A MAGNETIC RESONANCE STUDY OF

ELECTRO-RHEOLOGICAL FLUIDS

A thesis submitted by Phillip Bailey in candidature for
the degree of Doctor of Philosophy of the University of
London.

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The work in this thesis is dedicated to my parents who have given me all the support anyone could ask for.
ABSTRACT

Electro-rheological (ER) fluids, which are dispersions of solid particles in a non-conducting oil, have been studied for the first time at a molecular level using magnetic resonance spectroscopic techniques.

The group of fluids on which measurements were first made was the already widely used lithium polymethacrylate dispersed in 20 cs silicone oil. The problems associated with this fluid such as high conductivity, relatively low viscosity changes, and settling out of the solid particles, led to fluids containing zeolites also to be investigated.

Mechanical tests were performed on all these fluids including static yield stresses measured at zero shear rate, and then a new electroviscometer was designed and built to test fluid performances in the shear rate range from 1.5 to 43.8 s\(^{-1}\) and temperatures from +5 to +60°C.

NMR relaxation measurements were used to study the mobilities of the water and the ions in all these solids to investigate the relationship between these properties, and the performance of a solid as a constituent in an ER fluid. This is the first time that many of these systems have been studied in this way.

ESR was used to study the motion of spin probe radicals in partially hydrated zeolites for the first time. The effect of an electric field on the motion of the spin probe inside a zeolite particle was measured and decreased motion was observed as the strength of the electric field was increased in those zeolites which showed a significant ER
effect, while no effect on the probe motion was seen for those zeolites which constituted a weak ER fluid. The first saturation transfer ESR experiments have been performed on spin probes inside partially hydrated zeolites that previously had been out of the motional range of conventional CWESR, and the anisotropy of the probe motion has been highlighted.

I would like to show my appreciation to all the individuals who contributed to the design and development of the fluid cell used in the measurement of the anisotropy of the probe motion. These include Dr. Frank C. W. H. and Mr. Thomas G. C. for their technical assistance.

Finally, I would like to thank Mr. Thomas C. for his interest in the project and for his financial support. I would also like to thank Mr. W. H. for his encouragement and support during the course of my research.

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Some of the powdered zeolite samples were supplied by Dr. Frank Fitch (Laporte Inorganic Division, Widnes, Cheshire) for which I am extremely grateful.

I would like to also show my appreciation to all the technical staff at Royal Holloway and Bedford New College whose help I have sought at one time or another. In particular I would like to acknowledge the help of Mr. Brian Smethurst in the design of the electroviscometer, and Mr. Mike Slocombe whose excellent engineering skills were shown in the construction of both the electroviscometer, and the electric Field NMR cell.

Finally I would like to thank SERC and Castrol Ltd., (Whitchurch Hill, Pangbourne, Berkshire), for funding the CASE award for my Ph.D.
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<tr>
<td>a</td>
<td>Particle radius</td>
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| A      | i) Electrode area  
          ii) Hyperfine coupling constant |
| Å      | Angstroms (10^{-10} m) |
| B_z    | Static magnetic field in the Z direction |
| β      | Width of a distribution |
| C      | i) Concentration of solid  
          ii) Average circumference of plug |
| cs     | Centistokes |
| cp     | Centipoise |
| CWNMR  | Continuous Wave Nuclear Magnetic Resonance |
| d      | Electrode separation |
| δ      | Distribution parameter |
| e      | Unit charge (1.6 x 10^{-19} C) |
| E      | i) Electric Field  
          ii) Energy |
<p>| E_A    | Activation energy |
| E_1    | Energy between links |
| EF     | Electric Field |
| EV     | Electroviscous |
| ER     | Electro-rheology |
| ε      | Dielectric constant |
| ESR    | Electron Spin Resonance |
| f      | Microviscosity factor |
| FTNMR  | Fourier Transform NMR |
| FID    | Free Induction Decay |</p>
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<td>Flow modified permittivity</td>
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<td>( f_1 )</td>
<td>Force between links in a chain of particles</td>
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<td>( \phi )</td>
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<td>i) Volume fraction</td>
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<td>( g ) value of the free electron</td>
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<td>ii) Nuclear spin</td>
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<tr>
<td>i) Electric current</td>
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<td>ii) Square root of (-1) in an imaginary number</td>
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<td>( m )</td>
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<td>Van Vleck second moment</td>
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<td>Nuclear Magnetic Resonance</td>
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<td>( n_u )</td>
<td>Number of occupants in an upper energy level</td>
</tr>
<tr>
<td>( n_i )</td>
<td>i) Number of occupants of a low energy level</td>
</tr>
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<td>ii) Number of links in a chain</td>
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<td>( \eta )</td>
<td>Dynamic viscosity (Poise) = Density \times Kinematic Viscosity</td>
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<td>( \eta_0 )</td>
<td>Viscosity of supporting fluid</td>
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<td>( N )</td>
<td>Number of particles in chains of an ER fluid</td>
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<td>Outer diameter</td>
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<td>ppm</td>
<td>Parts per million</td>
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<td>( P_1 )</td>
<td>Orbital angular momentum</td>
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<td>PTFE</td>
<td>Polytetrafluoroethane</td>
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<tr>
<td>PVC</td>
<td>Poly vinyl chloride</td>
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<td>( \pi )</td>
<td>i) ( P_1 )</td>
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<td>ii) ( 180^\circ )</td>
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<td>Radio frequency</td>
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<td>Temperature</td>
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<td>Time</td>
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<td>Spin-spin relaxation time</td>
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<td>ii) Volume</td>
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<td>$W_0$</td>
<td>Weight of dehydrated solid</td>
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<tr>
<td>$W_L$</td>
<td>Weight of solid loaded with water</td>
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<td>W</td>
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<td>$\omega$</td>
<td>Angular frequency</td>
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<td>Force constant of the load cell</td>
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<tr>
<td>$y$</td>
<td>Thickness of shear plane</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Zeta (Electro-kinetic) potential</td>
</tr>
</tbody>
</table>
CHAPTER 1 INTRODUCTION

Fluids which reversibly change their apparent viscosity under the application of an electric field (electrorheological fluids) have received considerable amount of attention in recent years. However, only recently has it been realized that these fluids could be of real technological value.

Much of the work has focused on the effect of fields on the rheological properties, and then relating the dependence on various constituents of the fluid. Of course, many attempts were made as to the cause of the effect (banding, etc.), and explanations were made vague and unsatisfactory.

The aim of this work was to study the effect of the nature of the molecular component on the electrically induced changes. Techniques used included nuclear magnetic resonance (NMR), and electron spin resonance (ESR) in order to understand how the fluid worked. Previous work had been carried out on the effects using various resonance techniques with the main intent of achieving a better understanding of the effect. Knowledge gained from these studies was harnessed in turn to design new fluids. It was hoped to try to design new fluids to meet a need that there would have to be a significant amount of mechanical testing to check the efficiency of new fluids, and compare their rheological properties with the existing fluids.

The generation of fluids which were initially studied was based on the hydric polyacrylamide (HPMA) dispersed in DC or AC electric fields.
Section 1.1 AIMS OF THE WORK

Fluids which reversibly change their apparent viscosity under the application of an electric field (Electro-rheological fluids), have received a considerable amount of attention in recent years. However only recently has it been realised that these fluids could be of real commercial value.

Much of the early work into the effect involved simply examining the gross mechanical properties, and then studying the dependence on the various constituents of the fluid. Of course suggestions were made as to the cause of the effect based on these measurements, but these descriptions were rather vague and sketchy.

The aim of this work was to study the ER effect at the molecular level using various forms of magnetic resonance spectroscopy (nuclear magnetic resonance (NMR), and electron spin resonance (ESR)), in order to understand how ER fluids work. No previous work had ever been carried out on ER fluids using both magnetic resonance techniques with the specific intent of achieving a better understanding of the effect. Using knowledge gained from these studies it was hoped to try to design new fluids. This meant that there would have to be a significant amount of mechanical testing to check the efficiency of new fluids, and compare their gross properties with the existing fluids.

The generation of fluids which were initially studied comprised the hygroscopic polymer salt lithium polymethacrylate (LiPMA) dispersed in 20 cs silicone oil,
which acts as a non-conducting supporting medium. The major problems with these fluids are:

(i) limited temperature range of operation,
(ii) excessive electrical power consumption
(iii) settling out problems

These drawbacks led us to study ER fluids based on various zeolites as the solid constituents. Zeolites lend themselves readily to study by the spectroscopic techniques chosen. The work revealed the improved properties of these fluids with scope for even better performance. Also, for the first time, an insight has been obtained into what actually happens in certain ER fluids when the electric field is applied.

The engineering of practical devices was achieved some time ago, and these now await more efficient durable, long lasting, and commercially cheap fluids. It is hoped that this work as well as discovering a new original type of fluid, has also gone some way to revealing the mechanism that actually does cause the effect.

Section 1.2 Background of ER fluids Past and Present

Changes in the viscosity of a liquid by the application of an electric field were first measured by König [1] in 1885, using a potential difference of 14 kV across a glass capillary, which caused a 30% increase in the viscosity of turpentine. Other early work by Duff [2] in 1896 using an electric field of 2.7 kV mm⁻¹ observed an increase of 0.5% in the viscosity of Castor oil. All the early work has since
been found to contain certain inaccuracies, especially in the purity of the liquids used.

The 1930's saw a resurgence of interest into the original effect and Herzog et al. [3] used a tube of square cross section with opposite walls made of glass, and platinum respectively to apply fields of up to $0.22 \text{ kV/mm}$. No effect was noted with non-polar liquids eg. hexane and carbon tetrachloride, however an increase of 18% in the viscosity of ether was noted, which from later results indicates that the ether was wet. With a range of polar liquids increases in viscosity of between 1 and 17% were measured, but since the viscous flow is as much affected by the glass walls of the apparatus as by the walls contributing the voltage, the results are again open to question.

In 1935 Dobinski [4] examined the flow between a cylindrical metal rod of 1mm diameter, and a coaxial metal cylinder of 2mm internal diameter. The voltage did not exceed $0.44 \text{ kV/mm}^{-1}$ and no effects were reported for benzene, and carbon tetrachloride among other non-polar liquids. With dry ether no effect was observed, but a 12% increase in viscosity was observed at $0.22 \text{ kV/mm}^{-1}$ for wet ether. Using the same electric field strength polar liquids such as chloroform and nitromethane exhibited an increase in viscosity, whilst aromatic polar liquids such as toluene, and nitrobenzene showed no viscosity change. At the time this was termed the electroviscous (EV) effect, and this term is still used to describe viscosity changes in pure
liquids. Even today this term is sometimes misleadingly used to describe electro-rheological fluids even though this description is inappropriate as will be discussed later.

Sokolov and Sosinki [5] in 1939 used a tube of 0.6 mm square cross-section and applied electric fields of up to 1.7 kVmm\(^{-1}\). Potentials were also applied at various frequencies, but no systematic relationship was found between the viscosity and the frequency. This was the first work to suggest that a current accompanies the electroviscous effect, and offered an explanation for the effect in terms of a hydrodynamic description.

This theory was later proved to be incorrect by the work of Andrade and Dodd [6] who in 1946 used apparatus in which a liquid ran in a channel between metal electrodes which were used with fields up to 3.5 kVmm\(^{-1}\). It was shown that non-polar liquids, and non-conducting polar liquids show no EV effect, but polar liquids which do conduct, or can be made to conduct by the addition of water will show a viscosity change. This reaches a limiting value depending on the electrode separation and the frequency for an alternating field. Their explanation was that the field produces concentrations of free ions close to the metallic surface of the electrodes. These ions are thought to act as centres around which polar molecules form clusters. In 1951 the same authors [7] published further investigations of the EV effect, undertaken using more accurate measurements of viscosity. It was found that the increase in viscosity is proportional to the square of the electric field.
In 1977 Honda and Sasada [8] proposed a mechanism for the EV effect based on the electro-hydrodynamic effect of polar liquids. They used calculations of Eisenschitz and Cole [9] to disprove the theory of the orientation of polar molecules. Under the action of a dc electric field, it is proposed that charge carriers in a weakly conductive dielectric liquid are created in two ways. These are, dissociation of impurity salts, or the liquid itself, and by metal particles from the electrodes. The space charges put the liquid into motion, which transfers momentum, requiring a higher pressure gradient for a constant flow rate. This is concluded to be the same as an increase in viscosity, with electric fields of up to $5 \text{kV/mm}$ having been used.

Further work by Honda and Sasada [10] showed that increasing the conductivity of a dielectric liquid, by the addition of polar liquids eg. ethanol, acetic acid, or hydrochloric acid led to an increase in electroviscosity. This was in agreement with the work of Sokolov and Sosinki [5], some 40 years before. This paper also introduced the parameter $C$ which was said to be the ratio between the thickness of the space charge layer and the electrode gap. It was found that the largest increase in viscosity occurred when $C = 1$. It was believed that differing values of $C$ was the cause of some of the discrepancies of the early work on the subject. These effects of viscosity changes in "pure" liquids are of course of chemical and physical interest, but from a commercial viewpoint the changes in viscosity are not large enough for use in a practical device.
A much larger increase in viscosity was seen in suspensions of hydrophilic particles in an inert support fluid such as oil by Winslow [11] in work that was begun in the late 1930's but was not published in detail until ten years later. It was shown that certain particles suspended in low viscosity oils formed fibres when acted upon by an electric field. The most suitable particles at this time were found to be semi-conductive solids of high dielectric constant, such as moist silica gel. The largest effects were observed for particles of 1 μm diameter, in oil such as kerosene, with a particle concentration of between 40 and 50% by volume. Also dispersing agents eg. metallic soaps, sorbitol fatty acid esters were needed and it was suggested that particle migration was the cause of the chain formation. In disperse systems three electroviscous effects have been identified, and equations to explain the increase in viscosity have been put forward.

1) In dilute suspensions the first effect is caused by the distortion of the electrical double layer in shear flow. This gives rise to enhanced energy dissipation because of the perturbation of the interaction of charges in the double layer and those on the particle surface.

2) At higher volume fractions, particles are no longer isolated and double layers overlap and interact causing increased viscosity due to the electrical repulsion during particle collisions. When a sphere approaches another in flow they will be repulsed at small separations, with this repulsion occurring along a line perpendicular to the lines
of flow, which results in the increased viscosity.

3) Viscous energy loss in polymeric electrolytes occurs due to the change in the conformation of the polymer with the degree of ionisation, or the presence of screening electrolyte. Ionisation results in the expansion of the polymer coils which increases the free energy of the polymer.

Obviously in the case of dispersions of solid particles in a support fluid, the apparent viscosity may change on the application of the electric field, but what is actually happening is that the resistance to flow (rheology) of the fluids are being changed. So for this reason electro-rheology (ER) is a better description of the effect.

The magnitude of the ER effect by the Winslow type of fluids was now beginning to be sufficient for practical devices. In this situation there is also the need for instantaneous changes in the viscosity of fluids via sensors and electronic controllers. Of course this required the use of computers which is one of the reasons why the subject lay dormant until the late 1960's.

In two papers published in 1967, Klass and Martinek [12, 13] showed that the ER effect increases with increases in electric field and temperature. The viscosity of the suspensions under investigation were also seen to decrease with an increase in the frequency of the applied field. The suspensions used consisted of either silica, or calcium titanate, in a naphthenic oil. The volume fraction of the solid used was between 0.2, and 0.5 with a non-ionic
surfactant also present in the suspensions. The electrode spacing was typically 0.25 mm with fields of up to 3.2 kV mm$^{-1}$. The proposed mechanism was that the electric field induces polarisation of the double layers surrounding the solid particles, dispersed in the medium of low dielectric constant. It was also found that the dielectric constant of the dispersion increased approximately linearly with the volume fraction of the dispersed solid. The dielectric constant also increased as the temperature increased, but decreased as the frequency of the applied field increased. With a dc field it was found that the increase of viscosity was proportional to the square of the electric field, while current deviates to higher powers after initially following the same relationship as the voltage.

In 1971 Lykov et al. [14] investigated the effect of an electric field of up to 10 kV mm$^{-1}$ on suspensions of silica (particle diameter 0.1 - 0.2 μm), and diatomite in a 1% solution of polyisobutylene brand 180 (thickener), and kerosene. It was noted that with increasing content (above 2%) the viscosity increased, before passing through a maximum and then decreasing. The maximum was different at each field intensity, but in all cases it appeared at approximately 6% moisture content, and moved to lower moisture contents as the applied field increased. It was found that the ER effect decreases to a zero value at 20% moisture content.

Similar studies on the influence of water on the ER effect of dispersions was carried out by Uejima [14].
dispersion used consisted of crystalline cellulose (average diameter 10 μm) and insulator oil. The dielectric constant of the dispersion was found to increase by a factor of two as the amount of water present increased from 3 to 9%. It was thought that the water is first absorbed into the inner part of the solid particles, during which time no change is seen in the viscosity. Then as the particles are saturated further water is adsorbed on the surface of the particles which causes the increase in the ER effect.

This is attributed to the formation of electrical double layers described initially in reference [12]. In two articles Deinega et al. [16, 17] showed how, at high electric field intensities of 0.4 to 3.2 kVmm⁻¹, the dielectric constant rises, reaches a maximum and then falls as the water content increases from 0 to 30%. A steady increase, but no maximum, was found for lower electric field strengths. The ER effect also showed a similar dependence on the water content, with all experiments being performed on a dispersion of starch in vaseline oil. The conductivity of the samples was also found to increase with the increase in the water content above 20% for fields of 0.1 kVmm⁻¹, and above 5% for fields of 3.2 kVmm⁻¹. Reference [16] also reviews the possible explanations for the ER effect up to 1978.

Deinega et al. [17] used the same system as in the previous article, and varied the moisture content up to 40%. It was suggested that the ER effect is due to a change from a free, to a bound state of water, which is accompanied by
an organisation of its structure. Hydrogen bonds are said to be formed to the surface OH groups, and molecules of $H_2O$, and between adsorbed molecules of $H_2O$. This chain of water molecules on the surface is then said to enable proton transfer in the electric field. It was also found that electrical resistance is highest at the contact region of the solid particles, so causing a voltage drop. These are the perfect conditions for polarisation interaction between the solid particles. When free water appears on the particle surface, in this case above 35%, it is suggested that collars of water are formed at the contact sites, and the electrical resistance falls, reducing the polarisation interaction, and weakening the structure.

Also in 1982 Gorodkin et al. [18] examined the effect of temperature, and mechanical vibration on the ER properties of a suspension. This consisted of 10% by weight of diatomite activated with various amounts of water in the range 4 to 7%, in transformer oil. Oleic acid was dissolved in the dehydrated transformer oil to act as a surfactant. Electric fields of between 0.2 and 3.5 kVmm$^{-1}$ were used, and it was found that the mechanical vibration of the sample increased the number of bridged structures of solid particles, so increasing the current through the suspension. The result of increasing the temperature on the effective viscosity was to increase it until the temperature was approximately +60°C, after which the effective viscosity decreased. The value of the temperature for the maximum viscosity was also seen to decrease as the water content of
the solid particles decreased.

Investigations by Shulman et al. [19] on silica gel activated by moisture, and diethylamine were carried out in 1977. All the theories for the effect relating to water "bridges" are brought together, along with the findings of the authors. The idea of hydrogen bonds formed by the adsorbed water molecules inducing polarisation between the solid particles, and proton transfer after giving up electrons at the electrode is again used to explain the effect.

The idea of water "bridges" has been rejected in a recent paper by Brooks et al. [20] who measured conductivities, yield stresses, and viscoelastic properties and came to the conclusion that there is no charge flux across the particle-solvent interface.

Many solid particles have been tried in ER fluids as this was found to be the major variant in the magnitude of the ER effect. The supporting oil was found not to directly influence the effect and was purely present as a supporting medium which should be non-conducting and inert, with a viscosity in the range 10 to 30 cp. Occasionally gels have been used to reduce the settling out problem of the solid particles.

Of the more recent solids which have proved to make useful ER fluids many have been patented in anticipation of commercial exploitation. One example is that of a solid water-containing polyhydric alcohol which was patented in 1978 by Stangroom [21]. Similar hydrophilic polymer salts
eg. lithium polymethacrylate (LiPMA), were also patented by Stangroom [22] in 1980, with all the polymeric solids containing free, or neutralised acid groups, within certain limits of water absorbency, and density. Further polymer and phenolic salts were also patented by Stangroom [23] in 1985.

Other completely different types of solids have also been used such as aluminium silicates or zeolites, with a Si:Al ratio in the range 1.25 to 6.66 which were patented in 1987 by Goossens et al. [24]. A very similar patent has also been granted for zeolites with low Si:Al ratios to Fillisko and Armstrong [25] in 1988.

Very recently a new kind of approach to the kind of solid particles needed for ER fluids was undertaken by Inoue [26] and Fujii et al. [27]. This involved the use of a three-layer composition of the solid particle. An organic polymer centre eg. polystyrene, polyethylene was covered with a conducting layer of 1 μm thickness, this layer may be a metallic compound, or an organic conductor. This is then covered with an insulating layer again approximately 1 μm in thickness, which could be a PVC, or varnish, or an inorganic insulator. The major benefit of this type of solid is that it does not contain an activator such as water, which means that it has a wider operational temperature range.

Various theoretical models have been proposed to explain the ER effect. One of these by Shulman et al. [28], uses the idea of an inter-electrode bridge which stretches...
with the motion of one of the electrodes. Using calculations for the shear stress formulae have been derived which give good agreement with experimental data eg. variation of the ER effect with the activator content.

Arguelles et al. [29] have suggested a model for the flow of an ER fluid between parallel plates used to generate an electric field. This model does not give complete consistency with experimental data, but it does show that it is possible to calculate a concentration of solid particles which will give the maximum ER effect.

A further theoretical model for the primary electroviscous effect in a suspension of spheres with thin double layers has been calculated by Hinch and Sherwood [30]. The work is a continuation of earlier calculations of surface potentials created on the solid particles of dispersions. No comparison is made between the model and the experimental data which leaves the article open to criticism.

A theory for the ER effect was presented in 1983 by Menjivar and Rha [31] who predicted the effect of surface potential, particle radius, and ionic strength on the ER effect of colloidal dispersions of charged spherical particles. It is suggested that there is a "reasonable" agreement with the existing experimental data.

So far the papers which have been referred to have basically all contained similar ideas for the mechanism for the ER effect. However, in the last decade another possible cause for the ER effect has been formulated, which is not
dependent on water content, but is based on the dielectric properties of ER fluids. Much of the work has been carried out by Block and his co-workers using the Couette cell described in reference [32], to measure the flow modified permittivity (fmp) and viscosity of fluids under the application of an electric field. It was noted by Block et al. [33] that with a polymer dispersion in heptane, forced resonance peaks appeared in the variation of the relative permittivity (dielectric constant) with shear rate. Two peaks in the graph of dielectric loss against frequency occurred. The large dielectric loss at low frequencies i.e. $< 10^2$ Hz was attributed to interfacial polarisation caused by an ionic conductance process, due to trace impurity ions, over the surface of the particles. The high frequency process was thought to be due to a dipolar mechanism.

Block and Kelly [34] later used the results from the above work to describe their own mechanism for the ER effect. This mechanism is based on the fact that the resonance seen in the measurement of the relative permittivity with shear rate, results from an in-phase condition between the sinusoidal electric field, and the rotation of the polarisation vector for the particles in flow. The particle rotation is flow induced, which means that the polarisation vector, and the field direction are non-collinear, except at resonance. Also the "in", and "out" of phase polarisation components are a result of a time dependent polarisation. The extreme conditions of a very rapid, or very slow polarisation do not provide an out
of phase component. When an out of phase component is present, this component is orthogonal to the field direction, a particle torque is induced, and work is done to maintain the flow against the torque, which results in a larger viscosity of the sample.

Block used various anhydrous solids in ER fluids again to enhance the temperature range of operation. Various unsaturated, electron rich, fused-polycyclic systems comprising at least one heteroatom were used. Examples of these solids include phthalocyanines, and poly(acene-quinone) polymers which have been patented by Block and Kelly [35]. The above work suggests that Block's explanation for the mechanism for the ER effect may apply to certain fluids, but another mechanism is applicable to systems containing an activator such as water.

In a recent review article Block and Kelly [36] covered a large amount of the work in ER fluids carried out up until 1988, both on hydrated and anhydrous solid component based ER fluids.

Section 1.3 Variation of Shear Stress with Shear Rate of ER fluids with no Electric Field

With no electric field ER fluids normally show an approximate Newtonian variation of shear stress with shear rate i.e. linear relation. When an electric field is applied the behaviour is rapidly and reversibly changed to that of a Bingham plastic, and a yield point is observed under zero shear rate, which is observed to be a function of the
applied electric field. Shear stress ($\tau$) is defined by the Newtonian formula $\tau = \eta \dot{\gamma}$ where $\eta$ is the viscosity, and $\dot{\gamma}$ the shear rate. This means that the viscosity should remain constant as shear rate increases proportionally to shear stress as shown in Fig. 1.1. Other types of shear stress behaviour with shear rate are also shown.

Section 1.4 Practical Requirements of ER Fluids

In practical devices, the major properties of an ER fluid that determine its usefulness are as follows,

1) The ER effect should be as large as possible for a given electric field.
2) The conductivity of the fluid should also be as low as possible.
3) The properties outlined in 1), and 2) should hold over a large temperature range (e.g. -30°C to +90°C)
4) Solid particles should settle out as little as possible.
5) The zero field viscosity of the fluid should be as low as possible.
6) The material should ideally be relatively cheap to manufacture for bulk commercial applications.

From the engineers' point of view, the important aspects are the maximum levels and relationships between pressure and flow, the controlling electric field, and the size and efficiency of the controller.

An example of the expected requirements of practical ER fluids has been shown by Duclos (37). These calculations are a comparison of the performance level of a typical fluid.
Fig. 1.1 Shear Stress Behaviour with Shear Rate
of the present generation, with the necessary characteristics of a fluid of the future.

A typical fluid at the present time has the following parameters,

Yield stress \((\sigma) = 2 \text{ kPa}\) with a field of \(4 \text{ kV/mm}^{-1}\).

Zero field viscosity = \(1 \text{ Poise}\)

Current density = \(1 \mu\text{Acm}^{-2}\) also at \(4 \text{ kV/mm}^{-1}\).

There are many possible uses of ER fluids such as in clutches, valves and damper systems. Some of these uses will now be discussed in more detail, together with the characteristics of ER fluids required for use in practical devices.

1) The ER clutch where the fluid acts as the means by which torque is transmitted from the drive shaft. This may take one of two types, either a cylindrical, or a plate clutch. The calculations below are for a cylindrical clutch in which a drive shaft from an engine is inserted in a concentric cylinder. The gap between the central shaft and the outer cylinder is then filled with the ER fluid. The amount of torque transferred from the drive shaft to the outer cylinder will be dependent on the viscosity of the ER fluid.

In the plate clutch two plates are separated by a small gap which is filled with the ER fluid. One of the plates is again attached to a drive shaft, so on the same principle the amount of force transferred from the driven plate will depend on the viscosity of the separating fluid.

2) The ER damper in which the fluid changes viscosity to absorb shocks, such as in an engine mounting: such a
mounting promises to be the first widespread application of the ER effect. In this case a piston is connected to the area likely to take a shock. This piston is situated in a cylinder containing the ER fluid. When a sensor detects movement in the piston then an electric field is applied to the fluid to increase its viscosity and damp out the shock.

3) The first commercial ER device has been marketed in the past year, and is used to draw fibres, or material onto large reels. This device must be used in fairly stable temperature conditions, so as to reduce the fluctuations in the performance of the present ER fluids.

In the following calculations the definition of the symbols used are shown below.

Vol. = Fluid volume needed in the device (cm$^{-3}$)
P = Electrical Power (W)
$\sigma$ = Static yield stress (kPa)

$\omega_0$ = Relative speed between input and output shafts, this equals zero when engaged, and 700 rpm when disengaged (rpm).

$T_{ER}$ = Torque transmission in clutch when engaged (Nm)
$T_0$ = Torque transmission when disengaged (Nm)

$F_{ER}$ = Force resistance by fluid with the electric field on in the damper (N)

$F_0$ = Force resistance by fluid with electric field off in damper (N)

Vel. = Damper velocity (ms$^{-1}$).

The shear device such as the damper will always consume less power than a fixed plate device such as the clutch. ER fluids need an order of magnitude improvement in their
performance from that at present for use in clutches, but less than this for dampers.

The damper systems might seem to be achievable with the present generation of fluids, as this task is not the most

Table 1.1 (Data from reference L371)

<table>
<thead>
<tr>
<th></th>
<th>$T_{ER}$</th>
<th>$T_0$</th>
<th>$\omega_0$</th>
<th>Present Fluids</th>
<th>Future Fluids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clutch</td>
<td>500</td>
<td>5</td>
<td>700</td>
<td>Vol. 180000, $P_0$ 1800</td>
<td>Vol. 1800, $P_0$ 14</td>
</tr>
<tr>
<td>Damper</td>
<td>1000</td>
<td>100</td>
<td>0.5</td>
<td>Vol. 130, $P_0$ 5.2</td>
<td>Vol. 16, $P_0$ 0.07</td>
</tr>
<tr>
<td>Sliding</td>
<td>1000</td>
<td>100</td>
<td>0.5</td>
<td>Vol. 560, $P_0$ 23.4</td>
<td>Vol. 38, $P_0$ 0.14</td>
</tr>
<tr>
<td>Electrode</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

arduous that could be contemplated for an ER fluid. However what is not quite so obvious from the above table is that for a sliding plate damper with a present day ER fluid the electrode gap required in the device would be 0.25mm. Whilst this is not out of the question, it does require great precision in the manufacture of the device, which would increase its production time, and therefore cost. The dimensions of the devices with the fluids of the future are shown below.

1) Clutch diameter 15 cm, and length 10 cm.
2) Sliding plate damper has 4 cm by 4 cm plates, with a 1 mm gap.
3) Fixed electrode damper has 7.6 cm diameter, 15 cm long concentric cylinders, with a 1 mm gap.

The problem of abrasive wear from the solid particles is greatest for particles diameters in the range 10 to 25 μm as has been shown by Schofield and Fodor [38]. Below 5 μm diameter particles both adhesive, and abrasive wear will be kept to a minimum.

The commercial interest in ER fluids has led to various predictions as to their future use. One such prediction is given in an article by Cookson [39], who suggested that the world market for ER fluids and devices will begin to take off in 1991. The availability of highly sophisticated electronic sensing and control devices with the right microprocessors, and software should lead to a world market of $1.3 bn by 1995, and up to $12 bn by the year 2000.

Section 1.5 Constituents of ER fluids used in this Study

- Supporting Fluid

All the ER fluids used in this study contained solids which were dispersed in silicone oil. All of the silicone oil was supplied by Dow Corning Ltd, Barry, Wales. For the measurements of the viscosity of ER fluid viscosity with no electric field (Chapter 2) various silicone oils were used of viscosities 1, 20, and 50 cs to study the effect on the viscosity of the increase in the volume fraction of the solid. For all the other measurements carried out an oil of 20 cs viscosity was used. All of the silicone oils are made up from a mixture of silicones of various chain lengths as
shown in Fig. 1.2.

Fig. 1.2 Silicone oil formula

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\begin{array}{c}
\text{Si} \quad \text{O} \\
\text{Si} \quad \text{O} \\
\text{Si} \quad \text{CH}_3
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

For the 20 cs oil the average value of \( n \) is 2, and the properties of this oil include a boiling range of \( >200^\circ C \), and a Pour point (when the oil will not flow) of \( -60^\circ C \). The mixed nature of the silicone oil was also checked by \(^{29}\text{Si}\) NMR which showed a variety of silicon environments, and by mass spectroscopy which also showed a wide range of fragments due to all the slightly different silicone molecules in the mixture. The supporting oil should have a low dielectric constant so then it can withstand high electric fields without breaking down, and also have a low electrical conductivity. Both these conditions are satisfied in the case of silicone oil.

Section 1.6 Lithium Polymethacrylate (LiPMA)

The LiPMA solid samples were supplied by Laser Engineering Ltd. The formula of this compound is shown below in Fig. 1.3.

Fig. 1.3 Lithium polymethacrylate formula

\[
\begin{array}{c}
\text{H} \\
\text{H}
\end{array}
\begin{array}{c}
\text{C} \\
\text{H}
\end{array}
\begin{array}{c}
\text{H} \quad \text{COO}^- \quad \text{+Li} \\
\text{C} \quad \text{C}
\end{array}
\begin{array}{c}
\cdots \cdots \cdots \\
\text{CH}_3
\end{array}
\]

The samples were made by the neutralisation of
polymethacrylic acid of molecular weight of approximately 25,000 with lithium hydroxide to a pH of 9. The polymer salt was then spray dried to produce the final solid which has a density of 1.45 g cm\(^{-3}\). The total pore area is 17.54 m\(^2\) g\(^{-1}\), measured by a mercury porisometer, with a total pore volume of 0.698 cm\(^3\) g\(^{-1}\). This type of polymer salt is very hygroscopic, and contains approximately 20% by weight of water after the spray drying process. This salt is easily soluble in water, but not to any significant extent in any organic solvent.

Section 1.7 Zeolite Solids used in this Study

Zeolites are framework aluminosilicates, built from corner sharing SiO\(^4\)\(^+\) and AlO\(^5\)\(^-\) tetrahedra, and containing regular systems of intracrystalline cavities, with channels of molecular dimensions. The name zeolite was taken from the Greek for boiling stone as the first mineral of this type, stilbite, which was discovered some 200 years ago, loses water rapidly on heating, and seems to boil.

The negative charge of the framework, equal to the number of the constituent aluminium atoms, is balanced by exchangeable cations, M\(^{n+}\), typically sodium, located in the channels which normally also contain water. The general oxide formula of a zeolite is,

\[ M_{x/n} \left[ \text{AlO}_2 \right]_x \left[ \text{SiO}_2 \right]_y \cdot m \text{H}_2\text{O} \]

At present there are around 40 zeolite minerals which have been identified with the ratio \(y:x\) varying from 1 to 5
depending on the structure, and at least 120 synthetic species with a very wide range of aluminium contents. The zeolite channel systems, which are either one, two, or three dimensional, may occupy more than 50% of the crystal volume, and are normally filled with water.

Cations neutralising the electrical charge of the aluminosilicate framework can be exchanged for other cations from solution. Zeolites often possess high ion-exchange selectivities for certain cations eg. in zeolite Na-A sodium can be exchanged for n-alkylammonium cations, but not for branched alkyl ammonium, or tetramethylammonium ions. A very thorough review of the topology and geometry of most natural, and synthetic zeolites has been provided by Smith [40].

Several methods have been used to determine the lattice structure of zeolites, but much information can be gained using several different NMR techniques. Both silicon and aluminium nuclei may be studied by NMR: the chemical shifts give information on the different environments of those nuclei in the zeolite framework. This method is described in more detail later in Chapter 3. Another NMR based experiment that has been used to study zeolite structures is the $^{129}$Xe NMR study of xenon gas adsorbed into the zeolite channels. One of the main exponents of this technique is Fraissard who has published a number of papers on the subject, examples of which are given in references [41, and 42]. A good example of this type of technique was in the characterisation of the void spaces in mordenite type
zeolites by Ripmeester [43]. At high loading levels of Xe three peaks are seen. The one at low field is due to Xe in the more "dense" side pocket environment, while the middle band is due to the Xe in the main channels. The sharp high field resonance is due to the free gas on the external surface. As the cation is exchanged from Na\(^+\), to K\(^+\), and then NH\(_4\)\(^+\) the space available for Xe in the side pockets is reduced, and this is reflected in the relative size of the side pocket peak.

The zeolites used to test their use as ER fluids will now be discussed, but examples of both the structures of the different frameworks, and also photographs of several of the zeolites taken using an electron microscope are shown in the appendix. The density of zeolites is rather difficult to calculate accurately as the water content in the different zeolites significantly alters their density. For this reason a density of 2 g cm\(^{-3}\) was assumed for all zeolites, which should not incur more than a 10% error at most for any zeolite.

The chemical composition of the major zeolites which were tested in this study are shown in Table 1.2 on the following page.

