilution confirms the 60 MHz result. It may well be that Hertz and Spalthoff have determined the final slope of the $n\text{Bu}_4\text{NBr}$ salt shift plot. The 'linear' relationship they report (measured at 25.5 MHz), being determined over a large concentration range, could easily absorb the initial behaviour.

* Figure 6.4 is included by kind permission of a colleague, the shifts were measured as part of a related study.¹¹⁹

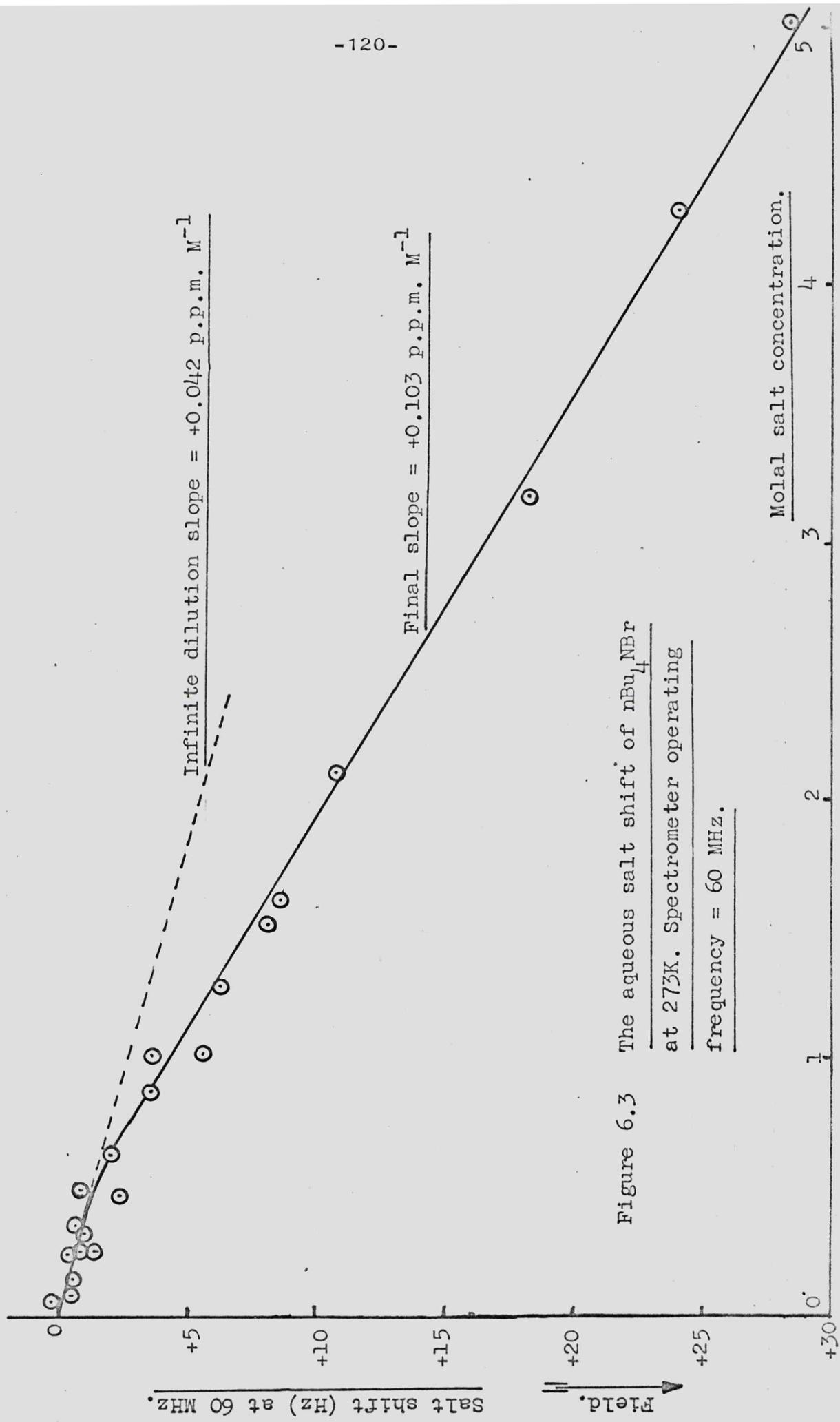


Figure 6.3 The aqueous salt shift of nBu_4NBr at 273K. Spectrometer operating frequency = 60 MHz.

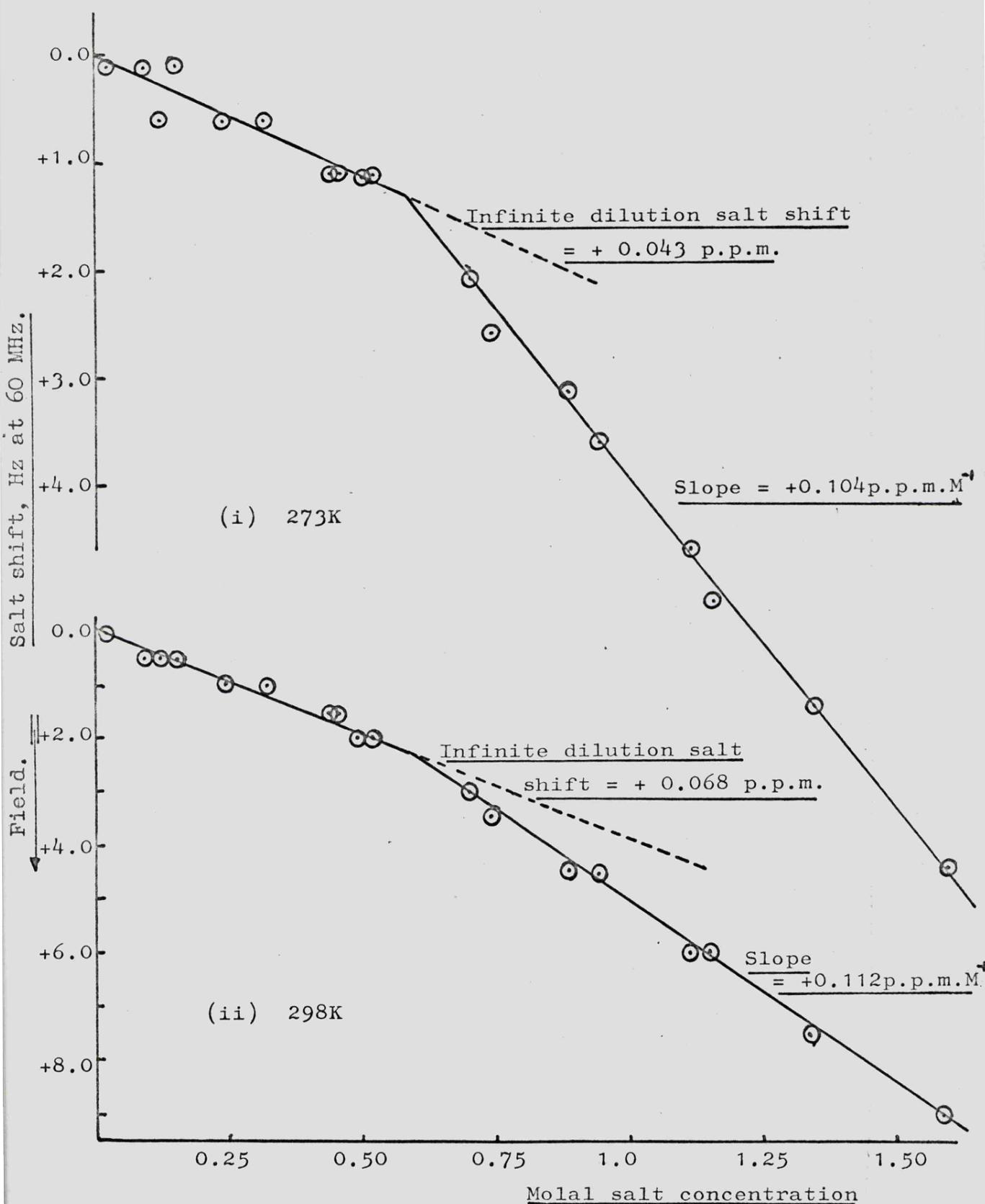


Figure 6.4 Aqueous salt shift of $n\text{Bu}_4\text{NBr}$.

spectrometer frequency = 60 MHz.

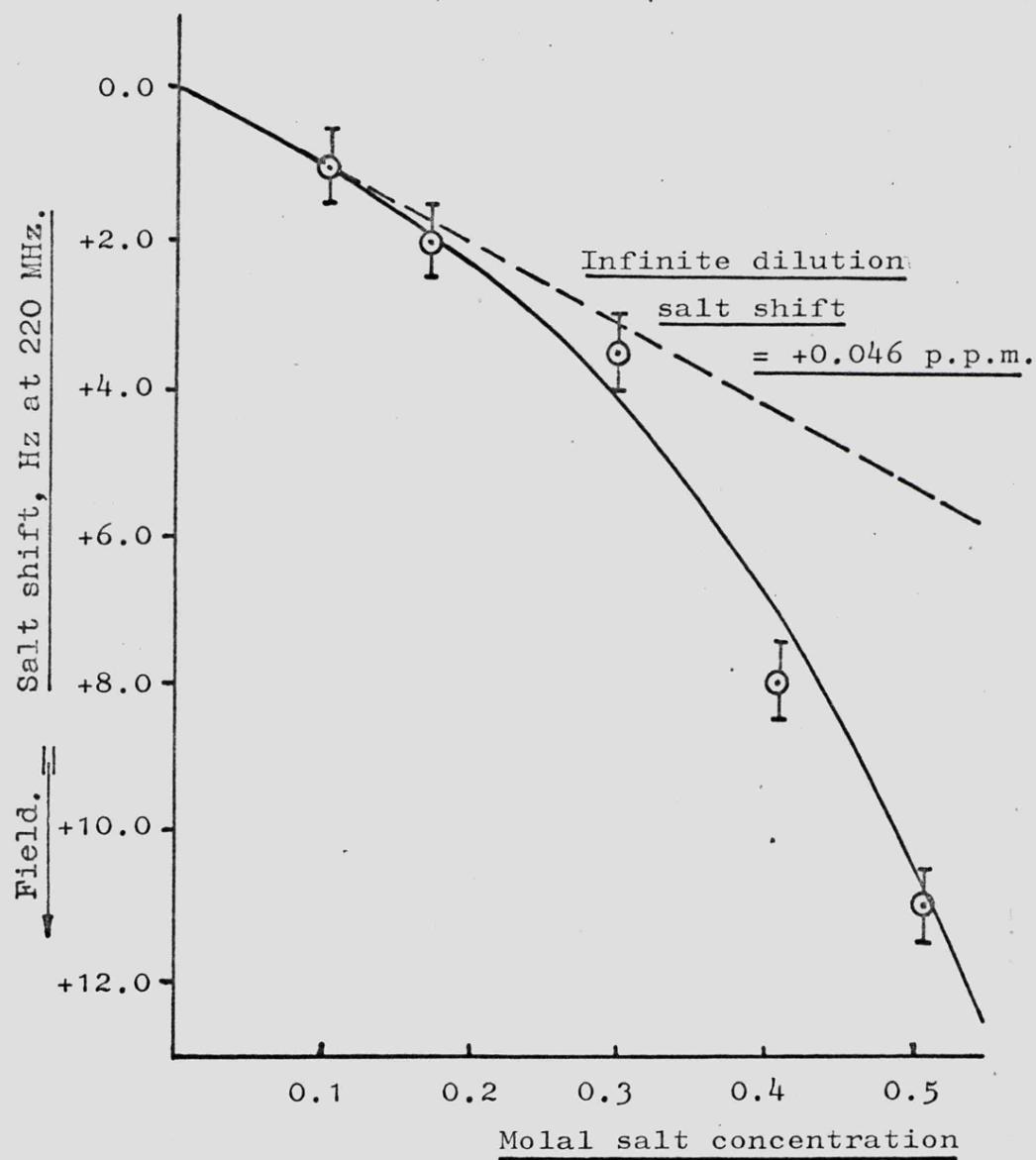


Figure 6.5 Aqueous salt shift of $n\text{Bu}_4\text{NBr}$ at 273K
spectrometer operating frequency = 220 MHz.

A possible explanation of the behaviour of the tetra *n* butyl ammonium bromide salt shift plot can be found by comparing the final slope, i.e. that beyond ~ 0.5 molal, with that of the bromide ion shift. The initial salt shift slope is taken to be due to the direct summation of the effect of the cation and the anion, the final slope being due to the anion only. This means that the tetra *n* butyl ammonium ion is assumed to have produced its maximum effect on the water structure when the salt concentration has reached approximately 0.50 molal. If this is the case, then the final slope should approximate to the shift of the bromide ion. The value found for the final slope at 273K is +0.103 p.p.m., this value compares favourably with the value of δBr^- at 273K, namely +0.113 p.p.m. This type of behaviour leads to concentration dependent shift plots as shown in Figure 6.6.

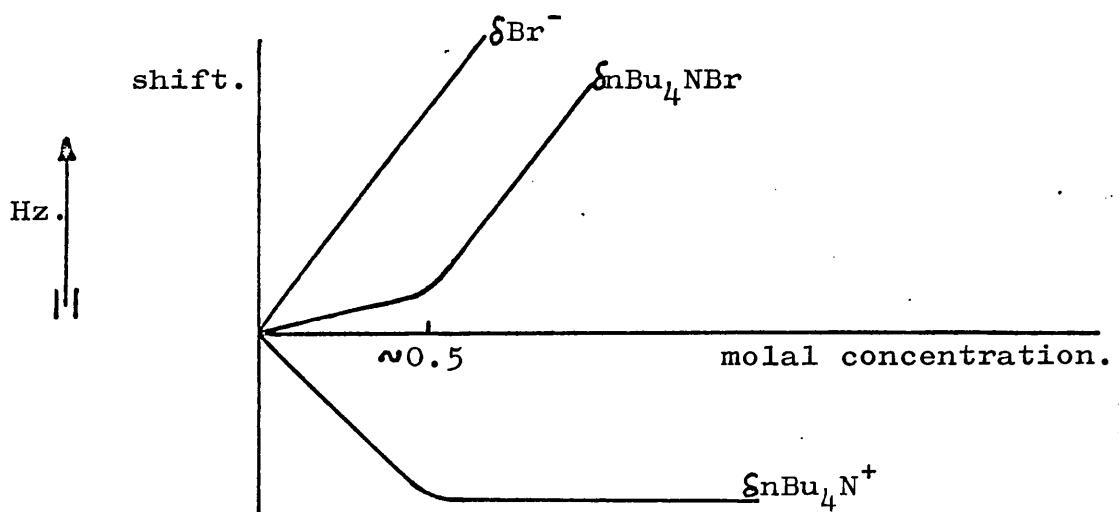


Figure 6.6 A possible form of the concentration dependent shift plots for the tetra *n* butyl ammonium bromide constituent ions.

It may well be that the type of behaviour indicated in Figure 6.6 is evident for other quaternary ammonium ions. If 220 MHz spectrometers were more readily available, such behaviour would seem worthy of further investigation.

The 'levelling off' of the shift of the tetra n butyl ammonium ion could be due to the formation of micelles. Wirth⁵³ has suggested that ethyl ammonium bromide forms micelles above a concentration of 4 molal and tetra n propyl ammonium bromide above 1.4 molal, if this trend continues then the tetra n butyl ammonium ion could well form micelles at or near 0.5 molal. Micellization removes hydrocarbon chains from contact with the water,⁵¹ consequently a reduced cation shift should become evident at concentrations in excess of the c.m.c. (critical micelle concentration).

It is interesting to note that if the above analysis is correct, then the bromide ion shift at 298K should compare with Hertz and Spalthoff's salt shift for tetra n butyl ammonium bromide, the relevant values are;

δ_{Br^-} , this work (298K).	<u>+0.092</u> p.p.m.
$\delta_{\text{nBu}_4\text{NBr}}$, Hertz & Spalthoff (298K).	<u>+0.095</u> p.p.m.
$\delta_{\text{nBu}_4\text{NBr}}$, this work (298K), initial.	<u>+0.073</u> p.p.m.
" " " " final.	<u>+0.112</u> p.p.m.

The values quoted are seen to be in reasonable agreement.

The occurrence of effects such as those described above, once again emphasises the need for measuring accurate infinite dilution salt shifts when studying ion-solvent interactions.

6.6 The behaviour of quaternary ammonium ions in aqueous solution.

The following factors would appear to be of direct relevance when interpreting the shifts of the quaternary ammonium ions in aqueous solution.

- i) Hydrophobic interactions.
- ii) Clathrate cage formation.
- iii) The symmetry of the ion.
- iv) Thermal motion of the hydrocarbon chains.
- v) Solvent temperature effects.

It would be expected that a correlation should exist between the size of these ions (length of the hydrocarbon chain) and the molal cation shift. In order to test this a set of values of ionic radius for the quaternary ammonium ions is necessary, unfortunately such values are difficult to estimate. In the past two main approaches have been employed;⁹⁷

- a) Using the summation of C-C, C-H and C-N bond lengths, i.e. a molecular model approach.
- b) Calculated from limiting ionic mobilities by making use of Stoke's law.

The values used in this work are based on a method which utilizes the continuity of cation shift versus charge/radius plots through the series K^+ to nBu_4N^+ . The method is fully described in appendix 2. Table 6.4 gives the values of the ionic radii used in this chapter. It should be noted that the values of ionic radius used are not critical to any of the arguments to be given, indeed

the radius and charge/radius plots are more of an aid to presentation.

Table 6.4

Ion	Radius p.m.	Charge/radius.
Me ₄ N ⁺	198.0	0.505 x 10 ⁻²
Et ₄ N ⁺	251.0	0.400 "
nPr ₄ N ⁺	303.0	0.330 "
nBu ₄ N ⁺	345.0	0.290 "
nHex ₄ N ⁺	380.0	0.264 "

Figure 6.7 shows a plot of salt shift versus radius, for temperatures in excess of 298K there appears to be a shift to higher applied fields as the hydrocarbon chain of the ion lengthens. For these elevated temperatures the present results have the same trend (upfield) as those of Hertz and Spalthoff,³⁶ however, at lower temperatures the trend reverses. The more meaningful cation shifts are plotted in Figure 6.8. The contrasting behaviour of these ions in methanolic and aqueous solution is apparent (cf Figure 6.2). The large quaternary ammonium ions leave methanol relatively undisturbed, whereas in aqueous solution the effect of the same ions on the water structure is both marked and noticeably temperature dependent. The temperature dependences of the salt (R₄NBr) and the cation (R₄N⁺) shifts are shown in Figures 6.9 and 6.10 respectively.

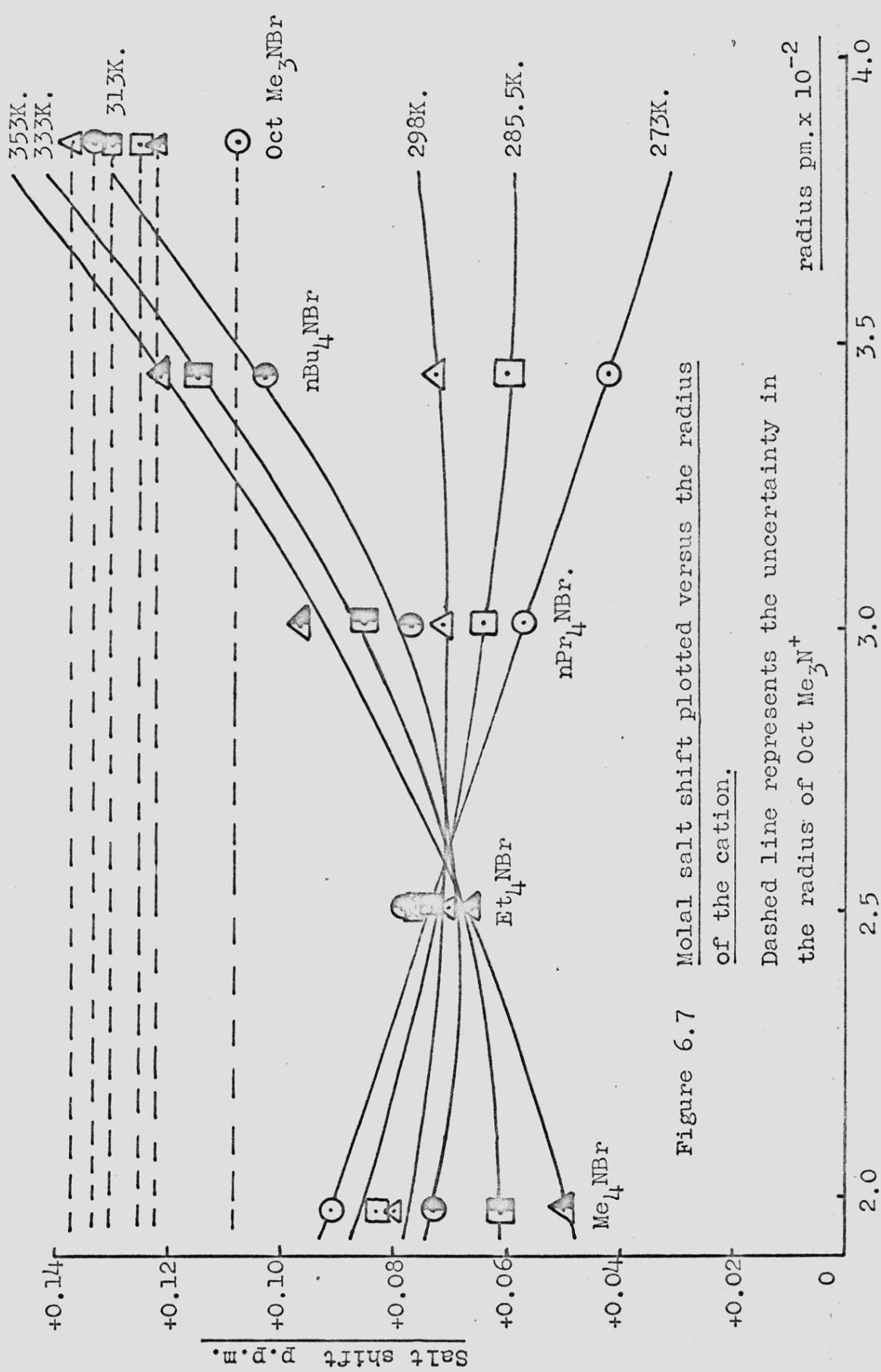


Figure 6.7 Molal salt shift plotted versus the radius of the cation.

Dashed line represents the uncertainty in the radius of Oct Me_3N^+

radius pm. $\times 10^{-2}$

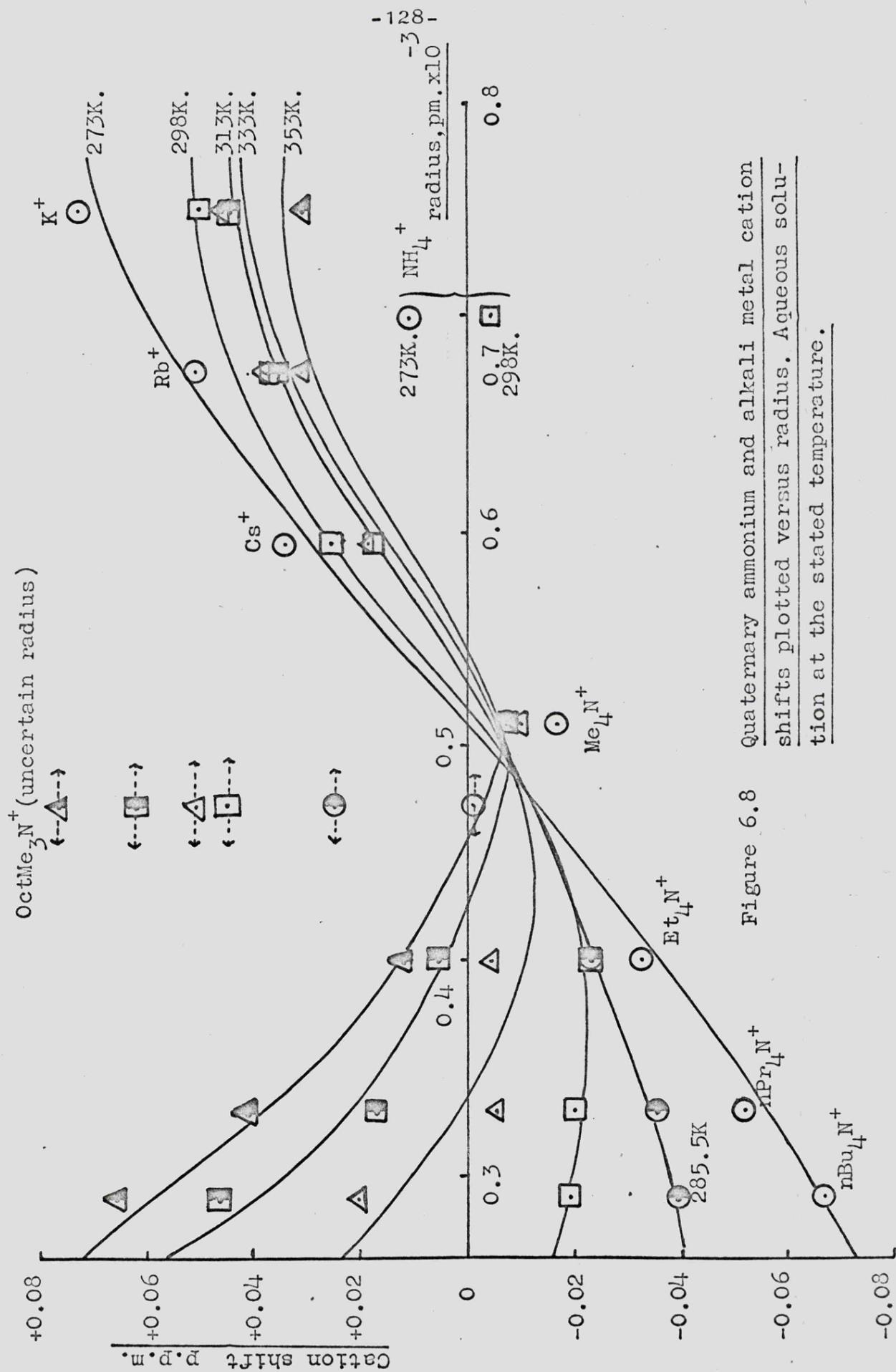


Figure 6.8
Quaternary ammonium and alkali metal cation
shifts plotted versus radius. Aqueous solu-
tion at the stated temperature.

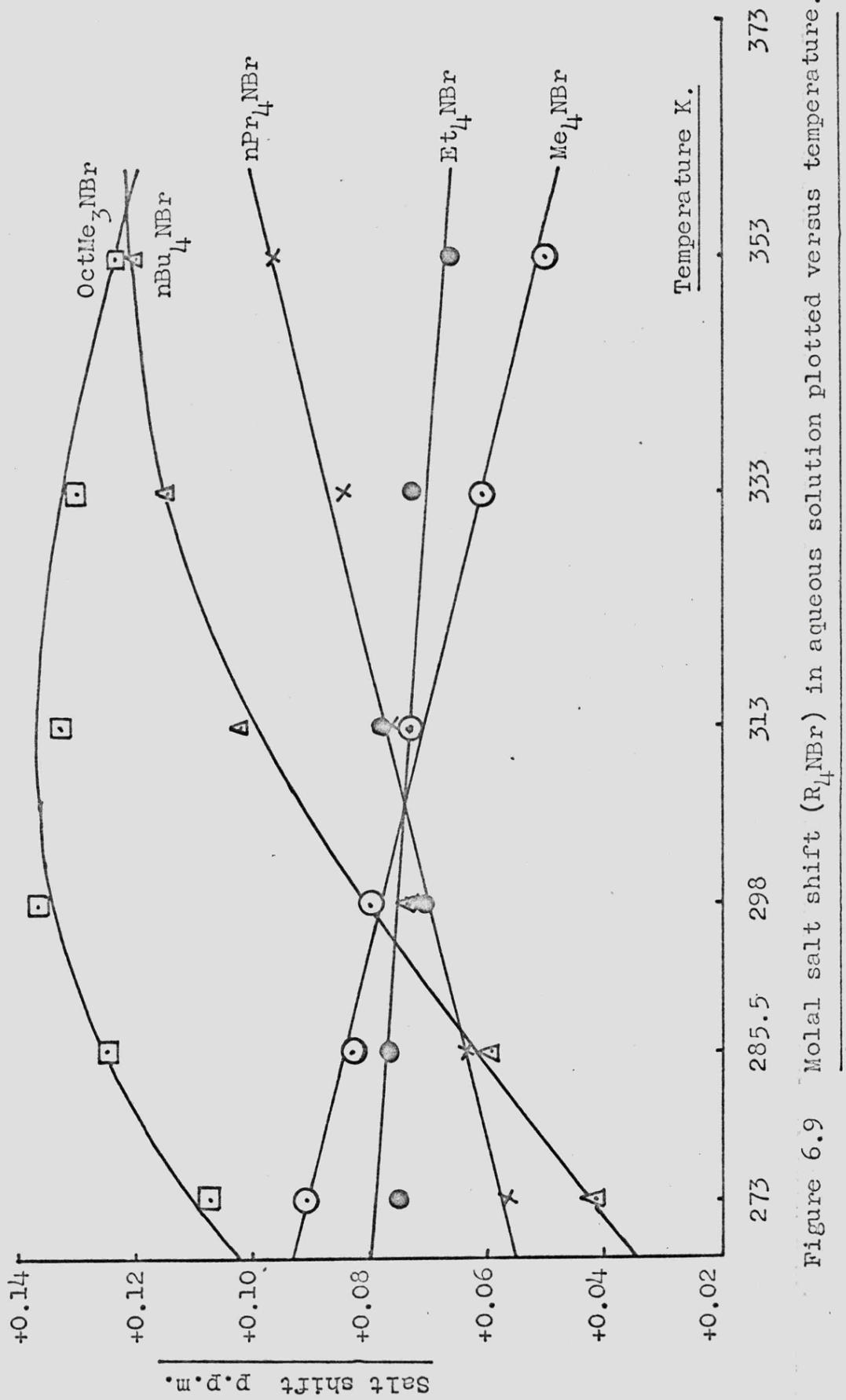


Figure 6.9 Molal salt shift (R_L₄NBr) in aqueous solution plotted versus temperature.

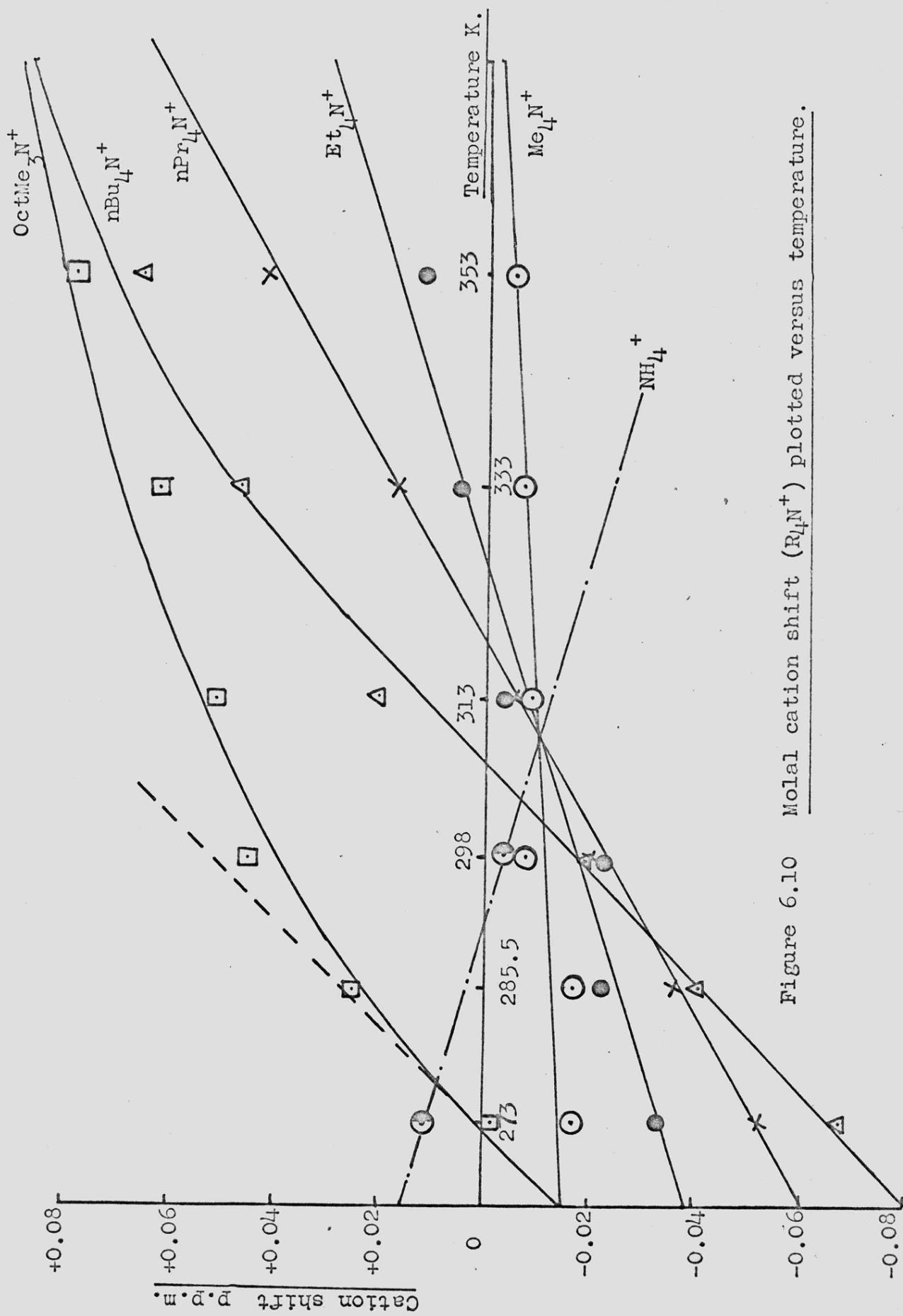


Figure 6.10 Molal cation shift (R_4N^+) plotted versus temperature.

Figure 6.8 shows that the quaternary ammonium ions seem to follow the downfield trend evident from K^+ to Cs^+ . There appears to be a common intersection at or near to the position of the tetra methyl ammonium ion, this ion has a small overall downfield shift at all the temperatures investigated and, furthermore, it is the least temperature sensitive of all the quaternary ammonium ions studied. The temperature coefficient of the tetra methyl ammonium ion, $\frac{d\delta}{dT} = +1.2 \times 10^{-4}$ p.p.m. K^{-1} . Gotto and Isemura⁴⁹ suggest that the tetra methyl ammonium ion induces the formation of clathrate cages, whereas, work concerning viscosity and Walden products^{98,99} indicates that the ion is an electrostrictive structure breaker. Evidence derived from heats of mixing¹⁰⁰ and entropy changes¹⁰¹ supports the latter conclusion. The results of the current work tend to ascribe to the Me_4N^+ ion a slight 'structure making' tendency at low temperatures (ca 273K), however, at more normal temperatures (> 300K) the ion (within the limits of experimental error) could be neutral in its effect on the water structure. It is interesting to compare the cation shift temperature coefficients for the two ions, Cs^+ and Me_4N^+ . If both ions formed similar clathrate cages⁴⁹ one might expect these coefficients to be of similar magnitude and sign. In fact, as is shown in Table 6.5, they are of opposite sign. Clathrate cage formation could well be the case for Me_4N^+ at low temperatures, however, self diffusion and spin-relaxation measurements⁷⁶ tend to rule out such behaviour for Cs^+ . It would seem reasonable to

expect the tetra methyl ammonium ion to be a 'transitional species', having properties resembling both the large mono-valent alkali metal cations and the long chain quaternary ammonium ions.