In the particle size analysis given this corresponds to three fractions of the particles i.e. 0.1, 0.5 and 0.9 which are less than the specified particle sizes in microns. The water contents were determined by the weight loss at 1000°C, and the Si:Al ratio by the molar ratio of SiO\(_2\):Al\(_2\)O\(_3\).
### Table 1.2 (Data supplied by Laporte Ltd)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>Fe(ppm)</th>
<th>Si:Al</th>
<th>H₂O%</th>
<th>Particle size analysis (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-A</td>
<td>35.5</td>
<td>41.7</td>
<td>22.0</td>
<td>250</td>
<td>1.0</td>
<td>22.2</td>
<td>6.4 13.9 22.8</td>
</tr>
<tr>
<td>Na-X</td>
<td>32.7</td>
<td>46.4</td>
<td>19.2</td>
<td>250</td>
<td>1.21</td>
<td>23.1</td>
<td>2.4  3.8  5.7</td>
</tr>
<tr>
<td>Na-Y</td>
<td>22.6</td>
<td>63.0</td>
<td>10.7</td>
<td>700</td>
<td>2.38</td>
<td>20.7</td>
<td>8.7  19.3 29.2</td>
</tr>
<tr>
<td>Deal-Y</td>
<td>24.9</td>
<td>71.8</td>
<td>0.13</td>
<td>1600</td>
<td>2.45</td>
<td>17.8</td>
<td>10.4 18.2 27.5</td>
</tr>
<tr>
<td>Na-mord</td>
<td>10.6</td>
<td>81.0</td>
<td>7.10</td>
<td>250</td>
<td>6.50</td>
<td>10.7</td>
<td>2.3  5.0  9.4</td>
</tr>
<tr>
<td>H-mord</td>
<td>7.25</td>
<td>91.4</td>
<td>0.03</td>
<td>200</td>
<td>10.7</td>
<td>10.4</td>
<td>2.2  4.6  9.1</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>3.78</td>
<td>94.5</td>
<td>0.06</td>
<td>100</td>
<td>21.3</td>
<td>10.0</td>
<td>2.9  4.7  7.2</td>
</tr>
</tbody>
</table>

### Section 1.8 Zeolite 4A

This zeolite is never found naturally, but it can be synthesised. The framework is formed from two types of polyhedra with double rings formed by sodalite units (also called truncated octahedra). The centre of the unit cell has a free diameter of 11.4 Å usually referred to as the α cage. The smaller β cages interlinking the sodalite units have apertures of 2.2 Å diameter, whilst the aperture for the α cages are 4 Å, although this does depend on the type of cation in the dehydrated zeolite as different cations obstruct the access to the α cage by varying amounts. The channel system is three dimensional, whilst the Si:Al ratio in this type of zeolite is always unity.
Section 1.9 Zeolite 13X

This type of zeolite is synthetically produced and has a Si:Al ratio of approximately 1 to 1.5. This framework structure is very open with a pore size for the channels of 8 Å which lead into supercages which have a diameter of 13 Å. This type of structure is formed from sodalite units which are linked together, and zeolite Y is also based on the same structure, the only difference being that in zeolite Y the Si:Al ratio is slightly higher in the range 1.5 to 3. This family of zeolites are known as faujasites, and once again the channel system is three dimensional. Of course, dealuminated -Y zeolite is also of the same framework, but the aluminium is removed from the lattice, although it is still present in the form of octahedrally co-ordinated Al\(^{3+}\) to six water molecules. The effect of removing the aluminium from the lattice is that the lattice no longer has a negative charge, and so requires only a very small number of cations to balance the small number of aluminium ions remaining in the lattice.

Section 1.10 Mordenite

Mordenite occurs naturally, but it can also be made synthetically. It is one of the most siliceous zeolites, and in the natural state has a Si:Al ratio of 5, which is almost constant, suggesting that there is an ordered distribution of Si and Al in the framework. The structure consists of cross-linked 5-membered rings, with chains combining to form twisted 12-membered rings which span
vertical, near cylindrical channels. This structure predicted a channel dimension of 6.7 Å but for natural mordenite it was found that only much smaller molecules could be adsorbed into the dehydrated zeolite: this led to the term "small port" mordenite. The synthetic material is characterised by free diffusion of molecules in the main channel, and has been termed "large port" mordenite. The main channels have side pockets of dimensions 2.9 Å by 5.7 Å with entrance pores of 2.8 Å. The cations in this zeolite are quite commonly Na⁺ or H⁺.

Section 1.11 ZSM-5 zeolite

This synthetic zeolite was originally produced by the Mobil Oil Company in 1972 and used to catalyse the synthesis of gasoline from methanol. This highly siliceous zeolite has the unit cell formula,

\[
\text{Na}_x\text{Al}_x\text{Si}_{16-2x}\text{O}_{96-2x}\text{H}_2\text{O}
\]

with \( x \) less than 27, and typically about 3, which corresponds to Si:Al ratios in the range 20 to 35, with this high value being indicative of a high thermal stability. This means that only a relatively small number of cations are needed to counteract the negative charge of the lattice with usually the cations being either Na⁺ or H⁺. The structure of ZSM-5 is based on two interlinked channel systems formed by 10-membered rings, of approximately 5.5 Å in diameter. The sorptive properties of this zeolite stem from its desirable pore size, and large internal volume. There have been several reports on the existence of two
X-ray crystallographically different phases of this zeolite, one having orthorhombic symmetry, and the other having monoclinic symmetry. Generally, the symmetry is orthorhombic. The transformation between the two symmetries involves only minor displacements of the atomic positions within the framework structure. The symmetry transitions which take place at high temperature (e.g., >500°C) do not change the size and shape of the channel openings, or the bond angle of the sinusoidal channel of the ZSM-5 structure.
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CHAPTER 2 MECHANICAL TESTING OF ER FLUIDS

Section 2.1 Experimental Procedure - Sample preparation

All the polymer and sepiolite samples required for mechanical testing were prepared in a similar fashion. The samples were first degreased for 3 to 4 days in a solvent to remove as much water as possible. The samples were dried at 120°C, and the sepiolite at 200°C. Each sample was treated and then left to pick up water from the atmosphere to the desired extent. The solid was then weighed.

$$\frac{W - W_0}{W_0} \times 100 = \text{percentage of water}$$

$W$ = weight of dehydrated sample
$W_0$ = weight of hydrated sample

To enhance the nicotine of the sepiolite, a 0.1N solution of nickel nitrate was added, followed by a solution of the nicotine solution containing the desired ratio of water. The samples were then dried for two days, after which time they were again treated with water and then continued to be soaked in a series solution of the hydrosol for five more days. After soaking and filtration, the samples were dehydrated before hydration as explained above. For those cases where the sepiolites were pretreated, the above procedure was carried out using a 15 solution of HCl rather than the saturated hydrosol solution.

After preparation, the solids were dispersed in 20 cc silicone oil obtained from Dow Corning, Inc. The silicone oil has a density of 0.96 g/cm³, while all the samples of polymer that were used were assumed to have a density of 1.03 g/cm³, although this will change slightly with the

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Section 2.1 Experimental Procedure - Sample preparation

All the polymer and zeolite samples required for mechanical testing were prepared in a similar fashion. The samples were first dehydrated for 3 to 4 days in an oven to remove as much water as possible. The polymer was dried at 150°C, and the zeolite at 200°C. Each sample was weighed, and then left to pick up water from the atmosphere to the desired content. The solid was then reweighed,

\[
\frac{W_L - W_0}{W_0} \times 100 = \text{percentage of water}, \quad (1)
\]

\( W_0 \) = weight of dehydrated sample
\( W_L \) = weight of sample loaded with water.

To exchange the cations in the zeolites, each sample was soaked in a saturated solution of the hydroxide solution containing the relevant cation for exchange. The samples were left for two days, after which time they were washed with water, and then continued to be soaked in a fresh solution of the hydroxide for two more days. Then after washing and filtration, the samples were dehydrated before hydrating as explained above. For those cases where the zeolites were protonated, the above procedure was carried out using a 1M solution of HCl rather than the saturated hydroxide solution.

After preparation, the solids were dispersed in 20 cs silicone oil (obtained from Dow Corning, Barry, Wales). This oil has a density of 0.96 g cm\(^{-3}\), while all the samples of polymer that were used were assumed to have a density of 1.43 g cm\(^{-3}\), although this will change slightly with water

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content. The samples of zeolite were also all assumed to have one value of density, in this case 2 g cm$^{-3}$. Again this is an assumption due to some inevitable variation in water content, but the error induced by these assumptions should not be more than 10%.

From these density values the solid was then made up to 25% by volume in a dispersion in the oil. Unless otherwise stated all the samples quoted in this study were of a 25% volume fraction of the solid component.

Section 2.2 Preparation of ER fluids with Surfactants

The dispersions were prepared using 50 cm$^3$ of silicone oil. The surfactant was then added in a fraction of 1% by weight, and the mixture was then heated to 60°C, so that the phases were well dispersed. This was then added to a 25% volume fraction of the solid. The suspensions were then left on a mechanical flask shaker for about 12 hours to ensure that the surfactant had a sufficient time to coat the solid particles.

Three different surfactants were used,
1) Oleic Imidazolene $\text{C}_3\text{H}_7^+\text{O}_{\text{C}(\text{CH})_2}\text{C}(\text{CH})_7\text{CH=CH(CH)}_7\text{CH}_3$
2) Dodecylamine $\text{CH}_3(\text{CH})_{11}\text{NH}_2$
3) Sympronc A2- which is the 2 mole ethoxylate of the fatty alcohol oleic Imidazolene.

The role of the surfactant is based on the fact that a colloidal dispersion can be prevented from settling out by an adsorbed layer of lyophilic material, namely the surfactant. This surfactant may be grafted, physisorbed, or
Section 2.3 Description of Measuring Devices

The viscosities of the various ER fluids were measured at zero electric field, and then with an applied field using two different devices for the applied field work.

1) The zero field viscosity data was collected using a conventional Ferranti viscometer.
2) The first of the electric field measurements was carried out using the static yield stress rig which measures viscosity changes at zero shear rate.
3) The second type of measurement allowed ER fluids to be studied at variable shear rate: this required construction of a novel electroviscometer.

Section 2.4 Zero Electric Field Viscosity Measurements

A conventional VM Model Ferranti rotating viscometer was used to measure the viscosities of the ER fluids at zero field. This type of measurement was not possible on the electroviscometer as the fluids at zero field are not viscous enough to be within its sensitivity range.

The Ferranti viscometer consists of two concentric cylinders which are immersed in the fluid. The outer cylinder is rotated by a motor at a pre-selected speed via a gearing system, which allows the investigation of different shear rates. The resulting movement of the fluid in the gap between the outer and the inner cylinder imposes a viscous drag on the inner cylinder, causing it to move an amount
that is directly proportional to the viscosity.

Section 2.5 The Static Yield Stress Rig

The static yield rig is capable of measuring the ER effect, and also the electrical conductivity of the sample. For two flat plates separated by a sample of oil, a force on the lower plate in the plane of the plates will cause the lower plate to move. When an ER fluid is placed between the plates no movement of the lower plate occurs until the applied force exceeds the static friction force (static yield stress). A description of this method is given by Stangroom [1].

This static friction force is sometimes known as "stiction", and usually increases as the voltage applied to ER samples increases. The static yield stress rig used in this study is shown in Fig.2.1.

The rig was made by Laser Engineering Development Limited. It has a lower earthed electrode which is a trough containing the sample. The trough is able to slide on a track underneath the stationary circular upper positive electrode. A micrometer screw is turned at a constant speed by a motor which loads the cantilever arm which in turn is pressing on the movable lower electrode. When the force on the arm is sufficient to overcome the resistance of the fluid the movable electrode will move forward ahead of the contact point with the arm. This will then produce a decrease in the stress detected from the sensors on the arm, before contact is re-established as the arm is moved by the
Fig. 2.1 a) The Static Yield Stress Rig (Top View)

Fig. 2.1 b) The Static Yield Stress Rig (Side View)
micrometer screw, and then the build up of the stress is renewed until the yield point is again attained and the process is repeated. Of course as the lower electrode is moving during the course of the measurement there will be an increase in the number of solid particles from the fluid which are trapped between the electrodes. This means that as the experiment proceeds there will be a slight increase in the yield stress for this reason, and an example of this is shown in Fig. 2.2. All yield stresses quoted in this section are the average peak values for each sample.

The control box of the static yield rig is capable of delivering up to 12 W of power, which means at the maximum voltage of 2.5 kV the largest current it is possible to draw is 5 mA. The accuracy of the ammeter in the control box is 1 μA, so this was taken as the lower limit for all the measurements. In the tables of results obtained from this device, any current which was below the sensitivity limit of the ammeter is indicated. The electrode area is 5.06 cm$^2$, and the gap used for all the measurements was 0.7 mm. By a switch selectable display, it is possible to apply electric fields from 0 to 2.5 kV, which correspond to 0 to 3.5 kV/mm$^{-1}$, with currents from 0 to 4 mA, and yield stresses from 0 to 20 kPa. A brief description of the standard method for the measurements taken with the static yield rig is outlined below.

1) First the movable electrode was thoroughly cleaned, before being filled with 4 cm$^3$ of the sample.

2) Next the movable electrode was positioned against the
Fig. 2.2 Output from Static Yield Stress Rig
cantilever arm using the spring pushrod on the safety cover. The position of the cantilever arm is determined by the setting of the micrometer screw, and this should be in the same starting position for all the samples.

3) The output of the yield stress was connected from a BNC socket on the main control box to a chart recorder, which was then set to run on an appropriate time base e.g. 20mm per minute.

4) The inhibit switch for the voltage was then moved to the position whereby the voltage could be applied, and the required electric field could be set.

5) The micrometer screw was then rewound two turns so that it no longer touched the cantilever arm, before the coupling to the electric motor was connected to the end of the micrometer.

6) The micrometer was rewound so as not to touch the cantilever arm at the beginning of the experiment. This is to ensure so that there is no stress measured by the sensors on the arm when the motor is switched on, and running smoothly. The motor to drive the micrometer was then switched on.

7) The experiment is then left to run at the chosen voltage, before disconnecting the motor and switching off the voltage, and replacing the movable electrode to the starting point. Commencement at a new electric field could then begin following the same procedure.

The temperature control method of the samples on this rig was only very approximate to within ±5°C. This involved in
the case of high temperatures i.e. above ambient, blowing heated nitrogen gas into the plexiglass safety box surrounding the rig. For temperatures below ambient nitrogen gas was passed through a coiled pipe submerged in a dewar of liquid nitrogen before being blown into the box containing the rig. For all temperature measurements a Comark electronic thermometer was placed inside the safety box, but obviously not in the direct flow of the nitrogen gas.

Section 2.6 The Electroviscometer

The design of the electroviscometer was made after considering the current designs available for both conventional viscometers, and commercial electroviscometers, the latter seem to be modifications of conventional viscometers, rather than being based on a fresh approach. The main aims of this new design was to be able to vary the following parameters on which the ER effect is known to depend.

1) Shear rate, either by altering the velocity of shear, or the gap between the electrodes.
2) Temperature of the sample.
3) Scanning speed of the applied electric field.

Section 2.7 Basics of the Construction

The design which we decided to base our electroviscometer on is shown in Fig.2.3. The outer pot which is made from brass contains the sample, of which
Fig. 2.3 a) The Electroviscometer (Side View)
Fig. 2.3 b) The Electroviscometer (Side View of the sensor arm)
approximately 70 cm$^2$ are required. An inner plug made from Tufnol is situated inside the pot, and this plug has a strip of brass set into it, so that when in operation the wall of the pot acts as the earthed electrode, and the brass surface of the plug acts as the positive electrode. The plug, and the pot have walls which are tapered at an angle of 10°, and the plug can be raised or lowered with a micrometer screw allowing the gap between the two electrodes to be varied from 0.69 to 2mm, while keeping the walls parallel. The micrometer scale was calibrated by filling the pot with cyclohexane, and then measuring the capacitance for different gaps.

The outer pot is driven by a belt drive from an electric stepper motor, which is operated from a BBC computer. The current stepper motor is capable of rotating the outer pot at speeds from 1 to 20 revs per minute, which of course varies the shear rate that the sample is subjected to from 1.5 to 43.8 s$^{-1}$.

On the same principle as the conventional viscometer the force transferred from the motion of the outer pot to the inner plug will be dependent on the viscous drag imposed by the fluid separating the two.

The amount of movement of the inner plug depends on the viscosity of the fluid, hence that movement has to be measured. This was done by a hollow spindle on which the plug is mounted. At this point, where the spindle emerges from the top of the viscometer, a brass bar was connected horizontally. One end of this bar was touching a load cell
which contained a spring. The spring was calibrated so that
the force needed to compress the spring by 1 mm was known.
To measure the distance of compression of the spring by the
bar, at the opposite end of the bar was positioned a
transducer (Radio Spares model DG 2.5), which is capable of
detecting movements of less than 0.1 μm in the position of
the bar. The transducer is powered by a Kingshill model 300
stabilised power supply at a constant 20 V, which causes the
transducer to produce 1200 mV for every 1 mm movement. The
output of the transducer was fed to a chart recorder (JJ
Instruments Model PL3).

The voltage supply for the experiment was a Vacuum
Generators programmed power supply, capable of scanning from
0 to 5 kV or any value in between, in times from 0.1 s to
1000 s. This power supply can provide up to approximately 3
W, i.e., 1 mA at 3 kV. The ramping of the voltage was also
taken to the chart recorder so that the typical type of
readout obtained (see Fig. 2.4) has a x axis corresponding
to increasing voltage, and a y axis which gives the movement
of the transducer, and so can be related to the viscosity of
the sample as will be explained shortly. The speed of
ramping of the voltage allowed the response time of the
fluid to be studied, as well as the magnitude of the effect.
The current drawn by the sample was followed using a
standard milliammeter, which can detect 0.01 mA.

The temperature of the system above ambient was
controlled by a bath of silicone oil which was situated in a
double walled, glass vessel surrounding the rotating pot.
Increasing Shear Stress

Output from Electroviscometer

Fig. 2.4 Output from Electroviscometer
Water was circulated between the vessel walls using a Colora N.40527 thermostat which was used up to +60°C. The silicone oil was stirred using a magnetic stirrer to ensure uniform temperature. The temperature of the sample inside the pot was followed using a Comark electronic thermometer the thermocouple of which was fed down through the hollow spindle attached to the inner plug. The thermocouple was situated in the sample on top of the inner plug: this was not in the applied electric field. Sample temperatures down to +5°C were obtained by cooling the pot in an ice bath.

The total electrode area of the device was increased to fifteen times that of the static rig ie from 5 to 72.12 cm⁻², thus providing increased sensitivity. The whole device was enclosed by a perspex safety screen, which was placed on a micro switch to prevent application of the electric field without having the safety screen in position.

Section 2.8 Theory of the Forces exerted in the Electroviscometer

A plan view of the electroviscometer is shown in Fig.2.5.

\[
F_2 \frac{R}{r} = F_1 r
\]

where \( A \) is the electrode area, \( \) (1)

\[
\text{Stress} = F_2 \frac{A}{r}
\]

\( \) (2)

Shear Stress = viscosity (\( \eta \)) x shear rate (\( \dot{\gamma} \)) \( \) (3)

Shear rate (\( \dot{\gamma} \)) = velocity of rotation (\( \nu \))

electrode separation (\( d \))

with (C) the average circumference of the plug, and (\( \nu \)) the frequency of rotation of the pot then,
\[ v = C \times \nu \]  \hspace{1cm} (5)

\[ \therefore \nu = 2\pi \times \text{average radius of plug} \times \nu \]  \hspace{1cm} (6)

Substituting (6) into (4) then,

\[ \nu = \frac{2\pi r \nu}{d} \]  \hspace{1cm} (7)

Now substituting (2) and (7) into (3),

\[ \frac{F_2}{A} = \frac{\eta \times 2\pi r \nu}{d} \]  \hspace{1cm} (8)

\[ \therefore \frac{F_2}{A} = \frac{\eta A \times 2\pi r \nu}{d} \]  \hspace{1cm} (9)

For the initial case,

\[ \Lambda = 72.12 \times 10^{-4} \text{ m}^2 \quad r = 2.91 \times 10^{-2} \text{ m} \]

\[ \nu = 1 \text{ rev per minute} = 1.667 \times 10^{-2} \text{ Hz} \]

\[ d = 2 \times 10^{-3} \text{ m} \]

\[ \eta = \text{dynamic viscosity} = \text{density} \times \text{kinematic viscosity} \]  \hspace{1cm} (10)

\[ \eta \text{ has units of poise} \quad 1 \text{ poise} = 1 \text{ g cm}^{-1} \text{s}^{-1} \]

\[ 1 \text{ centipoise} = 0.01 \text{ g cm}^{-1} \text{s}^{-1} = 0.001 \text{ kg m}^{-1} \text{s}^{-1} \]  \hspace{1cm} (11)
Two different springs were found to be able to cover the required range in the load cell, these had the compression rates shown below.

Heavy spring = 6.867 Nmm\(^{-1}\)  \hspace{1cm} Light spring = 4.415 Nmm\(^{-1}\)

The springs with these force constants were found to be repeatable and consistent in their performance, unlike springs of much lower compression rates. The calibrations of these springs were checked at regular intervals to ensure that there was no change in these values. Each spring has a maximum deflection of 2mm.

The magnitude of the forces measurable by these load cells eg. 0.132N from equation (9) with this value for \(F_2\) requires a viscosity of the sample around 12,000cp. This is 12,000 times greater than the viscosity of water under standard conditions, however glycerol does have this viscosity at about 0°C.

Section 2.9 Calibration of the Electroviscometer

A sample of glycerol was tested in the viscometer at a temperature of approximately 0°C, and was indeed found to give the type of forces in the region covered by the electroviscometer. However the temperature control of the sample in the electroviscometer is only accurate to ±1°C, which is large enough to produce significant variations in the viscosity of glycerol. For this reason a set of standard silicone oils supplied by Brookfield of viscosities 12,200, 32,000, and 53,920 cp at ambient temperature were used to calibrate the viscometer.
The force $F_2$ is equal to the force constant of the spring in the load cell ($X$) eg. 6.687 Nmm\(^{-1}\) multiplied by the distance moved by the spring ($m$).

$$F_2 = X \times m \quad . \quad (12)$$

The distance ($m$) moved by the spring will be equal to the voltage produced by the transducer and shown on the chart recorder in mV ($V$), divided by the sensitivity ($S$) of the transducer, which was stated earlier to be 1200 mVmm\(^{-1}\) movement of the transducer, hence,

$$m = \frac{V}{S} \quad . \quad (13)$$

This can be substituted into equation (12), and then placing this in equation (9) gives,

$$X \times V = \frac{\eta A 2\pi \nu r}{S} \quad . \quad (14)$$

Now rearranging this equation (14), the value of the viscosity can then be calculated from the chart recorder reading, as shown below in (15).

$$\eta = \frac{X V d}{A 2\pi \nu r S} \quad . \quad (15)$$

For an electrode separation of 2mm, at a rotation of 1 rev per minute, and with the heavy spring in the load cell, then the viscosity of the sample will be related to the voltage from the transducer by the equation (16),

$$\eta \text{ (kg m}^{-1}\text{s}^{-1}) = 0.52 \times V \text{ (in mV)} \quad . \quad (16)$$

To obtain $\eta$ in centipoise then multiply the right hand side of the above equation by 1000 (see equation 11).
Section 2.10 Standard Procedure for use of the Electroviscometer

1) Ensure that the outer pot, and all electrical connections are scrupulously clean.

2) Fill the outer pot with approximately 70 cm$^3$ of the sample fluid, and then attach the pot to the main flange below the drive belt using screws to fix the position of the pot.

3) At this point the temperature bath may be fitted to attain the desired temperature for the experiment, leave the sample for one hour to equilibrate at the desired temperature.

4) Enter the speed of rotation of the stepper motor that is required using the computer, and adjust the electrode gap to that required.

5) Next detach the connection from the transducer to the chart recorder, and move the recorder pen to the middle of the y-axis. Then re-attach the transducer lead to the recorder and adjust the position of the load cell using the screw thread around its collar. This ensures that the cross bar from the transducer to the load cell is horizontal, and results in the recorder pen moving back to its original position in the middle of the y-axis. Then reposition the recorder pen back to the origin.

6) Replace the safety screen around the device.

7) After switching on the power supply adjust the voltage using the manual control to find out the approximate maximum electric field that can be applied, with the limiting
parameter being the conductivity of the sample. Also fix the sensitivity of the y-scale on the recorder to ensure that the transducer output remains on scale.

8) Then scan the voltage range using 30 seconds for each scan.

9) Then after the number of required scans for a steady state output reading to be reached, usually 5 or 6 scans, switch off the power supply, and remove the safety screen. Then repeat the procedure from 4) again adjusting the shear rate as desired.

Section 2.11 Results on viscosity of ER fluids at Zero Electric Field

When the viscosity of both the polymer and zeolite dispersions were measured at zero electric field, using the Ferranti viscometer, the viscosity of the dispersions was found to increase in a far from linear manner as the volume fraction of the solid was increased. Some typical examples of this are shown in Fig. 2.6.

In Fig. 2.6 the graphs show the results gained from three families of fluids each based on a different viscosity of the base oil. It can be seen that the non-linear increase in viscosity with packing fraction is consistent no matter what the viscosity of the supporting oil.

This type of work has been of interest for a number of years, and several theoretical explanations have been proposed to account for this type of dependence of viscosity on packing fraction.
Fig. 2.6  Zero Electric Field Viscosity against Solid Volume Fraction

At low densities of solid, below a volume fraction of approximately 0.15, the variation of viscosity was modelled by both Einstein [2] (for suspensions), and Enskog [3] (for hard sphere gases). Without the consideration of particle-particle correlations Einstein obtained the result,

\[ \frac{\eta}{\eta_0} = 1 + \frac{5}{2} y \]

where \( y \) = packing fraction, \( \eta \) = viscosity of suspension, and \( \eta_0 \) = viscosity of solvent.
\[ \eta_0 = \text{viscosity of supporting oil.} \]

Above this lower region where the relationship between viscosity, and packing fraction loses its linearity a fresh approach is needed as departures from Einstein and Enskog theories are substantial.

In the paper presented by Woodcock [4] a hard sphere model is shown to give a better fit to this kind of viscosity vs packing fraction data over the whole fluid range of these suspensions, which are up to packing fractions of approximately 0.5. A thorough insight into the hard sphere fluid has been given by Alder et al. [5]. The relative contributions to the total shear viscosity are shown to arise from potential, kinetic, and cross components. None of these terms deviates significantly from Enskog theory up to the packing fraction of approximately 0.2. At this point the potential component begins to increase rapidly, while the kinetic component also rises slightly. The cross term deviates negatively, but to a much lesser extent than the positive deviation of the potential component. The actual shear viscosity was seen to follow the potential part very closely, and at packing fractions in the region of 0.5 the potential contribution to the shear viscosity is more than 90%.

Section 2.12 Results from Static Yield Rig

All the samples were made up to 25% by volume of the solid, and all values for yield stress quoted are those after subtraction of the zero volts yield stress. The value
of the zero volts yield stress was found to be quite similar for all the samples, and the variation with temperature is shown in Table 2.1.

Table 2.1

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Zero volts Yield stress (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30°C</td>
<td>0.8</td>
</tr>
<tr>
<td>+24°C</td>
<td>0.3</td>
</tr>
<tr>
<td>+60°C</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The current was monitored over the temperature range from +60°C to -40°C for two of the zeolite samples, and also one polymer sample. The results were obtained which are shown in Table 2.2.

This work is still only very approximate but it seems that this area is worth further investigation.

Table 2.2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy ($kJmol^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Error)</td>
</tr>
<tr>
<td>H-ZSM-5 Si:Al=21.25</td>
<td>75</td>
</tr>
<tr>
<td>1% H$_2$O</td>
<td>(19)</td>
</tr>
<tr>
<td>Na-X</td>
<td>64</td>
</tr>
<tr>
<td>2% H$_2$O</td>
<td>(0.5)</td>
</tr>
<tr>
<td>LiPMA</td>
<td>47</td>
</tr>
<tr>
<td>20% H$_2$O</td>
<td>(2)</td>
</tr>
</tbody>
</table>
### Format of Results Tables from the Static yield rig

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si:Al</th>
<th>Elec.Field (kVmm(^{-1}))</th>
<th>-30°C, +24°C, +60°C Stress/Current Density (kPa) (μAcm(^{-2}))</th>
</tr>
</thead>
</table>

As shown above all static yield stresses are quoted in kPa, whilst all the current densities quoted are in μAcm\(^{-2}\). The yield stresses and current densities are given in the form of a pair of numbers separated by a slash, as there are values of both stress and current densities at three different temperatures as shown in the plan above for each particular electric field. The ammeter used in this device was only sensitive down to 1 μA i.e. 0.2 μAcm\(^{-2}\), currents which were smaller than this lower limit are indicated by the symbol <1.

The current density from the oil was also measured and found to be less than 6 pAcm\(^{-2}\) even at 3 kVmm\(^{-1}\). Therefore the current generated by the fluids can be considered as being due to the solid particles alone.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Sl:Al</th>
<th>Elec. Field (kV mm$^{-1}$)</th>
<th>-30°C</th>
<th>+24°C</th>
<th>+60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-A 3% H$_2$O</td>
<td>1</td>
<td>1</td>
<td>-/-</td>
<td>0.18/37.5</td>
<td>-/-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>-/-</td>
<td>0.32/197.6</td>
<td>-/-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>-/-</td>
<td>0.78/418.9</td>
<td>-/-</td>
</tr>
<tr>
<td>Na-X 3% H$_2$O</td>
<td>1.21</td>
<td>1</td>
<td>0.57/&lt;1</td>
<td>0.15/&lt;1</td>
<td>0.21/2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>0.98/&lt;1</td>
<td>0.71/0.6</td>
<td>0.69/10</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>1.25/&lt;1</td>
<td>1.27/1.9</td>
<td>1.31/24</td>
</tr>
<tr>
<td>Li-X 5% H$_2$O</td>
<td>1.21</td>
<td>1</td>
<td>-/-</td>
<td>0.68/7.7</td>
<td>0.43/12</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>-/-</td>
<td>1.68/28.5</td>
<td>0.9/47</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>-/-</td>
<td>2.28/65.6</td>
<td>1.67/115</td>
</tr>
<tr>
<td>Na-X 3% HCONH$_2$</td>
<td>1.21</td>
<td>1</td>
<td>0.35/&lt;1</td>
<td>0.26/2</td>
<td>0.24/24</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>0.71/&lt;1</td>
<td>0.95/6.5</td>
<td>1.07/106</td>
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<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>1.69/&lt;1</td>
<td>1.59/13</td>
<td>1.9/500</td>
</tr>
<tr>
<td>Li-Y 0.5% H$_2$O</td>
<td>2.37</td>
<td>1</td>
<td>-/-</td>
<td>0.05/&lt;1</td>
<td>0.04/1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>-/-</td>
<td>0.2/0.6</td>
<td>0.21/2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>-/-</td>
<td>0.43/1.2</td>
<td>0.44/5</td>
</tr>
<tr>
<td>Deal-Y 15% H$_2$O</td>
<td>2.45</td>
<td>1</td>
<td>-/-</td>
<td>0.04/&lt;1</td>
<td>-/-</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>-/-</td>
<td>0.09/&lt;1</td>
<td>-/-</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>-/-</td>
<td>0.14/0.4</td>
<td>-/-</td>
</tr>
<tr>
<td>Na-mord 2% H$_2$O</td>
<td>6.5</td>
<td>1</td>
<td>0.1/&lt;1</td>
<td>0.16/4.4</td>
<td>0.03/2</td>
</tr>
<tr>
<td></td>
<td>2</td>
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<td>0.22/&lt;1</td>
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<td>0.29/23</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>0.47/0.6</td>
<td>0.87/53.4</td>
<td>0.77/67</td>
</tr>
<tr>
<td>H-mord 1% H$_2$O</td>
<td>10.7</td>
<td>1</td>
<td>0.07/&lt;1</td>
<td>0.37/&lt;1</td>
<td>0.16/&lt;1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>0.19/&lt;1</td>
<td>0.95/0.4</td>
<td>0.43/1.6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>0.39/&lt;1</td>
<td>1.28/1.6</td>
<td>0.69/2.9</td>
</tr>
<tr>
<td>Sample</td>
<td>Si:Al</td>
<td>Elec. Field (kV mm⁻¹)</td>
<td>-30°C</td>
<td>+24°C</td>
<td>+60°C</td>
</tr>
<tr>
<td>-------------</td>
<td>-------</td>
<td>-----------------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>21.25</td>
<td>1</td>
<td>0.1/1</td>
<td>0.26/1</td>
<td>0.4/1</td>
</tr>
<tr>
<td>0.5% H₂O</td>
<td></td>
<td>2</td>
<td>0.2/1</td>
<td>1.24/1</td>
<td>1.61/0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.39/1</td>
<td>3.78/1</td>
<td>3.85/1.6</td>
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<tr>
<td>H-ZSM-5</td>
<td>21.25</td>
<td>1</td>
<td>0.1/1</td>
<td>0.12/1</td>
<td>0.07/1</td>
</tr>
<tr>
<td>0% H₂O</td>
<td></td>
<td>2</td>
<td>0.14/1</td>
<td>0.33/1</td>
<td>0.25/1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.54/1</td>
<td>0.93/1</td>
<td>0.37/1</td>
</tr>
<tr>
<td>Na-ZSM-5</td>
<td>21.25</td>
<td>1</td>
<td>0.30/1</td>
<td>0.6/5.1</td>
<td>0.14/7.9</td>
</tr>
<tr>
<td>1% H₂O</td>
<td></td>
<td>2</td>
<td>0.88/1</td>
<td>3.23/17</td>
<td>0.4/43.5</td>
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<tr>
<td></td>
<td></td>
<td>3</td>
<td>1.55/1</td>
<td>6.9/24</td>
<td>0.87/102</td>
</tr>
<tr>
<td>Li-ZSM-5</td>
<td>21.25</td>
<td>1</td>
<td>0.27/1</td>
<td>0.31/0.8</td>
<td>0.23/2.7</td>
</tr>
<tr>
<td>1% H₂O</td>
<td></td>
<td>2</td>
<td>0.96/1</td>
<td>0.9/3.6</td>
<td>1.01/12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>2.08/1</td>
<td>2.17/6</td>
<td>1.92/32</td>
</tr>
<tr>
<td>Mg-ZSM-5</td>
<td>21.25</td>
<td>1</td>
<td>-/-</td>
<td>0.03/1</td>
<td>0.03/1</td>
</tr>
<tr>
<td>1% H₂O</td>
<td></td>
<td>2</td>
<td>-/-</td>
<td>0.05/1</td>
<td>0.07/1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>-/-</td>
<td>0.07/1</td>
<td>0.15/1</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>174</td>
<td>1</td>
<td>0.1/1</td>
<td>0.04/1</td>
<td>0.1/1</td>
</tr>
<tr>
<td>0.5% H₂O</td>
<td></td>
<td>2</td>
<td>0.2/1</td>
<td>0.33/1</td>
<td>0.35/1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.26/1</td>
<td>0.54/1</td>
<td>0.72/1</td>
</tr>
<tr>
<td>LiPMA</td>
<td></td>
<td>1</td>
<td>-/-</td>
<td>0.69/1.8</td>
<td>-/-</td>
</tr>
<tr>
<td>20% H₂O</td>
<td></td>
<td>2</td>
<td>-/-</td>
<td>1.22/4</td>
<td>-/-</td>
</tr>
<tr>
<td>ground</td>
<td></td>
<td>3</td>
<td>-/-</td>
<td>2.33/9.8</td>
<td>-/-</td>
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<td>LiPMA</td>
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<td>1</td>
<td>0.11/1</td>
<td>0.26/0.3</td>
<td>0.23/29</td>
</tr>
<tr>
<td>20% H₂O</td>
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<td>2</td>
<td>0.13/1</td>
<td>0.74/1.8</td>
<td>0.72/141</td>
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<tr>
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<td>3</td>
<td>0.47/1</td>
<td>1.4/4.7</td>
<td>1.0/711</td>
</tr>
</tbody>
</table>
Section 2.13 Results from the Electroviscometer

As shown previously in the section on the construction of the electroviscometer, the readout from the device gives a reading of the viscosity of the sample for the whole time that the electric field (being applied to the sample) is increasing. This allows other interesting characteristics of the fluid to be monitored other than the simple magnitude of the viscosity change of the fluid.

One important point is the magnitude of the electric field required to initiate the increase in viscosity. Another feature of the fluid that is of interest is the conductivity of the fluid as monitored by the ammeter: this will be quoted as a current density \( j_e \), the total current/electrode area = 72.12 cm\(^2\). How these two parameters, and the ER effect vary with temperature is also of interest.

The temperature range of operation of the electroviscometer is from +5 to +60°C at present. The results for each sample presented in the following section will take the form of comments on each characteristic of the fluid and its variation with temperature, as shown in the example below.

Fluid Example
a) Magnitude of the ER effect
b) Conductivity of the sample
c) Value of the electric field which initiates the ER effect

Section 2.14 Results from Zeolite Containing Samples

Sample 1) Li-A 3% H\(_2\)O, 25% by volume in 20 cs silicone oil
a) This sample only showed a relatively weak effect, at an electric field of 0.5 kVmm$^{-1}$ the viscosity of the sample was 4,000 cp at $+10^\circ$C, 10,000 cp at ambient, and 4,000 cp at $+60^\circ$C.
b) This sample was also very highly conducting eg. at 0.5 kVmm$^{-1}$ at $+10^\circ$C, 2.8 $\mu$Acm$^{-2}$, while at ambient this increased to 14 $\mu$Acm$^{-2}$, and at $+60^\circ$C it was 30 $\mu$Acm$^{-2}$.
c) The initiation voltage of the effect was approximately 0.23 kVmm$^{-1}$ over the whole temperature range.