Table 6.5

Ion	$\frac{d\delta}{dT}$ p.p.m. K^{-1}
Li^+ , Na^+ , K^+	-5.6×10^{-4}
Rb^+ , Cs^+	-1.5×10^{-4}
NH_4^+	-5.7×10^{-4}
Me_4N^+	$+1.2 \times 10^{-4}$
Et_4N^+	$+6.3 \times 10^{-4}$
nPr_4N^+	$+11.4 \times 10^{-4}$
nBu_4N^+	$+19.2 \times 10^{-4}$
$OctMe_3N^+$	$+15.5 \times 10^{-4}$

The cation shifts for the remaining symmetrical ions (Et_4N^+ to nBu_4N^+) and the asymmetric octyl tri-methyl ammonium ion are found to be markedly temperature dependent (Figures 6.9 and 6.10). At temperatures below 286K the symmetric ions give an increasing downfield shift with increasing hydrocarbon chain length, implying an increasing structure making tendency with both increasing hydrocarbon chain length and decreasing solution temperature. As the solution temperature approaches 300K a transition becomes evident. The cation shifts at 298K, although still downfield overall, appear to level off for ions of a size exceeding that of tetra ethyl ammonium. Such behaviour may be indicative of the onset of an 'entropy'

effect, thermal agitation of the hydrocarbon chains opposing any structure making properties. Such entropy factors would be expected to be dependent both on hydrocarbon chain length and solution temperature. At temperatures in excess of 298K the 'entropy' effect seems to become dominant, as a result shifts to higher applied fields are observed as the hydrocarbon chain of the ion lengthens (Figures 6.7 and 6.9). A thermal effect of this type would be expected to be more marked for a long chain asymmetric ion such as octyl tri-methyl ammonium. The shifts found for this ion tend to confirm this prediction. At 273K the octyl tri-methyl ammonium ion shift is only slightly downfield, resembling that of the tetra methyl ammonium ion at this temperature. As shown in Figure 6.10, the octyl tri-methyl ammonium ion shift rapidly moves upfield as the solution temperature rises. In the limit, at or near to 373K, the shift of this asymmetric ion tends to that of the tetra n butyl ammonium cation. It is interesting to note, that even for methanolic solutions (cf Figure 6.2) the shift of the assymetric ion is upfield of that of tetra n butyl ammonium.

The symmetry of the quaternary ammonium ions appears to have a profound effect on any hydrophobic structure forming tendencies. Such behaviour would seem probable if any structure enhancement was based on incipient clathrate cage formation, the structures of which resemble those found for the salt hydrates (cf Figure 6.1).

6.7 The behaviour of carboxylic acid and related anions in aqueous solution.

Additional information concerning the hydrophobic effects of single hydrocarbon groups should be forthcoming from n.m.r. studies of carboxylic and related anions.

Clifford and co-workers^{51,74} have studied aqueous solutions of sodium alkyl sulphates in this way, they found that an increase in the hydrocarbon chain length resulted in the water protons shifting to higher applied fields. The results were interpreted in terms of an increase in the co-valent character of the water hydrogen bonds upon the addition of hydrocarbon chains, so avoiding the necessity of postulating structure breaking.

The infinite dilution anion shifts (hence avoiding problems resulting from micelle formation⁵¹) shown in Table 6.2, as already stated in Chapter 5, are mainly dependent on the basicity of the anion. Figure 6.11 (i) shows a plot of the anion shift versus pKa of the conjugate acid. The downfield shift of the acetate relative to the formate ion seems to be directly attributable to the greater basicity of the former ion.

Over and above the basicity dependence, hydrophobic effects of the hydrocarbon groups would be expected to be evident for these anions. Figure 6.11 (ii) shows a plot of the anion shift versus the number of carbon atoms in the alkyl group of the carboxylate. From acetate to propionate the shift becomes more negative, however, beyond this point a slight trend to higher applied fields

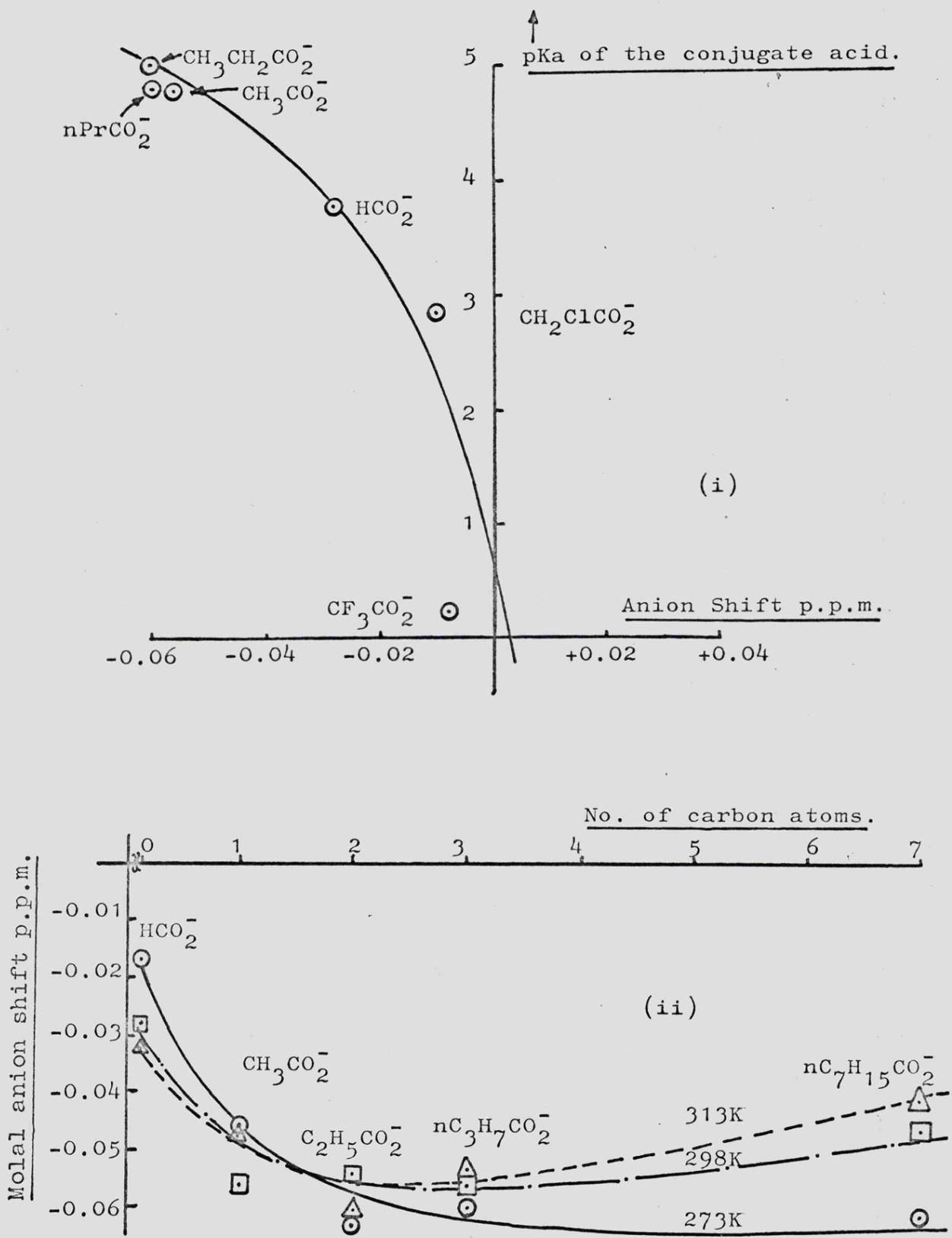


Figure 6.11 Molal anion shifts versus (i) pKa
and (ii) number of carbon atoms.

appears. This trend becomes more marked at higher temperatures. Such behaviour seems to indicate the presence of the previously mentioned 'entropy' effect for the longer chain carboxylate anions. Unfortunately, the smallness of the measured ion shifts means that too much emphasis cannot be placed on the results.

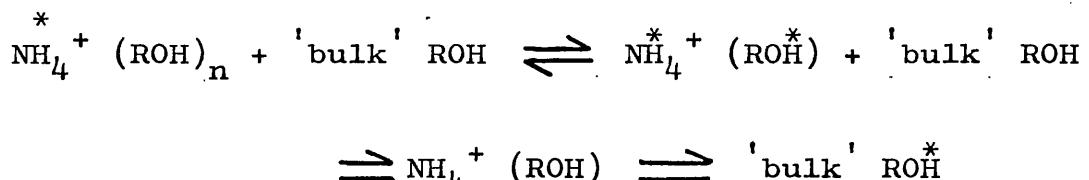
Greyson and Snell,¹⁰² using evidence based on entropies of transfer between heavy and normal water, have stated that there is a transition from structure breaking to making in passing from sodium formate to sodium caproate. Frank and Evans²⁴ postulate that the acetate ion causes the formation of 'icebergs'. The present results, being downfield for all the ions studied, support both of these statements. The basicity dependence of, and the 'entropy' effect on such carboxylate anion shifts must, however, be kept in mind.

6.8 The Ammonium Ion.

The ammonium ion, when viewed in the context of the cation shift versus charge/radius plots shown in Figure 6.8, seems to be anomalous. It has been stated that the ammonium ion by virtue of its tetrahedral shape fits into the water structure, causing very little disturbance.^{24,46,77,103} In the present results the ion does seem to give a much reduced shift when compared with cations of a similar size (e.g. Rb^+ , K^+), however, the value is markedly temperature dependent. The ammonium ion temperature coefficient, $\frac{d\delta}{dT}$, is almost identical

with that of the Li^+ , Na^+ , K^+ group. The individual values are shown in Table 6.5. It follows therefore, by similar reasoning to that used in Chapter 5, that the value of the temperature coefficient suggests a solvation number of four. This number is compatible with the ammonium ion being tetrahedrally bonded into the water network.

The ammonium ion has been widely used as a reference for the purpose of sub-dividing n.m.r. salt shifts.⁴⁶ For such purposes it has usually been given a zero shift. The temperature dependence of the ammonium ion shift, given above, must warn against any use of this ion as a primary standard. The suitability of the ammonium ion as a reference for hydroxylic solvents has been questioned elsewhere.¹⁰⁴ The presence of an exchange between the ammonium and solvent hydroxylic protons was shown to take place in methanolic solution.



The author states that exchange mechanisms such as the one shown above must cast serious doubts on the use of the ammonium ion as a primary n.m.r. standard.

6.9 Summary.

The results of this study seem to support the theories that regard the water structure as being enhanced by the presence of ions containing hydrocarbon groups.

An important qualification to this statement is that of thermal conditions, as the temperature is increased the shifts of the more bulky ions pass through zero and become positive. This behaviour is comparable with that of neutral molecules such as t butyl alcohol.⁸⁹ The data for the asymmetric octyl tri-methyl ammonium ion suggests that the symmetry of the quaternary ammonium ions is an important factor in relation to any structure making properties. Such behaviour is understandable in terms of a 'clathrate cage' structural theory that has in the past been utilized to explain other spectroscopic and ultrasonic data.^{86,87,89} Enclathration of quaternary ammonium ions requires considerable organisation of neighbouring water molecules, transient structural effects for aqueous solutions will be strongly opposed by increased thermal motion and loss of bulk water structure. At elevated temperatures it seems that the long chain, and in particular the long chain asymmetric, ions enhance the disorganisation, such behaviour overshadowing any residual structuring effects. The marked temperature effects do strongly point to the presence of water-structure phenomena.

It is interesting to compare the present n.m.r. results with those of a near infra-red study on quaternary ammonium bromide solutions.¹⁰⁵ Although in the latter study it was not possible to separate out the effect of the bromide ion, the variation of the structure making/breaking tendencies of the salts as the temperature is

varied agrees with the n.m.r. results.

Arnett and Campion¹⁰⁶ have measured the heat capacities of aqueous solutions of quaternary ammonium bromides. Their results lead them to warn against drawing any conclusions concerning the behaviour of aqueous solutions of salts of this type that are based on a single experimental temperature.

CHAPTER SEVEN

N.M.R. STUDIES OF IONIC BEHAVIOUR IN NON AQUEOUS SOLVENTS

7.1 General introduction.

The purpose of this chapter is to collate some n.m.r. results concerning various non-aqueous solvents.

The solvents that have been studied are;

- i) Methanol
- ii) Ethanol
- iii) Ethylene diol
- iv) Liquid Ammonia

It should prove very informative to compare the behaviour of electrolytes in these solvents with that found in an aqueous environment.

The results are best presented under three main headings;

- a) The hydroxy solvents.
- b) Ion pair formation in methanol.
- c) Liquid ammonia as a solvent.

7.2 Ion-solvent interactions in the hydroxylic solvents.

7.2.1 Introduction.

Butler and Symons^{54,107,108} have carried out an extensive study of ion-solvent interactions in methanol, a preliminary investigation was also undertaken on certain ethanolic solutions. In the present work, the ethanolic study has been extended and a series of salt shifts measured in the related solvent, ethylene diol.

The simple alcohols, unlike water, freeze at very low temperatures. This property is extremely useful in that it allows the resolution of cation solvation shells, even for dilute salt solutions, by slowing down the rate of solvent exchange. If the exchange of solvent molecules between various environments is slow (τ_{\pm} c.a. 10^{-4} sec), n.m.r. spectra similar to that shown in Figure 4.1a are obtained. Spectra of this type have made it possible to determine a set of absolute ion shifts in methanol, such derivations are fully described in section 4.2.

Separate resonances for solvation shell and bulk hydroxylic protons have also been reported for ethanolic solutions, using temperatures below 213K.^{34,109} It should therefore prove possible, using an identical procedure to that employed for the methanolic solutions, to determine a set of absolute ethanolic ion shifts. This has been carried out, and the results obtained are given in section 7.2.2.

As a compliment to the study of the mono-hydric

alcohols, the behaviour of electrolytes in the di-hydric alcohol, ethylene diol, has also been studied. The configuration of the diol, providing two active sites, should give rise to interesting ion-solvent interactions. Unfortunately the resolution of separate cation solvation shell resonances is not possible for ethylene diol, at the low temperatures required for such spectra the viscosity of the solvent increases and so broadens any n.m.r. signals.¹¹⁰ The n.m.r. spectrum of a solution of magnesium perchlorate in this solvent is shown in Figure 7.1. Reference to this figure shows that even at the relatively high temperature of 260K the resonances of both the methylene and hydroxyl protons are appreciably broadened, at 230K they are so broad that they can hardly be detected. In an attempt to overcome this viscosity problem, the co-solvent acetone was added in order to reduce the solution viscosity to a tolerable level. Even with very high acetone concentrations (>60%) the resonances were still very broad, at 223K no separate resolved cation shell could be detected. For ethylene diol an alternative procedure for sub-dividing the measured salt shifts is therefore necessary. The procedure adopted to achieve the sub-division is described in section 7.2.2.

7.2.2 Results, referencing and sub-division of the salt shifts.

In all three cases, the solvents themselves were able to provide a suitable internal reference. The secon-

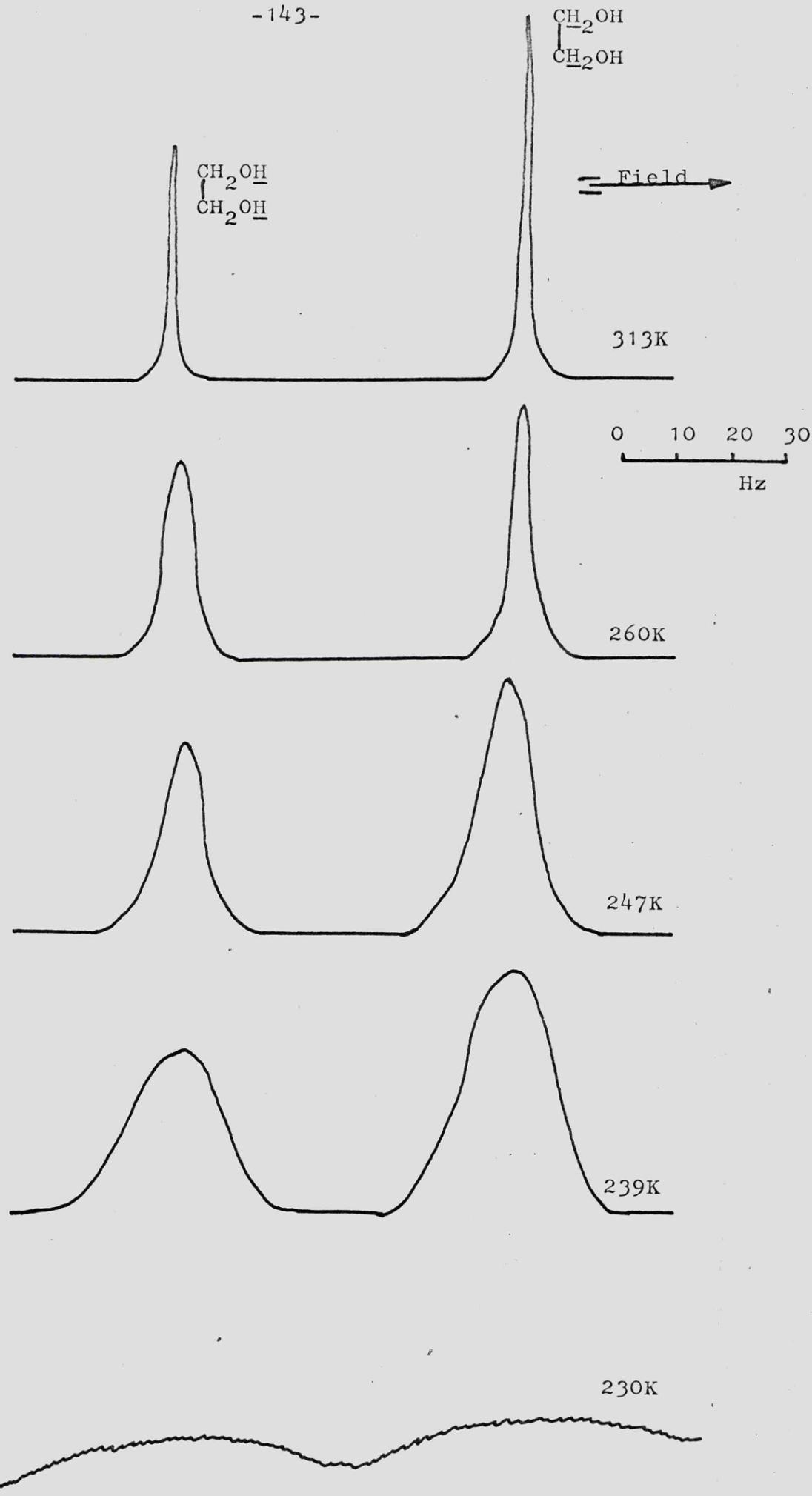


Figure 7.1 N.M.R. spectrum of $\text{Mg}(\text{ClO}_4)_2$ in ethylene diol.

dary reference, TMS, was used to test the suitability of such choices. There may be slight movements of the chosen reference resonance as the dissolved salt is varied,¹¹¹ however, the magnitude of such movements compared to the measured salt shifts is small and so they can be neglected without introducing serious errors. The individual resonances used for reference purposes were as follows;

Methanol; The methyl resonance.