Sample 2) Na-X 4% H$_2$O, 25% by volume in 20 cs silicone oil
a) At 1 kVmm$^{-1}$ the viscosity varies from 62,400 cp to 292,000 cp with the maximum effect under ambient conditions, and a decrease in the effect by raising, or lowering the temperature.
b) Conductivity is high eg. 27.7 $\mu$Acm$^{-2}$ at 1 kVmm$^{-1}$ at ambient, and decreases to 20.8 $\mu$Acm$^{-2}$ at 2.5 kVmm$^{-1}$ and $+10^\circ$C.
c) The ER effect begins at 0.38 kVmm$^{-1}$ at $+10^\circ$C, and this value decreases to 0.2 kVmm$^{-1}$ at ambient and above.

Sample 3) H-mordenite 1% H$_2$O, 25% by volume in 20 cs silicone oil.
a) This sample with an electric field of 1 kVmm$^{-1}$ had a viscosity of 20,000 cp at $+10^\circ$C, 70,000 cp at ambient, and 30,000 cp at $+60^\circ$C.
b) The conductivity was in the middle region for ER fluids of 19.5 $\mu$Acm$^{-2}$ at 1.6 kVmm$^{-1}$ in the ambient and high
temperature regions. At +10°C and 2.4 kVmm⁻¹ this value decreased to 5.6 μAcm⁻².

c) At the low temperature end of the scale the ER effect begins at 0.5 kVmm⁻¹, which decreases to 0.2 kVmm⁻¹ at ambient temperatures and above.

Sample 4) Na-mordenite 2% H₂O, in 25% by volume in 20 cs silicone oil.

a) At +10, and +60°C and an electric field of 1 kVmm⁻¹ the viscosity of the sample was 25,000 cp, which increased to 100,000 cp at ambient temperatures.

b) This sample was very conductive, with a current density of 14 μAcm⁻², at 2.5 kVmm⁻¹ and +10°C. This increased further to 28 μAcm⁻² at 0.65 kVmm⁻¹ by +60°C.

c) The starting voltage for the effect was quite low at 0.6 kVmm⁻¹ at +10°C, with a decrease to 0.22 kVmm⁻¹ at 60°C.

Sample 5) H-ZSM-5, 1% H₂O, 25% by volume in 20 cs in silicone oil.

a) The viscosity of the fluid at 1 kVmm⁻¹ was around 50,000 cp at ambient, and high temperature, whilst at an electric field of 2 kVmm⁻¹ was 100,000 cp at +10°C, 220,000 cp at ambient, and 150,000 cp at +60°C.

b) The conductivity of this sample was very low e.g. at 2.5 kVmm⁻¹ it varied from 1.7 μAcm⁻² at +60°C, to 0.4 μAcm⁻² at ambient, while at +10°C the conductivity was below the detection limit of the device.

c) The starting voltage for the effect varies from
1.4 kVmm⁻¹ at +10°C, to 0.7 kVmm⁻¹ at ambient, and 0.45 kVmm⁻¹ at +60°C.

Sample 6) Na-ZSM-5 2% H₂O, in 25% by volume, in 20 cs silicone oil.

a) In this case the viscosity at 1 kVmm⁻¹ varied from 80,000 cp at +10°C, to 111,000 cp at ambient temperature, and 160,000 cp at +60°C, thus showing one of the larger ER effects we have observed.

b) This conductivity ranged from 1.7 μAcm⁻² at +10°C, through 11.1 μAcm⁻² at ambient to 28 μAcm⁻² at 1 kVmm⁻¹ and +60°C.

c) The effect begins at 0.3 kVmm⁻¹ at +10°C, and this lowers to 0.16 kVmm⁻¹ at +60°C.

Sample 7) Li-ZSM-5 2% H₂O, in 25% by volume in 20 cs silicone oil.

a) The ER effect of this sample was large as shown by the following viscosities i.e. at 1 kVmm⁻¹ and +10°C, the viscosity was 30,000 cp, which increased to 200,000 cp at ambient, before decreasing to 100,000 cp at +60°C.

b) The conductivity varied considerably from 0.5 μAcm⁻² at 2 kVmm⁻¹ and +10°C, to 7 μAcm⁻² at ambient, and 28 μAcm⁻² at +60°C.

c) At a temperature of +10°C the ER effect begins at 0.4 kVmm⁻¹, which decreases to 0.2 kVmm⁻¹ at ambient temperature and above.

Samples containing both dealuminated-Y, and H-ZSM-5 with a
Si:Al ratio of 174 proved to be too weak in their ER effect to be measurable using the electroviscometer.

Section 2.15 Polymer Containing Samples

Sample 8) LiPMA 20% H₂O, 25% by volume in 20 cs silicone oil
a) With an applied electric field of 0.5 kVmm⁻¹ at both +10°C and ambient temperatures the viscosity was 100,000 cp while at +60°C this decreased to 60,000 cp.
b) At +10°C the current density with a field of 1.5 kVmm⁻¹ was 1 μAcm⁻². This increased to 14 μAcm⁻² at ambient, and still further to 28 μAcm⁻² at 0.5 kVmm⁻¹ and +60°C.
c) The initiating field for this sample was very low being approximately 0.1 kVmm⁻¹ at all temperatures.

Sample 9) LiPMA 10% H₂O, 25% by volume in 20 cs silicone oil
a) The effect in this sample was reduced at 1 kVmm⁻¹ to 100,000 cp at +10°C, although this did increase to 150,000 cp at ambient before decreasing at +60°C to 70,000 cp.
b) The conductivity of this sample was also reduced in comparison to the previous polymer sample to 1 μAcm⁻² at +10°C and 10 μAcm⁻² at ambient both with 2 kVmm⁻¹. This increased to 14 μAcm⁻² at 0.6 kVmm⁻¹ at +60°C.
c) The starting voltage for the effect was also increased from the previous sample to 0.3 kVmm⁻¹ at +10°C, with a similar value to that for sample 8 at ambient and high temperatures.

Sample 10) LiPMA 1% H₂O, 25% by volume in 20 cs silicone oil
a) The trend of the reduction of the ER effect with water content of the polymer was further shown as the viscosity at 2 kVmm\(^{-1}\) varied from 20,000 cp at +10°C, to 160,000 cp at ambient, and 80,000 cp at +60°C.
b) The conductivity was further reduced and was below the measurable limit of the device i.e. 0.1 \(\mu\text{Acm}^{-1}\) at all temperatures.
c) The effect needed a much greater starting voltage in this case of 1.2 kVmm\(^{-1}\) at +10°C, 0.7 kVmm\(^{-1}\) at ambient, and 0.2 kVmm\(^{-1}\) at +60°C.

Section 2.16 Zeolite Samples with Surfactants

The solid zeolite used was a sample of H-ZSM-5, with 1% H\(_2\)O, making it directly comparable to sample 5). For this reason the results for each surfactant will be presented in a similar form as previously by comparing the results with those for sample 5)

Sample 11) H-ZSM-5, and oleic imidazolene.
a) The ER effect was very similar.
b) The conductivity was very slightly reduced.
c) The starting voltage was exactly the same.

Sample 12) H-ZSM-5, and Sympronic A2
a) The effect was reduced to 70% of that at ambient and high temperatures, and 10% of that \(\Delta +10^\circ\text{C}\).
b) The conductivity was reduced to less than the detection level of the device at all temperatures.
c) Again the initiating value of the electric field was
unchanged.

Sample 13) H-ZSM-5, and dodecylamine.

a) The effect was reduced to 10% of that at high and low temperatures, and 30% of that at ambient.

b) As for the sample 12) the current was reduced to below the detection limit of the device.

c) As in the previous two cases the starting voltage for the effect was unchanged.

Section 2.17 Polymer Samples with Surfactant

In this case a sample of LiPMA with 20% H₂O was used with all the surfactants, and so the results are compared with sample 8).

Sample 14) LiPMA, with oleic imidazolene.

a) The ER effect was reduced by approximately a factor of 2.

b) The conductivity was increased enormously by a factor of 15, which meant that measurements above ambient were not possible as the current drawn was too great for the power supply.

c) The starting voltage was very similar.

Sample 15) LiPMA, with Sympronie A2.

a) The effect was reduced by a factor of 4.

b) The conductivity was increased by a factor of approximately 15.

c) Again the initial voltage required was little changed.
Sample 16) LiPMA, and dodecylamine.

a) The effect was not reduced quite so much in this case, and was 75% of the original fluid.

b) The increase in conductivity was also not quite so great, as this sample increased by a factor of 10.

c) As observed previously the electric field to initiate the effect showed little change.

Section 2.18 Variation of Shear Stress with Scanning speed of the Electric Field

The argument could be put forward that the trace of the variation of the shear stress with electric field is purely dependent on the rate that the voltage is ramped. To investigate this effect, and also to study the reaction time scale of the ER effect, the scanning time for the electric field was varied. It has commonly been stated that the ER effect takes place on the millisecond timescale, so let us take a typical reaction time to be $3 \times 10^{-3}$ s, with the average scan covering 0 to 3.5 kVmm$^{-1}$. This means that in 3 ms the electric field increases as shown in the following table for various scan speeds.

<table>
<thead>
<tr>
<th>Scan Speed (s)</th>
<th>1</th>
<th>3</th>
<th>10</th>
<th>30</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vmm$^{-1}$ per 3 ms</td>
<td>10.5</td>
<td>3.5</td>
<td>1.1</td>
<td>0.4</td>
<td>0.1</td>
</tr>
</tbody>
</table>

On increasing the scan speed, one difference that was observed occurred at low voltages where the initial increase of the shear stress was at a more gradual rate, and at a
higher value of the electric field than seen at longer scan times. Also in the remaining part of the trace where the stress increases linearly with electric field the stress measured decreased slightly as the scan speed was reduced. At a scan time of 30s and longer the output remained unchanged, so it seems that the ER effect can respond to electric field changes of 0.4 V mm$^{-1}$ per second or less. The result of larger changes in the electric field due to shorter scan times is to reduce the shear stress at any particular value of the electric field on the readout, which indeed is an artificial result. To ensure that this did not happen all measurements quoted in this section were taken with a scan time of 30s.

Section 2.19 Details of the Increase of the Shear Stress with Applied Electric Field

Staying on a similar subject of the increase of the shear stress with electric field, it was seen that the increase of viscosity was a gradual one initially following a curve proportional to some power of the electric field. An example of this is shown in Fig. 2.7. Also, for all the samples tested, it was seen that after the electric field had initiated the ER effect then the effect continued to rise linearly with electric field. These two field effects were explained by Sprecher et al. [6] to be due to polarisation of the particles, and the interaction of the subsequent dipoles with the strength ($S_i$) of induced dipoles given by,
Fig. 2.7 Initial Output From Electroviscometer
where \( k_1 \) is the polarising constant, and \( E \) the electric field. The strength of the mutual attraction of dipoles in an electric field is given by,

\[
S_2 = k_2 S_1 E^2
\]

where \( k_2 \) is the attraction constant. Substituting (18) into (19) gives,

\[
S_2 = k_2 k_1 E^2
\]

which is thought to be the cause of the power law dependence of the shear stress on the electric field strength. At higher electric fields then the dipoles will be saturated and \( S_1 \) will have a constant value \( k_3 \). Hence the strength of the induced dipoles in this case will be given by,

\[
S_2 = k_2 k_3 E
\]

Now this can be used to explain the linear behaviour of the shear stress with higher values of the electric field.

Only in very highly conducting samples of current density 30 \( \mu \text{Acm}^{-2} \) was the current heating large enough at high voltages to compete with the ER effect, and this caused a slight deviation from the linear relationship between shear stress, and field.

Section 2.20 Theory of the Variation of Shear Stress and Shear Viscosity with Shear Rate in ER fluids

The electroviscometer was capable of generating shear rates in the range 1.5 to 43.8 \( \text{s}^{-1} \) which is still at the low end of the shear rate scale.

Concentrated suspensions are known to exhibit often
non-Newtonian flow behaviour i.e. there is a variation of shear viscosity with shear rate, in general suspensions tend to be shear thinning, although examples of shear thickening can occur. There are three types of shear thinning,

1) Thixotropic flow is a time dependent decrease in shear viscosity.

2) Plastic flow has no variation in the shear viscosity with shear rate, just as in the case of a Newtonian fluid, but here the shear stress is non-zero at zero shear rate i.e. a plastic fluid possesses a yield stress at zero shear rate.

3) Pseudo-plastic flow shows a constant shear viscosity at high shear rates, but as the shear rate is lowered this type of flow shows no yield stress as there is a gradual decrease to zero shear stress at zero shear rate.

One parameter that is of interest in concentrated suspensions is that of the relaxation time for significant structural rearrangement \( \tau_r \) employed by Heyes [7] in Brownian Dynamics simulations. In a suspension this is the time taken by a macromolecule to diffuse through the macromolecular radius, and is given by equation (22),

\[
\tau_r = \frac{3\pi a^3 \eta_0}{4 k \theta},
\]

where \( \eta_0 \) is the viscosity of the supporting medium of the suspension. One typical plot is that of \( \eta/\eta_0 \) versus \( \dot{\gamma} \), where \( \eta \) is the viscosity of the dispersion, and takes the form seen in Fig.2.8.

From equation (22) it can be seen that the value of \( \tau_r \) is directly related to the size of the solid particles in
the suspension. Hence in Fig. 2.8 it would be expected that smaller particles would give the behaviour seen at low values of \( \dot{\gamma}_r \), i.e. shear thinning. Also since \( \tau_r \) is directly proportional to \( \eta/\text{temperature} \) then at low temperatures then the relaxation time will be large, therefore it might be expected to be more likely to witness shear thickening at low temperatures.

It has been shown by Woodcock [8] that the onset of
shear thickening moves to higher shear rates as the particle size of the solid in the dispersion decreases. It was also noted that the variation of the relative viscosity with shear rate depends on both hydrodynamic, and osmotic contributions.

Heyes [9] has shown that if the viscosities of the sample are within the range of the first Newtonian plateau (see Fig.2.8), and just in a subsequent shear thinning curve then \( \eta(\dot{\gamma}) \) can often be described by the Cross model shown in (23),

\[
\eta = \eta_0 + \eta_\infty \left( \frac{\eta_0 - \eta_\infty}{1 + \alpha \dot{\gamma} \gamma^n} \right)
\]

where \( \eta_0 \) and \( \eta_\infty \) are the limiting viscosities at \( \dot{\gamma} \to 0 \), and \( \dot{\gamma} \to \infty \), and \( \alpha \) is a constant. However, often the experiment is too far from \( \eta_0 \) for the above type of formula to be useful. The following formulae have been found to give a more accurate representation of experimental data, and have been described in more detail by Barnes [10]. For Bingham plastic fluids then equation (24) may be applied,

\[
\eta = \sigma_0 + \eta_\infty \left( \frac{\dot{\gamma}}{\gamma} \right)
\]

where \( \sigma_0 \) is the yield shear stress at zero shear rate, and \( \eta_\infty \) is the solvent viscosity. Two further similar models have also been used and these are shown in equations (25, 26). The Sisko model is given by,

\[
\eta = \frac{\gamma}{\gamma^n} + \eta_\infty
\]

The Herschel/Bulkley model is based on two powers of the inverse of the shear rate and is given by,
\[ \eta = \sigma_0 + \frac{\alpha}{\dot{\gamma}^{1-n}} \]  \quad (26)

In the treatment of my data I have assumed a Newtonian relationship between \( \sigma = \dot{\gamma} \eta \), so that the shear stress \( \sigma \), can be related to a shear viscosity \( \eta \). This viscosity was then fitted to the equation below which is similar to the Sisko model,

\[ \eta = b + c \dot{\gamma}^m \]  \quad (27)

In analysing the viscosity data equation (27) was used assuming the second term on the right hand side is insignificant compared to the first term on the right hand side. A straightforward plot of \( \log_{10} \eta \) vs. \( \log_{10} \dot{\gamma} \) yields \( m \) directly.

Section 2.21 Effect of shear rate on the shear viscosity of ER fluids

1) For all the polymer-based ER fluids the effect of increasing the shear rate by narrowing the gap between the electrode surfaces caused shear thinning i.e. the shear stress did not increase in a linear fashion with the shear rate: therefore the shear viscosity also decreased as the shear rate increased. These data were fitted to equation (27) and the value of the parameter \( m \), the power dependence of \( \dot{\gamma} \), was found to be in the range 1 to 2, with the majority in the range 1.4 to 2. The effect of increasing the shear rate by increasing the velocity of rotation between the electrodes did not affect the shear stress, although since
the apparent viscosity was calculated using $\sigma = \eta \dot{\gamma}$ then $\eta$ was still found to decrease even though the shear stress remained constant. Of course the apparent viscosity was then proportional to the inverse of the shear rate.

2) Of the zeolite based fluids the shear stress, and hence the shear viscosity, was again reduced by increasing the shear rate by narrowing the gap between the electrodes, apart from a few exceptions. There was only time to inspect H-ZSM-5 and H-mordenite zeolites by varying the shear rate by increasing the speed of rotation of the shear surfaces. The results that were obtained for these samples showed a decrease in the shear stress as the shear rate increased but not as great as that seen by reducing the electrode gap. Of course, since the shear viscosity was calculated using the Newtonian relation $\sigma = \dot{\gamma} \eta$, then as the shear rate was increased by the increased electrode rotation (even though the shear stress did not alter appreciably) the shear viscosity calculated still decreased.

The zeolites which showed shear thickening were Na-X, Na-mordenite, H-mordenite, Li-ZSM-5, and Na-ZSM-5 but only at low temperatures e.g. +10°C. The fluid containing H-ZSM-5 showed very little variation in $\sigma$ with $\dot{\gamma}$, even at low temperatures.

In the cases of shear thickening, the value of $\mu$ in equation (27) was found to be in the range -4 to -5.5, with the negative sign indicating the shear thickening phenomenon. Again in all the zeolite samples showing shear
thinning the value of \( m \) was again in the range 1 to 2 as was the case for the polymer samples.

This greater value for \( m \), the power of the shear rate on which the viscosity depends, in the case of shear thickening, compared with shear thinning (remembering of course that their signs are opposite), has also been observed by Heyes [11] for a Lennard-Jones liquid. Heyes describes the shear thinning of a liquid as being due to the fact that increasing shear rate distorts the local velocity profile, so that motion perpendicular to the velocity streamlines (which cause the shear stress) become less important. This means then that the shear stress does not increase in proportion to the shear rate, and so the apparent shear viscosity decreases. Shear thickening for a liquid is defined as the time when the increase in the shear rate reaches a value at which the molecules cannot react sufficiently quickly to the shear distortions, and overlap of molecules causes greater local structural disorder in the liquid, resulting in shear thickening. Heyes [11] and Woodcock [8] have shown that shear thinning is associated with a change in local and long range order in the dispersed particles. This can take the form of layers or lines of particles sliding over one another, depending on the shear rate. Shear thickening in contrast, happens at even greater shear rates still. This is caused by harsh particle collisions, which result in a partial redisordering of the particles and a dramatic (time dependent) rise in stress (viscosity). The liquid is often seen to fracture.
Increasing the shear rate from 12 to 43.8 s\(^{-1}\) increases the starting voltage of the ER effect, as measured by the electroviscometer, by a factor of approximately 2 for the zeolite based fluids, and a factor of 1.5 for the polymer fluids. However, the conductivity of both families of fluids remains unchanged on variation of the shear rate in this range. The physical changes taking place in a dilute ER fluid under shear on application of an electric field has been studied by Sprecher et al. [6]. Using an electron microscope it was seen that there is swirling in the fluid followed by immediate fibration on application of the electric field. This fibration broke down on shearing, with no fibres formed by the solid particles in the dispersion being left in the channel centre.

The decrease of the apparent shear viscosity with the increase in \(\dot{\gamma}\) was also measured by Klass and Martinek [12] on a series of silica based fluids. It was found that at a constant electric field at different electrode spacings (but increasing the velocity to maintain the shear rate) the ER effect is fairly constant. This, it is believed, is confirmation that wall effects are not important here. We are measuring a truly bulk property. This was observed for the zeolite samples considered. Although, in the case of the polymer, reducing the electrode gap and increasing the shear velocity to maintain the shear rate, caused a decrease in the shear stress. This therefore can be ascribed to surface artifacts. In reference [12] it was also found that the shear viscosity is approximately proportional to the
inverse of the shear rate \( \dot{ \gamma } \).

\[ \eta \sim \frac{1}{\dot{ \gamma }}, \tag{28} \]

All fluids tested which exhibited shear thinning behaved in a similar manner.

**Section 2.22 Result of Instantaneous Application of ER effect on Shear Stress**

When the electrode was rotating with no electric field the shear stress was scanned with time as the electric field was suddenly turned on from zero kV mm\(^{-1}\) to a steady voltage large enough to produce the ER effect in the sample. For both polymer, and zeolite based samples the behaviour of the shear stress on the application of the field was as shown in Fig. 2.9.

**Electric Field Applied**

![Electric Field Applied](image)

**Fig. 2.9** Overshoot of the Shear Stress after Application of an Electric Field
This type of behaviour of the overshoot of the shear stress followed by relaxation was also seen by Bullough and Peel [13]. A similar shear stress overshoot was observed by Heyes et al. [14] in simulation on applying a shear rate suddenly to a model liquid at equilibrium. It was suggested in reference [14] that the reason for the overshoot is the finite time for the fluid to respond structurally on the timescale of the change in conditions. The rate of increase of shear stress decreases until it reaches a limiting value governed by the shear viscosity, and then the sample relaxes back to a lower steady state value for the shear stress. In the case of ER fluids there is a time needed in which to charge the capacitative load, before the shear stress can begin to rise.

Section 2.23 The Effect of Settling Out on the ER effect

Settling out of the solid particles in dispersions is always a problem, so the effect was studied of leaving a sample of ER fluid containing H-ZSM-5 in the electroviscometer for one week without any rotation to agitate the fluid. After this time the ER effect of the fluid was measured, and there was found to be a 10% reduction in the value of the yield stress from the week previously. This obviously means that in a practical device that may be used only infrequently, surfactants are essential. From my results of surfactants on polymer samples the increase in conductivity, especially with ionic surfactants is unacceptable for practical applications.
This was also found by Marshall [15], who suggested that the increase in conductivity was due to the charged surfactant stripping off the particle surface. This problem was not encountered with the zeolites which had particles of very low conductivity, and the surfactants did not increase that conductivity.

Section 2.24 Variation of Shear Stress with the Solid Volume Fraction

Studies of the variation of the shear stress, with applied field were undertaken for both polymer based fluids, and also for fluids containing zeolite Na-X. The variation of the shear stress with volume fraction at a particular value of the applied field was proposed by Sprecher et al. [6] to be given by equation (29),

\[ \text{Shear stress} = k C^{2/3} \quad (29) \]

where \( C \) is the solid concentration, and \( k \) is a proportionality constant. This relationship was derived from the fact that the average spacing \( s \) between particles in a uniform mixture is given by,

\[ s \propto (1/\text{wt\%})^{1/3} \quad (30) \]

with the force of attraction between charged particles \( f \) being,

\[ f \propto \frac{1}{s^2} \quad (31) \]

Hence inserting (30) in (31) will give,

\[ f \propto (\text{wt\%})^{2/3} \quad (32) \]
from which equation (29) is drawn. In reference [6] this equation was used on silica based ER fluids of very low volume fractions of 1 or 2%, and very small particle size, so these equations had not been tested to see if they held for higher volume fractions of different solids.

From my results for the polymer-based fluids equation (29) provided a reasonable agreement to the data. However, the Na-X proved to be different with a value for the power of the concentration of the solid increased from $2/3$ to the range 2 to 3. Examples of the approximate fits on which these data are based are shown in Fig. 2.10.

It seems therefore that in the case of the polymer fluids they behave in a similar manner to the silica fluids as if the polymer was made up of much smaller particles than is actually the case, a type of behaviour that was also seen in the shear stress behaviour with shear rate. It had been derived earlier by Goodeve [16], that plastic flow may be expressed in terms of links in the chain of particles in a suspension ($n_1$), as shown in equation (33),

$$\text{Shear Stress} = \frac{1}{2} y n_1 f_1^2,$$  \hspace{1cm} (33)

where $y$ is the thickness of the shear plane, and $f_1$ is the force between the links in the chain. Obviously this expression gives a linear dependence on the shear stress with the solid concentration, which is directly proportional to the number of links in the chain. A more recent study by Michaels and Bolger [17] showed the shear stress was related to $(\text{volume fraction})^2$ in suspensions, by equation (34),
Fig. 2.10 Graph of Shear Stress vs. Volume Fraction for both Zeolite and Polymer containing Fluids with Applied Electric Fields

Shear Stress = \frac{3 \phi^2 E_1}{2 \pi^2 a^3}, \quad (34)

where \( a \) is the particle radius, \( \phi \) the volume fraction, and \( E_1 \) the energy required to separate particles. This relationship gives a reasonable agreement with my data for Na-X based ER fluids, but it would seem from the results from the polymer that for ER fluids the situation is unique.
in the manner that shear stress is generated. For this reason either there may not be one universal relationship between shear stress and volume fraction in all ER fluids, or else, if there is, it may be based on a theory different from that for the shear stress of suspensions with no electric field.

Section 2.25 Summary of Shear Testing Results

1) Shear thickening was never observed from the polymer particle dispersions. This is possibly due to the comparatively "soft" nature of the interparticle forces. This prevents "harsh" collisions taking place (which has already been stated causes shear thickening). In support of this, shear thickening has never been observed in emulsions, which also have a soft interaction between the particles, droplets in this case.

2) Zeolites show a variety of shear characteristics. All but H-ZSM-5 show thickening at low temperatures, which is a symptom of coagulation, and also show thinning at and above ambient temperatures.

3) Both zeolites and polymer based fluids have a similar rate of decrease of viscosity with shear rate. Whilst for zeolites the increase of viscosity with shear rate is much faster for shear thickening than thinning.

4) The shear stress remains fairly constant when increasing the shear rate by increasing the velocity of rotation in both polymer and zeolite based fluids i.e. \( \eta \propto \gamma^{1/3} \). However, for a particular speed of rotation increasing the
shear rate by decreasing the electrode gap lowers the shear stress considerably. Exceptions to this are H-mordenite at ambient and above, at all shear rates studied, and H-ZSM-5 at all temperatures at low shear rates 1 to 10 s\(^{-1}\).

5) At low shear rates of 1.5 to 2 s\(^{-1}\) and using \(\sigma = \eta \dot{\gamma}\) to calculate an apparent viscosity, the most effective ER fluids show a viscosity increase of between 2 and 3 orders of magnitude at electric fields in the range 1 to 2 kVmm\(^{-1}\). Of course increasing \(\dot{\gamma}\) by an order of magnitude by increasing the speed of rotation will reduce the effective shear stress by an order of magnitude as described in 4).

6) The ER effect was seen to take place on the millisecond timescale.

7) Both the polymer and zeolite samples require a larger electric field to produce the ER effect as the temperature is reduced. Also, in all cases the increase of shear stress with electric field is linear after the start of the effect.

8) The sample of H-ZSM-5 has the lowest conductivity of zeolites and requires the largest electric fields to begin the ER effect. In general other zeolites need a similar electric field as the polymer with 10% H\(_2\)O.

9) H-ZSM-5 is much less conductive than Na, or Li-ZSM-5 and the use of surfactants does not alter the conductivity of H-ZSM-5. In the case of polymer samples surfactants purely act to increase the conductivity of those fluids.

10) In the polymer fluids as the water content of the polymer increases in the range studied up to 20% the ER effect increases, as does the conductivity, while the
initiating voltage for the effect decreases.

11) The ER shear stress relationship with solid volume fraction seems to be dependent on the chemical nature of the solid particles themselves.

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Section 2.26 References


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CHAPTER 3 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

An electron's atomic magnetic moment is nuclear magnetic resonance (NMR), and electron spin resonance (ESR) spectroscopy. Both are based on the fact that electrons have certain properties that can be studied. This section will be focused on nuclear magnetic resonance. A basic description of magnetic resonance in solids is given, but a brief summary follows, with vector quantities underlined.

A magnetic dipole can be evaluated in terms of its angular momentum, as an example an electron describing a non-equatorial orbit corresponds to a non-zero term in the angular momentum. Then

\[ L = \sqrt{\frac{e}{2m} L} \]

where \( L \) is the moment of inertia of the system, and \( m \) is the mass of the electron. The time for one orbit is

\[ T = \frac{2\pi}{f} \]

Where \( f \) is the orbital frequency. This is equivalent to a current flowing in the opposite direction.

\[ i = n \cdot 2\pi \times 2\pi \]

where \( n \) is the electron in charge. This causes a dipole at the center of the orbit of

\[ \mathbf{B} = \mathbf{A} = \mathbf{n} \times \mathbf{r} \]

This shows that the orbital magnetic dipole vector is exactly opposite to the angular momentum vector of itself.
Section 3.1 Magnetic Resonance Theory

The two main areas of magnetic resonance are Nuclear Magnetic Resonance (NMR), and Electron Spin Resonance (ESR) spectroscopy. Both are based on the fact that electrons and certain nuclei have magnetic moments, caused by their electrostatic charge, and spin angular momenta, which can interact with applied magnetic fields. A basic description of magnetic resonance is provided by McLauchlan [1], but a brief summary follows, with vector quantities underlined.

A magnetic dipole can be evaluated in terms of its angular momentum, as an example an electron describing a Bohr orbit, radius \( r \), with angular velocity \( \omega \), has an angular momentum \( \ell \), given by,

\[
\ell = I\omega = mr^2\omega ,
\]

where \( I \) is the moment of inertia of the system, and \( m \) is the mass of the electron. If \( t \) is the time for one orbit then (1) becomes equivalent to,

\[
|\ell| = \frac{mr^2}{t} = 2mA . \tag{2}
\]

Where \( A \) is the orbital area. Now the motion of the electron is equivalent to a current flowing in the opposite direction \( i \),

\[
i = -\frac{e}{t} \tag{3}
\]

where \(-e\) is the electronic charge. This causes a dipole at the centre of the orbit of

\[
\mu_i = Ai = -\frac{e\ell}{2m} \tag{4}
\]

This shows that the orbital magnetic dipole vector is exactly opposite to the angular momentum vector. Small
splittings of energy levels occur due to magnetic interaction between orbital, and spin magnetic moments.

To measure the electron magnetic moments from orbital and spin motion, consider that the energy $E$, of a dipole $\mu$, in a magnetic field $B$ is given by,

$$E = -\mu \cdot B.$$  

(5)

The torque acting on the magnetic moment is equal to the rate of change of orbital angular momentum $P_\perp$, as shown by Bloch [2]. The result is that the magnetic moment precesses about the direction of field $B$, with angular frequency $\omega$, known as the Larmor frequency and given by,

$$\omega = \frac{\mu_\perp \cdot B}{P_\perp}.$$  

(6)

The energy of the system is given by the component of $\mu_\perp$ in the z direction, and from quantum mechanics it has been shown that the orbital angular momentum of any particle in say the z direction $P_{1z}$ is given by,

$$P_{1z} = m_1 \hbar.$$  

(7)

In this case $m_1 = +1, (1-1)\ldots (-1+1), -1$, where $l$ is the orbital angular momentum quantum number. Inserting this value into (1) and then (4) gives the following expression,

$$\mu_{1z} = -\frac{m_1 \hbar e}{2m}.$$  

(8)

If the electron has one quantum of angular momentum then,

$$\mu_{1z} = \frac{\hbar e}{2m} = \mu_B = \text{Bohr Magneton} = 9.2737 \times 10^{-16} \text{ J T}^{-1}. $$  

(9)

Combining (8) with (6) gives the Larmor frequency as,

$$\omega = \left[ \frac{-e}{2m} \right] \frac{B_z = \gamma_e B_z}{\gamma_e B_z},$$  

(10)

where $\gamma_e$ is the magnetogyracic ratio of the electron, and is
the proportionality constant between the magnetic moment and
the angular momentum \( \ell \), from which

\[ \mu_1 = \gamma_e \ell \] \hspace{1cm} (11)

Section 3.2 Nuclear Spin Angular Momentum

It has been shown that some nuclei have spin angular
momentum with observable components \( m_i \hbar \), having nuclear spin
quantum numbers that are not restricted to \( \frac{1}{2} \), but may be,
0, 1/2, 1, 3/2, 2, 5/2, 3, 7/2, 4, 9/2, 5, 6, and even \( \geq 7 \).

The magnetic moment of the nucleus including the
nuclear g factor \( g_i \) is,

\[ \mu_i = \left( \frac{g_i \mu_N}{\hbar} \right) I = \gamma_i I \] \hspace{1cm} (12)

This relationship was first shown by Bloch [2], who also
derived equations to express the components of the
magnetisation in three dimensions, which are known as the
Bloch equations.

The spin angular momentum, and magnetic moment of the
electron are by convention opposed to each other, but there
is no such requirement for nuclei and \( \gamma_i \) may be positive or
negative.

Section 3.3 Electron Spin Angular Momentum

In a similar vein the electron has a spin angular
momentum with measurable components \( m_s \hbar \), but in this case
\( m_s = \pm \frac{1}{2} \) only. The magnetic moment of the electron is
derived from,

\[ \mu_s = g_e \gamma_e S \] \hspace{1cm} (13)

with \( g_e \) being the g-value for the electron: for a free
From (5) it follows that with the magnetic field in the $z$ direction, $B_z$ that,

$$E = -\mu_z B_z.$$  \hspace{1cm} (14)

For particles with a spin of $\frac{1}{2}$ then $\mu_z$ has either of two values, with the magnetic field removing the spin degeneracy.

Fig. 3.1 Energy Level Splitting in a Magnetic Field

Transitions are caused when a quantum of energy is absorbed equal to the energy separation.

$$h\nu = \mu_z B_z - (-\mu_z B_z) = 2\mu_z B_z.$$  \hspace{1cm} (15)

NMR - For a nucleus with $m_t = \frac{1}{2}$, then from (12) $\mu_z = \frac{1}{2} \gamma_1 \hbar$ and hence the resonance condition is fulfilled when,

$$h\nu = \gamma_1 \hbar B_z \text{ or } \nu = \gamma_1 \frac{B_z}{2\pi}.$$  \hspace{1cm} (16)
This relationship was derived in the original paper by Bloembergen, Purcell, and Pound [3], in one of the first reports of NMR. It is customary to use $\gamma_1$ for nuclei (nuclear property), and $g$ for electrons. 

ESR - For the electron $m_s = 1/2$ and from (13) $\mu_z = 1/2 g_e \mu_B$, which substituted in (15) gives,

$$\hbar \nu = g_e \mu_B B_z \quad (17)$$

The two quantum states correspond to two opposite orientations of the magnetic moment vector, and each precesses about the field direction.

![Diagram of Magnetic Field and Dipole](image)

Fig. 3.2 Effect of the Magnetic Field on a Magnetic Dipole

A transition is defined as a vector passing from one orientation to the other, and the magnetic field $B_1$ has to
be applied perpendicular to the static field to produce the required torque. The field $B_1$ rotates at the Larmor frequency given by (10) in order to produce the transition.

For the particular system considered above, when in thermal equilibrium, the distribution of the particles between the two energy levels is given by the Boltzmann law.

$$\frac{n_1}{n_u} = \exp \left[ \frac{2 \mu_z B_z}{k T} \right] \approx 1 + 2 \frac{\mu_z B_z}{k T} \quad \text{since} \quad \mu_z B_z \ll k T$$

where $n_1$ and $n_u$ are the number of particles in the lower, and upper energy levels respectively. The ability to detect a net absorption of energy depends on the excess population in the lower level, but as this value is only very small then sensitive detection methods are required. A good account of the basic theory of NMR is provided by Emsley, Feeney and Sutcliffe [4].

Section 3.4 Axes for Description of Magnetisation

The above description of nuclear motions is based on a laboratory frame of reference. If however we rotate the laboratory i.e. the radio frequency (RF) field $B_1$, at the Larmor frequency then the nuclei would no longer appear to precess, but would become stationary and coincident with the $B_0$ axis of the constant magnetic field, as shown in Fig. 3.3.

The magnetic behaviour is now completely described by a stationary bulk magnetisation vector $M_0$. This system is referred to as the rotating frame and simplifies the practical description of NMR. This area is described in

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Section 3.5 Practical Aspects of Solution NMR

Much of this section is also applicable to solid state NMR, but it is best to introduce the subject by considering the most basic case initially. The special requirements of solid state NMR will be covered later.

The simplest form of NMR is known as Continuous Wave NMR (CWNMR) can be carried out using a balanced RF bridge with one arm containing the sample in the magnetic field. Then an alternating current with frequency in the RF range is passed through a coil perpendicular to the applied field $B_0$. This gives rise to an oscillating magnetic field which...
is then varied in frequency, with the sample being spun at approximately 30 Hz to reduce any residual magnetic field gradients in solution. When the frequency of the oscillating field matches the Larmor frequency of the nuclei then energy is absorbed by the sample causing a change in the spin orientation. This unbalances the bridge, and a Faraday current is induced in the receiver coil, and amplified and detected by standard RF methods. The signal is then recorded as a function of the frequency of the oscillating RF field. Signal averaging for samples of low sensitivity is done by repetitive scanning of the spectrum, followed by addition of the individual scans, which is time consuming.

Section 3.6 Fourier Transform NMR (FTNMR)

In this case a powerful pulse of RF current is sent through the transmitter coil. A situation results where the Larmor frequencies of nuclei within the spectral range are excited simultaneously. The nuclei as a result "phase up" into one precessing magnetisation vector which has a component in the xy plane. This component of the magnetisation induces a current in the receiver coil. The same coil is used to transmit the pulse, and detect the signal as the two processes occur at different times.

The amount of xy magnetisation is determined by the sine of the tip angle. The maximum signal is therefore obtained with an angle of 90°, this is known as the 90° pulse. The value of the pulse angle (ϕ), generated by
pulse of time $t$ is given by,

$$\phi = \gamma B_1 t \text{ (rads)} = \gamma B_1 t \frac{360}{2\pi} \text{ (degrees)} . \quad (18)$$

The frequency of the induced current in the receiver coil is equal to the precessional frequency of the nuclei. The current is then sampled at regular time intervals to monitor its decay, which is related to relaxation effects, which will be described later. The data thus collected in the time domain are then mathematically transformed using a computer to perform the following integration to obtain the signal in the frequency domain.

$$M(\nu) = \int_{-\infty}^{\infty} M(t) \exp(i2\pi\nu t) \, dt \quad . \quad (19)$$

This is known as the Fourier transform (FT) of the signal. The major advantage of this method is that the signal averaging can be done more efficiently as the only restriction on the repetition frequency of the number of pulses $N$, is that ideally the sample should have relaxed back to equilibrium after each pulse before the next is applied. The increase in sensitivity i.e. the signal to noise ratio, is theoretically equal to $\sqrt{N}$, which is one reason that nuclei of low sensitivity, such as $^{13}$C can be observed routinely. It is also possible to obtain $\sqrt{N}$ by doing a CW experiment $N$ times, but this is much more time consuming as all the nuclei are excited all the time in this experiment.

Section 3.7 Solid State NMR

In general solids have very broad lines several kHz in
width. There are several reasons for this which need to be taken into account in order to observe high resolution solid state NMR spectra.

1) There is dipolar broadening e.g. for $^{13}$C this is entirely heteronuclear due to C-H interactions. The local field $B$ is a direct function of the angle $\theta$ the inter-nuclear vector between the carbon, and hydrogen, makes with $B$.

$$B = \frac{\mu}{r^3} (3 \cos^2 \theta - 1) \quad (20)$$

In a powder there are a range of fixed values of $\theta$, which give a range of resonance frequencies, and are one contribution to the large linewidths. In a solution molecular tumbling ensures that dipolar interactions are averaged over all values of $\theta$.

The solution to this problem is to use very high power proton decoupling, in the case of $^{13}$C, over several kHz to remove the dipolar contribution to line broadening together with magic angle spinning.

2) Several interactions which have a direct influence on the NMR of solids contain the term $(3\cos^2 \theta - 1)$, where $\theta$ is the inter-nuclear vector. One of these interactions is the dipolar broadening in the solid as shown above. Any anisotropic property is averaged by molecular tumbling in the liquid state, but the absence of fast molecular reorientation in the majority of solid samples dictates that any anisotropy must be averaged mechanically. By spinning the sample at an angle which averages the value of $(3\cos^2 \theta - 1)$ to zero will also average all the anisotropic
interactions to zero, thus eliminating, or reducing their influence in the solid state spectrum. This situation corresponds to an angle of 54.7° (the "magic" angle), and the rate of spinning should also be of the order of the static bandwidth expressed in Hz. Typical spinning speeds are of the order 4 to 12 kHz. A precise and complete description of this facet of solid state NMR has been described by Harris [6].

3) In solids the molecular motion is reduced which causes a lengthening of relaxation times. This limits the repetition frequency of the RF pulses, so to surmount this problem cross polarisation is used to transfer relaxation information from a fast relaxing abundant nucleus, to a dilute one. In the case of $^{13}$C, cross polarisation is carried out with fast relaxing protons.

Section 3.8 Chemical Shifts

The magnetic field at the nucleus is never equal to the applied field, but depends upon several factors, one of which is the structure of the molecule in which the atom containing the nucleus is a part.

Nuclear magnets in other atoms in a molecule can cause changes in the magnetic field, by dipole-dipole interactions causing signal broadening, especially in solids. In liquids the rapid molecular motions averages these fields to zero.

The normal resonant condition already shown in (16), is amended by the introduction of an isotropic screening, or shielding constant, $\sigma_j$. 

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In the semi-empirical theory of chemical shifts, \( \sigma_j \) is equal to the algebraic sum of the shielding contributions from different sources.

\[
\sigma_j = \sigma_{D} \text{(local)} + \sigma_{P} \text{(local)} + \sigma_{N} + \sigma_{R} + \sigma_{E} + \sigma_{S}, \tag{22}
\]

- \( \sigma_{D} \) = local diamagnetic contribution
- \( \sigma_{P} \) = local paramagnetic contribution
- \( \sigma_{N} \) = neighbour anisotropy
- \( \sigma_{R} \) = effect of ring currents
- \( \sigma_{E} \) = electric field effects
- \( \sigma_{S} \) = solvent effects

Shielding differences are called the chemical shift, given by,

\[
\nu_1 - \nu_2 = \gamma \frac{B}{2\pi} \left[ \sigma_2 - \sigma_1 \right] \quad \text{and} \quad \frac{\nu_1 - \nu_2}{\nu_1} = \frac{\sigma_2 - \sigma_1}{1 - \sigma_1}, \tag{23}
\]

but since \( \sigma_1 \ll 1 \) then the fractional change, equal to the difference in shielding constants, is the chemical shift \( \delta \), expressed in ppm.

\[
\delta = \frac{\nu_1 - \nu_2}{\nu_1} = \frac{\sigma_2 - \sigma_1}{1 - \sigma_1}. \tag{24}
\]

Chemical shift is a relative term, so a scale has been developed with a standard reference substance set as zero. For \(^1\text{H}\), \(^{13}\text{C}\), and \(^{29}\text{Si}\) spectra the standard is \((\text{Me})_4\text{Si}\) (Tetramethylsilane TMS), since it is inert, well separated from most resonances, and gives an accurate narrow singlet reference. \( \delta \) is defined as positive to the high frequency (low field) of the reference.
Section 3.9 Relaxation theory Harris [6].

It has already been shown that when the resonance condition is achieved the nuclei absorb energy to occupy the next higher energy level. The nuclei then relax back to the lower energy level by a process due to a magnetic field fluctuating at a required frequency for the system in question. The components of the local field in the x and y directions both contribute an equal amount to induce relaxation transitions, though the z component does not. This means that the total relaxation transitions for a single quantum process are at a rate given by,

$$W_1 = \frac{1}{2} \gamma^2 \left[ B_{xy} \right]^2 J(\omega_0) , \quad (25)$$

where $B_{xy}$ is the random fluctuating magnetic field, and $J(\omega_0)$ is the transition efficiency from fluctuations at the resonance frequency $\omega_0$, known as the spectral density. Each transition alters the population difference between the energy levels by 2, and equilibrium is approached in exponential fashion with time constant $T_1$,

$$T_1 = \frac{1}{2 W_1} . \quad (26)$$

This was first proposed by Bloembergen, Purcell and Pound [3], for the relaxation of the magnetisation in the longitudinal direction, and is also known as spin-lattice relaxation.

An alternative description of the relaxation process is that the spin system, after it has absorbed energy, is equivalent to an increase in its temperature, with the relaxation process maintaining thermal equilibrium with the surroundings. Hence, this is called spin-lattice relaxation.
where lattice refers to the surroundings. In the particular case of a particle with a spin \( \frac{1}{2} \), including electrons, the fluctuating magnetic fields are set up due to the intrinsic magnetic moment of the particle. Again the magnetisation in the z direction relaxes in an exponential fashion with the time constant \( T_1 \). The \( T_1 \) of electrons is shorter than that for nuclei, because of the greater interaction of the magnetic moments of electrons with their surroundings.

The factors which cause line broadening are due to effects called spin-spin relaxation processes, characterised by the time constant \( T_2 \), as first determined by Bloch [4]. If two nuclei are precessing in phase at a given time, then as time runs on they will irreversibly lose their phase coherence, due to spin-spin relaxation, in effect this describes how the transverse magnetisation decays with time.

The mean value of a randomly fluctuating magnetic field is zero, whilst the mean square value on which relaxation processes depend is non-zero. The time scale of the fluctuations is the time scale of molecular motion. The faster the fluctuations the more different will be the magnetic field at time \( (t + \tau) \) i.e. \( B(t + \tau) \) from its value \( \tau \) seconds before \( B(t) \). This property is expressed by the autocorrelation function \( G(\tau) \),

\[
G(\tau) = \overline{B(t)B(t + \tau)} \text{ (average over all spins).} \quad (27)
\]

Another view of \( G(\tau) \) is that it expresses the average correlation in time of any particular configuration of the nuclei i, and j, i.e. it indicates the average persistence
in time of any given arrangement of nuclear moments relative to each other. Thus \( G(t) \) is intimately concerned with the statistical nature of the molecular motion in the system. In general it is assumed that the motion of molecules in fluids is statistically stationary. This means that the value of a particular correlation function depends only on the difference \( \tau \), between \( t \), and \( t + \tau \), and not on the absolute value of \( t \).

In principle it is necessary to choose a model for the molecular motion, and then to evaluate the necessary correlation functions. In practice it is almost always assumed that correlation functions may be written as,

\[
G(\tau) = \exp \left[ -\frac{|\tau|}{\tau_c} \right]
\]

where \( \tau_c \) is called the correlation time, which characterises the time scale of the molecular motion. The value of \( \tau_c \) is the time beyond which the configuration of the system will have changed significantly, and this is often given as the time for a molecule to rotate through an angle of one radian, or to diffuse through a distance of one molecular diameter.

The importance of the autocorrelation functions in calculating nuclear magnetic relaxation times, is that their form determines the spectral density of the interaction producing the relaxation as a function of frequency. The theory of almost random processes by McDonald [7], shows that the spectral density i.e. frequency domain function, of such an interaction, is given by the FT of its correlation
function i.e. time domain function. If $J(\omega)$ is the spectral density then,

$$J(\omega) = \int_{-\infty}^{\infty} G(\tau) \exp(i\omega \tau) d\tau.$$  \hfill (29)

One particular form is that of the Lorentzian spectral density as shown in (30), but this does not hold for every situation and usually the spectral density is modelled to fit the system it is applied to.

$$J(\omega) = \frac{2\tau}{1 + \omega^2 \tau^2}.$$  \hfill (30)

The energy available for producing relaxation transitions is distributed over a frequency range given by the equation of $J(\omega)$. The FT of an exponential (time scale), is a Lorentzian (frequency scale), however it is more usual to see $J(\omega)$ plotted as a function of $\log(\omega)$, which gives the appearance of a flat topped peak.

For a system of isolated spins the component at $\omega_0$ is required. If $\omega_0^2 \tau_c^2 \ll 1$ this is called extreme narrowing, whilst the most efficient relaxation occurs when $\omega_0 \tau_c = 1$ for the Lorentzian spectral density, which is at the point where the value of the spectral density suddenly drops in Fig.3.4. Also in Fig.3.4 $\omega_0$ is in extreme narrowing in one case, but outside in the other.

For long values of $\tau_c$ there is a large spectral density at low frequencies, but very little at high frequencies. The result of this is that as $\tau_c$ increases from zero, then $T_1$ goes through a minimum whilst $T_2$ continues to decrease. The reason for this is that the fastest dephasing of a group of precessing nuclei, due to the spread of the local magnetic field produced at the site of one of them by the
Fig. 3.4  The Variation of the Spectral Density $J(\omega)$ with $\omega$

... others, will occur when the nuclei are in fixed positions relative to one another. Any motion reduces the spread of the effective local field, and hence reduces the rate at which the nuclei lose phase coherence.

The behaviour of $T_1$ and $T_2$ with the change of $\tau_c$ is shown in Fig. 3.5. Thus by choosing a suitable model which fits the experimental data, the $T_1$ minimum can be located by
changing the temperature (i.e., changing $\tau_c$), or the frequency of observation ($\omega_0$). This model is based on the assumption that a molecular motion may be represented by a single $\tau_c$. In the case of molecules on solids for example, this model is often found to be insufficient, and a second value of $\tau_c$ needs to be invoked if the motion of the molecule is not isotropic on the average.

As $T_1$ and $T_2$ are largely determined by molecular motion, a study of the relaxation times with temperature variation can lead to information on the temperature dependence of the motion. This assumes that the temperature does not alter the mean square interaction energy of the
relaxation mechanism, which is reasonable if the relaxation is dominated by intramolecular interactions. If the motion involved is taken to be a thermally activated process showing Arrhenius type behaviour, Wert and Zener [8],

\[
\text{Rate} = A \exp \left( \frac{-E_A}{kT} \right),
\]

then plots of \( \log_e(T_1)^{-1} \), or \( \log_e(T_2)^{-1} \) against (Temperature)^{-1} can lead to an apparent activation energy for the process.

Next it is useful to bring together correlation times, molecular motion, and relaxation mechanisms. Only molecular rotational, and translational motions have frequency components appropriate for nuclear relaxation, since the vibrational motions occur on too fast a time scale.

For a spherical solute molecule of volume \( V \), in a medium of viscosity \( \eta \), the Stokes-Einstein-Debye theory gives the rotational correlation time as,

\[
\tau_c = \frac{\eta V f_{rot}}{kT},
\]

where \( f \) is the microviscosity factor.

Similarly the translational diffusion coefficient is given by

\[
D = \frac{kT}{6\pi\eta rf_{trans}},
\]

where \( r \) is the radius of the solute molecule. Stokes-Einstein-Debye theory effectively assumes that \( f = 1 \) in both cases, although since the pioneering work various models have been proposed to justify various values of \( f \). For example in the work of Glerer and Wirtz [9] values for \( f \) in pure liquids were proposed.
In extreme narrowing the relaxation equation is independent of the static magnetic field, and in this region the relaxation takes place by one, or a combination of the following relaxation mechanisms.

Section 3.10 Methods of Relaxation

1) Dipole-dipole relaxation with other nuclei for nuclei with spin $= \frac{1}{2}$. This mechanism may be between homo, or hetronuclear atoms. This leads to three possible equations for relaxation rates for nuclei separated by a distance $r$.

\[(\text{intra})(\text{homo}) \quad \frac{1}{T_1} = \left[ \frac{\mu_0}{4 \pi} \right]^2 \frac{3}{2} \frac{\gamma_A^4 \hbar^2 \tau_c}{r^6} \quad , \quad (34)\]

\[(\text{intra})(\text{hetero}) \quad \frac{1}{T_1} = \left[ \frac{\mu_0}{4 \pi} \right]^2 \frac{\gamma_A^2 \gamma_X^2 \hbar^2 \tau_c}{r^6} \quad , \quad (35)\]

\[(\text{inter})(\text{hetero}) \quad \frac{1}{T_1} = \left[ \frac{\mu_0}{4 \pi} \right]^2 \frac{2}{15} N_X \gamma_A^2 \gamma_X^2 \hbar^2 \quad , \quad (36)\]

$N_X$ = concentration of spins X (per unit volume)

$D$ = mutual translational coefficient of the two molecules

$a$ = distance of closest approach

2) The shielding at the nucleus of unsymmetric molecules varies with the molecular orientation in the magnetic field. The tumbling motion therefore causes the necessary fluctuations to cause relaxation. The method of detection is that the rate of relaxation is proportional to $B_z^2$, and the mechanism is known as Chemical Shift Anisotropy (CSA).
\[
\frac{1}{T} = \frac{2}{15} \gamma^2 \Delta \frac{B^2}{A} \Delta \sigma^2 \tau_e \quad \Delta \sigma = \sigma || - \sigma \perp
\]
(shielding anisotropy for axial symmetry)

3) Molecular Spin Rotation causes a magnetic field which varies at the nucleus due to molecular collisions. In this case the correlation time is a reflection of the time between collisions rather than a measure of the molecular tumbling. For liquids undergoing isotropic tumbling then,

\[
\frac{1}{T_1} = 2 I k T C^2 \tau_s \quad \text{and} \quad \tau_s \tau_s = \frac{I}{6 k T}
\]

where \(C\) is spin-rotation interaction constant, and \(I\) is the molecular moment of inertia.

4) Scalar interactions between nuclei which interact through their electrons can also cause relaxation. If the coupling constant \(J_{AX}\) varies due to a time dependent chemical exchange this is known as scalar relaxation of the first kind, whereas if the relaxation of the \(A\) nucleus is dependent on the relaxation of the coupled \(X\) nucleus this is known as scalar relaxation of the second kind. The equation is

\[
\frac{1}{T_1} = \frac{8\pi^2 J_{AX} I_X (I_X + 1)}{3} \frac{\tau}{1 + (\omega_X - \omega_A)^2 \tau^2}
\]

For relaxation of the first kind then \(\tau\) is the exchange rate, whilst for the second kind this is the relaxation rate of \(X\).

5) Interactions with unpaired electrons may be either dipolar or scalar. As stated previously the magnetic moment of the electron is so large that dipolar interactions are increased. If the electron exchanges between molecules then this would be scalar relaxation.
(Intra) dipolar \[
\frac{1}{T_1} = \left[ \frac{\mu_0}{4 \pi} \right]^2 \frac{\alpha_e^2 \hbar^2 S(S + 1)}{3 \gamma_n r^6} \tau_c ,
\]

scalar \[
\frac{1}{T_1} = \frac{8}{3} \pi^2 \alpha_n^2 S(S + 1) \tau_c ,
\]

S is the total spin of the unpaired electrons, and \( \alpha_n \) is the nucleus-electron hyperfine splitting constant.

6) Quadrupolar relaxation for nuclei of spin \( \frac{1}{2} \) depends on whether the molecule containing the nucleus is in the solid or liquid state. For the particular samples used in my work the nuclei were in environments which more closely resembled the liquid state whilst being trapped in solid particles.

The quadrupolar interaction is affected by the direction of the electric field gradient which is fixed in the molecular framework, so that molecular tumbling causes rapid changes in this energy which induces spin lattice relaxation when at the transition frequency.

\[
\frac{1}{T_1} = \frac{3}{10} \pi^2 \left[ 1 + \eta^2 \right] \frac{2I + 3}{I^2(2I - 1)} \lambda^2 \tau_c ,
\]

\( \lambda = \) nuclear quadrupole coupling constant \( = \frac{e^2 Q q_{zz}}{\hbar} \),

where \( Q \) is the quadrupole moment, and \( q_{zz} \) is the electric field gradient \( zz \) component. It is assumed that the electric field gradient is symmetric so reducing the asymmetry parameter \( \eta \) to zero, thus causing the term \( 1 + \eta^2/3 \) to equal 1.

When not in extreme narrowing then the \( \tau_c \) value in all of the above must be replaced by the appropriate spectral density expression which fits the data.
Section 3.11 Experimental Procedure - Sample preparation

All the polymer, and zeolite samples used in relaxation time analysis were prepared in a similar fashion. To fix the level of hydration of each sample the solid was dehydrated for 3 to 4 days in an oven to remove as much water as possible. For the polymer the temperature of the oven was 150°C, whilst that for the zeolite was 200°C. The structures of both compounds is unaffected by heating in this temperature range Krzyszowska [10] and Mumpton [11].

Each sample was weighed, and then placed in a humid atmosphere, which consisted of a dessicator containing a quantity of either $\text{H}_2\text{O}$, or $\text{D}_2\text{O}$ on a watchglass. The dessicator was then evacuated of oxygen and the sample was left to absorb water to the desired content. The solid sample was reweighed, and then sealed in a glass sample tube to ensure that the hydration level did not vary. The water content was defined as follows,

$$\frac{W_L - W_0}{W_0} \times 100 = \text{percentage of water} \quad (43)$$

$W_L =$ weight of dehydrated sample

$W_0 =$ weight of sample loaded with water

For replacement of cations in zeolites, the zeolite was left to soak in either saturated hydroxide solution, or 1M HCl to introduce the various metal or proton ions. After 2 days the samples were washed then soaked in fresh solutions, after a further two days the zeolite was filtered, washed with water to remove any solution from the surface, and then hydrated using the procedure described above.

From $^{23}\text{Na}$ NMR data it was possible to compare the
magnitude of the sodium signal in samples of the original zeolites with those of cation exchanged samples. From the comparison of the two signals the percentage of sodium exchanged was calculated. The determination of ion exchange by $^{23}\text{Na}$ NMR of zeolites has been previously shown by Macura et al. [12]. All the spectrometer parameters were unchanged, while the sample volumes and the sample positions in the coil were as similar as possible. Of course a certain error will occur in these factors, but the accuracy of the results should not be altered by more than $\pm 10\%$ at maximum.

Table 3.1

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Original $^{23}\text{Na}$</th>
<th>$^{23}\text{Na}$ after</th>
<th>$% ~^{23}\text{Na}$ exchanged</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-X</td>
<td>16.19</td>
<td>4.67</td>
<td>71</td>
</tr>
<tr>
<td>Na-Y</td>
<td>24.29</td>
<td>1.53</td>
<td>94</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>21</td>
<td>3</td>
<td>86</td>
</tr>
<tr>
<td>Na-Mord.</td>
<td>12.71</td>
<td>1.2</td>
<td>91</td>
</tr>
</tbody>
</table>

As expected this confirms that the majority of the cations in all the samples had been exchanged.

The samples were also checked by repeating the room temperature experiment to ensure that after measurements had been made at the highest temperature in the NMR magnet (110°C) no water had left the sample.

Section 3.12 NMR Procedure

All the measurements were performed on a Bruker MSL 300 spectrometer. The relaxation measurements were carried out using static samples, and employing broadline NMR. Each
sample was packed in a sealed glass tube of dimension 5mm o.d., and 46mm length for $^1$H measurements. For all other nuclei glass tubes of dimensions 10mm o.d. and 48mm length were employed. The solid samples were not degassed as it was thought that dissolved oxygen inside the zeolites would not cause significant line broadening, as the minimum linewidth for any of the nuclei was of the order of 100 Hz. Relaxation times at temperatures at ambient and below were attained using a flow of $N_2$ gas, while above ambient heated compressed air was used to achieve the required temperature.

The $^{13}$C spectra of the polymer were acquired using Cross Polarisation Magic Angle Spinning (CPMAS) NMR.

Section 3.13 $T_1$ Spin - lattice relaxation times

A Saturation Recovery pulse sequence was used, in which the magnetisation is saturated by a burst of pulses which flip the magnetisation $90^\circ$ and dephase it in the $x'y'$ plane a number of times. The saturation pulse sequence is designed to ensure that there is no magnetisation in either of the $z$ planes. There is then a time delay $\tau$, during which time the magnetisation has the opportunity to relax back in the $z$ direction. After this delay one of the situations is created as shown in Fig.3.6.
Then a $90^\circ$ pulse is applied with the following result.

So for a long delay the magnetisation has a larger resultant magnetisation component in the detection axis, rather than the case of a short delay where the final signal intensity is low after the $90^\circ$ pulse. This technique has
the added advantage that the $90^\circ$ pulse needs to be known only approximately as all signal intensities are relative, and the time constant is what is of interest.

The first point of the FID was sampled for each particular $\tau$ value as its intensity was proportional to the total magnetisation in the detection axis. The variation of the magnetisation intensity with increasing $\tau$ value was then fitted to find the value of $T_1$ using either a single or double exponential fit if that was significantly better. The program used to fit the data was the standard program SimFit as supplied by Bruker. Examples of the typical fits obtained using this method are shown in Fig.3.7.

A typical spectrum is shown in Fig.3.8, with typical parameters being a $90^\circ$ pulse of between 5 to 8$\mu$s, with the number of pulses ranging from 3 for protons, to 64 for sodium. Typical values of the spectral width were from 4 to 125 kHz, with 32 time delays used to calculate the $T_1$ value.

The Saturation recovery pulse sequence can be summarised as follows,

\[ \text{(Saturation pulse sequence)} - \tau - \frac{\pi}{2} \text{FID} \]

The recovery of the signal intensity in a saturation recovery experiment is from 0 to $M_\infty$, and obeys the equation for ideal pulses below.

\[ M(\tau) = M_\infty \left[ 1 - \exp \left( \frac{-\tau}{T_1} \right) \right] \]  \hspace{1cm} (44)

Typically fifteen values of $T_1$ were measured in the temperature range 193 to 373 K.

The time constant $T_{1p}$ can be measured using a separate NMR experiment, in order to gain information about molecular
Fig. 3.7 One and Two Component Fits of the Relaxation Data using the Saturation Recovery Sequence.
Section 5.15: Relaxation Time

An approximate value for $T_1$ was found from the relationship:

$$\frac{1}{T_1} = \frac{1}{T_{1a}} + \frac{1}{T_{1b}}$$

where $T_{1a}$ and $T_{1b}$ are the relaxation times for the two components.

Fig. 3.8 Typical NMR Static Wide line Spectrum
motions with a rate in the 50 kHz region. It was initially thought that this may be useful for the polymer in particular, however the data that were measured on the polymer proved difficult to analyse with any degree of accuracy for most of the samples. Another problem was that the high power required for these experiments frequently damaged the RF coil of the NMR probe, so it was decided not to pursue this type of experiment.

Section 3.14 \( T_2 \) Spin-spin relaxation times

An approximate value of \( T_2 \) was found from the relationship,

\[
B_{1/2} = \frac{1}{\pi T_2}, \quad (45)
\]

\( B_{1/2} \) = the linewidth in Hz at half the maximum peak intensity.

Section 3.15 Relaxation of molecules on surfaces

The \( T_1 \) relaxation time for a pair of nuclei each with spin \( \frac{1}{2} \) which experience a dipole-dipole interaction may be written as a linear combination of spectral densities.

\[
\frac{1}{T_1} = \frac{3}{2} \gamma^4 h^2 I (I + 1) \left[ J_1(\omega_0) + J_2(2\omega_0) \right]. \quad (46)
\]

This was first derived by Kubo and Tomita [13], and subsequently refined by Solomon [14]. One of the early examples where this was used was in the study of water on silica gel by Woessner [15]. In this case equation (46) was expressed as being the addition of the spectral densities at the resonance frequency, and twice the resonance frequency.
of quantities involving the distance and the angle of the line joining the two protons. The distance between the protons is included in the autocorrelation function in the evaluation of the spectral densities. This equation has now been recast as shown by Woessner [16], and is shown in (47).

\[
\frac{1}{T_1} = \frac{2}{3} m^2 \left[ \frac{\tau_1}{1 + \omega_0^2 \tau_1^2} + \frac{4\tau_1}{1 + 4\omega_0^2 \tau_1^2} \right] \quad . \tag{47}
\]

For amorphous or powdered samples the constant value \( m^2 \) in (47) is written as,

\[
m^2 = \frac{2}{3} \frac{g^4 h^2 I(I + 1)}{I} \frac{4}{5} \sum r_{ij}^{-6} \quad , \tag{48}
\]

where \( r_{ij} \) = distance between centres of molecules i and j.

This is known as the Van Vleck second moment [17].

For (47) the minimum value of \( T_1 \) (i.e. rate maximum) is achieved when,

\[
\omega_0 \tau_1 = 0.6158 \quad . \tag{49}
\]

This means that for a set of samples which have relaxation times measured at the same resonance frequency then the minimum values of \( T_1 \) at whatever temperatures they occur, will correspond to the same value of the correlation time.

The value of \( T_1 \) dipolar relaxation for molecules on surfaces was proposed by Resing [18] to be a combination of two terms, a translational one, and a rotational one. In this case each type of motion would give separate \( T_1 \) minima, with typical values of temperature of the minima, and associated \( E_A \) values shown below.

Translational diffusion minimum \( \approx +160^\circ C \quad E_A = 40 \text{ kJmol}^{-1} \)
Rotational process minimum \( \approx -100^\circ C \quad E_A = 12 \text{ kJmol}^{-1} \).
The electron magnetic moment is generally about a thousand times greater than nuclear moments. The magnetic fields from the paramagnetic centres swamp out those of the nuclei as far as relaxation is concerned. Zeolites contain iron which is incorporated into the lattice which can, under certain conditions, interfere by addition to the nuclear dipolar relaxation mechanism as shown in (50).

\[ T_1^{-1} = T_{1D}^{-1} + T_{1P}^{-1} \quad (50) \]

or Total Rate = Dipolar Rate + Paramagnetic Rate

Resing [19] showed that iron impurities above 6ppm can give a paramagnetic contribution to the dipolar relaxation. The samples used in this study contained the following paramagnetic quantities shown in Table 3.2.

Paramagnetic dipolar fields only have instantaneous relaxation effects in a small region around their centre Blumberg [20]. The relaxation mechanism for most nuclei is by movement of the nuclei, or the nuclear magnetisation to the paramagnetic sink. At higher temperatures, molecular diffusion is much faster than spin diffusion can ever be, so the molecular diffusion modulates the field of the paramagnetic species.

The contribution of \( T_{1P}^{-1} \) to the total relaxation rate is fairly constant and is not affected appreciably by temperature. This means at low temperatures when molecular motion is much reduced, the sole contribution to the relaxation rate is that of the paramagnetic species. In this region the time between molecular jumps \( \tau \) becomes
greater than $T_{1p}$ and relaxation is governed by the paramagnetic impurity. This leads to a constant value of the relaxation rate an example of which can be seen in the work by Resing [21]. In this work, the $^1H$ NMR $T_1$ data were measured for water on 13X, both for the zeolite with 150 ppm of iron, and also for 0 ppm. The iron impurity has the effect of lowering the value of $T_1$ at the minimum, so altering the value of the second moment. The magnitude of $E_A$ is also affected by the presence of iron but the temperature at which the $T_1$ minimum occurs is little changed. This means that as my samples all contain a certain amount of iron, then all the dipolar relaxation data can be treated relative to one another, but should not be taken as absolute values. It is expected that trends of behaviour should not be affected by the presence of iron.

Table 3.2

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Iron (III) Content ppm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-A</td>
<td>250</td>
</tr>
<tr>
<td>Na-X</td>
<td>250</td>
</tr>
<tr>
<td>Na-Y</td>
<td>700</td>
</tr>
<tr>
<td>Deal-Y</td>
<td>1600</td>
</tr>
<tr>
<td>Na-Mordenite</td>
<td>250</td>
</tr>
<tr>
<td>H-Mordenite</td>
<td>200</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>100</td>
</tr>
<tr>
<td>H-ZSM-5 Low Al content</td>
<td>100</td>
</tr>
</tbody>
</table>
Section 3.17 The Van Vleck Second Moment

For a single correlation time then the fraction $T_1/T_2$ is equal to 1.6 at the $T_1$ minimum, a larger fraction than this signifies that there is a distribution of sites and correlation times. The ratios found experimentally are shown in the results section. For the case of a single correlation time the second moment deduced from the value of $T_1$ at the minimum is the full second moment, as can be seen from my $T_1/T_2$ ratios. However, a single correlation time was not found in the systems under study.

The units of the second moment $m^2$ are $10^{-10} \text{(rad}^2\text{sec}^{-2})$, and the most efficient packing of non-rotating water molecules is in ice which has a value for $m^2$ of 2.63 units. Any adsorbed phase should have a second moment less than this, with the smallest possible value being for water molecules separated by large distances from their neighbours in a random fashion. Experimentally Kvlfividze [22] found that such a situation gave a value of 1.57 units. The least value of $m^2$ to be modulated by diffusion if the molecules were allowed fast spherical rotation would be slightly less than that calculated for ice of rapidly rotating molecules i.e. 0.4 units.

In summary the largest values of the second moment are found when the adsorbed molecules are close packed, and slow in their motion. A comprehensive review of theory and experimental applications of the use of NMR in the study of dipolar molecules adsorbed onto a heterogeneous surface is provided by Resing [23].
Section 3.18 Treatment of Relaxation of Quadrupolar Nuclei

It has been shown by Abragam [24], that the spin-lattice relaxation rate for any quadrupolar nucleus is given by equation (41) in the extreme narrowing region, i.e. for fast molecular motions. The extra proviso is that the relaxation is described by a single exponential, therefore

\[
\frac{dM_z}{dt} = - \frac{1}{T_1} \left[ M_z - M_z^0 \right], \quad (51)
\]

and also \( J(2\omega) = J(\omega) = 2\tau_c \). Out of extreme narrowing, the rate of relaxation is no longer proportional to \( \tau_c \) and the spectral density function shown previously for dipolar relaxation is invoked. Now equation (41) becomes,

\[
\frac{1}{T_1} = \frac{3}{100} \frac{\lambda^2}{I^2(2I - 1)} \left[ \frac{\tau_c}{1 + \omega_c^2} + \frac{4\tau_c}{1 + 4\omega_c^2} \right], \quad (52)
\]

Since \( J(\omega) + 4 J(2\omega) = 10\tau_c \) the equation must be divided by 10 on the right hand side. The Lorentzian form of the spectral density as shown in equation (30) means that by removing a factor of 2 from the bracketed term in (52) the final equation becomes for deuterium of \( I = 1 \),

\[
\frac{1}{T_1} = \frac{3}{10} \frac{\pi^2 \lambda^2}{I^2(2I - 1)} \left[ \frac{\tau_c}{1 + \omega_c^2} + \frac{4\tau_c}{1 + 4\omega_c^2} \right], \quad (53)
\]

and for nuclei with \( I = \frac{3}{2} \) such as \(^7\)Li then equation (54) is applicable. It has been shown by Geiger and Hertz [25], that the relaxation of \(^7\)Li is bi-exponential in principal but one component is so small as to be negligible, therefore it can be considered as a single exponential. The same treatment was followed for data on \(^{23}\)Na data which also has \( I = \frac{3}{2} \), in order to get an approximate picture of the
behaviour of the sodium cations.

\[
\frac{1}{T_1} = \frac{2}{25} \pi^2 \lambda^2 \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right]
\]  \hspace{1cm} (54)

In certain cases as seen in the results tables, it was found that a better fit to the data was achieved by assuming that the water occupied a fast, and a slow motional region. In these cases it was assumed that each region had a separate value for \(\tau_{298}\) and for \(E_A\). This led to the following type of equation based on that seen in (52).

\[
\frac{1}{T_1} = \frac{3}{100} \pi^2 \lambda^2 \frac{2I + 3}{I^2 (2I - 1)} \left[ J(\omega)_F + 4J(2\omega)_F + J(\omega)_S + 4J(2\omega)_S \right]
\]  \hspace{1cm} (55)

where the subscripts F and S refer to the fast and slow regions. Each region was given an equal weighting, and even though this is an artificial way of looking at the situation it was found that the fit to the data was improved. Examples of some of the fits of the \(T_1\) data are shown in Figs. 3.9, 3.10, and 3.11.

Section 3.19 Introduction to NMR of zeolite related systems

\(^1\text{H} \text{NMR of Protonated Zeolites}\)

Maiwald et al. [26], showed that in hydrophobic channel systems like H-ZSM-5, water can move more freely than in the sodium forms of zeolites X, Y, or A. It was also stated that proton exchange between sorbed water, and structural OH groups, is similar to other zeolites.

Vetrivel et al. [27], have simulated the OH groups in an infinite ZSM-5 lattice and found that the protons bind more strongly with Al substituted clusters than pure silicalite.
Fig. 3.9 Examples of the fits of $\nu_1$ Data with $\nu$ Temperature

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Fig. 3.10 Examples of the fits of $T_1$ Data with

\[
Y \text{ temperature}
\]
Fig. 3.11 Examples of the fits of $T_1$ Data with temperature
Several workers have studied the $^1$H MAS NMR of water on ZSM-5. Engelhardt et al. [28] showed that for the dealuminated form of the zeolite the resonances due to SiOH, AlOH, and SiOHAl were all quite distinguishable by their different chemical shifts. Using the same technique Hunger et al. [29], showed that the number of acidic groups is in good agreement with the number of framework Al atoms.

Section 3.20 IR Studies of Protonated Zeolites

A number of infra-red (IR) studies have been made of protonated zeolites and Vedri et al. [30, 31] found that the acid sites in H-ZSM-5 are slightly stronger than those in H-mordenite, whilst the pore size difference between the two is less than 1Å, and also stronger than HY and H-ZSM-11. The strength of the OH groups in H-ZSM-5 vary if the distribution of Al is uneven. Also using IR, Zholobenko et al. [32] showed that in ZSM-5 and mordenite, acidic structural OH groups are able to form strained intra-molecular hydrogen bonds with the neighbouring oxygen atoms of the zeolite framework. Finally Bankos et al. [33] showed that the strongest Brønsted sites in mordenites are localised in the narrow channels.

Section 3.21 $^1$H NMR of Zeolite A

Delinger et al. [34] showed that the zeolitic water becomes more tightly bound in the following order Na-X, Na-A, Ca-A and Mg-A with Mg-A having the longest values of $T^2$. 