Ethanol; The central line of the methyl triplet.

Ethylene diol; The methylene resonance.

Molal salt shifts measured during this study are given in Table 7.1. The results quoted for methanol, with the exception of that for octyl tri-methyl ammonium bromide, are taken from the work of Butler and Symons.⁵⁴

The insolubility of many of the alkali metal halides in ethanol is the reason for the many exclusions in Table 7.1 under this solvent. The ethanolic shifts quoted for the magnesium salts are taken from reference 111.

The salt shifts listed in Table 7.1 must be subdivided into ionic contributions before any discussion can be given. The procedure adopted for methanolic solutions has already been fully described (section 4.2). An identical procedure has been adopted for ethanolic solutions. Low temperature spectra essentially the same as those shown in Figure 4.1 are obtained for ethanolic solutions, an extra proton resonance from the methylene

Table 7.1

Salt	Methanol		Ethanol		Ethylene diol
	204K	313K	204K	313K	313K
LiCl	0.000	-0.116	+0.098	-0.055	-0.030
NaCl	-	-	-	-	+0.093
KCl	-	-	-	-	+0.161
RbCl	-	-	-	-	+0.147
CsCl	-	-	-	-	+0.121
KF	-0.108	-0.258	-	-	-0.195
NaI	+0.333	+0.250	+0.502	+0.311	+0.250
NaBr	+0.308	+0.158	-	-	+0.170
LiBr	+0.075	-0.040	+0.187	+0.141	-
Mg(ClO ₄) ₂	-0.050 ^b	-0.125	+0.283 ^b	+0.142	-
MgCl ₂	-0.216 ^b	-0.433	+0.007 ^b	-0.276	-
Me ₄ NBr	+0.350 ^a	+0.175 ^a	-	-	-
Et ₄ NBr	+0.216	+0.158	+0.265	+0.180	-
nPr ₄ NBr	-	-	+0.238	+0.160	+0.150
nBu ₄ NBr	+0.190	+0.116	+0.228	+0.158	+0.100
nHex ₄ NBr	-	-	-	-	+0.093
Me ₄ NC1	-	-	c	+0.093	+0.078
nBu ₄ NI	+0.200	+0.190	+0.280	+0.243	-
nHex ₄ NI	+0.200	+0.190	+0.268	+0.231	-
Et ₄ NC1	-	-	-	-	+0.080
OctMe ₃ NBr*	+0.190	+0.147	-	-	-
nHexane	0.00	0.00	-	+0.013	-
nC ₅ H ₁₁ OH	-	-	-	-	0.00
tBuOH	-	-	-	-	+0.001
2,2dimethoxy propane	+0.033	+0.033	-	-	-

Molal salt shifts (p.p.m.) at the quoted temperature.

a Approximate value, measured on solutions of up to 0.25M.

b Determined by combining the primary cation shift with the residual shift.

c Me₄NC1 is insoluble at 204K.

Methanolic shifts taken from ref. 54.

* Shift of OctMe₃NBr measured during this work.

group will, of course, be present for this solvent. The residual anion shifts in ethanol at 204K for the magnesium salts were determined as;¹¹

$$\delta_{\text{ClO}_4^-} (\text{Mg}(\text{ClO}_4)_2) = +0.208 \text{ p.p.m.}$$

$$\delta_{\text{Cl}^-} (\text{MgCl}_2) = +0.071 \text{ p.p.m.}$$

These reference ion shifts can be used to sub-divide the ethanolic salt shifts. The values of the ion shifts obtained in this way are shown in the third column of Table 7.2. The residual shift method is, however, only applicable to the determination of ion shifts at temperatures where separate solvation shell resonances can be resolved. At high temperatures an alternative method must be found. Butler and Symons⁵⁴ noted that the shift of the tetra nhexyl ammonium ion in methanol tended to a limiting value at both 204 and 313K. This type of behaviour is assumed to be exhibited in ethanolic solution, consequently the tetra nhexyl ammonium ion has been assigned the same shift at both 204 and 313K. It follows that the difference in the salt shifts for tetra nhexyl ammonium iodide at these two temperatures is wholly attributed to the iodide ion. The ethanolic ion shifts at 313K, derived in this way, are listed in column four of Table 7.2. It is encouraging to note that the values for the shift of the tetra nbutyl ammonium ion in ethanol at the two experimental temperatures are identical, as is also the case in methanolic solution.

The sub-division of the ethylene diol salt shifts

Table 7.2

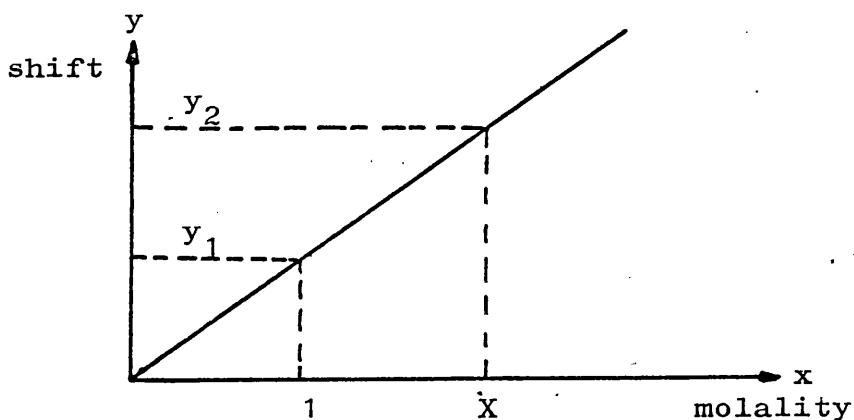
Ion	Methanol		Ethanol	
	204K	313K	204K	313K
Li ⁺	-0.062	-0.112	+0.027	-0.049
Na ⁺	+0.166	+0.090	+0.290	+0.136
K ⁺	+0.150	+0.116	-	-
Rb ⁺	+0.166	+0.116	-	-
Cs ⁺	+0.140	+0.116	-	-
Mg ²⁺	-0.300	-0.458	-0.135	-0.288
Me ₄ N ⁺	+0.208 ^a	+0.108 ^a	-	+0.087
Et ₄ N ⁺	+0.075	+0.090	+0.105	+0.090
nPr ₄ N ⁺	-	-	+0.078	+0.070
nBu ₄ N ⁺	+0.040	+0.040	+0.068	+0.068
nHex ₄ N ⁺	+0.033	+0.033	+0.056	+0.056
OctMe ₃ N ⁺	+0.050	+0.079	-	-
F ⁻	-0.258	-0.375	-	-
Cl ⁻	+0.066	-0.010	+0.071	+0.006
Br ⁻	+0.140	+0.068	+0.160	+0.090
I ⁻	+0.166	+0.158	+0.212	+0.175
ClO ₄ ⁻	+0.125	+0.166	+0.208	+0.215
nHexane	0.00	0.00	-	+0.013
2,2 dimethoxy propane.	+0.033	+0.033	-	-

Molal ion shifts (p.p.m.) at the quoted temperatures.

a Approximate value due to insolubility of tetra methyl ammonium salts.

is even more intractable. The lack of low temperature data, a direct consequence of viscosity effects, precludes any measurement of residual anion shifts. It is therefore necessary to resort to an indirect method. Such a method can be found by considering the behaviour of the tetra alkyl ammonium ions in the hydroxylic solvents.

When comparing salt shifts measured in various related solvents (in this case the alcohols) it is not valid to directly compare infinite dilution molal parameters. The parameter which must be employed is the infinite dilution shift of a mole of solvent hydroxyl protons brought about by the presence of one mole of solute particles. Shifts of this type will be referred to, for convenience of subsequent reference, as mole mole⁻¹ shifts. The interconversion between the molal and this latter parameter is made as follows:



$$y = m \cdot x, \text{ where } y_1 = m = \text{molal salt shift at infinite dilution.}$$

$$\text{If } X = \text{molality} \equiv 1 \text{ mole mole}^{-1}$$

$$\text{then } X = \frac{1}{W} \cdot 10^3, \text{ where } W = \text{molecular weight of the solvent.}$$

$$\therefore \text{mole mole}^{-1} \text{ salt shift at infinite dilution.} = y_2 = m \cdot X = m \cdot \frac{10^3}{W}$$

The individual ion shifts for methanol and ethanol, converted to a mole mole⁻¹ basis, are listed in Table 7.3. It is noted that the shifts for the tetra n hexyl ammonium cation in these two solvents, on a mole mole⁻¹ basis, are very nearly identical. Such behaviour would tend to suggest that the shift of this bulky ion, in the hydroxylic solvents, is moving towards a limiting value. Molal cation shift plots such as those shown in Figure 7.2 tend to support this hypothesis. The assumption is now made that the limiting shift of the tetra n hexyl ammonium cation, c.a. 1.15 p.p.m. (average), would also be expected in ethylene diol solution. There is, however, an important qualification that must be made for this latter solvent, namely, that it is di-hydric. One mole of ethylene diol contains two moles of 'active' hydroxyl protons, consequently allowances must be made when computing mole mole⁻¹ shifts. Table 7.4 lists molal, mole per two moles of hydroxyl and mole per mole of hydroxyl (mole mole⁻¹) salt shifts in ethylene diol at 313K. By making use of the assumed limiting tetra n hexyl ammonium cation shift (+1.15 p.p.m. per mole of hydroxyl protons) the mole mole⁻¹ salt shifts in ethylene diol have been sub-divided, the resulting ion shifts are listed in Table 7.5 together with (for comparison) those found in methanol and ethanol.

7.2.3 Discussion.

Butler and Symons⁵⁴ have accommodated their methanolic ion shifts in terms of a model which considers the relative effects of hydrogen bonding to methanol and

Table 7.3

Ion	Methanol		Ethanol	
	204K	313K	204K	313K
Li ⁺	-1.94	-3.50	+0.63	-1.12
Na ⁺	+5.19	+2.81	+6.60	+3.10
K ⁺	+4.69	+3.63	-	-
Rb ⁺	+5.19	+3.63	-	-
Cs ⁺	+4.37	+3.63	-	-
Mg ²⁺	-9.38	-14.35	-3.08	-6.58
Me ₄ N ⁺	+6.53 ^a	+3.37 ^a	-	+1.90
Et ₄ N ⁺	+2.34	+2.81	+2.49	+2.05
nPr ₄ N ⁺	-	-	+1.77	+1.59
nBu ₄ N ⁺	+1.25	+1.25	+1.57	+1.57
nHex ₄ N ⁺	+1.03	+1.03	+1.27	+1.27
OctMe ₃ N ⁺	+1.56	+2.47	-	-
F ⁻	-8.10	-11.71	-	-
Cl ⁻	+2.06	-0.31	+1.62	+0.13
Br ⁻	+4.37	+2.15	+3.65	+2.05
I ⁻	+5.19	+4.94	+4.82	+3.98
ClO ₄ ⁻	+3.90	+5.19	+4.75	+4.90
n Hexane	0.00	0.00	-	+0.29
2,2dimethoxy propane	+1.03	+1.03	-	-

Mole Mole⁻¹ ion shifts at the quoted temperatures.

a Approximate value due to insolubility of tetra methyl ammonium salts.

Shifts in p.p.m., positive shifts are upfield.

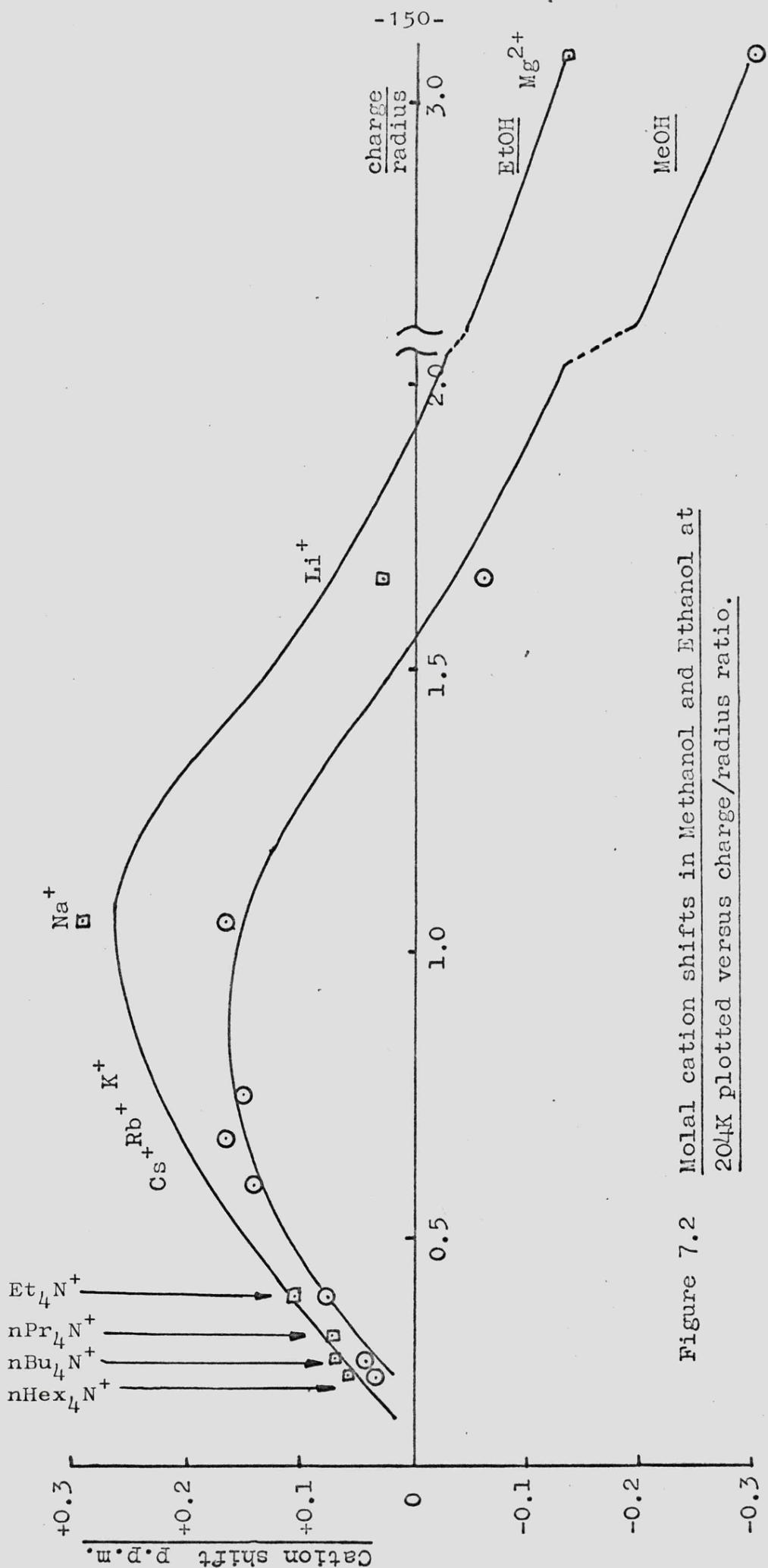


Figure 7.2 Molal cation shifts in Methanol and Ethanol at 204K plotted versus charge/radius ratio.

Table 7.4

Salt	Molal	Mole per two moles hydroxyl	Mole Mole ⁻¹
LiCl	-0.030	-0.48	-0.96
NaCl	+0.093	+1.50	+3.00
KCl	+0.161	+2.60	+5.20
RbCl	+0.147	+2.37	+4.74
CsCl	+0.121	+1.95	+3.90
KF	-0.195	-3.15	-6.30
NaI	+0.250	+4.03	+8.06
NaBr	+0.170	+2.74	+5.48
nPr ₄ NBr	+0.150	+2.42	+4.84
nBu ₄ NBr	+0.100	+1.61	+3.22
nHex ₄ NBr	+0.093	+1.50	+3.00
Me ₄ NCl	+0.078	+1.26	+2.52
Et ₄ NCl	+0.080	+1.29	+2.58
nC ₅ H ₁₁ OH	0.00	0.00	0.00
tBuOH	+0.001	+0.02	+0.03
Salt shifts (p.p.m.) in ethylene diol at 313K.			
positive shifts are upfield.			

Table 7.5

Ion	Methanol	Ethanol	Ethylene diol
Li ⁺	-3.50	-1.12	-0.33
Na ⁺	+2.81	+3.10	+3.63
K ⁺	+3.63	-	+5.83
Rb ⁺	+3.63	-	+5.37
Cs ⁺	+3.63	-	+4.53
OctMe ₃ N ⁺	+2.47	-	-
Me ₄ N ⁺	+3.37	+2.03	+3.15
Et ₄ N ⁺	+2.81	+2.05	+3.21
nPr ₄ N ⁺	-	+1.59	+2.99
nBu ₄ N ⁺	+1.25	+1.57	+1.37
nHex ₄ N ⁺	+1.03	+1.27	+1.15
F ⁻	-11.71	-	-12.13
Cl ⁻	-0.31	+0.13	-0.63
Br ⁻	+2.15	+2.05	+1.85
I ⁻	+4.94	+4.90	+4.43
Mole Mole ⁻¹ ion shifts (p.p.m.) at 313K.			
positive shifts are upfield.			

the bonding of methanol to the ions present. Such a model does not need to invoke any major contributions from structural changes remote from the ion. In chapter five of this thesis a similar model was proposed for aqueous solutions of diamagnetic ions, with the noteable exception of the quaternary ammonium species. The mole mole⁻¹ ion shifts for the related solvents methanol, ethanol and ethylene diol, listed in Table 7.5, show remarkable similarities. It appears therefore that the previously mentioned model will accommodate all three hydroxy solvents.

Anion shifts.

The values obtained for the halide ion shifts are very similar, indeed, within the the limits of computational and experimental error they could well be identical. Figure 7.3, being a plot of mole mole⁻¹ ion shift versus charge/radius ratio, underlines this behaviour, only one line is needed to accommodate the experimental points for all three solvents. The shift to higher applied fields that occurs through the series $F^- \rightarrow I^-$ is also found for the hydrogen halides in both the liquid and gaseous phase,¹¹⁰ pointing to the importance of short range interactions. In order to test such correlations plots of average of average mole mole⁻¹ shifts for the three solvents (listed in Table 7.6) versus bond dissociation energy and the liquid phase shift of the hydrogen halides are shown in Figures 7.4 and 7.5. Such correlations, as in the case of aqueous solutions, seem once again to point to the importance of short range interactions when

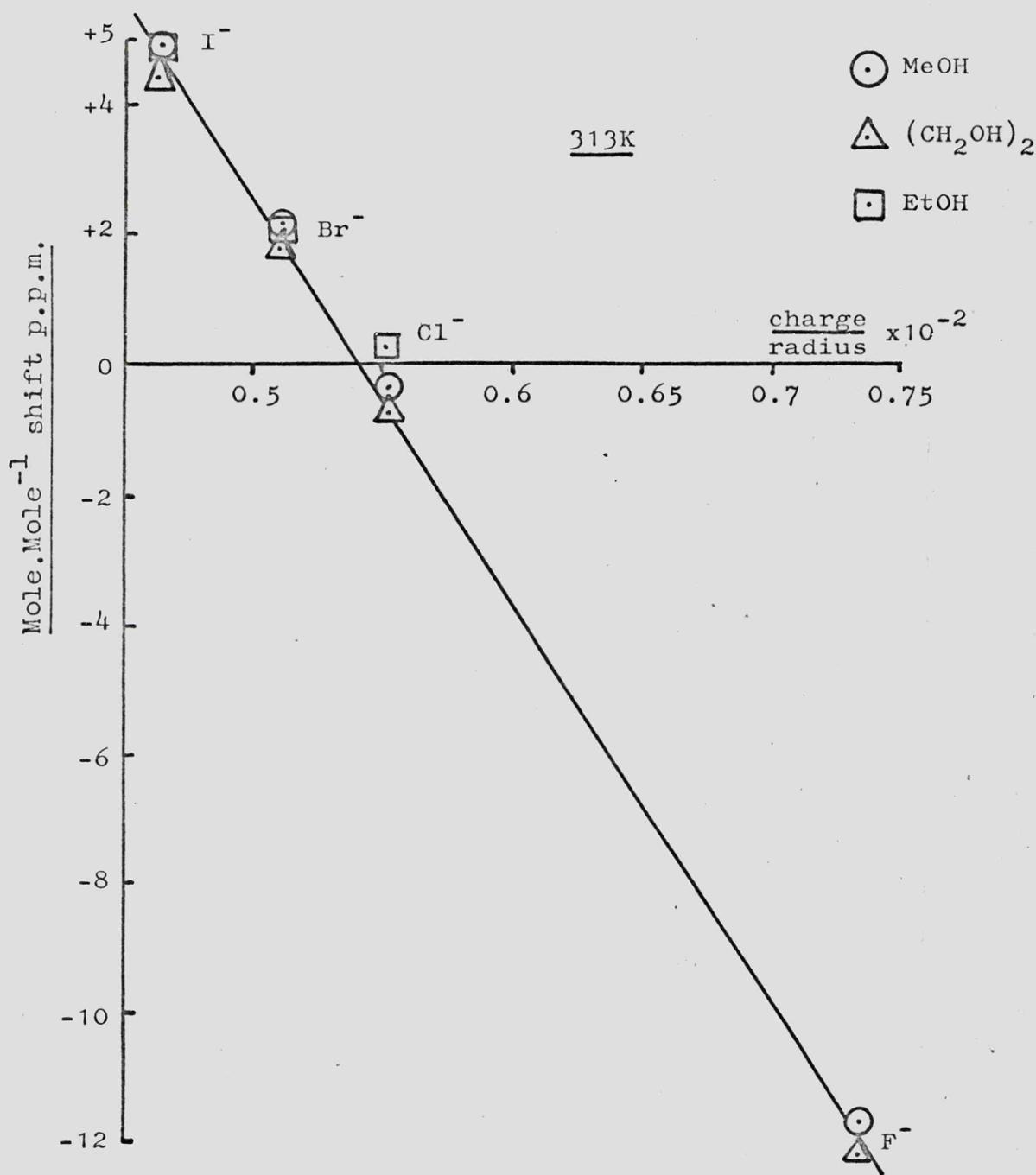
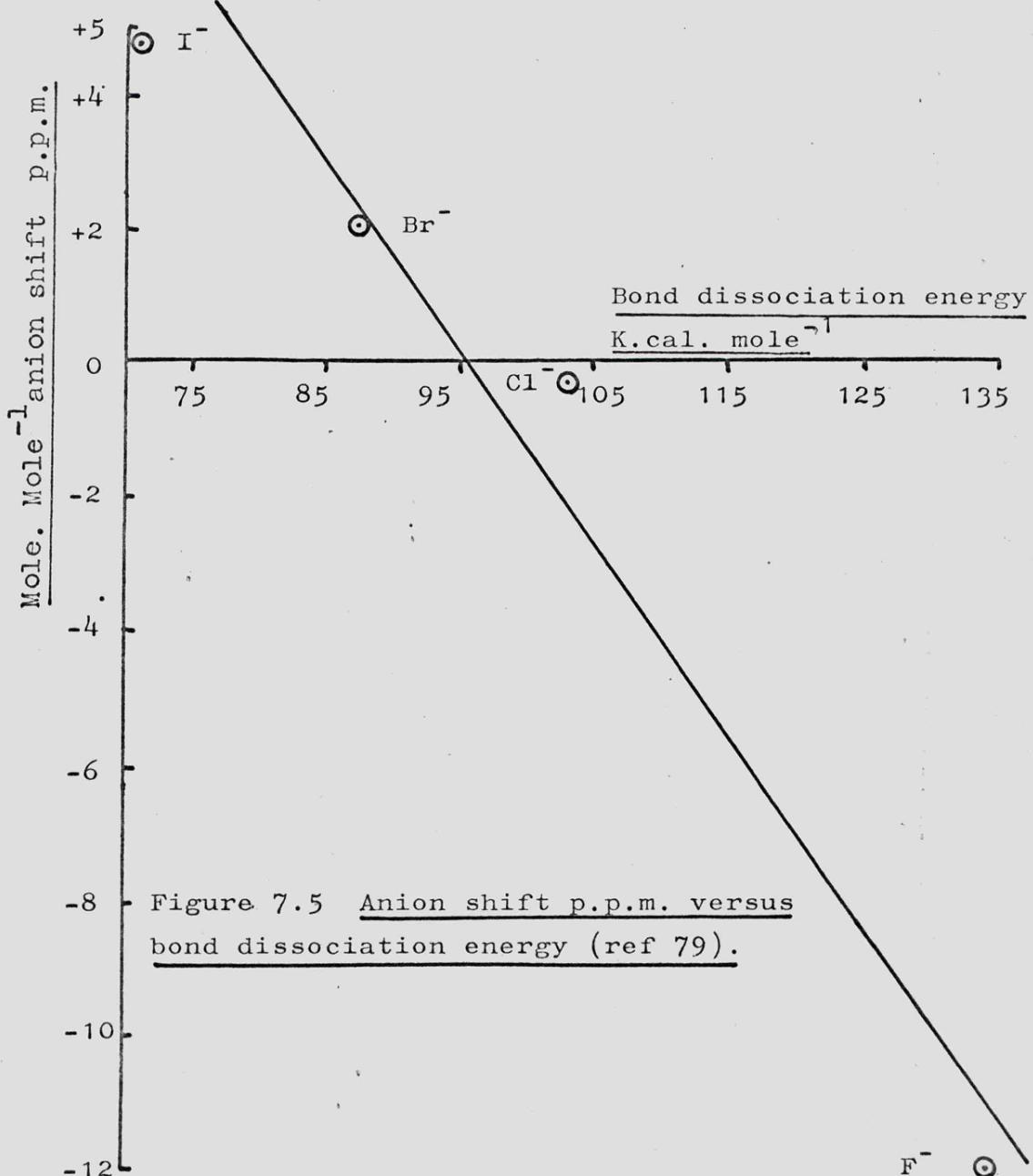
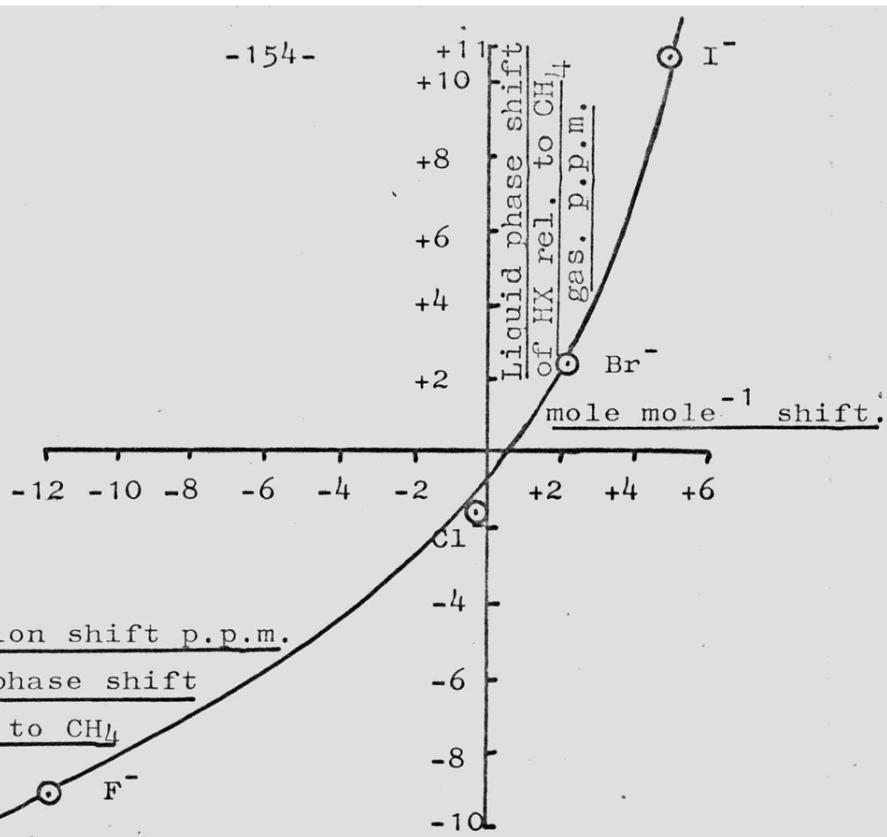


Figure 7.3 Mole Mole⁻¹ anion shifts in the hydroxy solvents versus charge/radius ratio.

Table 7.6

Anion	Average mole mole ⁻¹ shift. (methanol, ethanol and ethylene diol.) 313K.
F^-	-11.92 p.p.m.
Cl^-	-0.27 "
Br^-	+2.02 "
I^-	+4.76 "



discussing n.m.r. anion shifts, strong bases tending to give rise to downfield shifts (see also ref. 54).

It seems that the behaviour of the halide ions in the alcohols is, as far as n.m.r. is concerned, that of an anion directly interacting with a hydroxyl proton.

i.e. $\text{RO}-\text{H} \dots \text{X}^-$

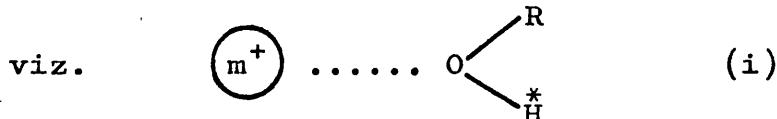
(c.f. the angular configuration postulated in Chapter five)

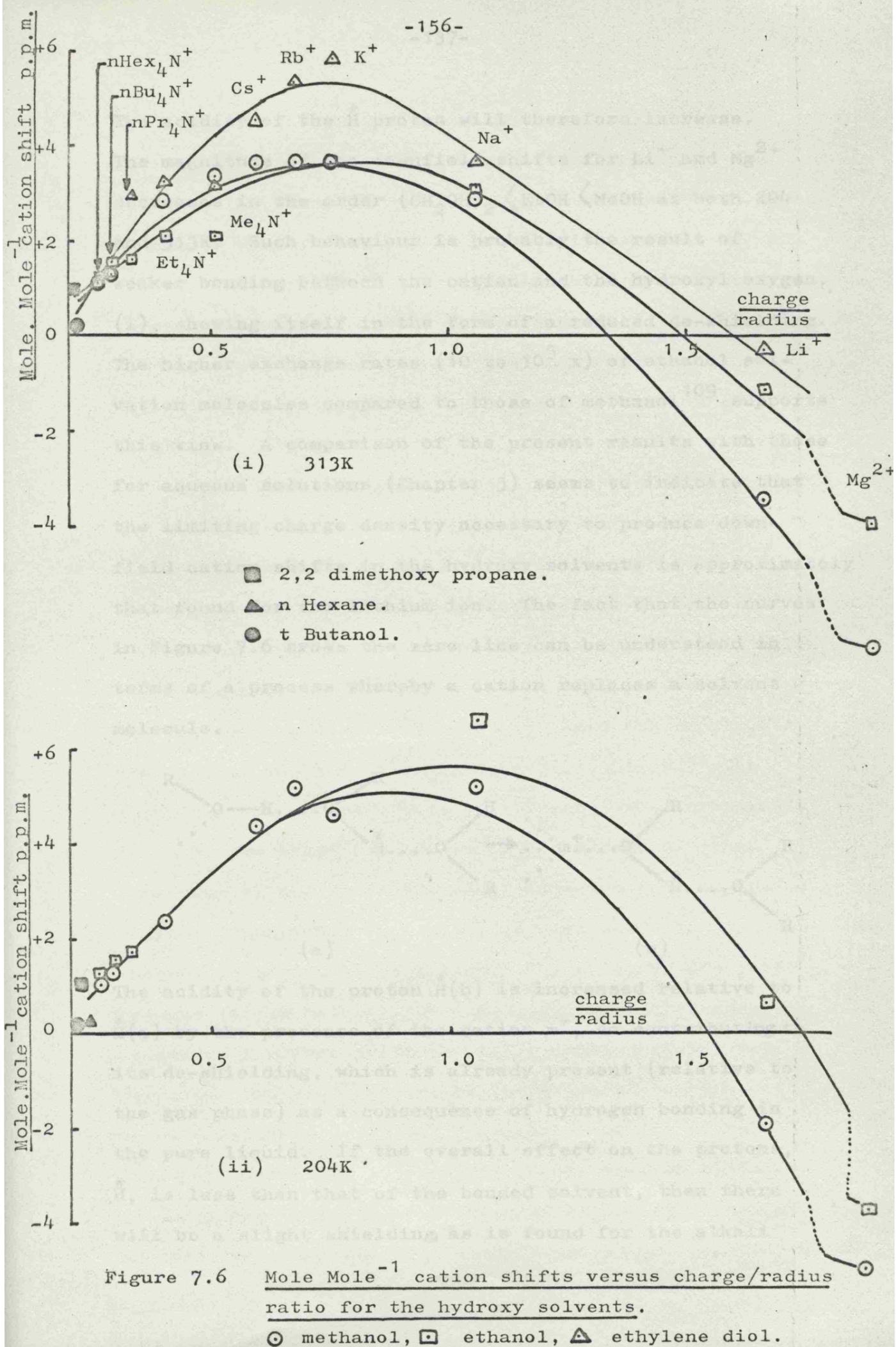
The nature of the alkyl group, R, seems to be of little significance. It is particularly encouraging that the di-hydric solvent, ethylene diol, is compatible with the mono-hydric alcohols in this respect.

Cation shifts.

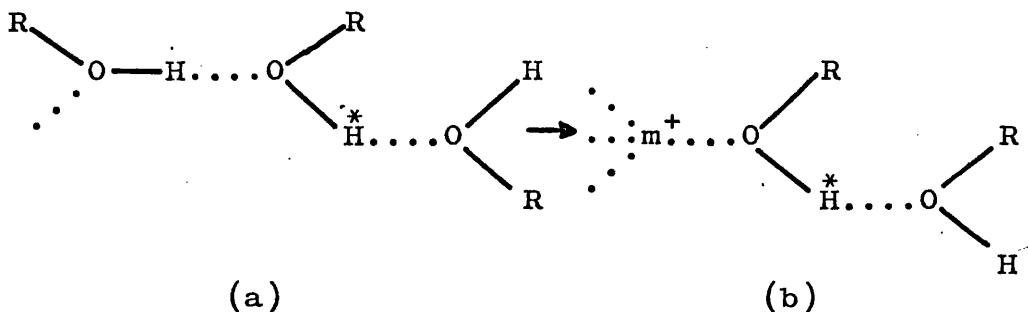
The mole mole⁻¹ cation shifts for these solvents are shown plotted versus charge/radius ratio in Figure 7.6 (i) and (ii). The curves have the same general form to that found in aqueous solution (cf. Figure 5.3), possessing the characteristic maximum found near to the potassium ion. The behaviour of the quaternary ammonium ions, however, shows marked deviations from that apparent in aqueous solution. The special structuring factors found in aqueous solution do not seem to be operative in the alcohols, even at very low temperatures (ca. 204K).

The cations of high charge density (e.g. Li^+ , Mg^{2+}) produce a de-shielding effect on the proton of a bonded solvent molecule.