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Klinowski [35] states that the water mobility decreases as the size of the cation increases as seen in the above trend, this article also provides a comprehensive review of the studies of zeolites using many aspects of NMR. One of the earlier articles by Resing [18] involved a description of the water adsorbed into Na-A and charcoal. The idea of exchange between physisorbed water, and surface hydroxyl groups is discussed along with the idea that the water is more viscous in the Na-A than in the charcoal.

Also in early work by Cohen-Addad and Farges [36], it was shown that even though the inter-cavity diffusion of water in Na-X is slow at room temperature, it is completely non-existent in Na-A at the same temperature. Basler [37], also found a two phase behaviour of water in Na-A, whilst Oehme et al. [38] have shown that the water molecules in the confined environments of the cubo-octahedra are predominantly intact.

Maiwald and Basler [39] suggested that the two phase behaviour of the proton resonance in zeolite A was due to firstly protons in water, and secondly protons in Al(OH)$_n$. It was thought that there is an enhanced accessibility of the $\beta$ cage protons for sorbate molecules in the $\alpha$ cages, when Na$^+$ ions are removed from the oxygen six ring window by exchange with ions of higher charge. One strange anomaly seen earlier [39] was that water in K-A had a very restricted molecular mobility but no explanation was offered as to why this should be.
The fact that mordenite zeolites have a more restricted water motion than that in faujasites was confirmed by the $^1$H MAS-NMR of Cholli and Pennino [40], who also calculated that in the unit cell faujasites have 235 water molecules when fully loaded, whilst mordenites have 24.

Pfeifer et al. [41], looked at the relaxation times of water in various zeolites which had ratios of Si : Al in the range 1.2 to 2.69.

The rate at which water molecules exchange between the large and the small cavities in Na-Y was measured by Basler [42], using $^1$H NMR to determine the rate of exchange between $^1$H and $^2$H isotopes.

It has been proposed by Pfeifer [43], that because of the short phase relaxation component in NMR measurements on water in faujasites due to the water in the cubo-octahedra, the results from NMR relaxation measurements are only valid for water adsorbed in the supercages. This is because in this instance the short phase does not contribute to the signal intensity in these measurements.

A review of the NMR study of the relaxation of molecules adsorbed on zeolites has been compiled by Pfeifer [44], with particular emphasis on water adsorbed on Na-X. Deininger et al. [34], also looked at the proton NMR of this system and found that as the water content decreases the water becomes more tightly bound as found from relaxation measurements.

Resing and Thompson [45] in their NMR study of this
system proposed a model based on an "inter-crystalline fluid" which is 30 times as viscous as bulk water at room temperature for the fully hydrated zeolite. In a theoretical report Kärger [46], showed how in heterogeneous systems the water may be described by two different diffusion coefficients, so justifying my fitting of the data to two motional environments.

Whipple et al. [47], found that for the diffusion of water in Na-Y the activation energy for the process was 16 kJ mol\(^{-1}\). It was also shown [47] that the lattice hydroxyl groups in zeolite Na-Y formed as previously described [11], can lead to structure degradation above approximately 16 per unit cell.

Section 3.23 IR Studies of Zeolites X and Y

The use of IR to examine water adsorbed on faujasites has helped to elucidate the picture of the structure at the zeolite surface. Both Subba Rao [48], and Hanke and Möller [49] proposed from IR measurements that in hydrated zeolites there is water hydrogen bonded to the zeolite lattice of the type shown below:

\[
\text{Na}^+ \quad ((\text{H})_{\text{zeolite}} \quad \text{O}^\cdot \quad \text{H})_{\text{zeolite}} \quad \text{H}_{\text{zeolite}}
\]

Section 3.24 \(^1\text{H NMR Self Diffusion Measurements of Water in Zeolites}\)

A number of workers including Kärger [50, 51] and Pfeifer [52] have pointed out that in the NMR self diffusion
measurements of water on both zeolite Na-X and Na-Y, it is possible to measure both inter- and intra-crystalline diffusion if the zeolite particles are small. Above approximately 15μm, only intra-crystalline diffusion is measured. In zeolite Na-Y the value for $E_A$ for inter-crystalline diffusion of water was shown [49] to be approximately 40 kJmol$^{-1}$. In Na-X the values for intra, and inter-crystalline diffusion were found to be in the order of 19 and 62kJmol$^{-1}$ respectively as measured previously [51, 52].

Pfeifer [53] has also discussed the self diffusion of water on Na-X, and found that the diffusion coefficient increases as the water content increases, whilst at the very highest coverages the self diffusion coefficient decreases again as the void spaces within the pores of the zeolite decrease.

Section 3.25 $^1$H NMR of Water in Zeolites under Pressure

A related study which is of interest is that by Brown [54], who used NMR to study the effect of pressure (of the order of several kbar) on the relaxation of water in hectorite, which is a layered mineral of the formula $\text{Al}_4\text{Si}_{10}\text{O}_{28}(\text{OH})_8$. The surface was found to be strongly hydrophilic due to hydroxyl groups, with a closely bound layer of water two to three molecules in thickness. The surface bound water has a lower $E_A$ than the free water, which was said to indicate the disruption of the hydrogen bond network in bulk water. The effect of pressures up to 5
kBar was to breakdown the remainder of the hydrogen bonds, as the variation in the $T_1$ seen for liquid $H_2O$ was not seen for water in the clay.

Section 3.26 NMR Relaxation of Quadrupolar Nuclei in Zeolites

$^7$Li NMR of Zeolites A, X, and Y

In work similar to that I have done Tokuhiro et al. [55] studied zeolites X, Y, and A with various concentrations of iron. In another study of the same system Basler [56] pointed out the errors that can occur in motional studies in these samples. Both papers assumed that all the Li$^+$ ions are either completely, or at least partially co-ordinated with water, which was thought to be realistic based on the work of Seff [57], and Basler [58].

The use of $^7$Li NMR was exploited by Macura et al. [59, 60] to study Li-A, and Li-X. In Li-A, two phases of cations were identified; those firmly bound in the aluminosilicate framework, and those distanced from it.

The work of Melchior et al. [61], showed that in partially exchanged LiNa-A the Li$^+$ ions have a definite preference for filling certain sites initially. In fully exchanged Li-A Freude et al. [62], found that the distance Li-Al is smaller than Na-Al thus supporting the fact that Li is not at the centre of the oxygen six ring. A mean lifetime of Li at a lattice site was calculated of 50µs with $E_A = 30$ kJmol$^{-1}$.

Electric conductivity measurements have been used by Jansen and Schoonheydt [63], to show that adding rubidium to
NaLi-X caused an increase in the \( E_A \) to 23 kJmol\(^{-1}\), and also an increase in the correlation time. This slowing of Li motion by the addition of a divalent ion was also seen by Schöllner and Herden [64], who again looked at dehydrated LiNa-A. As in reference [62], the lithium was found to be displaced towards the aluminium from the centre of the oxygen six ring, with a mean distance of Li-Al = 2.35 Å. Adsorbed organic molecules tended to reduce the activation energy and the correlation time, while different monovalent ions (H\(^+\), K\(^+\), Ag\(^+\), Tl\(^+\)) produce increases in these values. The \( E_A \) for the mobility of protons in NaH-A has been reported to be 43 kJmol\(^{-1}\) by Oehme [65], and for Tl\(^+\) in Tl-A it is 38 kJmol\(^{-1}\) as measured by Freude et al. [66].

Section 3.27 Deuterium NMR

Very few papers have been published on deuterium NMR of water adsorbed in zeolites as in most cases the use of proton NMR has been thought to suffice. One example of work that has been done is by Resing [67], which concentrated on calculations of the QCC in fully hydrated zeolites.

Section 3.28 Sodium NMR

It was shown by Hayashi et al. [68] using \(^{23}\)Na MASNMR that in Na-Y the level of hydration causes the Na ions to be in 3 different types of site, with only one of these sites being fully co-ordinated to water. This was shown by different lineshapes and chemical shifts for hydrated, dehydrated and re-hydrated samples.
Lechert [69], showed that in faujasites the $^{23}\text{Na}$ NMR linewidth first decreases with increased hydration as the asymmetry parameter is increased, and then decreases upon further hydration. It was also shown that in these zeolites the water became more mobile upon increased hydration.

In the report by Pfeifer [53], data for the sodium wide line spectra of Na-X, and Na-Y are also discussed. It was concluded that the non-localised Na$^+$ of the zeolite together with the adsorbed water form some kind of "cation" solution, the anion of which is represented by the skeleton of the zeolite. With decreasing water $0 < 0.7$ where $0$ is the fraction of the water coverage, there are not enough water molecules available to form symmetric hydration shells, and the electric field gradient at the nucleus increases broadening the $^{23}\text{Na}$ line. It is shown that even for maximum hydration, the non-localisable sodium ions are bound only to less than two water molecules. This assumes that in the "frozen" state these Na$^+$ are situated on the walls of the supercages c.f. "liquid" state where they form a cation solution. It is proposed that the reduced mobility of zeolitic water is not due to the Na$^+$ ions, because even in concentrated aqueous solutions of Na$^+$ the mobility of the water molecules is only slightly reduced.

Section 3.29 NMR of Organic molecules adsorbed on Zeolites

An excellent review of the NMR of adsorbed organic molecules on zeolites has been compiled by Pfeifer et al. [70], which is a useful starting point to the vast
amount of literature in this area.

In the following section the results on the NMR relaxation study of both lithium polymethacrylate, and various zeolites have been tabulated. Unless otherwise stated all the results were obtained using three component fits, although in some cases it was possible to fit the same data using five components. In these instances the five component parameters are reported directly below those calculated using three components.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T2 (ms)</th>
<th>T1 (ms)</th>
<th>T2 (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiPMA</td>
<td>0.25</td>
<td>4.29</td>
<td>3.29</td>
</tr>
<tr>
<td>LiPSZ</td>
<td>1.26</td>
<td>8.69</td>
<td>11.25</td>
</tr>
<tr>
<td>LiTSA</td>
<td>0.86</td>
<td>4.05</td>
<td>4.09</td>
</tr>
<tr>
<td>LiTFA</td>
<td>0.71</td>
<td>6.65</td>
<td>0.05</td>
</tr>
<tr>
<td>LiTSA</td>
<td>0.71</td>
<td>6.65</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Observations

1. The solvent deuterium is little changed as T2 increases.
2. T2 decreases very slightly as T1 increases.
3. The T2 moment increases as T1 increases.
4. With H2O in deuterium, the T2 moment is little changed as T1 increases.
5. T2 increases as T1 moment increases.
6. T2 moment increases slightly with increasing H2O.
### Table 3.3
Lithium Polymethacrylate Proton \(^{(1)H}\) NMR Relaxation Data

<table>
<thead>
<tr>
<th>Hydration (^{(1)H})</th>
<th>(\tau_{298}) (ns) ((\text{Error}))</th>
<th>(E_A) (kJmol(^{-1})) ((\text{Error}))</th>
<th>2nd moment ((\text{rad}^2\text{s}^{-2})) ((\text{Error}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% (H_2O)</td>
<td>5.15 (0.47)</td>
<td>4.14 ((0.47))</td>
<td>2.10E+10</td>
</tr>
<tr>
<td>20% (H_2O)</td>
<td>5.04 (1.19)</td>
<td>5.25 ((1.19))</td>
<td>2.18E+10</td>
</tr>
<tr>
<td>30% (H_2O)</td>
<td>4.80 (0.62)</td>
<td>8.49 ((0.62))</td>
<td>2.25E+10</td>
</tr>
<tr>
<td>40% (H_2O)</td>
<td>4.22 (1.18)</td>
<td>11.68 ((1.18))</td>
<td>2.63E+10</td>
</tr>
<tr>
<td>0% (H_2O)</td>
<td>0.89 (0.37)</td>
<td>3.77 ((0.37))</td>
<td>4.50E+9</td>
</tr>
<tr>
<td>11% (D_2O)</td>
<td>1.07 (0.55)</td>
<td>5.64 ((0.55))</td>
<td>4.05E+9</td>
</tr>
<tr>
<td>38% (D_2O)</td>
<td>1.75 (0.71)</td>
<td>6.48 ((0.71))</td>
<td>6.0E+9</td>
</tr>
<tr>
<td>56% (D_2O)</td>
<td>1.70 (1.58)</td>
<td>6.72 ((1.58))</td>
<td>6.0E+9</td>
</tr>
</tbody>
</table>

**Observations**

With \(D_2O\) i.e. Observing polymer protons

1) \(\tau_{298}\) is little changed as \(D_2O\) increases.

2) \(E_A\) increases very slightly as \(D_2O\) increases.

3) The 2nd moment increases as \(D_2O\) increases.

With \(H_2O\) i.e Looking at polymer and water protons.

4) \(\tau_{298}\) shortens (motion increases) as \(H_2O\) increases.

5) \(E_A\) increases as \(H_2O\) content increases.

6) The 2nd moment increases slightly with increasing \(H_2O\).
Table 3.4

Lithium Polymethacrylate Deuterium ($^2$H) Relaxation Data

<table>
<thead>
<tr>
<th>Hydration</th>
<th>$\tau_{298}$ (ns) (Error)</th>
<th>$E_A$ (kJmol$^{-1}$) (Error)</th>
<th>Quad. Coup. Const. (kHz) (Error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14% $D_2O$</td>
<td>3.15 (0.38)</td>
<td>9.04 (1.57)</td>
<td>86.56 (2.89)</td>
</tr>
<tr>
<td>25% $D_2O$</td>
<td>2.62 (0.09)</td>
<td>11.50 (0.60)</td>
<td>92.54 (1.54)</td>
</tr>
<tr>
<td>40% $D_2O$</td>
<td>2.21 (0.49)</td>
<td>11.01 (1.74)</td>
<td>99.95 (10.71)</td>
</tr>
</tbody>
</table>

Observations

1) $\tau_{298}$ lowers (motion increases) as the $D_2O$ content increases.

2) $E_A$ increases with the increase of $D_2O$.

3) The Quadrupole Coupling Constant (QCC) increases as the $D_2O$ content increases.
Table 3.5
Lithium Polymethacrylate Lithium ($^7\text{Li}$) NMR Relaxation Data

<table>
<thead>
<tr>
<th>Hydration</th>
<th>$\tau_{298}$ (ns)</th>
<th>$E_A$ (kJmol$^{-1}$)</th>
<th>Quad. Coup. Const. (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Error)</td>
<td>(Error)</td>
<td>(Error)</td>
</tr>
<tr>
<td>0% $\text{H}_2\text{O}$</td>
<td>53.30</td>
<td>12.74</td>
<td>63.98</td>
</tr>
<tr>
<td></td>
<td>(3.67)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% $\text{H}_2\text{O}$</td>
<td>13.62</td>
<td>20.07</td>
<td>55.41</td>
</tr>
<tr>
<td></td>
<td>(2.62)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35% $\text{H}_2\text{O}$</td>
<td>14.65</td>
<td>20.39</td>
<td>67.86</td>
</tr>
<tr>
<td></td>
<td>(4.87)</td>
<td>(0.50)</td>
<td>(22.62)</td>
</tr>
<tr>
<td>61% $\text{H}_2\text{O}$</td>
<td>5.17</td>
<td>25.26</td>
<td>55.41</td>
</tr>
<tr>
<td></td>
<td>(0.61)</td>
<td>(1.40)</td>
<td>(4.62)</td>
</tr>
</tbody>
</table>

Observations

1) $\tau_{298}$ shortens (motion becomes faster) as the $\text{H}_2\text{O}$ content increase.

2) The $E_A$ increases as the $\text{H}_2\text{O}$ content increases.

3) The QCC is fairly constant around 65kHz as the water content is varied.
Table 3.6
Zeolite Lithium (\textsuperscript{7}Li) NMR Relaxation Data
Range of $T_1/T_2$ from 10 to 200

<table>
<thead>
<tr>
<th>Zeolite Hydration</th>
<th>$\tau_{298}$ (ns) (Error)</th>
<th>$E_A$ (kJ mol\textsuperscript{-1}) (Error)</th>
<th>Quad. Coup. Const. (kHz) (Error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-A 0% H\textsubscript{2}O</td>
<td>24.24 (2.65)</td>
<td>50.13 (1.98)</td>
<td>225.07 (18.19)</td>
</tr>
<tr>
<td>Short $T_1$</td>
<td>15.60 (3.06)</td>
<td>40.02 (2.22)</td>
<td>311.80 (49.23)</td>
</tr>
<tr>
<td>Long $T_1$</td>
<td>13.10 (3.02)</td>
<td>38.52 (2.78)</td>
<td>123.90 (24.78)</td>
</tr>
<tr>
<td>Li-A 9% H\textsubscript{2}O</td>
<td>8.18 (0.73)</td>
<td>40.38 (1.42)</td>
<td>131.90 (7.76)</td>
</tr>
<tr>
<td>Short $T_1$</td>
<td>7.14 (1.18)</td>
<td>48.70 (4.50)</td>
<td>214.60 (35.77)</td>
</tr>
<tr>
<td>Long $T_1$</td>
<td>8.85 (5.59)</td>
<td>31.00 (3.94)</td>
<td>115.34 (62.11)</td>
</tr>
<tr>
<td>Li-X 0% H\textsubscript{2}O</td>
<td>4.02 (0.22)</td>
<td>27.78 (1.68)</td>
<td>106.10 (2.41)</td>
</tr>
<tr>
<td>Li-X 10% H\textsubscript{2}O</td>
<td>5.11 (0.59)</td>
<td>33.39 (1.87)</td>
<td>129.94 (11.81)</td>
</tr>
<tr>
<td>Short $T_1$</td>
<td>2.32 (0.39)</td>
<td>40.01 (4.12)</td>
<td>237.24 (43.13)</td>
</tr>
<tr>
<td>Long $T_1$</td>
<td>2.38 (0.38)</td>
<td>36.42 (3.35)</td>
<td>90.48 (11.31)</td>
</tr>
<tr>
<td>Li-X 20% H\textsubscript{2}O</td>
<td>3.29 (0.29)</td>
<td>30.57 (1.15)</td>
<td>123.90 (8.26)</td>
</tr>
</tbody>
</table>
Table 3.7 Further Zeolite Lithium ($^7$Li) NMR Relaxation Data

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>$\tau_{298}$(ns) (Error)</th>
<th>$E_a$(kJmol$^{-1}$) (Error)</th>
<th>Quad. Coup. Const.(kHz) (Error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Y</td>
<td>6.25 (1.01)</td>
<td>24.68 (0.80)</td>
<td>327.80 (39.02)</td>
</tr>
<tr>
<td>10% $H_2O$</td>
<td>2.92 (0.50)</td>
<td>24.09 (1.80)</td>
<td>407.80 (43.92)</td>
</tr>
<tr>
<td>Short $T_1$</td>
<td>2.96 (0.28)</td>
<td>27.54 (1.05)</td>
<td>206.08 (13.9)</td>
</tr>
<tr>
<td>Long $T_1$</td>
<td>2.11 (0.12)</td>
<td>24.73 (0.78)</td>
<td>410.96 (16.19)</td>
</tr>
<tr>
<td>Li-Y</td>
<td>10.25 (1.79)</td>
<td>36.80 (2.64)</td>
<td>208.50 (24.50)</td>
</tr>
<tr>
<td>20% $H_2O$</td>
<td>5.25 (0.99)</td>
<td>28.44 (2.01)</td>
<td>221.63 (27.70)</td>
</tr>
<tr>
<td>Li-Mord.</td>
<td>2.80 (0.23)</td>
<td>21.94 (0.80)</td>
<td>186.53 (10.97)</td>
</tr>
<tr>
<td>Li-ZSM-5</td>
<td>18.2 (3.37)</td>
<td>45.87 (3.75)</td>
<td>242.60 (39.90)</td>
</tr>
<tr>
<td>0% $H_2O$</td>
<td>2.52 (0.28)</td>
<td>19.9 (1.30)</td>
<td>226.20 (45.20)</td>
</tr>
<tr>
<td>Li-ZSM-5</td>
<td>6% $H_2O$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Observations

1) For A, X, Y, ZSM-5, and Mordenite, $\tau_{298}$ and $E_a$ decrease (motion increases) as water content increases.

2) For A, ZSM-5, and Mordenite, the QCC decreases slightly as the $H_2O$ increases. $A \approx 130$ kHz, ZSM-5 $\approx 200$ kHz, and Mordenite $\approx 180$ kHz.

3) In X, and Y QCC fairly constant X $\approx 120$ kHz, Y $\approx 400$ kHz.
Table 3.8 Zeolite Sodium ($^{23}$Na) NMR Relaxation Data

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Hydration</th>
<th>$\tau_{298}$(ps) (Error)</th>
<th>$E_A$(kJmol$^{-1}$) (Error)</th>
<th>Quad. Coup. Const.(MHz) (Error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-A</td>
<td>32% $D_2O$</td>
<td>223.5 (159.5)</td>
<td>65.67 (26.67)</td>
<td>1.17 (0.85)</td>
</tr>
<tr>
<td>Na-X</td>
<td>26% $D_2O$</td>
<td>65.07 (21.25)</td>
<td>44.02 (5.21)</td>
<td>1.32 (0.33)</td>
</tr>
<tr>
<td>Na-X</td>
<td>40% $D_2O$</td>
<td>82.22 (33.42)</td>
<td>44.23 (6.61)</td>
<td>1.54 (0.57)</td>
</tr>
<tr>
<td>Na-Y</td>
<td>0% $H_2O$</td>
<td>1000.00 (60.00)</td>
<td>8.93 (1.11)</td>
<td>0.72 (0.02)</td>
</tr>
<tr>
<td>Na-Y</td>
<td>20% $H_2O$</td>
<td>60.40 (21.90)</td>
<td>64.20 (9.35)</td>
<td>0.94 (0.27)</td>
</tr>
<tr>
<td>Na-Y</td>
<td>36% $D_2O$</td>
<td>31.41 (9.37)</td>
<td>44.93 (3.66)</td>
<td>1.58 (0.47)</td>
</tr>
</tbody>
</table>

Note

The results for H-ZSM-5, and Dealuminated -Y zeolites were rather inaccurate due to the low concentration of sodium ions. However, the following observations were possible.

1) For H-ZSM-5 the sodium ions are very restricted in their motion with $\tau_{298}$ in the range 6000 to 12,000ps with water contents of 5 to 20% $D_2O$. The value of $E_A$ is fairly constant around 4kJmol$^{-1}$.

2) For dealuminated-Y values of $\tau_{298}$ were even larger up to 20,000 ps, and $E_A$ was slightly smaller 3kJmol$^{-1}$ for water contents in the same range as used in H-ZSM-5.

3) For the samples in the table the value of $\tau_{298}$ was
similar in all the zeolites, however it did increase (i.e. motion slowed) when the sample was dehydrated.

4) The value of $E_A$ was largest for samples with a higher water content.

5) In all cases the value of QCC was in the range 0.7 to 1.6 MHz, with the majority of the samples being close to 1.3 MHz.
Table 3.9 Zeolite Deuterium ($^2$H) NMR Relaxation Data

Range of $T_1/T_2$ from 5 to 190

<table>
<thead>
<tr>
<th>Zeolite Hydration</th>
<th>$\tau_{298}$ (ps) (Error)</th>
<th>$E_A$ (kJmol$^{-1}$) (Error)</th>
<th>Quad. Coup. Const. (kHz) (Error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-A</td>
<td>471.7 (27.81)</td>
<td>27.81 (133.59)</td>
<td></td>
</tr>
<tr>
<td>22% D$_2$O</td>
<td>(40.70)</td>
<td>(1.31)</td>
<td>(12.02)</td>
</tr>
<tr>
<td>Five</td>
<td>442.90</td>
<td>36.80</td>
<td></td>
</tr>
<tr>
<td>Compon.</td>
<td>(48.70)</td>
<td>(2.70)</td>
<td>167.92</td>
</tr>
<tr>
<td>Fit</td>
<td>2703.00</td>
<td>1.80</td>
<td>(12.81)</td>
</tr>
<tr>
<td></td>
<td>(341.00)</td>
<td>(1.06)</td>
<td></td>
</tr>
<tr>
<td>Na-A</td>
<td>476.00</td>
<td>30.80</td>
<td>133.59</td>
</tr>
<tr>
<td>32% D$_2$O</td>
<td>(77.90)</td>
<td>(2.60)</td>
<td>(22.67)</td>
</tr>
<tr>
<td>Five</td>
<td>276.00</td>
<td>51.00</td>
<td></td>
</tr>
<tr>
<td>Compon.</td>
<td>(59.00)</td>
<td>(5.70)</td>
<td>147.55</td>
</tr>
<tr>
<td>Fit</td>
<td>1873.00</td>
<td>5.20</td>
<td>(18.62)</td>
</tr>
<tr>
<td></td>
<td>(348.00)</td>
<td>(2.50)</td>
<td></td>
</tr>
<tr>
<td>Na-X</td>
<td>170.50</td>
<td>36.01</td>
<td>165.77</td>
</tr>
<tr>
<td>14% D$_2$O</td>
<td>(25.40)</td>
<td>(1.99)</td>
<td>(21.52)</td>
</tr>
<tr>
<td>Na-X</td>
<td>166.86</td>
<td>31.30</td>
<td>158.07</td>
</tr>
<tr>
<td>26% D$_2$O</td>
<td>(10.95)</td>
<td>(0.86)</td>
<td>(9.93)</td>
</tr>
<tr>
<td>Na-X</td>
<td>200.90</td>
<td>35.70</td>
<td>154.64</td>
</tr>
<tr>
<td>40% D$_2$O</td>
<td>(26.40)</td>
<td>(1.99)</td>
<td>(20.77)</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Hydration</td>
<td>$\tau_{298}$ (ps) (Error)</td>
<td>$E_A$ (kJmol$^{-1}$) (Error)</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
<td>---------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Na-Y</td>
<td>8% D$_2$O</td>
<td>193.40 (17.20)</td>
<td>22.30 (1.01)</td>
</tr>
<tr>
<td>Na-Y</td>
<td>22% D$_2$O</td>
<td>251.70 (29.90)</td>
<td>23.70 (1.41)</td>
</tr>
<tr>
<td>Na-Y</td>
<td>30% D$_2$O</td>
<td>222.80 (26.37)</td>
<td>24.83 (1.39)</td>
</tr>
<tr>
<td>Five</td>
<td></td>
<td>94.12</td>
<td>38.51</td>
</tr>
<tr>
<td>Compon.</td>
<td></td>
<td>(17.62)</td>
<td>(3.90)</td>
</tr>
<tr>
<td>Fit</td>
<td></td>
<td>2835.12 (173)</td>
<td>1.35 (0.75)</td>
</tr>
<tr>
<td>Dealum-Y</td>
<td>2% D$_2$O</td>
<td>606.61 (3.96)</td>
<td>3.96 (1.73)</td>
</tr>
<tr>
<td>Dealum-Y</td>
<td>11% D$_2$O</td>
<td>339.22 (33.84)</td>
<td>12.15 (0.92)</td>
</tr>
<tr>
<td>Dealum-Y</td>
<td>20% D$_2$O</td>
<td>180.93 (33)</td>
<td>14.74 (11.22)</td>
</tr>
<tr>
<td>Dealum-Y</td>
<td>37% D$_2$O</td>
<td>152.62 (60.63)</td>
<td>16.32 (4.11)</td>
</tr>
</tbody>
</table>
Table 3.11
Further Zeolite Deuterium ($^2$H) NMR Relaxation Data

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>$\tau_{298}$ (ps)</th>
<th>$E_A$ (kJ mol$^{-1}$)</th>
<th>Quad. Coup. Const. (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>739.04 (15.10)</td>
<td>6.29 (0.18)</td>
<td>108.52 (1.55)</td>
</tr>
<tr>
<td>4% D$_2$O</td>
<td>317.36 (60.71)</td>
<td>8.13 (0.93)</td>
<td>122.44 (22.44)</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>194.21 (32.22)</td>
<td>13.97 (1.22)</td>
<td>122.44 (17.49)</td>
</tr>
</tbody>
</table>

Observations

1) For A, X, and Y the value of $\tau_{298}$ and $E_A$ remain fairly constant over the hydration range studied.

2) For H-ZSM-5 and dealuminated-Y $\tau_{298}$ decreases (i.e. motion gets faster) as the water content increases. Also for these zeolites $E_A$ increases as D$_2$O increases.

3) The QCC of Y and X are approximately 160 kHz, and for A is 140 kHz.

4) The QCC for H-ZSM-5 is in the range 108 to 122 kHz and for dealuminated-Y is in the range 150 to 170 kHz.
Table 3.12

Zeolite Proton (^H) NMR Relaxation Data

Range of $T_1/T_2$ from 7 to 1000

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Hydration</th>
<th>$\tau_{2g}$ (ps)</th>
<th>$E_A$ (kJmol$^{-1}$)</th>
<th>2nd moment (rad$^2$sec$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Error)</td>
<td>(Error)</td>
<td>(Error)</td>
</tr>
<tr>
<td>Na-A</td>
<td>10% H$_2$O</td>
<td>527.62</td>
<td>14.92</td>
<td>13.4E+10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(19.31)</td>
<td>(0.32)</td>
<td>(0.3E+10)</td>
</tr>
<tr>
<td>Na-A</td>
<td>17% H$_2$O</td>
<td>586.22</td>
<td>22.92</td>
<td>13.8E+10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(34.53)</td>
<td>(0.93)</td>
<td>(0.8E+10)</td>
</tr>
<tr>
<td>Five</td>
<td></td>
<td>296.21</td>
<td>26.22</td>
<td></td>
</tr>
<tr>
<td>Compon.</td>
<td></td>
<td>(44.11)</td>
<td>(1.45)</td>
<td>3.6E+10</td>
</tr>
<tr>
<td>Fit</td>
<td></td>
<td>1310.53</td>
<td>24.66</td>
<td>(0.9E+10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(426.53)</td>
<td>(6.14)</td>
<td></td>
</tr>
<tr>
<td>Li-A</td>
<td>5% H$_2$O</td>
<td>450.02</td>
<td>13.24</td>
<td>5.50E+10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(13.92)</td>
<td>(0.33)</td>
<td>(0.09E+10)</td>
</tr>
<tr>
<td>Li-A</td>
<td>9% H$_2$O</td>
<td>863.84</td>
<td>16.57</td>
<td>5.42E+10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(48.41)</td>
<td>(0.41)</td>
<td>(0.38E+10)</td>
</tr>
<tr>
<td>H-A</td>
<td>0% H$_2$O</td>
<td>1413.2</td>
<td>16.83</td>
<td>6.24E+10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(378.1)</td>
<td>(6.33)</td>
<td>(0.24E+10)</td>
</tr>
<tr>
<td>H-A</td>
<td>5% H$_2$O</td>
<td>1767.1</td>
<td>11.93</td>
<td>7.68E+10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(303.2)</td>
<td>(0.91)</td>
<td>(1.08E+10)</td>
</tr>
<tr>
<td>Na-X</td>
<td>6% H$_2$O</td>
<td>267.72</td>
<td>12.55</td>
<td>11.8E+10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(33.97)</td>
<td>(1.25)</td>
<td>(0.9E+10)</td>
</tr>
<tr>
<td>Five</td>
<td></td>
<td>298.93</td>
<td>8.73</td>
<td></td>
</tr>
<tr>
<td>Compon.</td>
<td></td>
<td>(36.67)</td>
<td>(0.84)</td>
<td>7.10E+10</td>
</tr>
<tr>
<td>Fit</td>
<td></td>
<td>217.92</td>
<td>32.58</td>
<td>(0.53E+10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(44.65)</td>
<td>(5.44)</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.13 Further Zeolite Proton (\textsuperscript{1}H) NMR Relaxation Data

<table>
<thead>
<tr>
<th>Zeolite Hydration</th>
<th>( r_{298} ) (ps)</th>
<th>( E_A ) (kJmol\textsuperscript{-1})</th>
<th>2nd moment (rad\textsuperscript{2}sec\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-X 20% H\textsubscript{2}O</td>
<td>303.92 (12.88)</td>
<td>22.65 (0.77)</td>
<td>13.4E+10</td>
</tr>
<tr>
<td>Five Compon.</td>
<td>131.10</td>
<td>30.55</td>
<td></td>
</tr>
<tr>
<td>Fit</td>
<td>477.33 (7.52)</td>
<td>20.22 (0.92)</td>
<td>7.20E+10</td>
</tr>
<tr>
<td>H-X 0% H\textsubscript{2}O</td>
<td>2625.94</td>
<td>10.56</td>
<td>6.84E+10</td>
</tr>
<tr>
<td>H-X 20% H\textsubscript{2}O</td>
<td>996.53 (90.88)</td>
<td>10.95</td>
<td>12.0E+10</td>
</tr>
<tr>
<td>Na-Y 3% H\textsubscript{2}O</td>
<td>213.13 (2.82)</td>
<td>14.59 (0.24)</td>
<td>107.1E+10</td>
</tr>
<tr>
<td>Na-Y 18% H\textsubscript{2}O</td>
<td>224.12 (15.36)</td>
<td>20.38 (0.85)</td>
<td>107.90E+10</td>
</tr>
<tr>
<td>Five</td>
<td>339.04</td>
<td>16.63</td>
<td></td>
</tr>
<tr>
<td>Compon.</td>
<td>49.55 (7.23)</td>
<td>37.34 (0.25)</td>
<td>65.7E+10</td>
</tr>
<tr>
<td>Fit</td>
<td>49.55 (6.68)</td>
<td>37.34 (1.98)</td>
<td></td>
</tr>
<tr>
<td>Mg-Y 1% H\textsubscript{2}O</td>
<td>237.55 (7.73)</td>
<td>14.12 (0.68)</td>
<td>90.7E+10</td>
</tr>
<tr>
<td>Mg-Y 17% H\textsubscript{2}O</td>
<td>198.54 (8.71)</td>
<td>19.12 (0.93)</td>
<td>88.8E+10</td>
</tr>
<tr>
<td>Al-Y 1% H\textsubscript{2}O</td>
<td>222.23 (12.48)</td>
<td>12.25 (0.62)</td>
<td>94.2E+10</td>
</tr>
</tbody>
</table>
## Table 3.14 Further Zeolite Proton ($^1$H) NMR Relaxation Data

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>$\tau_{298}$ (ps)</th>
<th>$E_A$ (kJmol$^{-1}$)</th>
<th>2nd moment (rad$^2$sec$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Error)</td>
<td>(Error)</td>
<td>(Error)</td>
</tr>
<tr>
<td>Dealum-Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% $H_2O$</td>
<td>1055.23 (203.12)</td>
<td>8.76 (1.15)</td>
<td>69.6E+10</td>
</tr>
<tr>
<td>Dealum-Y</td>
<td>1095.27 (110.45)</td>
<td>8.62 (0.29)</td>
<td>77.4E+10</td>
</tr>
<tr>
<td>Li-Mord.</td>
<td>443.06 (9.53)</td>
<td>13.22 (0.21)</td>
<td>18.3E+10</td>
</tr>
<tr>
<td>5% $H_2O$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li-Mord.</td>
<td>440.63 (11.56)</td>
<td>10.32 (0.27)</td>
<td>11.7E+10</td>
</tr>
<tr>
<td>10% $H_2O$</td>
<td>(11.56)</td>
<td>(0.27)</td>
<td>(0.14E+10)</td>
</tr>
<tr>
<td>Na-Mord.</td>
<td>288.14 (6.72)</td>
<td>11.14 (0.37)</td>
<td>20.55E+10</td>
</tr>
<tr>
<td>5% $H_2O$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na-Mord.</td>
<td>392.24 (7.02)</td>
<td>12.61 (0.17)</td>
<td>21.15E+10</td>
</tr>
<tr>
<td>10% $H_2O$</td>
<td>(7.02)</td>
<td>(0.17)</td>
<td>(0.3E+10)</td>
</tr>
<tr>
<td>Mg-Mord.</td>
<td>391.26 (10.28)</td>
<td>11.66 (0.41)</td>
<td>19.5E+10</td>
</tr>
<tr>
<td>1% $H_2O$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-Mord.</td>
<td>453.02 (7.91)</td>
<td>15.91 (0.18)</td>
<td>22.8E+10</td>
</tr>
<tr>
<td>6% $H_2O$</td>
<td>(7.91)</td>
<td>(0.18)</td>
<td>(0.3E+10)</td>
</tr>
<tr>
<td>Al-Mord.</td>
<td>326.32 (12.35)</td>
<td>9.81 (0.56)</td>
<td>18.45E+10</td>
</tr>
<tr>
<td>1% $H_2O$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Mord.</td>
<td>404.25 (9.54)</td>
<td>14.98 (0.26)</td>
<td>22.5E+10</td>
</tr>
<tr>
<td>5% $H_2O$</td>
<td>(9.54)</td>
<td>(0.26)</td>
<td>(0.45E+10)</td>
</tr>
</tbody>
</table>
Table 3.15 Further Zeolite Proton (¹H) NMR Relaxation Data

<table>
<thead>
<tr>
<th>Zeolite Hydration</th>
<th>$\tau_{298}$ (ps) (Error)</th>
<th>$E_A$ (kJmol⁻¹) (Error)</th>
<th>2nd moment (rad²sec⁻²) (Error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Mord. 0% H₂Ο₂</td>
<td>2756.25 (1544.43)</td>
<td>14.13 (0.81)</td>
<td>19.35E+10 (9.75E+10)</td>
</tr>
<tr>
<td>H-Mord. 10% H₂Ο₂</td>
<td>296.95 (23.99)</td>
<td>8.03 (0.69)</td>
<td>8.7E+10 (0.3E+10)</td>
</tr>
<tr>
<td>Five</td>
<td>130.94 (11.92)</td>
<td>11.87</td>
<td></td>
</tr>
<tr>
<td>Compon</td>
<td>2260.1 (747.9)</td>
<td>11.85 (1.94)</td>
<td></td>
</tr>
<tr>
<td>H-ZSM-5 0% H₂Ο₂</td>
<td>1486.34 (160.73)</td>
<td>17.28</td>
<td>75.2E10 (4.7E10)</td>
</tr>
<tr>
<td>H-ZSM-5 5% H₂Ο₂</td>
<td>849.95 (32.56)</td>
<td>13.02</td>
<td>84.45E10 (1.8E10)</td>
</tr>
<tr>
<td>H-ZSM-5 5% D₂Ο₂</td>
<td>2896.53 (1763.43)</td>
<td>9.86</td>
<td>170.4E10 (96E10)</td>
</tr>
<tr>
<td>Five</td>
<td>1419.94 (49.98)</td>
<td>17.95</td>
<td></td>
</tr>
<tr>
<td>Compon</td>
<td>2216.55 (854.76)</td>
<td>6.15</td>
<td>55.50E10 (7.40E10)</td>
</tr>
<tr>
<td>Fit</td>
<td>1042.34 (39.87)</td>
<td>10.23</td>
<td>27.0E10 (0.6E10)</td>
</tr>
</tbody>
</table>
Table 3.16 Further Zeolite Proton (^H) NMR Relaxation Data

<table>
<thead>
<tr>
<th>Zeolite Hydration</th>
<th>$\tau_{298}$(ps) (Error)</th>
<th>$E_A$ (kJmol^-1) (Error)</th>
<th>2nd moment(rad^2sec^-2) (Error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-ZSM-5</td>
<td>312.92 (4.52)</td>
<td>8.26 (0.12)</td>
<td>15E+10 (1.1E+10)</td>
</tr>
<tr>
<td>1% H_2O</td>
<td>314.73 (8.94)</td>
<td>9.48 (0.25)</td>
<td>15E+10 (0.3E+10)</td>
</tr>
<tr>
<td>Li-ZSM-5</td>
<td>217.23 (6.35)</td>
<td>10.52 (0.29)</td>
<td>15.9E+10 (0.3E+10)</td>
</tr>
<tr>
<td>1% H_2O</td>
<td>188.82 (6.67)</td>
<td>9.97 (0.35)</td>
<td>17.25E+10 (0.45E+10)</td>
</tr>
<tr>
<td>Na-ZSM-5</td>
<td>442.45 (67.95)</td>
<td>13.32 (1.16)</td>
<td>506E+10 (37E+10)</td>
</tr>
<tr>
<td>3% H_2O</td>
<td>158.46 (19.83)</td>
<td>17.72 (0.74)</td>
<td>360E+10 (7.4E+10)</td>
</tr>
<tr>
<td>Five</td>
<td>2730.58 (1083.42)</td>
<td>31.53 (7.78)</td>
<td>(21E+10)</td>
</tr>
<tr>
<td>Compon.</td>
<td>625.46 (67.83)</td>
<td>9.33 (0.57)</td>
<td>320E+10 (16.05E+10)</td>
</tr>
<tr>
<td>Low Al 7% H_2O</td>
<td>285.18 (18.13)</td>
<td>11.68 (0.22)</td>
<td>223E+10 (6.75E+10)</td>
</tr>
<tr>
<td>Fit</td>
<td>5642.65 (1593.5)</td>
<td>28.23 (1.88)</td>
<td>(6.75E+10)</td>
</tr>
</tbody>
</table>
Section 3.30 A Summary of the Proton NMR Relaxation Data for Zeolites

The discussion is presented by considering the zeolites with the largest values of $\tau_{298}$ initially followed by considering samples with successively decreasing values of $\tau_{298}$, together with any relevant comments.