The acidity of the $\overset{*}{\text{H}}$ proton will therefore increase. The magnitude of the downfield shifts for Li^+ and Mg^{2+} decreases in the order $(\text{CH}_2\text{OH})_2 < \text{EtOH} < \text{MeOH}$ at both 204 and 313K. Such behaviour is probably the result of weaker bonding between the cation and the hydroxyl oxygen, (i), showing itself in the form of a reduced de-shielding. The higher exchange rates (10 to 10^3 x) of ethanol solvation molecules compared to those of methanol¹⁰⁹ supports this view. A comparison of the present results with those for aqueous solutions (Chapter 5) seems to indicate that the limiting charge density necessary to produce down-field cation shifts in the hydroxy solvents is approximately that found for the lithium ion. The fact that the curves in Figure 7.6 cross the zero line can be understood in terms of a process whereby a cation replaces a solvent molecule.



The acidity of the proton $\overset{*}{\text{H}}(b)$ is increased relative to $\overset{*}{\text{H}}(a)$ by the presence of the cation m^+ , so contributing to its de-shielding, which is already present (relative to the gas phase) as a consequence of hydrogen bonding in the pure liquid. If the overall effect on the protons, $\overset{*}{\text{H}}$, is less than that of the bonded solvent, then there will be a slight shielding as is found for the alkali

metal cations other than lithium. As the size of the cation increases, then ultimately such bonding to the cation will become unimportant and therefore the solvent molecules will revert almost completely to their normal state. The maximum that occurs in the cation shift versus charge/radius plots can be explained, as was done for aqueous solutions, by postulating a decreasing effective solvation number for ions of a size in excess of that of potassium.

The quaternary ammonium ions do not seem to exhibit any structure making properties in the alcohols. The shifts of these large cations, as shown in Figure 7.6, converge on those of the bulky non-polar solutes (e.g. n hexane and 2,2 dimethoxy propane) at both 20⁴ and 313K. Such behaviour is also evident when tertiary butanol is the solute. No downfield shift is found for this latter species, as was the case for aqueous solutions,⁸⁹ the structure making properties of t butanol that are evident in water are therefore absent in the alcohols. The behaviour of the octyl trimethyl ammonium ion, as the solvent temperature is varied, is also found to be more 'normal' in methanolic solution. The value of its shift changes little between 20⁴ and 313K, whereas in aqueous solutions a marked shift to higher applied fields (cf. structure breaking) occurs as the solution temperature rises (Figure 6.8). The hydrocarbon groups of the quaternary ammonium ions appear to become more effective in shielding the effect of the central positive charge as their size increases. In terms of the previously

mentioned cation shift theory such shielding implies that the shifts of the large quaternary ammonium cations, in the absence of any special structuring effects, will tend to approach those of the bulky non-polar solutes. The slight upfield shift of the octyl trimethyl relative to the n hexyl ammonium ion could be a measure of the reduced screening of the positive charge by the asymmetric ion or, alternatively, a result of slight structure breaking (see Figure 6.2).

The general tendency of the cation shift to move to lower applied fields as the alcoholic solvents are heated is probably associated with the fact that there are more non-hydrogen bonded hydroxyl protons at higher temperatures. The relationship derived in chapter five reproduces the observed trend.

$$\text{i.e. } n = - \frac{10^3}{m} \left[\frac{dW}{dT} \right] \left[\frac{dT}{dX} \right]$$

where, n = the solvation number.

m = molecular weight of the solvent.

$\frac{dW}{dT}$ = temperature coefficient of the cation shift.

$\frac{dX}{dT}$ = temperature coefficient of the pure solvent.

For the alcohols $\frac{dX}{dT}$ is positive (the general shift to higher applied fields found when the hydroxy solvents are heated) and so $\frac{dW}{dT}$ will be negative. For the large quaternary ammonium ions $\frac{dW}{dT}$ tends to zero, consequently $n \rightarrow 0$. The implication is that the solvation of these

ions is not the same as found for simple cations, supporting the view that the large quaternary ammonium ions leave the alcoholic solvents relatively undisturbed.

7.3 Solvent-shared ion-pairs in methanolic electrolyte solutions.

7.3.1 Introduction.

For solutions of certain magnesium salts in methanol, the hydroxyl proton resonance from methanol molecules directly bonded to Mg^{2+} shifts with concentration in a manner which closely resembles the OH proton shift for the bulk solvent. This section investigates the origin of such shifts. The work reported was jointly carried out with Dr R.N. Butler, who investigated the acetate and perchlorate shifts, whilst the present author carried out the work on the nitrate and bromide solutions.

7.3.2 Experimental.

Experimental procedures were as described in chapter two except for the following. The salts $Mg(NO_3)_2 \cdot 6H_2O$ and $MgBr_2 \cdot 6H_2O$ were dried by distilling dry methanol on to them, refluxing, and pumping off, at least four times. The resulting vacuum line prepared solutions gave well resolved n.m.r. spectra with no indication of water signals. All transfer operations were carried out in a dry box and the solutions were analysed with E.D.T.A. to determine the magnesium concentration. Traces of the

respective acids were added to the salt solutions in order to give well resolved solvation shell signals.

The methyl resonance of the alcohol was used as a reference, small shifts which probably occur in this reference have been ignored. A typical spectrum is shown in Figure 7.7. Spectra were measured at 204K.

7.3.3 Results.

The shifts in the resonance lines obtained for the Mg^{2+} solvation shells with increasing salt concentration are shown in Figure 7.8a for the nitrate, bromide and perchlorate, and the corresponding residual shifts in Figure 7.8b. The results for the acetate are given in Figure 7.9.

The effect of adding lithium chloride or magnesium chloride solutions to those of magnesium perchlorate was to shift the single solvent-shell resonance to the position expected for statistical collisions. In contrast, addition of magnesium acetate gave a resonance which strongly favoured the acetate value.

7.3.4 Discussion.

i) Nitrates, Bromides and Perchlorates.

The close correlation between the concentration shifts for both OH peaks suggests that the same factors are operative. Unless an unusual number of coincidences are involved, it seems that these anions affect the

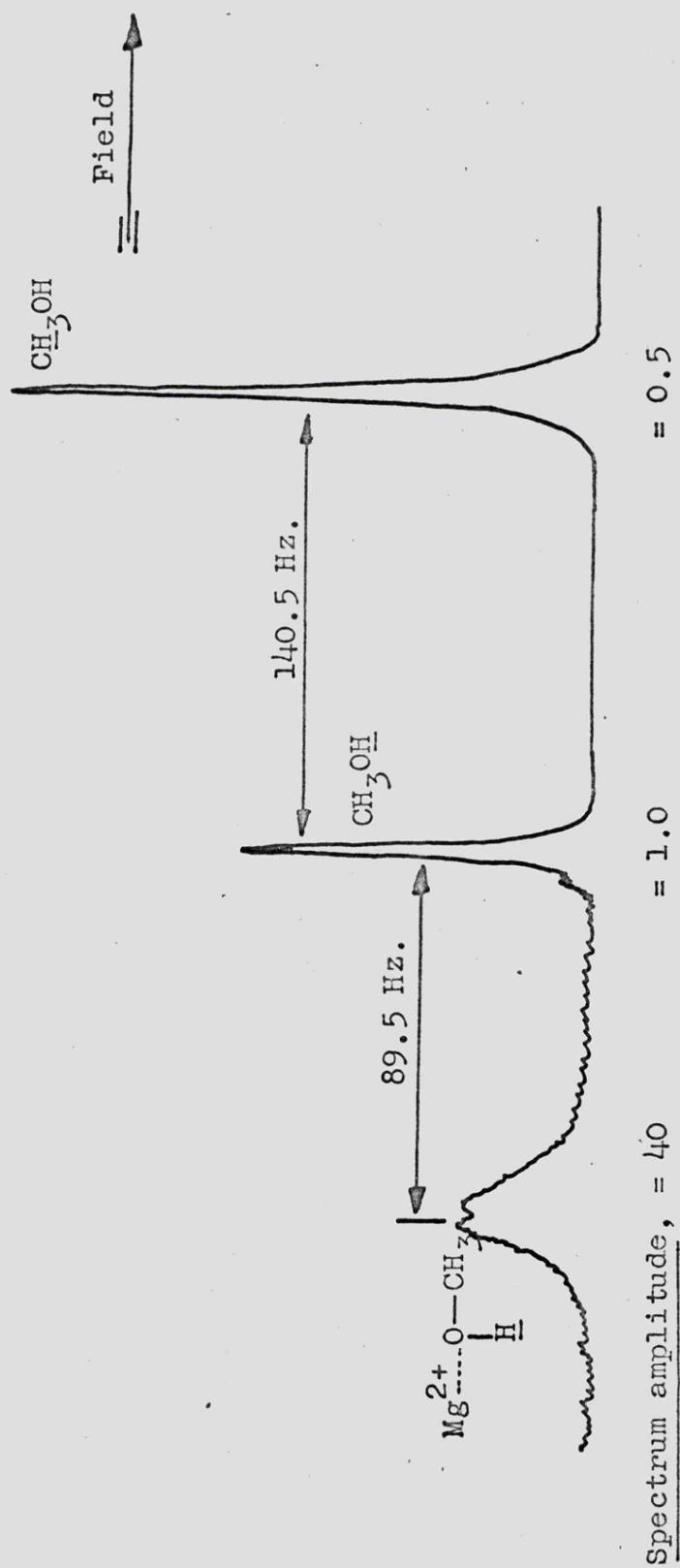
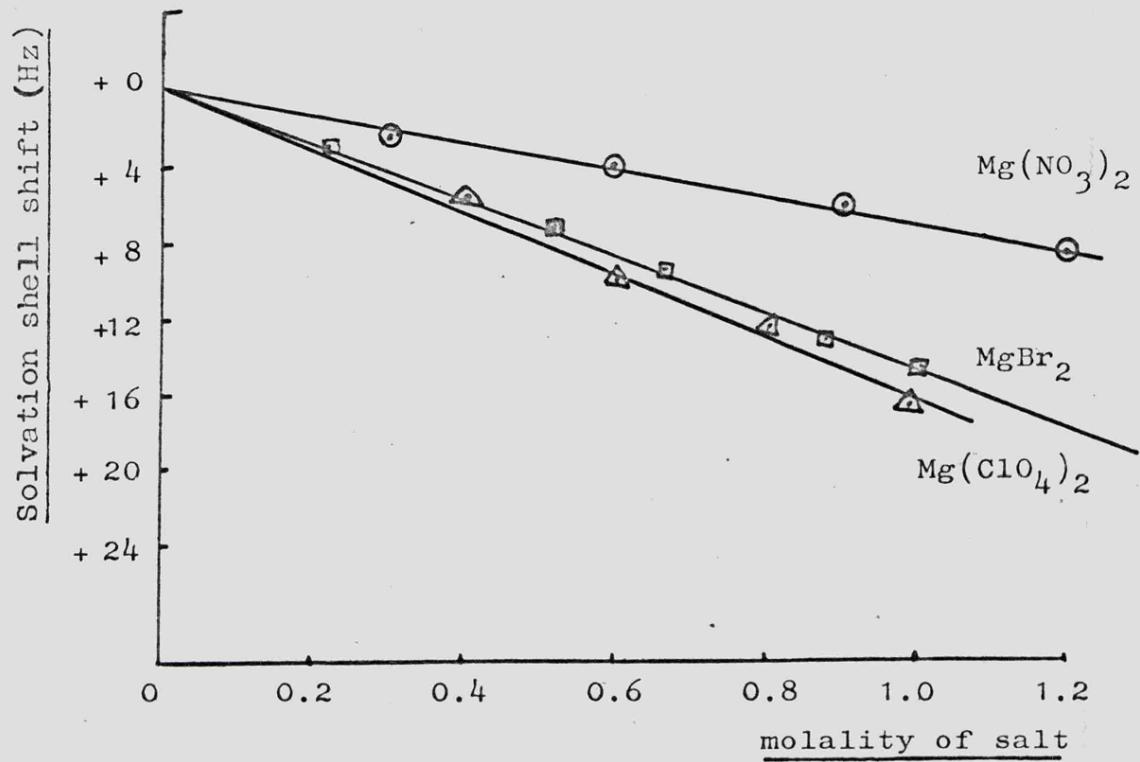
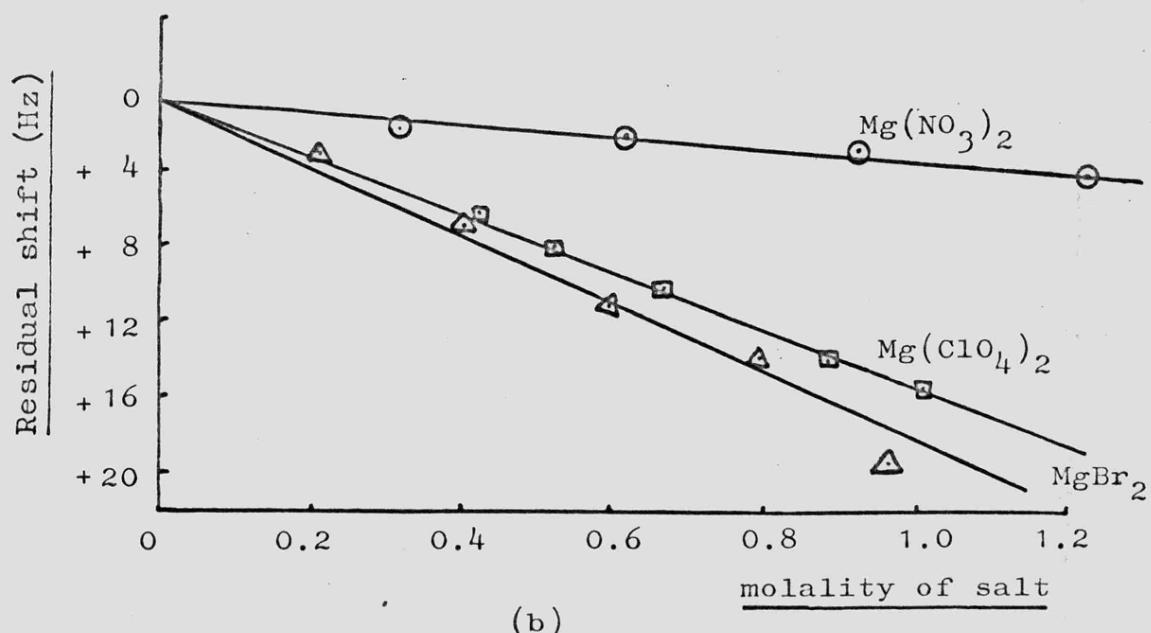


Figure 7.7 A typical p.m.r. spectrum (at 60 MHz.) of a 1.52 molal solution of Mg(NO₃)₂ in Methanol at 204K.



(a)



(b)

Figure 7.8 Shifts in the solvation shell (a) and residual bulk OH (b) (Hz at 60 MHz) for magnesium salts at 204K. Positive shifts are upfield.

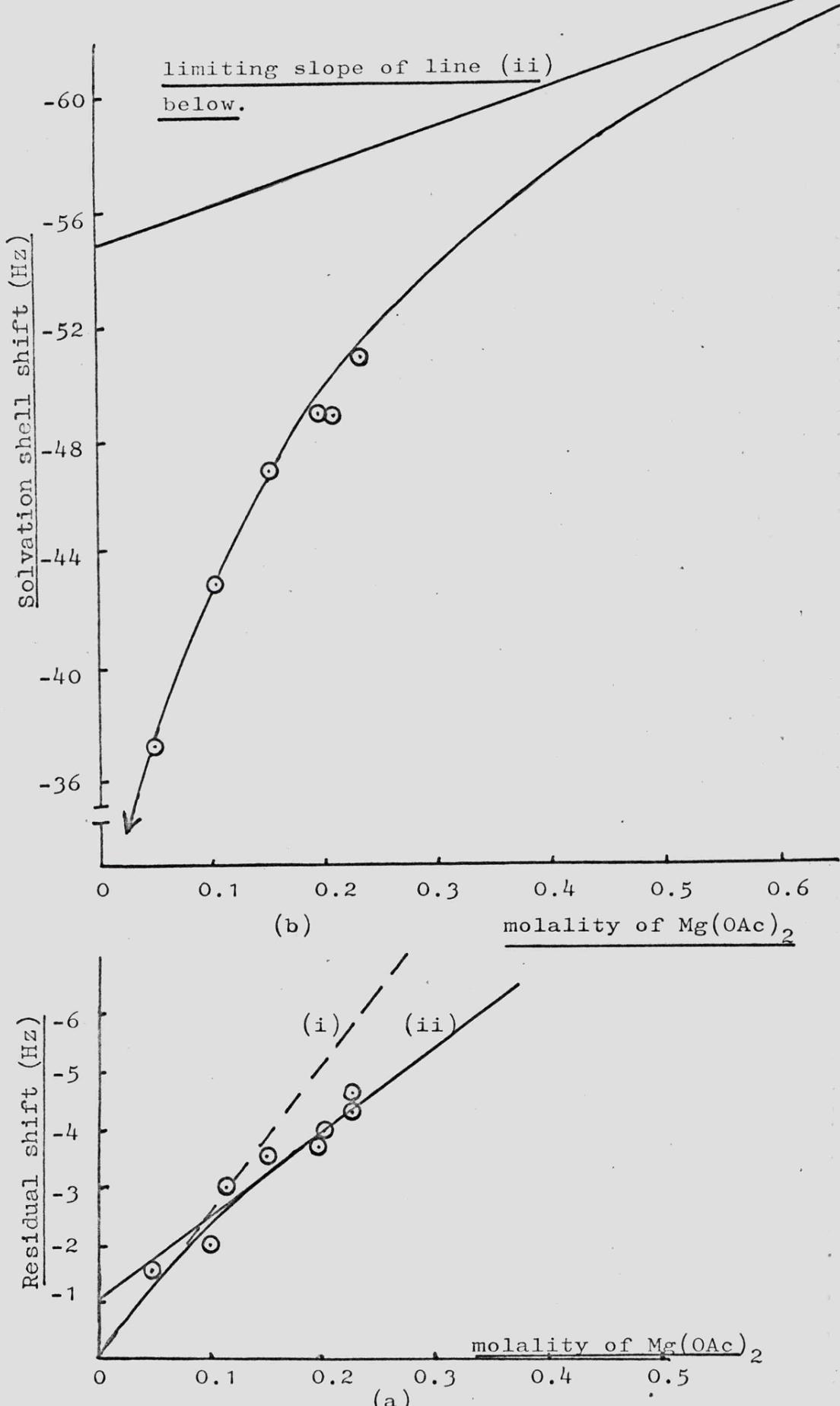
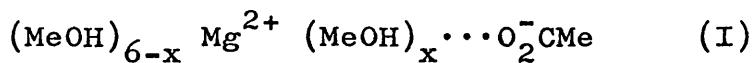


Figure 7.9 Solvation shell (b) and residual (a) shifts in the OH resonance for methanolic solutions of $\text{Mg}(\text{OAc})_2$ at 204K. i, predicted line derived from NaOAc data⁵⁴. ii, line with half slope of (i).

the hydroxyl protons equally, whether or not the methanol molecules are bonded to magnesium ions. The observed behaviour would also indicate that the mean interaction time between the anions and either type of proton must be about the same. Under such circumstances, a purely statistical interaction occurs, and both hydroxyl peaks are equally shifted. This conclusion is further supported by the effect of adding sodium perchlorate to the magnesium perchlorate solutions. One would expect these extra perchlorate ions to influence the magnesium solvation shell resonance in a similar and proportional way. The effect of adding sodium perchlorate to a 0.12 M solution of magnesium perchlorate is shown in Figure 7.10. The slope of $+9 \text{ Hz M}^{-1}$ is close to half of the slope obtained from pure $\text{Mg}(\text{ClO}_4)_2$ ($+17.8 \text{ Hz M}^{-1}$). It does indeed seem that it is the anion that is influencing the solvation shell resonance.

ii) Acetates.