1) All the protonated zeolites have the largest values of $\tau_{298}$; these lie in the region of 1000 ps to 3000 ps, but these values shorten on the addition of water as obviously water is included in the average value of the correlation time, which can be as low as 300 ps for H-mordenite. For a sample of H-ZSM-5 which was hydrated with D$_2$O this also shortened the value of $\tau_{298}$ obviously some exchange will be possible with deuterium and hydrogen, but there will not be total exchange.

Structural hydroxyl groups may also be introduced into zeolites by cation hydrolysis. Normal dehydration causes dissociation of water molecules by the electric field of the association cation (Mumpton [11]). So all zeolites will have a certain amount of the characteristics of the hydroxyl groups in their proton relaxation behaviour.

Maiwald et al. [26], showed that in systems like ZSM-5, water is more mobile than in zeolites based on a cubo-octahedra framework. This point is more clearly demonstrated by the deuterium NMR which has contributions only from framework cations. It was also stated that proton exchange between sorbed water, and structural OH
groups, is similar to other zeolites. In reference [26], the difference between water mobility in H and Na forms of ZSM-5 was small as the zeolite crystals were <1μm in diameter so water could have been adsorbed on the surface. My results show that the water is much more mobile at room temperature in the Na form.

My results have been confirmed by Vetrivel et al. [27], who using simulation studies found protons are more strongly bound with Al clusters in ZSM-5. In my work the low Al content ZSM-5 has a shorter value for $\tau_{298}$ than does the sample with the larger Al content where the protons are more rigidly held.

In my results the second moments for H-ZSM-5 and H-mordenite are exceptionally high because of the very short $T_1$ relaxation times for these samples, the values are less for the samples of H-X and H-A.

2) Dealuminated-Y also has a very long value for $\tau_{298}$ of the order 1000 ps, together with a very large second moment. The term dealuminated means that although the aluminium has been removed from the zeolite framework, it is still present in the form of non-framework octahedral $\text{Al(H}_2\text{O)}_{6}^{2+}$ ions. These ions have a lower mobility than Na⁺ in Na-Y which is the reason for the longer values for the correlation time of the associated water at room temperature.

3) Li-A has $\tau_{298}$ in the range 500 to 1000 ps increasing with the increase in water, as does $E_A$. 

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4) As previously mentioned, the H-ZSM-5 low Al content has a value of $\tau_{298}$ 400 to 600 ps, again increasing with larger water contents, but with $E_A$ decreasing.

5) Na-A has a fairly constant value of $\tau_{298}$ around 500 ps but made up of two components, with the average value of $E_A$ increasing from 15 to 22 kJmol$^{-1}$ as the water content increases. I certainly found that the water was more restricted in A than in X with the same cation, agreeing with Deininger et al. [34].

Oehme et al. [38] showed that the water in the cubo-octahedra of Na-A is more mobile than that in Na-X at 300K, which is explained by absence of the stabilising influence of the sodium ions. Below 160K, the water molecules in Na-A are thought to be rigid i.e. $\tau_c > 10$ μs. The two phase behaviour of water in zeolite A has been seen by Basler [37], and by Maiwald and Basler [39].

6) Li-mordenite had a $\tau_{298}$ of approximately 450 ps which remains fairly constant as water content increased, whilst $E_A$ decreases. The mordenite zeolites have less mobile water than faujasites, which has also been shown by Cholli and Pennino [40].

7) Al and Mg-mordenite have similar values of $\tau_{298}$ from 380 to 420 ps which increases with water content as does the value of $E_A$. 
8) Na-mordenite has $t_{298}$ ranging from 300 to 380 ps, which increases with the level of hydration: the value of $E_A$ also increases slightly.

9) Li-ZSM-5 has a fairly constant value of $t_{298}$ around 310 ps with $E_A$ constant as well.

10) Na-X was calculated to have $t_{298}$ from 270 to 300 ps increasing with water content as does $E_A$ in the range 13 to 22 kJmol$^{-1}$. Pfeifer et al. [41] proposed, from relaxation measurements, that in faujasites the restriction of the adsorbed water was thought to be caused by the oxygen lattice of the zeolite, as they found no significant influence of the sodium ions. This was supported by the experimental finding that there was no unusual distribution of correlation times. My $T_1$ results are rather inconclusive as to whether water is more tightly bound as its content decreases, because the trend of the results is not clear because the difference in $t_{298}$ for the various degrees of hydration is in the region of the errors on these values. However, the linewidth of the water on Na-X does substantially increase on the reduction of water indicating a more restricted water motion.

11) Na-Y, Mg-Y and Al-Y all have $t_{298}$ of 220 ps which increases slightly with added water. The value of $E_A$ ranged from 15 to 20 kJmol$^{-1}$ also increasing with water content,
which is similar to the activation energy measured by Whipple et al. [47], for the diffusion of water in Na-Y.

12) In Na-ZSM-5 the value of $\tau_{298}$ decreases slightly with extra water and is approximately 200 ps, whilst the activation energy increases with the increase of water.

The increase in activation energy seen in most of my samples as the water content is increased can be accounted for by the work of Brown [54], who studied water on hectorite under pressure. The surface bound water had a lower $E_A$ than the free water which was said to indicate a disruption of the hydrogen bond network in the bulk water which gradually reforms as the water content of the sample increases.

Section 3.3.1 Discussion of NMR Relaxation times of Quadrupolar Nuclei in Zeolites - Lithium

In the work of Tokuhiro et al. [55], zeolites were studied having the following concentrations of iron Li-A, 309 ppm, Li-X 297 ppm and Li-Y 920 ppm. The zeolites were hydrated with $H_2O$, and $D_2O$ to find the dipolar contribution to the $^7Li$ relaxation time. Only zeolites A and Y had any dipolar contribution and that was only below -60°C, and above that the quadrupolar mechanism dominated. At very low temperatures i.e. $<-100°C$ the paramagnetic electron - nuclear dipolar interaction was the method of relaxation, but as was pointed out by Basler [56], this is only true if spin diffusion is the mechanism for the interaction, but
diffusion of Li$^+$ ions gives a temperature dependence to the paramagnetic relaxation.

The $T_1$ values found by Tokuhiro et al. [55], were regarded as the average values of all the cations in all the sites in the zeolite structure. It was also assumed that all the Li$^+$ ions are also either completely or at least partially co-ordinated with water, this is thought not to be unreasonable due to the work of Seff [57], and Basler [58]. Based on these same proposals for a model, the comparison of my values of $\tau_{298}$ and $E_A$ are as follows. It must be remembered that all their samples were completely hydrated but the values of activation energy should not be severely influenced by this, however the trend of an increase in $E_A$ in going from A to X to Y, was in complete opposition to the trend that is reported here. Their trend of a decrease in the value of $\tau_{298}$ from A to X to Y was mirrored by my results, although of course my actual correlation times were much longer as my samples contained less water. These facts can be explained by reference to earlier work described in [56], where the $^7$Li relaxation times for Li-X with various iron contents were studied. It was found that on going from 19ppm to 110ppm of iron, the activation energy was lowered considerably, whilst the value of $\tau_{298}$ although affected was not altered to such an extent. As previously stated the correlation time is not affected so seriously by the iron content hence the reason for the similar behaviour to the results presented here.

The values of QCC found by Tokuhiro et al. [55] also
follow the same trend as my results, that is they increase in magnitude in going from A = X < Y. Discrepancies could be due to a number of factors which will be discussed shortly.

The QCC increases with increase in the Si : Al ratio. It was suggested [55], that as there are fewer cations in the lower Al containing zeolites then the number of water molecules bonded to them increases which causes the QCC to increase. This should mean that as the water content of a particular zeolite increases then QCC should also increase: this was found for X, and Y but not for A.

Tokuhiro et al. [55] suggested that the larger value of the QCC in Li-Y, compared with Li-X, was due to a lower symmetry of co-ordination of the Li⁺ ions to water. Basler [56], disagreed with this explanation as the value of the QCC is determined by the actual magnitude of the various T₁ values and these are directly influenced by the iron content of the sample. So the fact that the apparent QCC of Li-Y is larger than those of the other samples is due to the higher iron content. The samples of Li-X, and Li-A are similar in iron content and hence have similar values for QCC, however my sample of Li-mordenite had a similar iron content to X, and A but the value of the QCC in this case was indeed larger. This would appear to agree with the argument that the QCC increases with the Si : Al ratio, especially as the QCC increases again for Li-ZSM-5. The reason that the increase for Li-ZSM-5 is not as large as might have been expected is caused by the fact the Li-ZSM-5 only contains 40% of the amount of iron compared with X, A, and mordenite.
The cations in the zeolite behave in a way comparable with that in an associated liquid such as glycerol. In these types of systems there are motions on two timescales. The librational motion of the water causes fluctuations in the field gradient at the quadrupolar nuclei on the sub pico-second timescale, while the rotation of the hydrated cation is much slower, and this determines the relaxation rate.

The use of $^7\text{Li}$ NMR was exploited by Macura et al. [59, 60] to study Li-A, and Li-X. In Li-A, two phases of cations were identified; those bound to the zeolite lattice and those not. From electric conductivity measurements, the $E_A$ for the low temperature process was 33 kJmol$^{-1}$, and for the high temperature process it was 66 kJmol$^{-1}$ c.f. 30 kJmol$^{-1}$ and 72 kJmol$^{-1}$ for Li-X also from electric conductivity measurements. Due to the larger cavities in Li-X, besides the ions in the rigid lattice there exists a phase of ions which undergo surface diffusion, and a phase which moves relatively freely within one cavity. It was stated that the electric conductivity of these systems is connected with the regular crystal structure, and not its defects or impurities.

The work of Melchior et al. [61] showed that the situation of Li$^+$ in a tetrahedral arrangement results in a uniformly contracted sodalite cage with all the Si equivalent, therefore there is a strong possibility that Li$_4$Na$_8$-A has long range order.

In fully exchanged Li-A Freude et al. [62], found that
the distance Li-Al is smaller than Na-Al verifying that Li is not at the centre of the oxygen six ring.

Section 3.32 Deuterium

In one of the few papers published in this area Resing [67] concentrated on calculating the QCC in a number of zeolites, none of which have been studied in my work.

The QCC for D₂O in the form of ice is approximately 214 kHz (Waldstein et al. [73]), while that for zeolitic water was found to be in the region of 230 kHz. The reason that my QCC's are down on these values is due to the fact that all my samples were made up with different degrees of hydration. However, for certain materials Resing [67] did find that the QCC of the aluminium hydroxides was in the 190 to 200 kHz range for Boehmite, and Diaspore. In ²H NMR the influence of the paramagnetic species is reduced by a factor of 42.4, the squared ratio of the proton magnetogyric ratio to that of deuterium. Though as indicated by Basler [56] even for quadrupolar nuclei the influence of paramagnetic species is not negligible.

The samples of zeolites A,X,Y and dealuminated-Y all have very similar values for QCC with only H-ZSM-5 showing any significant further decrease. My values showed a decrease in τ₂₉₈ as the water content increased for samples of a large enough difference in hydration contents. As in the proton NMR results, the zeolites with the most restricted water motion were Na-A, and dealuminated-Y with low water contents. The zeolites Na-X and Na-Y have a
middle range of water mobilities although the activation energies for Na-Y are much less than those for Na-X due to the higher iron content once again. The sample of H-ZSM-5 again show the most mobile water.

Section 3.33 Sodium

My results from $^{23}$Na NMR, as previously mentioned are only very approximate but it was seen that the ion mobility does increase as the water content increases. Those zeolites containing very small amounts of sodium ions e.g. H-ZSM-5 and dealuminated-Y, were found to have immensely immobile Na ions, whilst in all cases the value of the sodium QCC is centred around 1.3 MHz c.f. gas phase value for NaI, NaBr, NaCl of 5 MHz by Logan et al. [74].

Section 3.34 Summary of the NMR Relaxation work on samples of polymer – Proton Results

For the samples hydrated with $D_2O$, in effect the protons of the polymer chain were being studied, and it was found that as the water content increased then the motion of these protons was little changed at ambient temperatures. Even for the most hydrated example the correlation time at room temperature was still longer than that for the protons in the zeolites. For samples containing $H_2O$ the overall correlation time decreased as the water content increased but of course this is now made up of an added contribution from the protons of the water molecules. The values for the activation energies and the second moments were also much
lower than those obtained for the zeolites.

McBrierty and Douglass [73], stated that the ability to probe heterogeneity over a small to intermediate range in polymers derives from two quite distinct consequences of NMR relaxation:

a) The short range nature of the dipole-dipole interaction, which is dominated by near neighbour events.

b) The transport of spin energy through the spin system by the mechanism of spin diffusion through like spins, or cross relaxation between unlike spins.

Spin diffusion can probe molecular environments over distances in the order of several tens of nanometres. In the absence of spin diffusion a two component decay would be observed, representing a simple superposition of the amorphous and crystalline phases in the polymer, and containing separate information on each. In my experimental results all the $T_1$ values are single component indicating the presence of spin diffusion.

Bryant and Shirley [74] studied hydrated solid protein systems, and found that the relaxation is dominated by motions in the water phase, and not by motions in the solid phase such as methyl group rotations. In this system the motion of the water was thought to be fast and anisotropic.

From $T_2$ studies of samples containing H$_2$O it was found by Sung et al. [75] that the values of $T_2$ are fairly constant when there is only bound water, or bound water with a small amount of intermediate water present. Beyond this region, $T_2$ rapidly increases indicating the presence of an
increasing amount of free and intermediate water. This can be compared with the $T_2$ values for the $^1$H NMR of the samples containing $D_2O$, and it is found in this case that the $T_2$ value increases linearly as the percentage of $D_2O$ increases, an example of which is shown in Fig. 3.12.

Sung et al. [75] suggested that the interaction of water with methacrylate polymers occurs in three ways:

1) Water strongly bound to the hydroxyl, or ester groups within the polymer network behaving as part of the polymer chain both dynamically and thermodynamically.

2) Water weakly bound to the hydrophilic sites, or structured around the polymer.

3) Water behaving dynamically, and thermodynamically as free water.

All these proposals were made for water interactions with the methacrylate polymers, but no NMR work of the polymer salts has ever been undertaken in the past.

Section 3.35 Deuterium

Again as the water content increases the values of $\tau_{298}$ lower indicating a more mobile phase of water, however their values are still one order of magnitude greater than the most restricted $D_2O$ in the zeolites. The values of the QCC in the polymer are in the range 86 to 100 kHz, and increase as the water content increases.

Section 3.36 Lithium

As for the case of the deuterium NMR, the lithium ions
Fig. 3.12 Graph of $T_2$ Variation with Water Content in Lithium Polymethacrylate Samples
become more mobile as the water content increases, but the values of $\tau_{298}$ are still on average twice as long as those in the zeolites with much lower values for the activation energies for the polymer. The QCC is fairly constant in the polymer with values of approximately 65 kHz which is similar to zeolites A and X.

Section 3.37 Overall Summary

1) The water behaviour in the zeolites gives some idea that, in the protonated forms, something very strange and unique is happening because the proton cations have a $\tau_{298}$ of 2 ns which is a remarkable coincidence with the lithium ions in the various zeolites. In those zeolites showing an ER effect Y, X, ZSM-5, and mordenite the correlation time at room temperature was in the range 2 to 5 ns, this is a rough guide with variance due to different water contents. For zeolite A which does not have a strong ER effect the value of $\tau_{298}$ was outside of this range at 6 ns or longer.

2) Dealuminated-Y was found to contain very few sodium cations, and those that were present were virtually immobile, and this zeolite also has a weak ER effect.

3) Both the zeolites which had the poorest ER effects were the ones which have the most restricted water, and consequently restricted cation motion.

4) In none of the above was it found beneficial to fit the data using a distribution of correlation times, even though from the ratio of relaxation times $\tau_1/\tau_2$ as shown by Resing [67], there was quite definitely water in more than one site.
or environment in all the species. Two different distributions of correlation times were attempted as outlined in the paper by Connor [76]. Both methods had originally been employed to interpret dielectric data and the equations for them are shown below.

a) Fuoss-Kirkwood [77].
\[
\frac{1}{T_1} = A \frac{\beta}{\omega} \left[ \frac{(\omega \tau)^\beta}{1 + (\omega \tau)^{2\beta}} + 2 \frac{(2\omega \tau)^\beta}{1 + (2\omega \tau)^{2\beta}} \right], \quad (56)
\]

A is the second moment as described by Kubo and Tomita [13], and $\beta$ is the width of the distribution $0 < \beta \leq 1$.

b) Cole-Davidson [78].
\[
\frac{1}{T_1} = A \delta \left[ B + C \right], \quad (57)
\]
where
\[
B = \frac{\tau}{(1 + \omega^2 \tau^2)^{5/2} (1 + \delta^2 \omega^2 \tau^2)^{1/2}}
\]
and
\[
C = \frac{4\tau}{(1 + 4\omega^2 \tau^2)^{5/2} (1 + 4\delta^2 \omega^2 \tau^2)^{1/2}}
\]

In this case $\delta$ is the distribution parameter $0 < \delta \leq 1$. In both distributions more data points were needed to reduce the errors using these functions, so the method of data fitting I originally employed had to suffice.

Section 3.38 Characterisation of Zeolite Samples using $^{27}$Al NMR Spectroscopy

$^{27}$Al NMR gives information on the relative amounts of tetrahedral and octahedral Al in the zeolite lattice. The chemical shift reference was taken from a solution of $\text{Al(NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Since this has octahedral symmetry, the
aluminium shift is by convention taken as being 0 ppm. Any
tetrahedrally co-ordinated Al has a chemical shift around 50
ppm. As expected all the zeolite samples contain a certain
amount of tetrahedral Al. Those which contain octahedral Al
atoms are due to the non-framework Al content in the
zeolite. This technique proves to be very sensitive to even
very small amounts of Al, as shown by the spectrum of
dealuminated-Y in Fig. 3.13. This was also seen by Klinowski
et al. [79] for a sample dealuminated by heating to 700°C in
the presence of steam. All the samples were rotated at the
magic angle at a frequency of approximately 4300 Hz, with a
delay time of at least 100 ms.

As expected the heating of the H-ZSM-5 samples in a dry
atmosphere even to temperatures as high as +600°C had no
effect on the Al structure in the lattice, although the
small amount of non-framework Al present in the original
sample was removed by heating. For perfectly crystalline
H-ZSM-5 the $^{27}$Al NMR should consist of a purely tetrahedral
peak as shown by Scholler and Veeman [80]. The treatment of
the zeolites with strong acid e.g. 1M HCl, did cause a
certain amount of the aluminium to be removed from the
lattice and remain as octahedral Al as seen for H-A and H-X.
This effect was recorded by Engelhardt et al. [81] when
looking at a sample of NaH-Y zeolite, though that sample was
prepared by shallow bed calcination for one week.

The $^{27}$Al chemical shifts of the remaining samples of
Na-X, Na-Y, Na-A, and mordenite have been previously
verified by Lippmaa et al. [82], so confirming the
Fig. 3.13  Typical $^{27}$Al NMR Spectra from Zeolites

a) Na-Y 20% H$_2$O

b) Dealuminated-Y 17% H$_2$O

c) H-mordenite 0% H$_2$O
aluminium structures in the zeolites.

Table 3.17

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical Shift ppm (Intensity %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-4A 6% H₂O</td>
<td>54.85 (48) 0.06 (52)</td>
</tr>
<tr>
<td>H-X 0% H₂O</td>
<td>53.45 (60) 0.68 (40)</td>
</tr>
<tr>
<td>Na-Y 20% H₂O</td>
<td>59.58 (100)</td>
</tr>
<tr>
<td>Dealuminated-Y 17% H₂O</td>
<td>58.89 (70) 0.13 (30)</td>
</tr>
<tr>
<td>H-Mordenite 0% H₂O</td>
<td>54.25 (85) -1.39 (15)</td>
</tr>
<tr>
<td>H-ZSM-5 10% H₂O Si:Al=21</td>
<td>53.75 (95) -1.83 (5)</td>
</tr>
<tr>
<td>H-ZSM-5 0% H₂O Si:Al=21</td>
<td>54.15 (100)</td>
</tr>
<tr>
<td>H-ZSM-5 0% H₂O Si:Al=173</td>
<td>52.53 (100)</td>
</tr>
</tbody>
</table>

Section 3.39 Characterisation of Zeolite Samples using ²⁹Si NMR Spectroscopy

The chemical shifts for ²⁹Si NMR are referenced to TMS as 0 ppm. All the samples were again rotated at approximately 4300 Hz, with a minimum pulse delay of 18 s. Typical ²⁹Si spectra are shown in Fig. 3.14 and 3.15.

In an alumino-silicate each silicon atom is bonded tetrahedrally to 4 oxygen atoms. These in turn are bonded to another silicon or an aluminium atom. The chemical shift depends on the number of OSi or OAl groups bonded to the silicon described in detail by Engelhardt and Michel [83]. The range of chemical shifts is roughly from -70 ppm for four OAl groups, to -120 ppm for zero OAl groups. The lines in the ²⁹Si spectra may be broadened either for large amounts of aluminium present, or else due to large amounts
Fig. 3.14 Typical $^{29}$Si NMR Spectra from Zeolites

a) Na-A 20% H$_2$O

b) Na-X 18% H$_2$O

c) Dealuminated-Y 20% H$_2$O
Fig. 3.15 Typical $^29$Si NMR Spectra from Zeolites

a) H-mordenite 9% H$_2$O

b) Na-mordenite 10% H$_2$O

c) H-ZSM-5 10% H$_2$O
of disorder in the lattice structure.

The spectrum of Na-A has previously been published by Engelhardt et al. [84], while confirmation of chemical shifts of Na-X Si : Al = 1.17 have also been shown by Engelhardt et al. [85]. The spectrum from Na-X is interesting as the signals due to silicon atoms surrounded by all the combinations of OAl groups can be seen, with the exception of zero OAl as this peak is very weak for this particular Si : Al ratio. The $^{29}$Si spectrum from the dealuminated-Y sample was also shown in reference [79], so both the silicon and aluminium NMR spectra show the behaviour expected for a dealuminated sample.

The samples containing the proton cations H-A, and H-X both have very broad peaks similar to that for NaH-Y in reference [81]. As stated previously, the acid used to exchange sodium for proton cations disrupts the zeolite framework, which consequently broadens the signal as the silicon is present in many slightly different environments.

The mordenite samples show two large characteristic peaks due to the inequivalent sites in the structure. These have also been examined previously by Fyfe et al. [86]. The two line spectrum is characteristic of mordenite with a Si:Al ratio of less than 10. A sample with an order of magnitude less aluminium would give a much sharper spectrum.

A large number of papers have been published on the $^{29}$Si NMR of ZSM-5 type zeolites, pointing out subtle changes due to slight modifications in their treatment. The expected result from this zeolite is a strong peak around
-112 ppm due to the four OSi bonded silicon atoms as most ZSM-5 samples have low aluminium contents. A shoulder as seen for my samples at -110 ppm is due to the small amount of silicon bonded to one OAl, and three OSi groups. An example of the typical type of result is shown by Fyfe et al. [87], so confirming that my sample is indeed ZSM-5.

This section has shown that all the samples of zeolites used in these studies are in fact the structures they are claimed to be, as well as demonstrating the usefulness of the study of the silicon, and aluminium nuclei by NMR in the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical Shift ppm (Intensity %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-A 20% H₂O</td>
<td>-89.34 (100)</td>
</tr>
<tr>
<td>H-A 6% H₂O</td>
<td>-98.77 (100) Broad peak</td>
</tr>
<tr>
<td>Na-X 18% H₂O</td>
<td>-85.3 (70) -89.6 (22) -94.9 (10)</td>
</tr>
<tr>
<td>H-X 0% H₂O</td>
<td>-99.2 (8)</td>
</tr>
<tr>
<td>Dealuminated-Y 17% H₂O</td>
<td>-100.90 (100) Broad peak</td>
</tr>
<tr>
<td>H-Mordenite 0% H₂O</td>
<td>-95.7 (3) -102.4 (10)</td>
</tr>
<tr>
<td>H-Mordenite 10% H₂O</td>
<td>-108.4 (80) -112.3 (7)</td>
</tr>
<tr>
<td>Na-Mordenite 10% H₂O</td>
<td>-111.8 (100) Broad peak</td>
</tr>
<tr>
<td>Mg-Mordenite 8% H₂O</td>
<td>-104.6 (40) -112.7 (60)</td>
</tr>
<tr>
<td>H-ZSM-5 10% H₂O Si:Al=21</td>
<td>-105.9 (55) -112.8 (45)</td>
</tr>
<tr>
<td>LiZSM-5 0% H₂O Si:Al=21</td>
<td>-106.03 (50) -113.2 (50)</td>
</tr>
<tr>
<td>H-ZSM-5 0% H₂O Si:Al=173</td>
<td>-106.4 (10) -113.3 (90)</td>
</tr>
<tr>
<td>LiZSM-5 0% H₂O Si:Al=173</td>
<td>-106.4 (10) -113.3 (90)</td>
</tr>
<tr>
<td>H-ZSM-5 0% H₂O Si:Al=173</td>
<td>-110.1 (5) -113.62 (95)</td>
</tr>
</tbody>
</table>
determination of solid structures.

Section 3.40 Lineshapes from wideline NMR $^7$Li NMR

For this particular branch of the NMR work it was found that the vast majority of the samples give a single peak in the spectrum from the static sample. However, in certain cases it was found that the peak is two component, with a sharp peak superimposed on a broader component. In particular this was found for Li-X 10% $H_2O$, and Li-mordenite 0, and 10% $H_2O$, as shown in Fig. 3.16. Herden et al. [88], found a similar two component peak for partially exchanged LiNa-Y, with the sharp component being attributed to the lithium in the supercages. In their investigation of LiNa-X, the narrow component peak was only seen for higher degrees of exchange i.e. once the supercage sites had been occupied.

Melchior [61] observed a two component peak in LiNa-A, with the broad component explained as being due to the central transition of the quadrupolar spin system, and the narrow component being due to all the transitions of the $^7$Li spin system with no quadrupolar splitting. A further explanation for the lineshape has been given by Nagy et al. [89], in their investigation of Li-ZSM-5. The broad line was said to be due to partially hydrated, or anhydrous Li\textsuperscript{+}, with the sharp line being caused by the hydrated cation. The evidence for their model is that as the concentration of Li\textsuperscript{+} cations decreases, the intensity of the narrow peak increases relative to the broad component as a larger number
Fig. 3.16 Spectrum to show Two Component Character of 
$^7\text{Li}$ Spectra
of cations are fully hydrated. No previous work was found which showed the two component behaviour for Li-mordenite as seen in this study.

Section 3.41 Deuterium NMR

For the samples of H-ZSM-5 with Si : Al = 21 with various water contents of 4, 12 and 22 % D$_2$O, a splitting of the peak was seen as shown in Fig. 3.17.

In my samples the central peak is only seen very slightly for the two most heavily hydrated samples, and not at all for the 4% D$_2$O sample, which in fact formed shoulders on the main peak rather than the splitting seen for the larger water contents. The splitting of the peaks for the 12% D$_2$O sample did decrease as the temperature was raised as shown below. This could be due to coupling of the deuterium spin to the protons as shown by Harris [90], but this is unlikely as the proton concentration is relatively low c.f. $^2$H.

Table 3.19

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Splitting (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>223</td>
<td>4285</td>
</tr>
<tr>
<td>238</td>
<td>4107</td>
</tr>
<tr>
<td>263</td>
<td>3571</td>
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<td>273</td>
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<tr>
<td>283</td>
<td>2142</td>
</tr>
<tr>
<td>297</td>
<td>0</td>
</tr>
</tbody>
</table>

Section 3.42 Proton NMR

A number of the mordenite samples gave proton spectra
Fig. 3.17 $^2$H NMR Line Splitting in H-ZSM-5 with 12% D$_2$O
which consisted of a triplet. These include H, Na, Mg, and Al Mordenite and examples of these are shown in Fig. 3.18 and 3.19. The central peak is due to hydroxyl groups, leaving the actual lineshape of the water signal as being a doublet according to Pfeifer et al. [91]. Since the lineshape of ice at 93K is a flattened Gaussian function the difference seen for water in zeolites means that the molecular arrangement of water molecules in the cavities of zeolites at low temperatures must be due to the limited space available in the cavities: this is added to the fact that the water is relatively isolated. An interesting study of how the freezing point of water is affected by the size of the cavity in which it is contained has been made by Deodhar and Luner [92]. Using water in capillaries of various diameters it was shown that as the size of the capillary is decreased the freezing point of the water is also lowered.

In the mordenite samples two types of behaviour were seen in the size of the peak splitting as the temperature was raised. Either the splitting simply decreased as in the H and Mg forms, or increased, then decreased as seen for the Na, and Al forms, examples of both are shown in the following tables.
Fig. 3.18 $^1$H NMR Line Splitting in Na-mordenite with 5% H$_2$O
Fig. 3.19 $^1$H NMR Line Splitting in Mg-mordenite with 5% $H_2O$
Table 3.20 Mg-Mordenite 5% H₂O

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Splitting (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>243</td>
<td>6434</td>
</tr>
<tr>
<td>263</td>
<td>5515</td>
</tr>
<tr>
<td>273</td>
<td>4595</td>
</tr>
<tr>
<td>283</td>
<td>3676</td>
</tr>
<tr>
<td>297</td>
<td>2757</td>
</tr>
</tbody>
</table>

Table 3.21 Na-Mordenite 5% H₂O

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Splitting (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>193</td>
<td>0</td>
</tr>
<tr>
<td>233</td>
<td>3846</td>
</tr>
<tr>
<td>273</td>
<td>7051</td>
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<tr>
<td>297</td>
<td>8125</td>
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<tr>
<td>323</td>
<td>8333</td>
</tr>
<tr>
<td>343</td>
<td>6410</td>
</tr>
<tr>
<td>363</td>
<td>3846</td>
</tr>
</tbody>
</table>

Again the simple decrease of the splitting as the temperature increases, seems to indicate only a less restricted motion at higher temperatures. However, the behaviour of a maximum splitting being observed as the temperature rises is more in line with orientational effects which cause the splitting of a line to vary according to the equation,

\[ \text{Splitting} \propto (3 \cos^2 \theta - 1), \quad (58) \]

where \( \theta \) is the angle between the static magnetic field and
the inter-nuclear vector. These type of orientational effects have been seen for water adsorbed on fibres, and on layered aluminosilicates such as hectorite by Fripiat et al. [93]. This does not occur simply by increasing the temperature of the sample, but by aligning the sample in the magnetic field. However, in the polycrystalline samples used in this study orienting the sample will not produce line splitting, which leaves the reason for the splitting open to debate. The splitting may be due to water in two environments with one relatively more mobile than the other. The immobile water would therefore be responsible for the splitting of the peak.

Section 3.43 Chemical Shifts in $^{13}$C NMR Spectra of Lithium Polymethacrylate

Typical $^{13}$C NMR spectra of samples of the polymer are shown in Fig. 3.20. A feature that was noticed was that as the water content of the sample was raised the chemical shift of the peak due to the methyl groups around 20 ppm shifted to higher $\delta$ values indicating a decreased shielding for that particular group. None of the other peaks in the spectra were affected, so the chemical shift of the methyl group is able to act as an indicator of the water content of the sample. Of course as the water content increases in these samples so does the magnitude of the ER effect, so the chemical shift could also be said to be an indicator of the efficiency of a particular sample of the compound in an ER fluid. Typical chemical shifts are shown below.
Fig. 3.20 \[ ^{13}\text{C} \] NMR Spectra of Lithium Polymethacrylate

Water Content Increasing
The sample used in the above study had been prepared by neutralising polymethacrylic acid with LiOH until a pH of 9 had been achieved. Another sample of the polymer was also prepared by neutralising the acid with the hydroxide until a pH of 7.5 was reached. A sample of this polymer was hydrated with 25% H$_2$O and its ER effect was found to be weaker than a sample of the polymer neutralised to pH 9 with the same water content. In fact the sample of polymer pH 7.5 with 25% H$_2$O was found to have an ER effect intermediate between that of the samples with 4 and 20% H$_2$O neutralised to pH 9. When the $^{13}$C spectrum of the polymer pH 7.5 25% H$_2$O was run the methyl chemical shift was also found to be intermediate between samples with 4 and 20% H$_2$O neutralised to pH 9 at a value of 22.6 ppm. So again it may be tentatively proposed that for samples of lithium polymethacrylate the chemical shift of the methyl group may give an indication of the strength of that polymer in an ER fluid, but more samples of the polymer would need to be investigated to confirm this. A full assignment of all the chemical shifts in polymethylmethacrylate has been performed by Neppel and Butler [94], which correspond quite closely.
for the similar types of carbon nuclei environments as those
for lithium polymethacrylate.

**Section 3.44 NMR Studies of ER Fluids in the presence of an
Electric Field - Background**

The use of NMR in the presence of an electric field
(not for ER measurements) has only found limited success as
shown by the relatively small amount of literature on the
subject. The earliest study was by Buckingham and
McLauchlan [95], in 1967 who used an electric field to
orient molecules in order to find the absolute value of
their coupling constant. Following this Hilbers and Maclean
[96], in 1969 studied how the splitting of the lines in the
$^{14}\text{N}$ spectra of nitromethane and nitrobenzene were dependent
on the strength of the applied electric field.

Holz and Muller [97], encountered problems in the
measurement of internal magnetic field gradients caused by
the current in electrolyte solutions. These were due to the
current in the NMR cell being perpendicular to the direction
of the static magnetic field in the NMR experiment, so the
cell design was later refined. In 1984, Holz et al. [98, 99]
designed a probe with the electric and magnetic fields
parallel. They used this to simultaneously measure ionic
mobilities, transference numbers, and self-diffusion
coefficients of an electrolyte solution using an NMR pulsed
field gradient experiment. During the experiment only very
small electric fields were needed 0.002 to 0.005 kVmm$^{-1}$,
which caused currents of up to 80 mA to flow.
In 1980 Plantenga et al. [100], used an NMR cell for use at high electric fields in superconducting magnets, again with the electric and magnetic fields aligned. For this particular study the cell was used to determine the orientation of the dipole moment of molecules from $^{13}$C NMR of molecules which are partially aligned by an electric field. The cell design is also explained in more detail by Ruessink [101], and has been used for the study of a number of different systems [102, 103, 104, 105, 106, 107, 108]. More recently the pretransitional phenomena in liquid crystals has been studied by Emsley et al. [109], by measurement of the deuterium quadrupolar splittings induced by an electric field. The electric field NMR cell used for this work was very much based on Ruessink's design [101].

Electric field NMR has also been applied in some diverse areas such as by Shenton et al. [110] who studied the muscle of the human arm under electrical stimulation by $^{31}$P NMR. While the work of Douglass et al. [111], was interested in examining the charge-density wave state in a single crystal of Rb$_2$Mo$_{0.3}$O$_3$ with an applied electric field. Only very small voltages were applied e.g. 0.1 Vmm$^{-1}$.

Section 3.45 Experimental

The electric field cell used in reference [101], proved to be the basis for the design used in my work. All my measurements were carried out using a super-conducting magnet so, as explained earlier the direction of the electric field is the same as that of the magnetic field as
shown in the drawing of the cell in Fig. 3.21.

The tube was 10mm od. to keep to NMR standards, with the lower half of the body of the tube made from PTFE. A PTFE ring was machined to act as a spacer between the electrodes, with an inner diameter of 5mm, and an outer one of 8mm. The depth of the ring was 3mm which acted as the electrode separation, and the total volume of sample it was possible to use was 0.059 cm$^3$.

The PTFE tube was sealed with a PTFE screw, and this lower section was a push fit into an upper body made from Tufnol which was more rigid and gave added support. The upper electrode was electrically positive and the wire leading from there was soldered to a wire from the power supply unit. Any other type of connection proved troublesome because of RF interference. The negative electrode wire was threaded through the NMR probe via the dewar normally used to supply nitrogen gas for variable temperature studies, and then back to the power supply box shown in Fig. 3.22.

An earthed metal box was needed to make all the other connections as once again spurious RF signals had to be excluded. The voltage was generated by a Brandenburg Ltd model 2907 power supply capable of giving 0 to 60 kV, at 0.5mA, and this supply was taken into the shielding box where an accurate voltage was measured using a Brandenburg Ltd. model 1390 voltmeter. The top of the box was made from a metal gauze with holes small enough to prevent RF pickup, but large enough to be able to see through to read the
Fig. 3.21  The Electric Field (EF) Cell
Fig. 3.22 Diagram of Electrical Circuit for Use with the EF Cell

H.T. POWER SUPPLY

V

A

11MΩ

B

E.F. cell

©
meters. The voltage was then taken out of the box and put through the sample, and the lead from the negative electrode was returned to the shielding box, where it was then passed through a resistance of 11 MΩ before measurement of the current with a Keithley model 485 autoranging picoammeter. The purpose of the 11 MΩ resistance was to act as a buffer to protect the ammeter should the sample short out. Of course this meant that in all measurements a certain voltage of

$$V = 11 \times (\text{current in } \mu\text{A})$$

will be dropped across the resistors and not across the cell, but this was taken into account in all calculations of the voltage dropped across the samples. All the transference of the high voltages was done via high voltage coaxial cable (No.URM43) supplied by Radiospares. Again the copper braid around this wire was found to be necessary to shield the wire from picking up stray RF signals.

Section 3.46 Results

Two nuclei were investigated with the application of an electric field. These were $^2\text{D}$ to look at $\text{D}_2$ in the samples and $^7\text{Li}$ to monitor the behaviour of the cations. The length of time required to accumulate enough spectra to perform an accurate $T_1$ measurement made the idea impractical, so the linewidths of the spectra were measured to act as a sensor of the molecular motion.
Section 3.47 Deuterium NMR

It was found that for the polymer typical water contents of 10 to 50% D\textsubscript{2}O produced manageable conductivity levels, and also the deuterium NMR signal was sensitive enough to record.

However the zeolite samples which are much more conductive require hydration levels of less than 5% D\textsubscript{2}O to keep the conductivity at a reasonable level, but this was found not to be sufficiently sensitive for deuterium NMR, consequently only the polymer could be examined using this nucleus.

It was found that the lineshape from the polymer dispersed in oil contained a very sharp line imposed on a broader peak, as shown in Fig. 3.23. This is due to the fact the polymer "sweats" while it is in the oil, and releases tiny droplets of D\textsubscript{2}O, which give rise to the sharp component. The water left in the solid gives the broad line of comparable width to the solid samples in the sealed tubes. The D\textsubscript{2}O in the silicone oil was confirmed by letting the solid settle out, and then decanting off a portion of the oil. This sample of oil gave a deuterium signal confirming the presence of D\textsubscript{2}O. Zeolite based ER fluids were tested in this way but no deuterium could be detected re-enforcing the fact that the water is retained by the zeolite.

Electric fields of up to 3 kVmm\textsuperscript{-1} were applied to the samples of polymer based ER fluids, but in all samples of varying degrees of hydration no effect was seen by
Fig. 3.23 $^2$H NMR of Lithium Polymethacrylate in the EF Cell

a) 56% $\text{D}_2\text{O}$ in glass tube

b) 25% $\text{D}_2\text{O}$ in glass tube

c) 25% $\text{D}_2\text{O}$ shorted out Line Broadening = 0 Hz

d) 25% $\text{D}_2\text{O}$ shorted out Line Broadening = 600 Hz
monitoring the linewidth of the signal to detect any changes in the $T_2$ value brought about by the electric field. The only small decrease in linewidth was put down to the heating effect of the current, so within the limits of sensitivity of NMR no gross effects were produced by the electric field.

When an excessive voltage is applied to the sample the fluid breaks down and a large current flows. This produces a large amount of heating which narrows the linewidth as expected. When the voltage was switched off, the sample returned to its initial ambient temperature, and the linewidth was again monitored. It was found that even after 2 hours the water motion was still considerably faster than that before breakdown.

Table 3.23 Lithium Polymethacrylate 25% $D_2O$

<table>
<thead>
<tr>
<th>Applied Field kVmm$^{-1}$</th>
<th>Sharp peak Hz width</th>
<th>Broad peak Hz width</th>
</tr>
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</tr>
<tr>
<td>0.665</td>
<td>950</td>
<td>22,000</td>
</tr>
<tr>
<td>0.999</td>
<td>800</td>
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<tr>
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<td>860</td>
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<td>680</td>
<td>17,100</td>
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<tr>
<td>3.000 shorted out</td>
<td>single peak</td>
<td>1,640</td>
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<tr>
<td>0 1 hour later</td>
<td>single peak</td>
<td>3,900</td>
</tr>
<tr>
<td>0 2 hours later</td>
<td>single peak</td>
<td>5,100</td>
</tr>
</tbody>
</table>
This is in agreement with the mechanical findings for this fluid that after breakdown the ER performance of this variety of fluid is reduced, and the value of the breakdown voltage progressively decreases.

Section 3.48 Lithium NMR

It was possible to detect the signals from polymer and zeolite solid particles for this nucleus, and still maintain hydration quantities at reasonable levels to produce workable conductivities. Examples of the spectra are given in Fig. 3.24.

In this case for the polymer only a broad single peak was seen indicating that despite the fact some water escapes from the solid particles, the \( \text{Li}^+ \) ions remain in the solid. This single peak was also noted for zeolite samples.

Again using the same method of detection of monitoring the peak width no changes for either the zeolite or the polymer could be detected on the \( \text{Li}^+ \) motion by increasing the electric field. Again, as for deuterium when the breakdown voltage was attained the linewidths of both types of fluid decreased, and the recovery after switching off the field was again monitored. As shown in the following tables 3.24 and 3.25.
Fig. 3.24  $^7$Li NMR of Polymer and Zeolite Containing Fluids in the EF Cell

a) LiPMA 25% D$_2$O 1 kVmm$^{-1}$ Line Broadening = 0 Hz

b) LiPMA 25% D$_2$O shorted out Line Broadening = 0 Hz

c) Li-X 1% H$_2$O shorted out Line Broadening = 0 Hz

d) Li-X 1% H$_2$O shorted out Line Broadening = 200 Hz
Table 3.24  Li-X 5% H₂O

<table>
<thead>
<tr>
<th>Electric field (kV mm⁻¹)</th>
<th>Half height width (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1680</td>
</tr>
<tr>
<td>0.497</td>
<td>1728</td>
</tr>
<tr>
<td>0.987</td>
<td>1600</td>
</tr>
<tr>
<td>1.467</td>
<td>1680</td>
</tr>
<tr>
<td>2 shorted</td>
<td>600</td>
</tr>
<tr>
<td>0 1/2 hour later</td>
<td>1550</td>
</tr>
<tr>
<td>0 1 hour later</td>
<td>1559</td>
</tr>
<tr>
<td>0 1 1/2 hours later</td>
<td>1719</td>
</tr>
</tbody>
</table>

Table 3.25  Lithium Polymethacrylate 25% D₂O

<table>
<thead>
<tr>
<th>Electric Field (kV mm⁻¹)</th>
<th>Half height width (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2500</td>
</tr>
<tr>
<td>0.998</td>
<td>2620</td>
</tr>
<tr>
<td>1.990</td>
<td>2700</td>
</tr>
<tr>
<td>shorted out</td>
<td></td>
</tr>
<tr>
<td>0 1/2 hour later</td>
<td>2260</td>
</tr>
<tr>
<td>0 1 hour later</td>
<td>2460</td>
</tr>
<tr>
<td>0 1 1/2 hours later</td>
<td>2430</td>
</tr>
<tr>
<td>0 2 hours later</td>
<td>2370</td>
</tr>
<tr>
<td>0 2 1/2 hours later</td>
<td>2300</td>
</tr>
<tr>
<td>0 3 hours later</td>
<td>2280</td>
</tr>
<tr>
<td>0 3 1/2 hours later</td>
<td>2350</td>
</tr>
</tbody>
</table>

The zeolite samples showed recovery back to the starting value of the linewidth in 1 hour, but again the...
polymer did not achieve its original value even after 3 hours. The zeolites show mechanical performances that can be reproduced even after breakdown, unlike the polymers. It can be seen that the large breakdown currents produce a permanent damage to the polymer fluids by increasing cation and water mobility, which would be undesirable in a practical situation.
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CHAPTER 4 ELECTRON SPIN RESONANCE SPECTROSCOPY

As stated in Chapter 3, in the theory of magnetic resonances for Electron Spin Resonance (ESR) the energy needed to cause the transition in the spin state of the unpaired electron is given by equation (1):

\[ E = h \nu = h \frac{g \mu_B B}{2} \]

The values of the field and frequency were chosen due to coincidence at the time of the development of the technique (at the end of the Second World War). The development of radar during the war meant that the manufacture of microwave sources in the region of 30 MHz to 300 MHz, which is not an extreme, and can be achieved with an electromagnet.

These parameters correspond to an energy level difference of approximately 20 J mol\(^{-1}\) at ambient temperature. The relative populations of the low energy levels, as given by the Boltzmann distribution, described in Chapter 3, is 0.9991. If the rate of transition to the higher energy level is much greater than the population of that of the lower level, then this is known as saturation. The conditions for saturation are dependent on the intensity of the microwave radiation, and also the relaxation time of the unpaired electron, that is its interaction with its environment. The area of ESR is expanding with applications in all branches of chemistry, as well as having found uses in other related disciplines, as in the case of EPR. For this reason it is impossible for
Section 4.1 Theory

As stated in Chapter 3 in the theory of magnetic resonance for Electron Spin Resonance (ESR) the energy needed to cause the transition in the spin state of the unpaired electron is given by equation (1),

$$h \nu = g_e \mu_B B_z$$  \hspace{1cm} (1)

The values of the field and frequency were chosen due to circumstance at the time of the development of the technique (at the end of the Second World War). The development of radar during the war meant that the manufacture of microwave sources in the region of 9.5 GHz was already well advanced. This corresponds to a magnetic field $B_z$ in the order 340 mT (3400 G), which is not too extreme, and can be achieved with an electromagnet.

These parameters correspond to an energy level difference of approximately 3.8 Jmol$^{-1}$. At ambient temperature the relative populations of the two energy levels, as given by the Boltzmann distribution, described in Chapter 3, is 0.9984. If the rate of transition to the higher energy level is such as to cause its population to equal that of the lower level then this is known as saturation. The conditions for saturation are dependent on the intensity of the microwave radiation, and also the relaxation time of the unpaired electron, that is its interaction with its environment. The area of ESR is enormous with applications in all branches of chemistry, as well as having found uses in other related disciplines, just as in the case of NMR. For this reason it is impossible for
every area of the subject to be covered, so I will concentrate on the points which are basic essentials or aspects relevant to my work. Relatively few reviews of the subject have been published, but Symons book [1] proves to be a useful starting point.

Section 4.2 The g Value

The g value determines the amount of energy needed to be absorbed by the sample in order for resonance to occur. In this respect it is equivalent to the chemical shift in NMR. If the electron spin is the only source of magnetism, then \( g = g_e = 2.0023 \). However orbital angular momentum can also act as a source of magnetism which can alter the value of \( g \). For most radicals the orbital angular momentum is largely removed, as the degeneracy of the orbitals involved is removed by the covalent bond. This means that the electron will be in an isolated orbital, and the value of \( g \) will be close to that of \( g_e \) as other sources which affect the magnetism are small. In spite of this, small amounts of orbital angular momentum can still affect the spin magnetism after mixing has been induced by the applied field, but changes in \( g \) are rarely larger than \( \pm 1\% \). These changes can still easily be measured down to 0.005% differences. The magnetic moment for an electron arising from spin orbital angular momentum is 1 rather than 2, so the g value will move below 2. Whilst for coupling via a filled, compared with an empty level, the g value moves in the opposite direction, e.g., \( V^{IV} < 2 \) and \( Cu^{II} > 2 \).
All the atoms in the radical which possess some of the unpaired electron spin density will provide contributions to the g value. In this study, nitrooxide radicals were used which are systems in which the majority of the unpaired electron spin density is in a π orbital of the N—O bond. Again in these radicals, the applied field in encouraging the unpaired spin to orbit the nucleus in a plane perpendicular to the applied field, creates the magnetic field which is spin orbital angular momentum, to counteract the applied field. It has been shown by Atkins and Symons \[2\] that in all bent molecules, such as the nitrooxide radicals used in this study, none of the π orbitals are degenerate.

The g value of a radical or ion oriented in space, for example inside a crystal, depends upon the direction along which it is measured, therefore it is anisotropic. There are three principal components of the g value which are averaged to a single value in normal liquids due to Brownian motion. The principal components can be found in crystals when the field can be applied in definite directions, and this can be applied in the analysis of crystal structure determination. In a powder the spectrum is the envelope of all the possible orientations of the radical, but the principal components of g may be measured directly. The powder spectrum is obtained when the correlation time of the radical is slower than \(\approx 10^{-6}\)s, with the fast motion limit of conventional ESR being \(10^{-9}\)s.
Section 4.3 Hyperfine Coupling

The magnetic coupling that can occur between the spin of the unpaired electron ($S$), and the spins of closely situated magnetic nuclei which also have a spin $I$, is termed the hyperfine coupling.

For solutions of radicals there are $2nI + 1$ lines produced in the spectrum, where $n$ is the number of equivalent nuclei. This is consistent with an interaction which has an energy dependent on the relative orientations of the magnetic moments, and consequently the angular momenta of the particles. As shown in Fig. 4.1 below, $m_1$ has $(2I + 1)$ values in the applied field, and $m_S$ has $(2S + 1)$ values. Now $S = 1/2$ for the electron, so for a nuclear spin of $1/2$ this gives,

\[
m_1 = \pm 1/2 \quad m_S = \pm 1/2
\]

Fig. 4.1 Energy Level Splitting by the Magnetic Field
Since the selection rules are such that $m_g = \pm 1$, and $m_I = 0$ then there are $(2I + 1)$ transitions leading to $2I + 1$ lines.

For $^{14}$N then $I = 1$, and so in a nitroxide there are $(2nI + 1) = (2 \times 1 \times 1 +1) = 3$ transitions giving the same number of lines in the spectrum. For complex interactions with more than one nucleus the number of transitions is given by (2),

$$\text{Total transitions} = (2nI + 1)^A \times (2nI + 1)^B \times (2nI + 1)^C \ldots \ldots \ldots (2)$$

Like the $g$ value, the hyperfine interactions are usually anisotropic, with three principal values, which may be determined by the study of the orientational dependence of a single crystal sample, an example of which is shown by the work of Preston et al. [3].

Section 4.4 Practical aspects of ESR

There are various microwave frequency ranges used for ESR spectroscopy, ranging from 1 to 35 GHz. The range which was used in these studies was from 8.8 to 9.6 GHz which is known as X-band and is the most common range in use. The basic description of a spectrometer given below varies slightly for different manufacturers specifications, but the basic components are similar in all spectrometers.

Section 4.5 Basic Description of the Spectrometer

(See Fig. 4.2)

A microwave source generates energy in the range 8.8 to 9.6 GHz for sample excitation, and this output is applied to an isolator, and then to an attenuator. The attenuated
Fig. 4.2  Plan Drawing an ESR Spectrometer

Microwave

Phase Detector

Recorder

Phase shifter

Amplifier

Detector

Amplifier

Sample

Phase shifter

cavity

Field modulation coils

magnet

Sample

0 Hz Osc.
microwave energy is then transmitted to the cavity, which is situated in between the poles of the magnet which produce the modulated magnetic field. The reflected energy from the cavity is directed to the crystal detector. The detected signal is amplified by a frequency selective amplifier, and then demodulated by a phase sensitive detector, with the resulting dc voltage being displayed on a recorder.

The result of the use of magnetic field modulation is that the demodulated signal is equal to the first derivative of the adsorbed power, if the frequency of the detected signal by the frequency selective amplifier is equal to the field modulation frequency. The signal detected at double the field modulation frequency gives the second derivative of the adsorbed power. It is easier to vary the magnetic field than the frequency $v$, because the cavity acts as a high Q tuned circuit, where Q is a measure of the sensitivity of the spectrometer defined as,

$$Q = \frac{\text{Energy stored in cavity}}{\text{Energy lost per cycle}}$$  \hspace{1cm} (3)

If the frequency were swept the cavity would have to be automatically retuned.

Now some of these components will be discussed in a little more detail, but for a full description from the electronic engineer's viewpoint it is best to consult Alger [4].

**Section 4.6 Source of microwave Radiation**

The source of microwave radiation of 3cm wavelength
i.e. 9.5 GHz, in older machines was a klystron valve capable of varying \( \pm 3\% \) about its central frequency. This is stabilised against temperature variation by forced air or water cooling. In newer spectrometers, solid state technology has been used to produce the microwave radiation from a Gunn diode. A feedback automatic frequency control (AFC) circuit using a fraction of the signal fed back from the cavity stabilises the klystron, or Gunn diode frequency to approximately \( 1 - 10 \) ppm, and output powers of up to 200 mW are standard.

Section 4.7 Waveguide and Attenuators

The microwave output is applied to an isolator, this is a unidirectional attenuator made from ferrite, which prevents reflected energy from reaching the microwave oscillator. The radiation is then conducted to the sample situated in the microwave bridge by the waveguide. The waveguide is a hollow rectangular tube of copper or brass, often plated with gold or silver. The dimensions of the waveguide will obviously depend on the wavelength of the radiation, but for X band the cross section is 2.25 cm by 1 cm. The microwave power can be decreased at this stage by inserting a variable attenuator, consisting of a piece of resistive material, into the waveguide.

Section 4.8 The microwave Bridge

The bridge can be of the "magic-T", or "circulator" type. Both serve the same purpose, so for brevity only the
description of the "magic-T" type will be considered here. In the "magic-T" as shown below in Fig. 4.3 power from the waveguide enters A, and then is divided between B and C. If the impedances of B and C are the same, then no power will enter D to the detector, and the bridge is said to be balanced. However, if the impedance of B changes because the Q of the cavity changes when the sample absorbs energy, then the bridge is unbalanced and the power reflected from B and C enters into arm D, and is detected.

**Fig. 4.3  Diagram of the Magic T**

![Diagram of the Magic T]

- B: cavity and sample
- C: matched load
- A: microwave radiation
- D: detector
Section 4.9 The Iris, and Cavity

The cavity is a piece of waveguide one or more half-wave lengths long, in which a standing wave is set up. This standing wave is composed of both magnetic, and electric fields at right angles to each other. The RF magnetic field interacts with the sample, so the sample is placed where this is largest, and the RF electric field is minimum. Both rectangular, and cylindrical cavities can be used, with typical values of $Q$ of 7000 for the rectangular variety.

Matching of the waveguide elements is established by changing the microwave oscillator frequency slightly. A metal tipped nylon screw, known as the iris, is used to couple the cavity. This screw varies the size of the hole from the waveguide to the cavity, through which the microwave radiation passes, so as to set up a standing wave.

Section 4.10 The Magnetic Field

The homogeneity of the magnet is less than that needed for NMR, since line widths are not less than 0.01 mT with the sweep of the magnetic field produced by increasing the current supplied to the electromagnet. The signal from the sample is increased in sensitivity if it is modulated at a specific frequency, typically 100 kHz. This is accomplished by a small alternating variation of the magnetic field, by supplying an ac signal to modulation coils oriented in the same direction as the magnetic field. For modulation frequencies larger than 1 kHz the coils are mounted inside
the cavity, as they cannot penetrate metal effectively. An alternative is that the cavity may be constructed of a non-metallic material, such as ceramic, or quartz, with a thin silver plating. The amplitude of the modulation of the magnetic field may be from 0.002 mT up to 2 mT, but values of larger than 1 mT, do cause heating of the cavity, which can result in dimensional changes which obviously affect the wavelength of the standing wave, and thus the tuning of the cavity. Also the magnitude of the modulation amplitude should not be larger than approximately \( \frac{1}{\gamma} \) of the natural linewidth of the sample, otherwise the lineshape will be distorted, and also small couplings may be obscured.

Section 4.11 Detectors

From the unbalanced cavity, when energy has been absorbed by the sample, the signal from the microwave bridge is then amplified, first using a frequency selection amplifier. In a standard spectrometer this will typically amplify signals at a preset frequency in the range of 12.5 to 200 kHz. Then the signal passes through another circuit controlled by the receiver gain selector on the console, and then to a phase sensitive detector. Detectors for microwave radiation above 3 GHz are diodes that convert the RF radiation to dc, for display on the recorder. The bias current of the detector is of the order of 100\( \mu \)A and is set by adjustment of the iris.

The reference signal used in the phase sensitive detector is generated by the phase controller, and the
signal passes into a low pass filter of a narrower band after the phase sensitive detector, which removes any residual harmonics from the signal. Additional filtering is then provided by an R-C circuit set by the time constant control on the console.

Section 4.12 Effect of motion on ESR linewidths

The speed of tumbling of a radical in a sample governs by how much the ESR spectrum will be motionally broadened, as shown by Spielberg and Gelerinter [5]. Fast tumbling will give spectra which consist of well-resolved Lorentzian lines from which line heights and widths can be easily measured, which has been explained in some detail by Freed [6].

The opposite case is true for slowly tumbling radicals which cause spectra to consist of lines which are often broad and poorly resolved, and are no longer Lorentzian: analysis can still be performed on these spectra, as described by Nordio [7]. The radicals used to probe the molecular motions in this study gave fast tumbling spectra when rotational correlation times ($\tau_c$) are in the range of $10^{-9}$ s and smaller, with slow tumbling spectra for $10^{-6}$ s < $\tau_c$ < $10^{-9}$ s. The radicals are assumed to undergo "stochastic" rotation via a series of very small stepwise jumps, and $\tau_c$ is a measure of the time for rotation through $2\pi$ radians by this mechanism. The first accurate model to account for the ESR linewidth in the fast tumbling region was proposed by Klivelson [8], based on the theory of Kubo.
and Tomita [9]. The Kivelson model assumes that the only modulation acting on the spin system is due to the radical movement through the solvent. Given this then the contributions to the ESR linewidth can be considered to arise from three processes:

1) Secular processes due to electron spin-spin relaxation.
2) Pseudo-secular processes when nuclear spins relax but electron spins are unaffected.
3) Non-secular processes which are due to electron spin-lattice relaxation.

The secular contribution is the major cause of line broadening for the conditions under which all the measurements were taken with other factors being negligible as will be shown later. The secular contribution to the linewidth of the line with nuclear quantum number \( I \) is given by \( (T_2(M_1))^{-1} \). The dependence of the linewidth on \( \tau_c \) is shown in Fig.4.4.

The \( T_2 \) time results from fluctuations in the energies of the ground and excited states, or in local fields experienced by electrons. The Kivelson [8] theory also assumes that all the inter-molecular spin interactions are neglected, so the radical concentration should be low (\( \approx 10^{-4} \text{M} \)) to avoid these interactions.

The equation for the secular contribution to linewidth is based on the assumption that the three following conditions hold,

\[
1) \tau_{c}a^2x_1 \quad 2)a^2 < \gamma^2B^2 \quad 3)c^2 < \gamma^2B^2
\]

where \( a \) is the isotropic hyperfine coupling constant, \( B \) the
Temperature Decreasing

Fig. 4.4 Variation of ESR Spectra with Tumbling Rate
applied field, γ the isotropic gyromagnetic tensor in the fixed co-ordinate system, and σ is a term based on components of the dipole tensor for the anisotropic hyperfine interaction. For the radicals used in the experiments described here, a is approximately 1.3 mT which means that the secular contribution equation is valid for τ < 3 × 10^{-8} s i.e. in the fast tumbling region, whilst B was approximately 341 mT c.f. 0.5 mT which is the minimum value required for the equations to hold.

The equations for the secular contribution to the linewidth also simplifies if only one nuclear spin interacts with the unpaired electron spin. The radicals used in this study also possess A and g tensors which fulfill the condition for axial symmetry which further simplifies matters.

The axial symmetry of the g tensor allows the following for 14N spectra,

\[ γ = \frac{-e \mu_B}{h} \]

therefore \( \gamma_{XX} = \gamma_{YY} \neq \gamma_{ZZ} \)

The simplified secular linewidth equation now becomes

\[ (T_2(M_1))^{-1} = \tau_c \left[ \frac{4}{45} (A^2 B^2) + \frac{3}{20} b^2 - \frac{4}{15} (A \mu B M_1) + \frac{1}{8} b^2 (M_1)^2 \right] \]

where,

\[ A = \frac{\mu_B}{h} \left[ g_{ZZ} - \frac{1}{2} (g_{XX} - g_{YY}) \right] \]

and

\[ b = \frac{4}{3} \pi \left[ A_{ZZ} - \frac{(A_{XX} + A_{YY})}{2} \right] \]

and \( M_1 \) is the component of nuclear spin angular momentum. A major condition for these equations to hold is that the
radical should rotate isotropically which is explained by Nordio [7]. In some cases this may be a major assumption.

By increasing the value of $\omega_0 \tau_c$ (where $\omega_0$ is the operating frequency of the spectrometer), this decreases the non-secular and pseudo-secular contribution to linewidth. Since the value of $\omega_0$ used in the ESR experiments was around 9.1 GHz corresponding to $6 \times 10^{10}$ rads$^{-1}$. Thus $(1 + (\omega_0 \tau_c)^2)^{-1}$ is less than 0.1 for $\tau_c$ values down to $5 \times 10^{-11}$ s, non-secular and pseudo-secular contributions to linewidth can be ignored down to this value.

The simplified secular linewidth equation now holds for $\tau_c < 10^{-9}$ s.

$$\left( T_2(M_I) \right)^{-1} = A' + B' (M(I)) + C' (M(I))^2, \quad (8)$$

where,

$$A' = \left[ \frac{4}{45} \Delta^2 b^2 + \frac{3}{20} b^2 \right] \tau_c, \quad (9)$$

$$B' = \frac{4}{15} \Delta b B \tau_c, \quad (10)$$

and

$$C' = \frac{1}{8} b^2 \tau_c. \quad (11)$$

The value of the correlation time calculated using (10) is more accurate than that using (11) as $B'$ is the average of both the A and the g values, while $C'$ is only the average of the A values.

The lines for the radicals can be regarded as Lorentzian, as there are no hyperfine couplings other than with $^{14}N$ and the following Lorentzian equation therefore applies,
\[ f(\omega) = \frac{(\pi)^{-1} (T_s)^{-1}}{(T_s)^{-2} + (\omega_0 - \omega)^2} \]  

where \( \omega_0 \) = angular frequency at position of maximum absorption, and \( \omega \) = angular frequency displacement from \( \omega_0 \) and \( (T_s)^{-1} \) = half width of the absorption peak at half the maximum height.

Since the spectra were recorded in the first derivative form, the most easily measurable feature is the peak-to-peak width. The width \( W \) corresponds to the width between the points of steepest slope in the absorption line. \( (T_s)^{-1} \) is related to \( W \) by

\[ (T_s)^{-1} = \frac{\sqrt{3}}{2} W \]  

\( (T_s)^{-1} \) the secular Lorentzian linewidth is found from the first derivative using,

\[ (T_s)^{-1} = \frac{\sqrt{3}}{2} W \]  

For radicals in the fast tumbling region the changes in the linewidth, particularly of the centre, and low field lines, maybe so small as to make the measurement difficult. However, each line contains the same area \( A \), and the first derivative pure Lorentzian line is related to the width, and height \( (h) \) by the expression,

\[ A = \frac{1}{2} h W^2 \]  

The final linewidth equations which can be used for motionally broadened \(^{14}N\) spectra are

\[ B' = \frac{\sqrt{3}}{2} W (+1) \left[ 1 - \frac{h (+1)}{h (-1)} \right] \]  

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and \[ C' = \frac{\sqrt{3}}{2} W(0) \left[ \begin{bmatrix} h(0) \\ h(+1) \\ h(-1) \end{bmatrix} \right] \frac{1}{2} \right] + \left[ \begin{bmatrix} h(0) \\ h(+1) \\ h(-1) \end{bmatrix} \right] \frac{1}{2} - 2. \] (17)

The first expression relating the radius (r) of a molecule, rotating isotropically in a solvent of viscosity \[ \eta, \] at a temperature \[ T \] to the rotational correlation time \[ \tau_c \] was formulated by Debye [10].

\[ \tau_c = \frac{4 \pi \eta r^3}{3 k T}. \] (18)

For the Debye equation to hold a radical must satisfy three main criteria,

1) It must be spherical, otherwise the shape of the molecule may lead to preferential rotation about the molecular axis which possesses the smallest interaction potential.

2) It should be non-polar, because a significant dipole moment can lead to association of the molecules into large slowly rotating groups, whose calculated radii would be much larger than that of the true value.

3) Freed [11] showed the molecule should rotate by a stochastic process which has \[ \tau_c \] smaller than the correlation time for the stepwise translation of the radical molecule through the solvent.

Section 4.13 Experimental

All the simple ESR CW experiments were carried out using a Varian E-4 spectrometer. For temperatures below ambient nitrogen gas was used to lower the temperature, and a copper constantan thermocouple connected to a Comark digital thermometer Model 5000 was used to monitor the
temperature to $0.1^\circ C$.

For the Saturation Transfer ESR (STESR) experiments a Jeol (JES-RE1X) spectrometer was used again, with nitrogen gas used to lower the temperature below ambient, with the whole temperature system monitored and run by a Jeol DVT2 temperature controller. All the variable temperature work was carried out with the samples contained in glass tubes of 5mm od.

Section 4.14 Electric Field Apparatus

All the electric field work was performed using the same cell as used for the NMR measurements. The only slight modification of the design of the electric field cell was in the spacer used to separate the electrodes, and contain the sample. For ESR experiments only a very small volume of the sample is detected, so the spacer was this time a ring of PTFE 3mm in depth, with only a 2 mm diameter hole to contain the sample.

Section 4.15 Sample Preparation

The spin probe molecules were those which had originally been used by Martini et al. [12] in their work on the molecular motion of water in fully hydrated zeolites. These consisted of,

1) Tempol (4-hydroxy-2,6,6-tetramethyl-piperidine-1-oxyl).
2) Tempyo$^-$ (2,2,5,5-tetramethyl-pyrroline-1-oxyl-3-carboxylate) as the succinimidyl salt.
3) TempTMA$^+$ (4-trimethyl-ammonium-2,2,6,6-tetramethyl-pipe-
ridine-1-oxyl) as the iodide salt. The Tempol was purchased from Aldrich Chemicals Ltd, while the other probes were obtained from Molecular Probes Inc. (Eugene, Oregon, USA) and are shown in Fig. 4.5.

It was hoped that by using probes of different charges would help in the study of water in different regions of the zeolite cavities.

\[
\begin{align*}
&\text{TempTMA}^+ \\
&\text{Tempyo}^- \\
&\text{Tempol}
\end{align*}
\]

Fig. 4.5 Structure of the Spin Probes Used

The zeolite samples were prepared by soaking them for four days in a 10^{-2}M aqueous solution of the radical. After this time the zeolite was filtered, and then washed with water to remove any radical from the surface of the solid. The sample was then dehydrated at 120°C until the desired water content was attained. A final water content of approximately 60% could be obtained by dehydrating for 15 minutes, or 10% by dehydration for one hour. The sample was then removed from the oven, and part of the sample was dispersed in oil, while the remaining fraction was dehydrated completely at 500°C to check the water content. Then the zeolite was dispersed in Dow Corning 20 cs
silicone oil to maintain the water content.

To observe any motion of the spin probe in the zeolite requires the zeolite to be hydrated. This means that the sample should be sealed as soon as it is prepared, or else it must be stored under silicone oil. A portion of the oil that had been used to contain a sample of zeolite impregnated with radical was separated from the solid, and then inspected on its own. Radicals could not be detected in the oil, indicating that radicals had not escaped from the solid.

Section 4.16 Discussion of previous work on Zeolites studied by ESR

Na-X

As mentioned previously, Martini et al. [12] used the same charged spin probes to investigate the water in fully hydrated zeolites X, and Y. It was shown that all the spin probes used have diameters of approximately 7.25Å. The diameter referred to is that of the smallest cylinder that can circumscribe the molecule. This means that in the zeolites X, Y, and Dealuminated-Y the radical will be predominantly in the supercages after entering through the external pore of 8Å diameter, since to pass between supercages requires that the molecule should pass through a much smaller pore of roughly 2Å diameter. Martini et al. [12] also showed that even for fully hydrated zeolites the water is less mobile in zeolitic cavities than in bulk water. The TempTMA⁺ will be largely affected by the water.
layers close to the cavity walls, since the zeolite framework is negatively charged. In the study on fully hydrated zeolites it was found that TempTMA* showed a tighter binding with surface sites in Y, than in X. This was attributed to the fact that in Y a higher fraction of the negative surface charge is neutralised by sodium ions located on more definite sites.

The use of spin labelled molecules was exploited by Rigo et al. [13], who found that labels adsorbed on to zeolites X, Y, and A resulted in asymmetric ESR slow motion spectra. This was said to be due to the spin label binding to Na+ sites which result in restricted rotation of the label, simultaneously tumbling within a cone.

The use of Cu2+ as a probe, by exchange with the cations in faujasite zeolites has been investigated by Packet and Schoonheydt [14]. The ESR spectra allowed different sites of the copper ions to be identified, as they have different g, and A values. The same ion was also used by Narayana and Kevan [15] in zeolite X. It was found that in Tl-X the adsorption of polar molecules can move the copper ions from the hexagonal prisms into the supercages, whereas migration of Cu2+ never occurs in Na-X.

Barry and Ley [16] used Mn2+ to study the several sites occupied by metal ions in zeolite X, and found that ions such as Mg2+ do not replace the sodium ions from the sites not accessible to water. The Mg2+ ions were also found to be able to approach the centre of the oxygen six rings, while still remain more strongly bound than the
larger cations.