The acetate ion possesses a relatively high basicity, (cf. Table 5.6), consequently it is able to differentiate between the bulk methanol and the more acidic methanol molecules that are bonded to magnesium. The slope of the curve in Figure 7.9b decreases as the concentration increases, tending towards the limiting value found for the bulk methanol peak. Such behaviour has been interpreted⁶¹ in terms of an equilibrium involving the relatively long lived species;



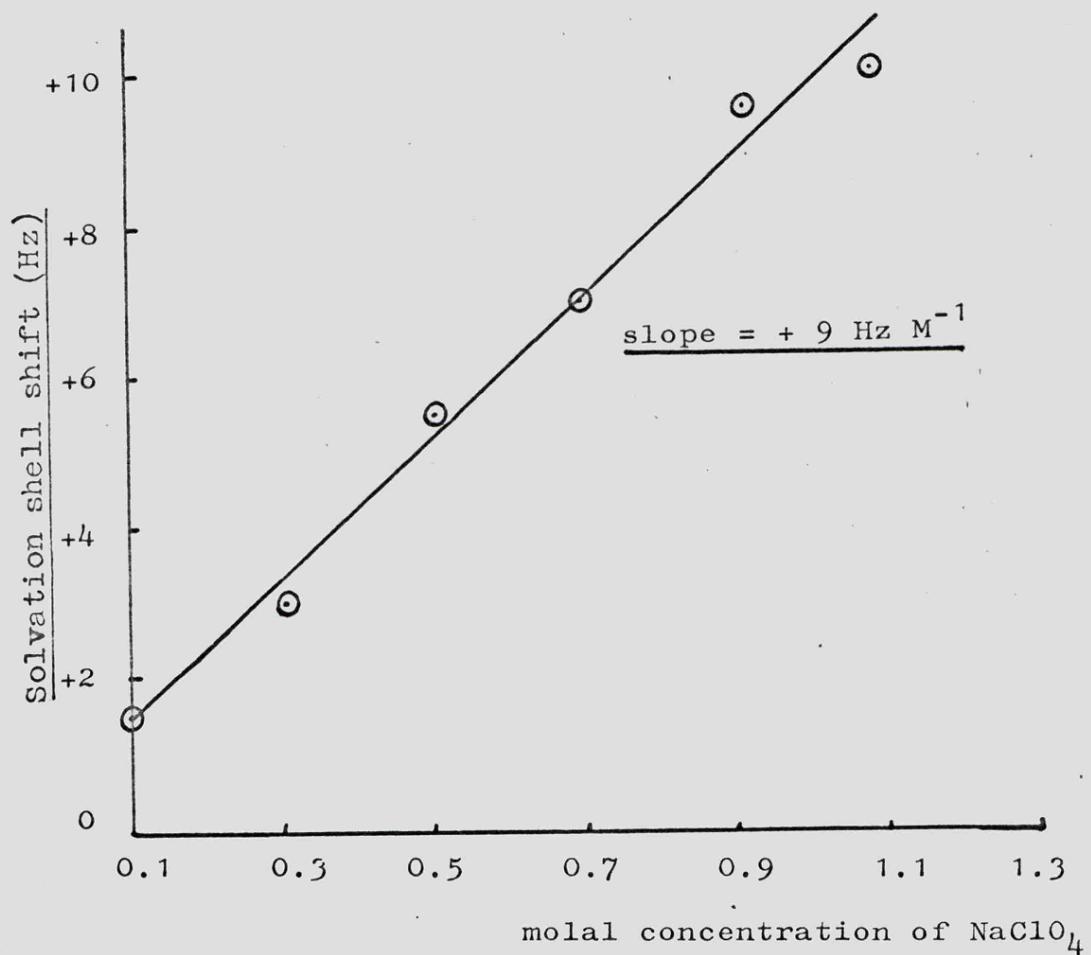
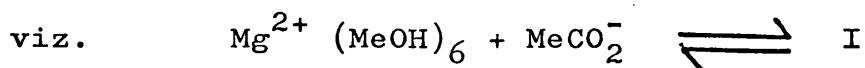


Figure 7.10 The upfield shift (Hz at 60 MHz) in the solvation shell OH signal of a 0.12 M solution of $\text{Mg}(\text{ClO}_4)_2$ in methanol, on addition of NaClO_4 at 204K.



The equilibrium nears completion in the 0.4 M region.

It is concluded that solvent-shared ion-pairs⁶² are responsible for the observed shifts, however, ion-pair formation seems to be purely statistical except for the acetate, which shows a strong preference for such behaviour. In all cases the lifetimes of the ion-pairs was low, and so no separate resonances were detected.

7.4 Liquid ammonia as a solvent.

7.4.1 Introduction.

The results presented in this section were determined during a preliminary study carried out on solutions of magnesium and sodium nitrates in liquid ammonia.

Allred and Wendricks¹¹² have measured an extensive series of salt shifts in liquid ammonia at 298K. The shifts were externally referenced, and reported before and after bulk susceptibility corrections had been performed. The authors made no attempt to sub-divide the salt shifts, however, they noted that shifts to higher applied fields, relative to pure liquid ammonia, did not occur for any of the salts investigated. It was suggested that some of the ions may have produced high field shifts, but these were out-weighed by low field shifts of the gegen ions.

It is evident that sub-dividing the salt shifts is, once again, a major problem. One solution, for

aqueous work, has been to assign to the ammonium ion a zero shift.⁴⁶ To ascribe to the ammonium ion a zero shift in liquid ammonia would seem unwise, it would be equivalent to assigning H⁺ a zero shift in aqueous solutions.³⁰ It has proved possible to detect separate solvation shell resonances for certain cations in liquid ammonia.¹¹³ The direct determination of primary cation shifts (at low temperatures) should therefore be possible, using the same procedures as previously employed for methanolic and ethanolic solutions. Given below are details of such an attempt.

7.4.2 Experimental.

When working with liquid ammonia solutions, it is best to use high vacuum techniques. The vacuum line apparatus used during this work is shown in Figure 7.11.

Anhydrous ammonia was prepared by repeated distillation in and out of a potassium - ammonia solution.

Anhydrous solutions of Mg(NO₃)₂ and NaNO₃, were prepared from 'analar' grade salts, the drying being accomplished by repeated distillation of the solvent ammonia in and out of the potassium-ammonia solution.

The analysis of the ammoniacal solutions presents some difficulty. The n.m.r. sample tubes were sealed on the vacuum line, after the spectra had been run the tubes were exploded into a known excess volume of standard hydrochloric acid. The ammonia was then determined by back titration with standard sodium hydroxide solution.

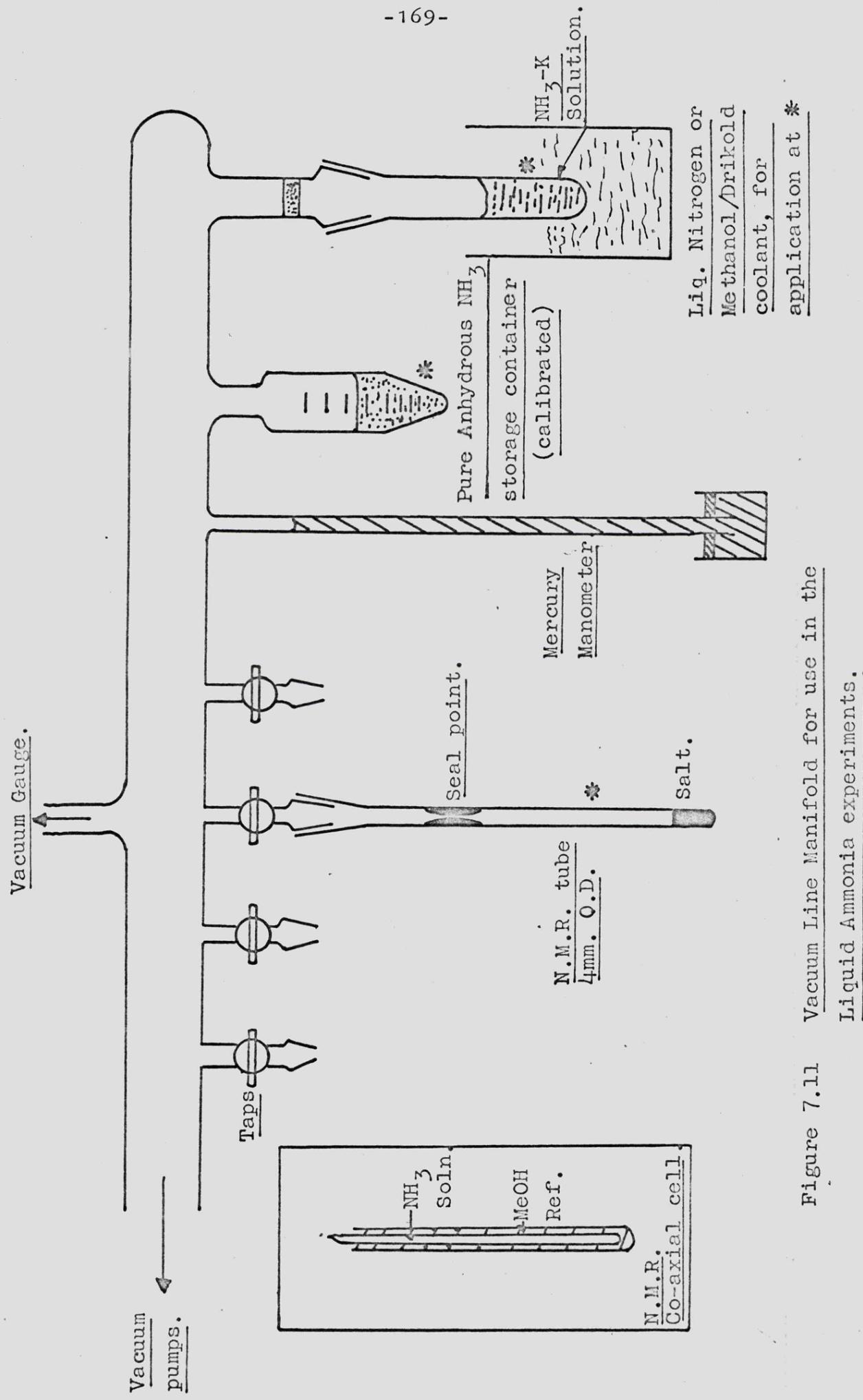


Figure 7.11 Vacuum Line Manifold for use in the
Liquid Ammonia experiments.

The magnesium concentration was determined by E.D.T.A. titration, whilst that of sodium was determined from the initial weight of the dry salt.

The solutions were externally referenced, methanol for this purpose being contained in the annulus of the co-axial n.m.r. cell (see the inset in Figure 7.11). The methanol served the double purpose of n.m.r. reference and temperature sensor, cf. section 2.3.

Spectra were measured on a Varian Associates A60. spectrometer operating at a frequency of 60 MHz.

The temperature of the determinations was 200K, at this temperature there is no risk of the cells exploding as a result of the pressure of ammonia gas.

7.4.3 Results and Discussion.

A typical low temperature spectrum, showing a magnesium solvation shell, is given in Figure 7.12a. The uncorrected salt shift plot for sodium nitrate is shown in Figure 7.12b, whilst the cation shell and residual shift plots for magnesium nitrate are given in Figure 7.13a,b.

It is at once evident that there is a considerable scatter in both sets of results. Such scatter is to be expected in view of the experimental difficulties involved in preparing, handling and analysing the liquid ammonia solutions.

The uncorrected molal shift of the magnesium solvation shell (Figure 7.13a) was determined as -1.2 p.p.m.

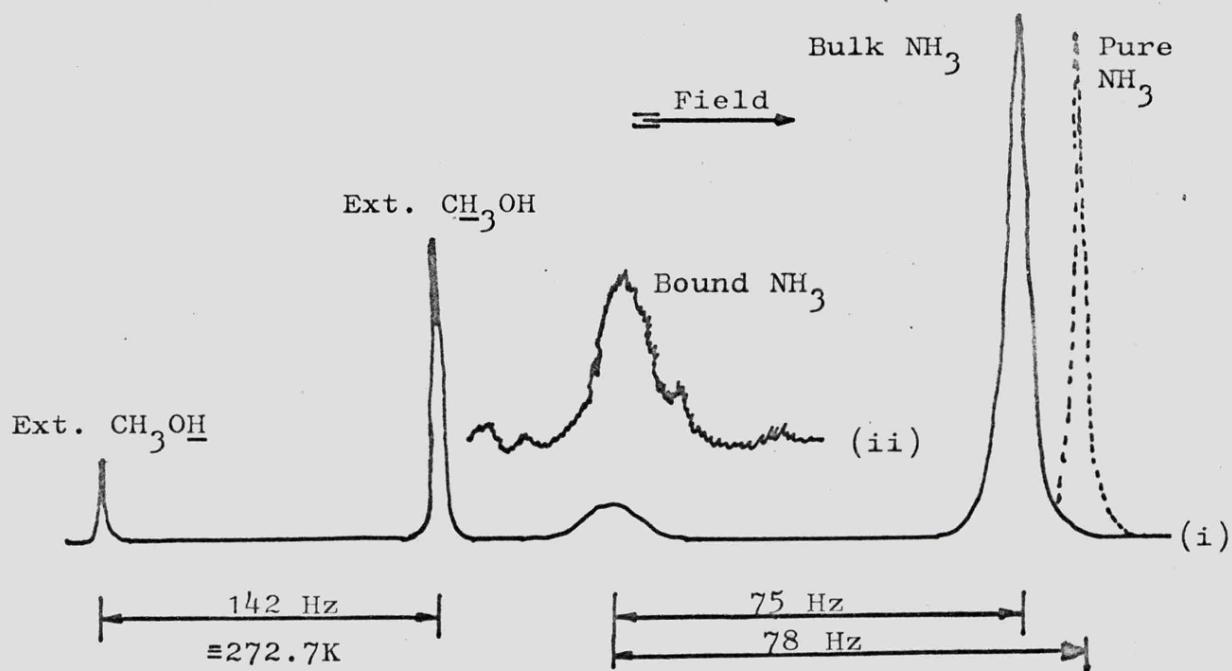


Figure 7.12a Low temperature proton n.m.r., 60 MHz. spectrum (not to scale) of a 0.4 M solution of $\text{Mg}(\text{NO}_3)_2$ in liquid ammonia.

(i) spectrum amplitude = 0.8

(ii) spectrum amplitude = 80

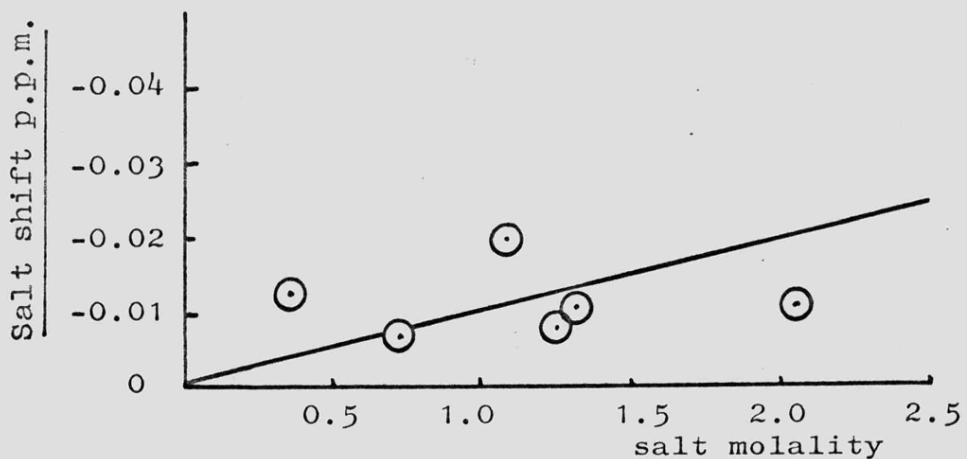


Figure 7.12b Uncorrected NaNO_3 salt shift plot in liquid ammonia at 200K.

Molal uncorrected shift = -0.011 p.p.m.

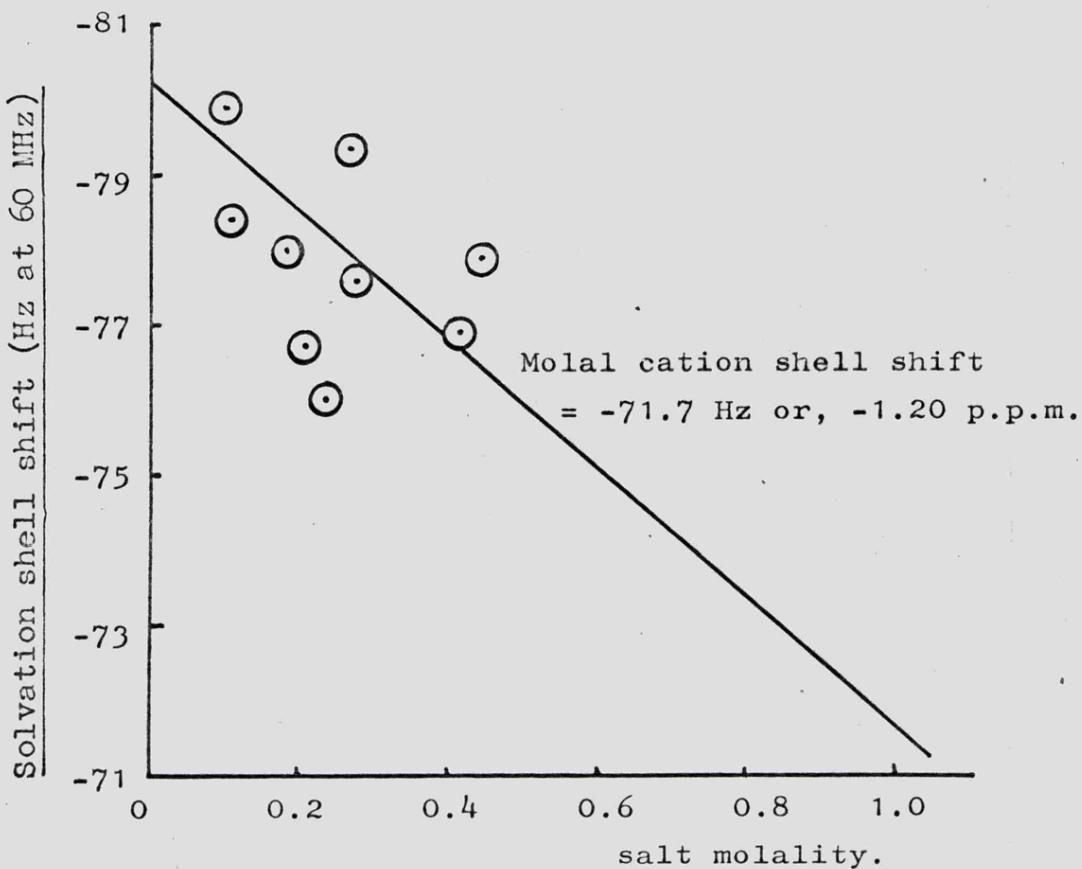


Figure 7.13a The cation shell shift, for a solution of $\text{Mg}(\text{NO}_3)_2$ in liquid ammonia at 200K, plotted versus salt concentration.

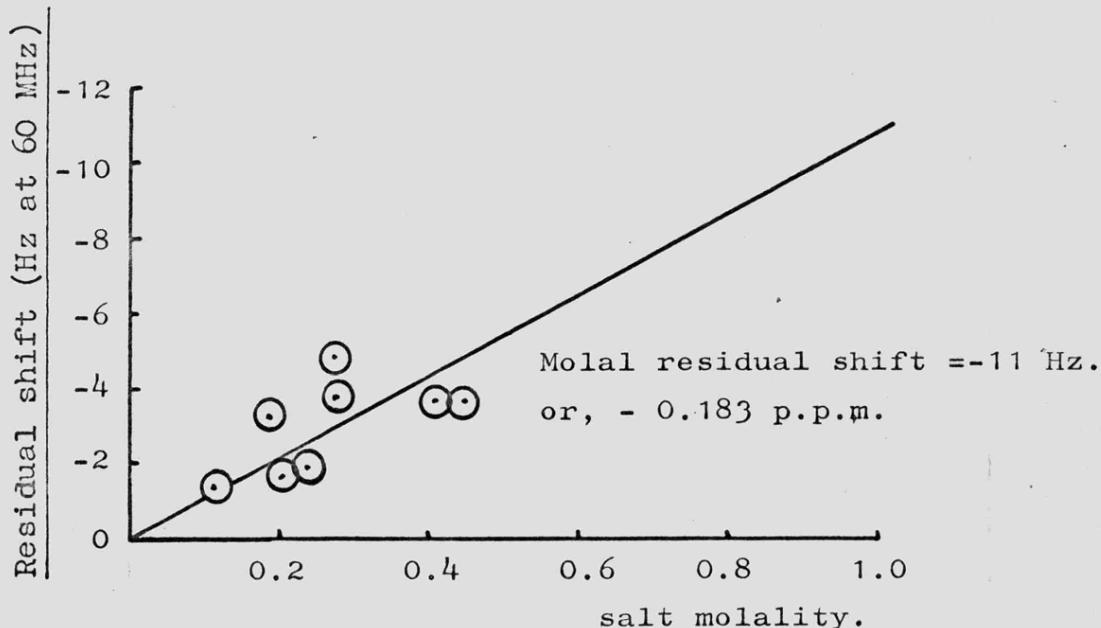


Figure 7.13b The residual shift, for a solution of $\text{Mg}(\text{NO}_3)_2$ in liquid ammonia at 200K, plotted versus salt concentration.

(i.e. downfield from the pure ammonia resonance)., This shift must be weighted with the pure ammonia resonance in order to obtain the Mg^{2+} molal cation shift. Such a calculation requires the knowledge of the primary solvation number of the magnesium ion in this solvent. Swift and Lo^{113,114} have determined this number to be 6.0 (at 198K). The method of calculation is essentially the same as that given in section 4.3, and it results in a primary cation shift (uncorrected) for the magnesium ion of -0.121 p.p.m. at 200K.

The residual shift plot, shown in Figure 7.13b, gives a molal value of -0.183 p.p.m. If, by comparison with the methanolic and ethanolic work (ref 54 and sections 4.2 and 7.2.2 of this thesis), this shift is taken as due to the anions only (i.e. assuming that secondary cation effects are not present) then the molal uncorrected nitrate shift becomes, $-0.183 + 2 = -0.091$ p.p.m.

By making use of the above values the uncorrected shifts listed in Table 7.6 have been derived.

Table 7.6

Salt	Salt shift	Ion	Ion shift
$Mg(NO_3)_2$	-0.304	Mg^{2+}	-0.121
$NaNO_3$	-0.011	Na^+	+0.080

Molal uncorrected shifts (p.p.m.) in liquid ammonia at 200K. Positive shifts are upfield.

The shifts listed in Table 7.6, being externally referenced, must be corrected for bulk susceptibility effects before true comparisons with other results can be made. Such corrections present special difficulties when working with liquid ammonia, in particular, there is a lack of readily available density data. Allred and Wendricks¹¹² assumed the equality of certain apparent molar volumes in order to approximate certain solution densities. In the present study, a correction for the magnesium nitrate shift has been obtained by assuming that the partial molar volumes of $Mg(NO_3)_2$ and $Ba(NO_3)_2$ are equal. Available literature data for $Ba(NO_3)_2$ can thus be used.¹¹⁵ Proceeding in this way, the correction was obtained by application of the equation;

$$\Delta = \delta_{obs} - \frac{2\pi}{3} \left[\chi_m^{solv} (d_{soln} - d_{solv}) - \frac{(\chi_m^{solv} - \chi_m^{solute}) M.W.}{10^3} \right]$$

where the symbols have the same meaning as given in section 3.1.

i.e. $\delta_{Mg(NO_3)_2} = \delta_{obs} - 0.07 \text{ p.p.m.}$

The correction for sodium nitrate is taken to be the same as that given in Allred and Wendricks paper¹¹², namely

$$\delta_{NaNO_3} = \delta_{obs} - (-0.033) \text{ p.p.m.}$$

It must be pointed out that such corrections can only be regarded as approximate. The corrected salt shifts are therefore; $\delta_{Mg(NO_3)_2} = -0.377 \text{ p.p.m}$ and $\delta_{NaNO_3} = +0.022 \text{ p.p.m.}$

In order to apportion the susceptibility corrections to the ion shifts it has been assumed that the correction is equally divided between the ions concerned. The corrected ion shifts, not significantly altered, become;

$$\text{Mg}^{2+} = -0.14 \text{ p.p.m.}$$

$$\text{Na}^+ = +0.09 \text{ p.p.m.}$$

$$\text{NO}_3^- = -0.10 \text{ p.p.m.}$$

The results indicate that upfield cation shifts (e.g. Na^+) do exist in liquid ammonia solutions, at least at low temperatures. The upfield shift is probably indicative of the weakness of the $\text{Na}^+ \dots \text{H-NH}_2$ bond, compared to that of $\text{H}_2\text{NH} \dots \text{NH}_3$. The molal shift of the magnesium ion is considerably reduced in magnitude compared to that found in methanol and ethanol at 204K (cf. Table 7.2) as is the downfield position of the cation shell resonance. Such behaviour is again probably due to the weaker intensity of the $\text{NH}_3 \dots \text{Mg}^{2+}$ interaction compared to that of $\text{RO} \dots \text{Mg}^{2+}$.

These preliminary results have not allowed a full discussion of ionic interactions in liquid ammonia. A more complete study, covering a larger range of ions should prove very fruitful. In view of the difficulties and errors involved in correcting externally referenced results in this solvent, the use of an internal reference would seem desirable. Tetra methyl ammonium nitrate would appear to be a reasonable choice for such a purpose, the chloride cannot be used in view of the fact that ammonolysis takes place in the presence of ions such as Mg^{2+} .

CHAPTER EIGHT

CONCLUDING REMARKS

The purpose of the work described in this thesis has been the investigation of ion-solvent, and to a lesser extent, ion-ion interactions by means of the n.m.r. solvent shift technique. The technique is a powerful one and is therefore capable of providing valuable information concerning systems of this type. The related nuclear spin relaxation time experiments, which provide information concerning the time dependence of molecular motions, have not formed part of the present investigations.

The time scale of the n.m.r. experiment, namely 10^{-2} s., is such that it is the diffusion controlled solvent structure that is observed.⁵ This is because the technique probes the average, rather than the instantaneous, magnetic environment of the particular resonating nucleus (in this thesis exclusively the proton).

The n.m.r. solvent shift technique does, however, suffer from two inherent disadvantages;

- (i) Referencing problems. (Chapter Three)
- (ii) The sub-division of salt shifts into 'single ion' quantities. (Chapter Four)

In order to overcome the first of these, it is suggested that the best solution is to use a suitable internal reference in very low concentration. The use of an internal standard does give rise to doubts concerning possible adverse interactions, however, on balance this type of reference is believed to be preferable to the alternative external system. In suitable cases, it is possible to use the solute itself as the internal reference, e.g. the quaternary ammonium and carboxylic acid salts.

Problems connected with the sub-division of salt shifts have proved to be one of the major drawbacks in the n.m.r. solvent shift field. The problem was tackled in Chapter four where two independent methods for arriving at the molal chloride ion shift were discussed. The ion shift values listed in the text are thought to be close approximations to the true absolute ones.

The overall impression from the determined ion shifts (in the various solvents studied) is that it is short-range ion-solvent interactions that are, in the main, responsible for determining the nature of such parameters. The quaternary ammonium cations, in aqueous solution, do seem to be the only species to exhibit any shift phenomena directly attributable to marked solvent structural changes.

In future work concerning n.m.r. solvent shifts it would seem desirable to employ either 100 or 220 MHz. spectrometers. By the use of such instruments, concentration phenomena such as those found for the large quaternary ammonium salts can be more positively determined. High frequency instruments also facilitate the use of solutions containing very low concentrations of added salts.

For the hydroxy solvents, a useful extension to the present work would be to determine absolute O^{17} ion shifts along similar lines to those given in Chapter four. The O^{17} resonance should be a more direct measure of the ion-solvent interaction.

APPENDICES

Appendix 1.

Computer programme for the external reference bulk magnetic susceptibility correction.

The programme calculates Δ in the equation;

$$\Delta = \xi_{\text{obs}} - \frac{2\pi}{3} \left[\chi_m^{\text{solv}} (d_{\text{soln}} - d_{\text{solv}}) - \frac{(\chi_m^{\text{solv}} - \chi_m^{\text{solute}}) M.W.}{10^3} \right]$$

where, Δ = Shift corrected for bulk susceptibility effects.

ξ_{obs} = Uncorrected observed shift, P.P.M.

χ_m^{solv} = Mass susceptibility of the pure solvent.

χ_m^{solute} = " " " " " solute.

d_{soln} = Density of the solution.

d_{solv} = Density of the pure solvent.

M = Molecular weight of the solute.

W = Molarity of the solution.

The input data is as follows;

n = number of observed shifts to be corrected.

x1 = χ_{mass} of the pure solvent.

x2 = χ_{mass} of the solute.

x3 = molecular weight of the solute.

x4 = molality of the solution at density x5.

x5 = density of the solution at molality x4.

x6 = density of the pure solvent.

x7 = temperature of the determination.

M I

molality

*

*

V I

observed shift p.p.m.

*

*

Section 2 calculates the density of the solution at molality M I, assuming a linear dependence.

Section 3 converts molality to molarity, the parameter used in the bulk susceptibility correction equation.

The programme listing, given overleaf, was written in Elliot Autocode for use on an Elliot 803 computer.

::BULK MAGNETIC SUSCEPTIBILITY CORRECTION J DAVIES
SETS IN
SETV X(7)V(500)D(500)M(500)Y(500)Z(500)W(500)R(500)
SETR 6

1)READ N
READ X1
READ X2
READ X3
READ X4
READ X5
READ X6
READ X7
CYCLE I=1:1:N
READ MI
READ VI
REPEAT I
WAIT

2)CYCLE I=1:1:N
DI=X5-X6
DI=DI/X4
DI=DI*MI
DI=DI+X6
REPEAT I

3)CYCLE I=1:1:N
WI=MI*DI
WI=WI*1000
RI=MI*X3
RI=RI+1000
RI=WI/RI
REPEAT I

4)TITLE BULK MAGNETIC SUSCEPTIBILITY CORRECTIONS AT
PRINT X7,4:2
TITLE DEG. K
LINES 5
TITLE
MOLALITY MOLARITY DENSITY OBS SHIFT. PPM
CORR SHIFT PPM

Cont.

```
5) CYCLE I=1:1:N
ZI=DI-X6
ZI=ZI*X1
YI=X1-X2
YI=YI*X3
YI=YI*RI
YI=YI/1000
YI=ZI-YI
YI=YI*2.095
YI=VI-YI
REPEAT I
```

```
6) CYCLE I=1:1:N
PRINT MI,2:4
SPACES 3
PRINT RI,2:4
SPACES 3
PRINT DI,2:4
SPACES 3
PRINT VI,2:4
SPACES 3
PRINT YI,2:4
LINE
REPEAT I
LINES 30
WAIT
JUMP@1
```

START 1

Appendix 2..

The radii of ions in solution.

The most commonly used model for a simple monatomic ion, regards such a species as a uniformly charged, incompressible sphere. In this way it is possible to assign to the ion a radius that can be taken to be independent of environmental effects.

Two distinct sets of ionic radii are in general use at the present time, one due to Pauling¹⁷ and the other based on a value of 1.33×10^2 pm. for the radius of the fluoride ion, assigned by Wasastjerna¹¹⁶ and extended by Goldschmidt and others.¹¹⁷ Crystal radii such as these are derived in a semi-empirical fashion, so as to obtain a set of values that are self-consistent with observed interatomic distances.⁵⁹

The radii of ions in solution are not precisely known.⁵⁶ It is therefore usual to equate such radii to those suggested for crystals. Blandamer and Symons²⁰ have suggested that the 'experimental' ionic radii proposed by Gourary and Adrian⁵⁷ are more appropriate to solvation phenomena in aqueous solution. These latter radii were derived after consideration of observed electron density contours based on X-ray measurements.⁵⁸

The problems associated with assigning radii to simple monatomic ions in solution are greatly magnified for ions of a more complex nature. Anions such as acetate and perchlorate have been assigned a parameter known as

the thermochemical radius.¹¹⁸ Such a parameter is derived by application of the Kapustinskii equation, using a known difference in lattice energies. Thermochemical radii are found to vary in approximately the way that one would expect from a knowledge of the variation of the bond lengths and the radii of monatomic ions. It is doubtful whether or not the term radius is truly meaningful for complex ions which are geometrically asymmetric. There are also uncertainties associated with the charge distribution of complex ions in solution. In view of these two factors it was thought unwise to give any discussion relying on ionic radius parameters for the many complex anions listed in Chapter five of this thesis.

It is less contentious to refer to the radii of species such as the symmetrical quaternary ammonium cations. The radii of these ions have been derived, in the past, by the use of two main approaches:-⁹⁷

- i) By the summation of C-C, C-H and C-N bond lengths, i.e. a molecular model approach.
- ii) Calculated from limiting ionic mobilities by making use of Stoke's law.

In the context of the radii of quaternary ammonium cations in solution, the following is of interest.

In order to obtain a truly smooth and continuous curve for the cation shift versus charge/radius ratio plots (cf. Figure 7.6) through the K^+ , Cs^+ , Me_4N^+ region, it was found necessary to increase the Me_4N^+ charge/radius ratio by a factor of +0.22 compared to that derived from molecular model radii.⁹⁷ This factor was found to apply

equally well in both aqueous, methanolic and ethylene diol solutions. It was not possible to determine the factor for ethanolic solutions as a result of the lack of alkali metal cation shift data, this being due to solubility problems. Proceeding in this way, an adjusted radius for the solvated tetra methyl ammonium cation was arrived at. Other quaternary ammonium ionic radii were then calculated by adding known bond length increments to the adjusted Me_4N^+ radius. The values so obtained are given in Table 6.4, and are the radii that have been used throughout this thesis. It is interesting to note, that on this new basis, the radius of the tetra methyl ammonium cation (198.0 pm.) closely approaches the Stoke's law value (204.0 pm.).⁹⁷

The radius of an asymmetric ion such as that of octyl trimethyl ammonium, presents a somewhat paradoxical situation. The indeterminate nature of this parameter has led to the 'dashed line' representation used when plotting the Oct Me_3N^+ cation shift versus radius and charge/radius ratio, cf. Figures 6.2, 6.7 and 6.8.

Ionic radius values can be found in the following tables:-

- (i) Metal cations and the halide anions; Table 4.2 (p 58)
- (ii) Quaternary ammonium cations; Table 6.4 (p 126)

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