Na-Y

The use of copper ions in this zeolite was again exploited by Martini and Burlamacchi [17], who found that the mean viscosity coefficient for the motion of the ionic surroundings is about one order of magnitude greater in the fully hydrated faujasite cavity, than in bulk water. It was thought that a reduction of the hydrogen bonding, which is disrupted by the restrictions imposed by the zeolite cavities may well be responsible for the peculiar properties of water. The water mobility in practically the whole faujasite cavity was found to be largely influenced by the type of exchanged cation, which was an important observation. Other transition metal cations such as Mn$^{2+}$ have also been used in the study of Y. The work of Tikhomirova et al. [18, 19] showed that if the zeolite contains ions with different water affinities, then on dehydration, the remaining water will preferentially congregate around the more hydrophilic ions.

Na-A

In a slightly different use of ESR, Morton and Preston [20], exchanged the Na$^+$ ions for Ag$^+$ in a sample of A zeolite where the silver ions form clusters. The sample was then submitted to γ irradiation, and the resulting Ag$_6^+$ centre was detected. It was found that the Ag$_6^+$ core was surrounded by a cube of eight Ag$^+$ ions, and the
"superhyperfine" interactions of the silver ions in the outer cage were used to study the effects on the cluster of dehydration at various temperatures.

**H-ZSM-5**

This zeolite has found particular use as a catalyst for reactions involving the synthesis of gasoline from methanol, and for this reason a number of the ESR studies previously performed have concentrated on this aspect. Kucherov et al. [21] found that cation radicals were formed on adsorption of different aromatic compounds e.g. benzene, anthracene, and p-xylene. It was shown that the concentration of the strong radical forming sites is not lower than that in H-mordenite, with the majority of the aromatic radicals formed being located in the channels of the H-ZSM-5.

Kucherov et al. [22] also looked at Cu\(^{2+}\) in H-ZSM-5 and mordenite, and found that clustering at higher concentrations of the copper ions was not so prominent in H-ZSM-5 as in mordenite. In both zeolites at low concentrations the ions were found to be isolated, and co-ordinately unsaturated. The work of Sendoda and Ono [23] also involved the use of Cu\(^{2+}\) and showed that the adsorption of ammonia, or pyridine caused the copper ions to migrate to sites where the adsorbed molecules could co-ordinate.

**Silica gel**

A positive nitroxide radical (TM-Tempamine\(^{+}\)) was used
by Romanelli et al. [24] on silica gel. The ESR spectrum showed the slow motion in the first water layers near the negatively charged surface, while fast motion was seen in a secondary interaction region, as was noted in some of my results.

Martini [25] used a negative nitroxide spin probe on gels with pore sizes from 40 to 100Å. It was found that the water mobility increased with pore size, in concordance with both my NMR and ESR results. The activation energy for probe motion was increased as the motion increased i.e. as pore size increased therefore water is more like bulk water in the large pores.

Martini et al. [26] used the probe Tempydo⁻ and examined the water on silica gels once more. In samples with a pore size of 40Å it was found that the motion of the probe was anisotropic, while the free motion of the probe down to 235K indicated that even at this temperature not all the water has frozen. The following reasons were put forward to account for the anisotropic motion of the probe molecule. ESR cannot quantitatively distinguish between the three contributions:

1) the spherical symmetry of the solvated molecule is distorted to an ellipsoid due to the different ordering of the water, and to the surface effects that extend well inside the pores.

2) the rate of the interconversion of the probe molecule between its different conformations is reduced as a consequence of the increased mean viscosity.
3) finally the collisions among the probe are not strictly controlled by diffusion due to the presence of a viscosity gradient.

The two phase behaviour of spin probe molecules adsorbed into a water containing solid has also been observed using Tempol in silica glass by Yoshioka [27].

Alumina

A study that was made by McBride [28] may be of use in the study of surfactants on solid particles in ER fluids. The work of McBride involved the use of fatty acid spin probes bonded to alumina by a carboxylic acid group, with the aliphatic chain undergoing wagging motions in a solvent. Evidence for at least two different degrees of motional restriction of the molecules on the alumina was presented.

Section 4.17 Results from Zeolite Samples with Various Water Contents

When fully hydrated all the radicals gave mobile isotropic spectra for all the zeolite samples that were tried. As the water content was reduced the zeolites each show the radical motion beginning to slow.

Results

The probe motion in the zeolites was studied with different hydration contents. The results that were found are shown in an approximate fashion (1) if the motion is described as mobile then the value of $\tau_c$ is less than $10^{-9}$s.
(ii) if the motion is described as slow then this means the value of $\tau_c$ is larger than $10^{-9}$s. In certain cases it was found that in a single spectrum there was a contribution from some radicals in the slow phase, and some in the fast region. The cases which are included in this category are signified by the description "2 compo" and are shown in Table 4.1.

Obviously these results are only very approximate, however a number of points can be made:

1) most zeolites require more than 60% by weight of water to be present in order to show isotropic tumbling of the spin probe in purely the fast motional region.

2) the exception to statement 1) is H-ZSM-5 Si:Al=21 which shows isotropic probe motion even at water contents of 50 to 60%.

3) some zeolites show a phase where as the water content is reduced, before immediately changing from mobile to slow probe motion, there are radicals showing both régimes to be present.

4) the TempTMA* quite definitely is more restricted in its motion in all zeolites, compared with Tempol and Tempyo* which both have very similar mobilities.
<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Hydration</th>
<th>Radical</th>
<th>Motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-A</td>
<td>23%</td>
<td>TempTMA⁺</td>
<td>slow</td>
</tr>
<tr>
<td>Na-A</td>
<td>27%</td>
<td>TempTMA⁺</td>
<td>slow</td>
</tr>
<tr>
<td>Na-A</td>
<td>42%</td>
<td>Tempyo⁻</td>
<td>slow</td>
</tr>
<tr>
<td>Na-A</td>
<td>55%</td>
<td>Tempyo⁻</td>
<td>slow</td>
</tr>
<tr>
<td>Na-X</td>
<td>58%</td>
<td>TempTMA⁺</td>
<td>slow</td>
</tr>
<tr>
<td>Na-X</td>
<td>60%</td>
<td>Tempol</td>
<td>mobile</td>
</tr>
<tr>
<td>Na-Y</td>
<td>60%</td>
<td>TempTMA⁺</td>
<td>slow</td>
</tr>
<tr>
<td>Na-Y</td>
<td>60%</td>
<td>Tempol</td>
<td>mobile</td>
</tr>
<tr>
<td>Dealuminated-Y</td>
<td>80%</td>
<td>TempTMA⁺</td>
<td>slow</td>
</tr>
<tr>
<td>Dealuminated-Y</td>
<td>48%</td>
<td>Tempol</td>
<td>slow</td>
</tr>
<tr>
<td>Dealuminated-Y</td>
<td>95%</td>
<td>Tempol</td>
<td>mobile</td>
</tr>
<tr>
<td>Dealuminated-Y</td>
<td>60%</td>
<td>Tempyo⁻</td>
<td>2 compo</td>
</tr>
<tr>
<td>H-mordenite</td>
<td>63%</td>
<td>TempTMA⁺</td>
<td>2 compo</td>
</tr>
<tr>
<td>H-mordenite</td>
<td>27%</td>
<td>Tempol</td>
<td>2 compo</td>
</tr>
<tr>
<td>H-mordenite</td>
<td>29%</td>
<td>Tempyo⁻</td>
<td>slow</td>
</tr>
<tr>
<td>Na-mordenite</td>
<td>18%</td>
<td>TempTMA⁺</td>
<td>slow</td>
</tr>
<tr>
<td>Na-mordenite</td>
<td>60%</td>
<td>TempTMA⁺</td>
<td>mobile</td>
</tr>
<tr>
<td>Na-mordenite</td>
<td>40%</td>
<td>Tempol</td>
<td>2 compo</td>
</tr>
<tr>
<td>Na-mordenite</td>
<td>100%</td>
<td>Tempyo⁻</td>
<td>mobile</td>
</tr>
<tr>
<td>H-ZSM-5 Si:Al=21</td>
<td>40%</td>
<td>TempTMA⁺</td>
<td>mobile</td>
</tr>
<tr>
<td>H-ZSM-5 Si:Al=21</td>
<td>39%</td>
<td>Tempol</td>
<td>2 compo</td>
</tr>
<tr>
<td>H-ZSM-5 Si:Al=21</td>
<td>53%</td>
<td>Tempol</td>
<td>mobile</td>
</tr>
<tr>
<td>H-ZSM-5 Si:Al=21</td>
<td>16%</td>
<td>Tempyo⁻</td>
<td>2 compo</td>
</tr>
<tr>
<td>H-ZSM-5 Si:Al=21</td>
<td>54%</td>
<td>Tempyo⁻</td>
<td>mobile</td>
</tr>
<tr>
<td>H-ZSM-5 Si:Al=173</td>
<td>20%</td>
<td>TempTMA⁺</td>
<td>2 compo</td>
</tr>
<tr>
<td>H-ZSM-5 Si:Al=173</td>
<td>13%</td>
<td>Tempol</td>
<td>slow</td>
</tr>
</tbody>
</table>
Section 4.18 ESR Results of Zeolites under the application of an electric Field - Theory

The changes that might be expected in the probe motion were totally unknown at the outset of this investigation as to my knowledge no previous work on the influence of electric fields on the motion of spin probes had ever been carried out before. For this reason the probe motion was followed as closely as possible to detect even very small changes in the probe mobility.

For this reason the correlation times were accurately measured from the line heights, and widths in the spectra as explained earlier. The values for the anisotropic values of the \( A \) and \( g \) tensors were taken to be those for Tempone as measured by Griffith et al. [29]. The structure of Tempone is shown below together with the values of the components of \( A \) and \( g \).

\[
\begin{align*}
A_{xx} &= 0.52 \text{ mT} & g_{xx} &= 2.0104 \\
A_{yy} &= 0.52 \text{ mT} & g_{yy} &= 2.0074 \\
A_{zz} &= 3.1 \text{ mT} & g_{zz} &= 2.0026
\end{align*}
\]

Tempone

Fig. 4.6 Structure of Tempone

From equation (7) this gives a value for \( b = 10.807 \text{ mT} \).

Whilst equation (6) gives a value for \( \Delta = -5.54 \times 10^8 \text{ T}^{-1}\text{s}^{-1} \).
Now from equation (1) \( h v = g \mu_B B \), and with a value of
\( \mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1} \) then,
\[
\nu = 2.803 \times 10^{10} \text{(T}^{-1} \text{s}^{-1}) \times B,
\]
if \( B \) is in mT then \( 1 \text{ mT} = \nu = 2.803 \times 10^7 \text{ s}^{-1} \)
This factor can then be used to convert the value by,
\[
\Delta = -5.54 \times 10^8 \text{(T}^{-1} \text{s}^{-1}) / 2.803 \times 10^{10} \text{(T}^{-1} \text{s}^{-1}), (20)
\]
\[
\Delta = -0.0198
\]
Combining equations (10), and (16) for \( B' \) gives the following equation (21),
\[
\frac{\sqrt{3}}{2} \frac{W(\pm 1)}{2} \left[ 1 - \frac{h(\pm 1)}{h(-1)} \right]^{1/2} = \frac{4}{15} \Delta b B \tau_c \times 2.803 \times 10^{-7}
\]
Hence by inserting the value of \( \Delta \) from (20), and using the value of \( b \) already calculated the value of \( \tau_c \) may be calculated from the line height and widths in the spectrum.
All the measurements were taken with a static magnetic field \( B \) of 341 mT.

Section 4.19 Results
1) Firstly the silicone oil was examined on its own with Tempol as the spin probe. There was found to be no change in the motion of the probe with applied fields of up to 7 kV mm\(^{-1}\). So from the start of the investigation we can be sure that the viscosity changes produced in ER fluids are due to the solid particles, with the oil purely acting as a supporting medium.

2) Na-X with Tempol, and 96% H\(_2\)O, a typical set of results are shown in the following table with a typical spectrum.
from an ER fluid in the electric field cell shown in Fig. 4.7.

Fig. 4.7 ESR Spectrum of a Spin Probe in an ER Fluid in the Electric Field Cell eg. Na-mordenite, Tempyo\(^-\), 81% \(\text{H}_2\text{O}\), M.A.=1 G, Pow. = 2 mW, SW = 100 G

Table 4.2

<table>
<thead>
<tr>
<th>Electric Field kVmm(^{-1})</th>
<th>(h(-1))</th>
<th>(h(+1))</th>
<th>(W(+1))(mT)</th>
<th>(\tau_c) ((x10^{-10}) s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>77</td>
<td>61.5</td>
<td>0.327</td>
<td>1.31</td>
</tr>
<tr>
<td>0.201</td>
<td>71</td>
<td>47</td>
<td>0.402</td>
<td>3.26</td>
</tr>
<tr>
<td>0.399</td>
<td>69</td>
<td>42</td>
<td>0.327</td>
<td>3.34</td>
</tr>
<tr>
<td>0.637</td>
<td>63</td>
<td>32</td>
<td>0.377</td>
<td>5.81</td>
</tr>
<tr>
<td>0.710</td>
<td>47</td>
<td>23</td>
<td>0.452</td>
<td>7.50</td>
</tr>
<tr>
<td>0</td>
<td>57</td>
<td>32</td>
<td>0.352</td>
<td>4.37</td>
</tr>
</tbody>
</table>

As can be seen for this sample the motion of the probe appears to slow as the voltage is increased. At the highest electric fields then the largest currents of 100 \(\mu\)A, corresponding to a current density of 3 \(\text{mAcm}^{-2}\) will be...
flowing, this will produce a heating effect which will be in direct opposition to the slowing of the radical by the electric field. This fact must be remembered for all these samples in this part of the study as all have a significant current flow at higher voltages. One important point to note is that after removal of the electric field the motion of the radical only partially returned to its initial value, which could be due to a retention of the polarisation after removal of the electric field.

3) For Na-X with Tempol and 110% methanol the data are shown in Table 4.3 and it can be seen that again as the electric field is increased there is a decrease in the probe motion. The reduction in the probe motion is less than that seen for water which agrees with the static yield test results on samples containing methanol rather than water, which were found to be less effective as ER fluids. Again in this sample at higher voltages the current heating also affects the results. Once more there is no recovery when the field is removed in this case.

**Table 4.3**

<table>
<thead>
<tr>
<th>Electric Field kV mm⁻¹</th>
<th>h(-1)</th>
<th>h(+1)</th>
<th>W(+1)(mT)</th>
<th>( \tau_c \times 10^{-10}\text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>123</td>
<td>86</td>
<td>0.251</td>
<td>1.72</td>
</tr>
<tr>
<td>0.330</td>
<td>125</td>
<td>89</td>
<td>0.276</td>
<td>1.77</td>
</tr>
<tr>
<td>0.635</td>
<td>135</td>
<td>90</td>
<td>0.264</td>
<td>2.10</td>
</tr>
<tr>
<td>0.909</td>
<td>150</td>
<td>101</td>
<td>0.226</td>
<td>1.74</td>
</tr>
<tr>
<td>1.122</td>
<td>153</td>
<td>95</td>
<td>0.276</td>
<td>2.68</td>
</tr>
<tr>
<td>1.234</td>
<td>126</td>
<td>78</td>
<td>0.251</td>
<td>2.46</td>
</tr>
<tr>
<td>0</td>
<td>161</td>
<td>96</td>
<td>0.264</td>
<td>2.84</td>
</tr>
</tbody>
</table>
3) For Na-Y with Tempol and 96% H₂O again showed a similar behaviour to Na-X with electric fields as might be expected since their structures are very similar. A typical set of data is shown in Table 4.4.

Table 4.4

<table>
<thead>
<tr>
<th>Electric Field kVmm⁻¹</th>
<th>h(-1)</th>
<th>h(+1)</th>
<th>W(+1)(mT)</th>
<th>τ_c (×10⁻¹⁰s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40</td>
<td>23</td>
<td>0.377</td>
<td>4.43</td>
</tr>
<tr>
<td>0.150</td>
<td>33</td>
<td>14</td>
<td>0.389</td>
<td>8.39</td>
</tr>
<tr>
<td>0.467</td>
<td>27</td>
<td>10</td>
<td>0.402</td>
<td>10.86</td>
</tr>
<tr>
<td>0.740</td>
<td>25.5</td>
<td>9</td>
<td>0.377</td>
<td>10.98</td>
</tr>
<tr>
<td>0.802</td>
<td>22</td>
<td>9</td>
<td>0.402</td>
<td>9.23</td>
</tr>
<tr>
<td>1.077</td>
<td>23</td>
<td>8</td>
<td>0.352</td>
<td>10.49</td>
</tr>
<tr>
<td>0</td>
<td>16</td>
<td>8</td>
<td>0.327</td>
<td>5.20</td>
</tr>
</tbody>
</table>

For this sample the current heating begins to increase the probe motion at higher voltages, but otherwise the magnitude of the change in correlation time is very similar to that seen for Na-X.

4) A sample of Na-Y, with Tempol, and 99% methanol showed very little change in correlation time with the increase of voltage. This was probably due to the fact that the very small changes in the case of Na-X, and methanol were obscured by the errors inherent in the experiment as well as heating from the current.

5) The dispersion of Na-Y with Tempol, and 110% formamide
showed a very small change in the correlation time when the electric field was applied. This is shown in Table 4.5.

Table 4.5

<table>
<thead>
<tr>
<th>Electric Field kVmm⁻¹</th>
<th>h(-1)</th>
<th>h(+1)</th>
<th>W(+1)(mT)</th>
<th>(\tau_c \times 10^{-11}s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>120</td>
<td>109</td>
<td>0.176</td>
<td>2.82</td>
</tr>
<tr>
<td>0.322</td>
<td>121</td>
<td>108</td>
<td>0.188</td>
<td>3.60</td>
</tr>
<tr>
<td>0.649</td>
<td>121</td>
<td>106.5</td>
<td>0.201</td>
<td>4.35</td>
</tr>
<tr>
<td>0.979</td>
<td>115.5</td>
<td>104.5</td>
<td>0.188</td>
<td>3.15</td>
</tr>
<tr>
<td>1.308</td>
<td>112</td>
<td>102</td>
<td>0.188</td>
<td>2.93</td>
</tr>
<tr>
<td>1.643</td>
<td>108</td>
<td>96</td>
<td>0.188</td>
<td>3.74</td>
</tr>
<tr>
<td>1.974</td>
<td>107</td>
<td>92</td>
<td>0.188</td>
<td>4.87</td>
</tr>
<tr>
<td>0</td>
<td>118</td>
<td>106</td>
<td>0.201</td>
<td>3.62</td>
</tr>
</tbody>
</table>

Whether or not the effect in this sample is real is open to debate as this sample has again a much weaker ER effect than the same water containing sample.

6) The samples of H-ZSM-5 with Tempol, and 90% H₂O also showed motional changes by the probe molecule with the electric field as was expected as this sample also shows an ER effect. A typical data set for this sample is shown in Table 4.6.

In this case there is an over recovery by the sample after the removal of the electric field. Once more the current causes heating at the higher voltages which increases the probe motion. This sample has a larger effect on the probe motion with the applied electric field than the faujasite containing methanol samples, but not as large an
Table 4.6

<table>
<thead>
<tr>
<th>Electric Field kVmm^-1</th>
<th>h(-1)</th>
<th>h(+1)</th>
<th>W(+1)(mT)</th>
<th>(\tau_c(\times 10^{-10}s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>115</td>
<td>86</td>
<td>0.352</td>
<td>1.89</td>
</tr>
<tr>
<td>0.253</td>
<td>117</td>
<td>74.5</td>
<td>0.327</td>
<td>2.97</td>
</tr>
<tr>
<td>0.52</td>
<td>96</td>
<td>67</td>
<td>0.359</td>
<td>2.47</td>
</tr>
<tr>
<td>0.89</td>
<td>90</td>
<td>62.5</td>
<td>0.364</td>
<td>2.55</td>
</tr>
<tr>
<td>1.18</td>
<td>89</td>
<td>55</td>
<td>0.364</td>
<td>3.58</td>
</tr>
<tr>
<td>1.53</td>
<td>87</td>
<td>55</td>
<td>0.377</td>
<td>3.49</td>
</tr>
<tr>
<td>0</td>
<td>149</td>
<td>121</td>
<td>0.327</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Effect as the water containing faujasites.

7) The sample of H-ZSM-5, with Tempol, and 96% methanol showed very little change with the electric field very much as in the case of Na-Y with methanol. The H-ZSM-5 with methanol showed a much weaker ER effect on the static yield rig than its hydrated counterpart.

8) A sample of Na-mordenite with Tempol and 81% \(H_2O\) which proves effective as an ER fluid also showed a change in the correlation time of Tempol with the application of the electric field as shown in Table 4.7.

This sample has an ER effect similar to that of the faujasites so it is not too surprising that its ESR probe mobility should also be very similar to the faujasites. In this particular case there is a full recovery of the probe mobility after removal of the electric field.
Table 4.7

<table>
<thead>
<tr>
<th>Electric Field kVmm(^{-1})</th>
<th>h(-1)</th>
<th>h(+1)</th>
<th>W(+1)(mT)</th>
<th>(\tau_c\times10^{-11}s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>116</td>
<td>102</td>
<td>0.201</td>
<td>4.39</td>
</tr>
<tr>
<td>0.64</td>
<td>84</td>
<td>66</td>
<td>0.201</td>
<td>8.71</td>
</tr>
<tr>
<td>1.333</td>
<td>59</td>
<td>47</td>
<td>0.201</td>
<td>8.16</td>
</tr>
<tr>
<td>0</td>
<td>57</td>
<td>50</td>
<td>0.201</td>
<td>4.47</td>
</tr>
</tbody>
</table>

9) The samples of dealuminated-Y with all the different probe molecules showed no changes which could be detected in the radical mobilities with the application of an electric field. This is not surprising as this sample also showed a very poor ER effect when mechanically tested.

10) One interesting finding was that none of the samples containing charged spin probes shows any effect in the presence of an electric field.

Section 4.20 Summary

1) The onset of the ER effect seems to be accompanied by a decrease in the motion of the zeolitic water i.e. an apparent increase in the viscosity of the zeolitic water.

2) The faujasite zeolites show the largest changes in the motion of the spin probes, with Na-mordenite also having a similar behaviour.

3) The H-ZSM-5 has a reduced slowing of the probe motion but this may be also related to the fact that, in this zeolite
the cavities of the framework are smaller than those of the faujasites.

4) All the samples tested showed a smaller change in the motion of methanol impregnated zeolites than with their hydrated analogues. This was also confirmed by their weaker effect as ER fluids.

5) ESR can be used as a crude method of rating ER solids.

Section 4.21 Saturation Transfer ESR (STESR)

Introduction

In "conventional" ESR spectroscopy the normal method of recording the spectrum is to vary the magnetic field in a continuous passage, and monitor the first harmonic of the absorption spectrum, which is then recorded in the form of the first derivative as explained earlier. However, this type of spectrum ceases to allow measurements of tumbling of the radical once the correlation time exceeds $10^{-7}$s.

As defined earlier the fast tumbling region is given by correlation times from $10^{-12}$ to $10^{-9}$s, and the theoretical description of the treatment of data in this time domain is also given. The $10^{-9}$ to $10^{-7}$s range is known as the slow tumbling region, but the interpretation of the data is still under investigation by a number of workers, and no simple treatment of the data is available.

For correlation times larger than $10^{-7}$s, known as the very slow tumbling region, it was necessary to develop a different type of ESR spectroscopy which was achieved by Thomas et al. [30], which is sensitive to correlation times.
in the range $10^{-7}$ to $10^{-3}$s. This type of ESR is known as Saturation Transfer ESR (STESR) because the response of the signal is dependent on diffusion of saturation between different portions of the spectrum. The subject has been reviewed by both Hyde and Dalton [31], and by Marsh [32].

Originally the experiment was developed to follow the motions of large biological molecules, labelled with nitroxide groups. Examples of the work in this area are included in the articles of Hyde and Thomas [33], and Esmann et al. [34], with another facet of this technique demonstrated by Marsh [35] in the study of lipids in gel phase bilayers.

In my work it was attempted to try to use (STESR) to look at the motion of the spin probes in rather restricted environments in solids. Even though the probes are relatively small molecules of one order of magnitude smaller than biological molecules, their environment is such as to cause them to tumble relatively slowly.

Section 4.22 Theory of the technique

The diffusion of nitroxides is largely governed by the rotational modulation of the Zeeman and hyperfine interactions. If the diffusion of saturation in the spectrum takes place at a similar rate to the loss of saturation from the spin system then there is effective transfer of saturation. The diffusion process causes a reduction in the number of spins on resonance, and off resonance spins become more saturated i.e. the rate of
saturation transfer is zero at the turning points, while this rate reaches a maximum at intermediate positions.

The sensitivity of the saturation transfer spectrum to changes in the correlation time ($\tau_c$) is at its highest when $\tau_c$ is approximately equal to $1/\nu$, where $\nu$ is the frequency of modulation of the magnetic field. The phase sensitive detector then selects the signal in the range of the highest sensitivity. All relaxation processes, not just rotational diffusion, can be studied using saturation transfer.

Section 4.23 Experimental

There are two methods which show greatest sensitivity to STESR, one is measured in the dispersion, and the other in the absorption mode. Since the spectrometer measured absorption signals, the experiment of choice involved the use of measurement of the absorption detected $90^\circ$ out of phase with respect to the second harmonic of the modulation. The transverse component of the magnetisation perpendicular to the microwave field is then detected. The magnetic field is modulated at 50 kHz, half the frequency of the phase sensitive detection.

The standard protocol for STESR has been documented by Hemminga et al. [36], but a brief description of the method followed in this work is outlined below.

First of all the signal was determined as out of phase by measurement of the null signal at low power, as follows.

1) The microwave power was reduced from the normal 1 mW for conventional ESR to 0.1 mW.
2) The modulation amplitude of the magnetic field was increased to 0.32 mT, from the normal 0.1 mT.
3) The frequency of the modulation of the magnetic field was changed from the normal 100 kHz to 50 kHz.
4) The detector was changed from that of the first derivative to that of the second derivative.
5) The phase of the detector was set 90° away from the phase of the field modulation.
6) Under these conditions the exact phase of the detector was then accurately adjusted to obtain a null signal of less than 1% intensity.
7) The power was then increased to 63 mW to record the STESR spectra.

Section 4.24 Analysis of Results

The original STESR work in reference [30], defined the parameters shown in Fig. 4.8 as variants to be monitored to follow the changes in the spectra.

Correlation times were obtained by carrying out experiments on model systems, and Horvath and Marsh [37], showed how each ratio was dependent on \( \tau_c \) by the simple polynomial of the form,

\[
f(x) = \sum_{i=0}^{4} a_i x^i \quad \text{or} \quad f(x) = \sum_{i=0}^{4} a_i (\log_{10} x)^i .
\]

In this case \( f(x) = \tau_c \), and \( x \) is the value of the relevant ratio, and \( a \) is the unknown coefficient. In reference [37] the coefficients were shown for spin labelled haemoglobin in glycerol-water solutions of different viscosities. These
coefficients should also be applicable for isotropic rotation in other systems, Marsh [38], and this is how the data shown later were analysed.

The values of the coefficients in [37] used to treat my data are shown below.

Table 4.8

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Fitted Range</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L''/L$</td>
<td>0.1 to 2</td>
<td>-7.529</td>
<td>10.94</td>
<td>-13.99</td>
<td>7.68</td>
<td>-1.36</td>
</tr>
<tr>
<td>$C'/C$</td>
<td>-1 to 1</td>
<td>-5.333</td>
<td>1.032</td>
<td>-1.269</td>
<td>1.387</td>
<td>1.57</td>
</tr>
<tr>
<td>$H''/H$</td>
<td>0.1 to 2</td>
<td>-8.406</td>
<td>15.68</td>
<td>-20.26</td>
<td>10.99</td>
<td>-2.012</td>
</tr>
</tbody>
</table>

The correlation time was assumed to obey an Arrhenius
relationship of the kind,

$$\tau = \tau_{298} \exp\left[\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{298}\right)\right],$$  \hspace{1cm} (23)

therefore

$$\log_e \tau = \log_e \tau_{298} - \frac{E_A}{R} \left(\frac{1}{T} - \frac{1}{298}\right),$$  \hspace{1cm} (24)

The value of $\tau$ was calculated at each temperature using STESR data with the coefficients given by Horvath and Marsh [37]. The best fit of $\log_e \tau$ versus $1/T$ was then obtained to find the values of $\tau_{298}$ and $E_A$. An example of the type of result obtained is shown in Fig. 4.9.

The Debye [10] equation for Brownian rotational diffusion shown in equation (18), takes no account of any additional external forces due to effects such as hydrogen bonds, or electrostatic forces, which would increase the effective radius for the probe molecule.

Section 4.25 Results

The spin probe molecules used in this study are the same as those used previously in my earlier work on zeolites. This time it was decided to test initially these radicals in a pure liquid to check the performance under the conditions of the Saturation Transfer experiment. The radicals were therefore dissolved in a suitable liquid, namely glycerol.

It was found from my results that in the glycerol samples, the three line height ratios each gave similar values for $\tau_{298}$ and the activation energies, but in the
Fig. 4.9 Fit from STESR Data of $\log \tau$ vs $1/\text{Temp}$, eg. H-ZSM-5, TempTMA* and 11% H$_2$O zeolite samples the value of these parameters were different when obtained using the high and low fields, c.f. that at centre field. The centre field ratio corresponds to faster motions whilst the outer field ratios are representative of what would seem to be slower motions.
This phenomenon of anisotropic rotational diffusion has been examined using STESR by Robinson and Dalton [39]. In this work it was explained how the parameters $L^\alpha$, $C^\beta$, and $H^\gamma$ could be described by two rotational correlation times $\tau_\parallel$ and $\tau_\perp$ for axially symmetric tensors, and also by other correlation times for systems characterised by non-axially symmetric ones. Nitroxide spin labels are said to come under the non-axially symmetric class. The $H^\gamma$ parameter was thought to be indistinguishable from that of isotropic diffusion, whilst $C^\beta$ is sensitive to the anisotropic diffusion model provided that a static, unique, relationship exists between the magnetic, and diffusion tensors. The differences between $L^\alpha$ and $H^\gamma$ may only be slight, but large differences from $C^\beta$ may result. This suggests that the different parameters are a direct consequence of different molecular motions.

For systems undergoing anisotropic diffusion, as the derivative of the spectrum increases so the computer time needed to analyse, and simulate them becomes prohibitive. Hence, in reference [39] only first derivative dispersion spectra detected $90^\circ$ out of phase with respect to the Zeeman modulation could be simulated. It was found that the $L^\alpha$ and $H^\gamma$ monitor the magnetic tensor elements, with $C^\beta$ more sensitive to the minor ones. When there are a mixture of rotational motions the spectra tend to reflect preferential weighting of the faster modes. It was found that the anisotropic spectra cannot simply be reproduced by the summation of isotropic spectra.
An example of the type of results for the anisotropic motion of a spin labelled molecule is that by Marsh [40], who studied spin labelled haemoglobin in the gel phase of the phospholipid DPPC. The calibration of the line height ratios was that in the original paper by Thomas et al. [30]. The values of $\tau_c$ at various temperatures are shown in the following table.

Table 4.9 $\tau_c$ of haemoglobin in DPPC

<table>
<thead>
<tr>
<th>Temperature</th>
<th>12°C</th>
<th>25°C</th>
<th>30°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>$L''/L$</td>
<td>$H''/H$</td>
<td>$C'/C$</td>
<td>$H''/H$</td>
</tr>
<tr>
<td>$L''/L$</td>
<td>$4.0 \times 10^{-4}$</td>
<td>$2.0 \times 10^{-4}$</td>
<td>$0.8 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>$H''/H$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$2.0 \times 10^{-4}$</td>
<td>$0.8 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>$C'/C$</td>
<td>$0.8 \times 10^{-4}$</td>
<td>$5.0 \times 10^{-6}$</td>
<td>$0.9 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

In the paper by Fajer and Marsh [41], it was stated that none of the line height ratios are absolutely diagnostic of either axial, or off axial motion, although certain regions of the spectra do have a quite definite preference. The $C'/C$ ratio is relatively insensitive to $\tau_c$ of larger than $3 \times 10^{-5}$s. This means that if the off-axial $\tau_c$ from $H''/H$ is of this magnitude, or larger, then $C'/C$ should reflect purely axial rotation. It was also noted that the nitroxide as well as performing a slow rotation may also execute a fast wobble relative to the rotation axis.
Section 4.26 Spin Probes in Glycerol

The accuracy of the measurements was not as good as hoped for due to the scatter in the data, but the correlation times quoted are certainly accurate well within an order of magnitude. The error in the activation energies is less pronounced, however the results from glycerol are shown in the following table 4.10. A typical set of STESR spectra from a spin probe in glycerol are shown in Fig. 4.10.

An interesting feature from the results is the calculated value of the correlation time of the probes in glycerol at room temperature. According to the radii of the probe molecules calculated by Martini et al. [12], of approximately 3.5 Å, and the viscosity of glycerol at 25°C of 0.954 kg m⁻¹ s⁻¹, and using the Debye equation (18) the value of $\tau_c$ is 40 ns.

Also from the temperature variation of the viscosity of glycerol shown in [42] the activation energy was calculated by fitting $\log \eta / T$ versus $1 / T$ which has a gradient equal to $E_A / R$. The viscosity data used were those between 273 and 241 K as this was approximately the range of the STESR measurements. The value of $E_A$ calculated was 40.6 ± 3.5 kJ mol⁻¹. This agrees reasonably well with the activation energy calculated by other methods e.g. by Forster and Gillies [43] who used glycerol diluted with water.

If the error on a particular set of line height ratios was too large to be of any use then this is signified as having data that is too scattered in the following table.
Fig. 4.10 Typical Variation of STESR Spectra for a Spin Probe in Glycerol

Temperature

293 K

258 K

243 K

233.3 K

230.3 K
The above table may be summarised by the following average values of correlation times and activation energies, shown in Table 4.11.

From these results it is possible to see that the values for both the correlation time and the activation
energy are in the same region as the calculated values. The

<table>
<thead>
<tr>
<th>Probe</th>
<th>$\tau_{298},(\text{ns})$</th>
<th>$E_A,(\text{kJ mol}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tempol</td>
<td>12</td>
<td>65</td>
</tr>
<tr>
<td>TempTMA$^+$</td>
<td>6</td>
<td>80</td>
</tr>
<tr>
<td>Tempyo$^-$</td>
<td>40</td>
<td>60</td>
</tr>
</tbody>
</table>

fact that the activation energies for all the radicals is larger than that calculated could be due to hydrogen bonding between the glycerol and the radicals which of course all contain nitroxide groups, as well as a hydroxide group in the case of Tempol, and a carboxyl group in the case of Tempyo$^-$. 

Section 4.27 Spin Probes in Zeolites

The zeolite samples were prepared as explained earlier in the section on fast tumbling ESR, but in this case they were dehydrated to a greater extent in order that the rate of tumbling decreased sufficiently to be observed by STESR. It was not possible to accurately predict the water content that would produce the correct probe motion for STESR, as a result of which the production of the samples was a case of trial and error as no work has ever been tried using this type of experiment on samples of this kind.

A summary of the STESR results determined from various zeolite samples is shown in Table 4.12. It was found not to be possible in all cases to calculate the value of $\tau_{298}$ and $E_A$ for every line height ratio as the error on the results
<table>
<thead>
<tr>
<th>Zeolite and Spin Probe</th>
<th>$\tau_{298}$ ($\mu$s)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Error)</td>
<td>(Error)</td>
</tr>
<tr>
<td>Dealum-Y, Tempol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>96% H$_2$O c'/c</td>
<td>0.75</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>(0.22)</td>
<td>(1.8)</td>
</tr>
<tr>
<td>48% H$_2$O c'/c</td>
<td>3.84</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>(0.15)</td>
<td>(0.5)</td>
</tr>
<tr>
<td>Y, TempTMA* 48% H$_2$O c'/c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>298K to 271K</td>
<td>0.04</td>
<td>127.2</td>
</tr>
<tr>
<td></td>
<td>(0.01)</td>
<td>(10.0)</td>
</tr>
<tr>
<td>271K to 232K</td>
<td>5.08</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>(0.48)</td>
<td>(1.2)</td>
</tr>
<tr>
<td>X, Tempol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24% H$_2$O c'/c</td>
<td>1.40</td>
<td>22.1</td>
</tr>
<tr>
<td></td>
<td>(0.30)</td>
<td>(3.14)</td>
</tr>
<tr>
<td>H-ZSM-5, Tempyo$^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13% H$_2$O c'/c</td>
<td>57.71</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>(16.39)</td>
<td>(4.2)</td>
</tr>
<tr>
<td>13% H$_2$O L''/L</td>
<td>2.65</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td>(0.53)</td>
<td>(3.8)</td>
</tr>
<tr>
<td>H-ZSM-5, TempTMA$^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11% H$_2$O c'/c</td>
<td>3.65</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>(0.15)</td>
<td>(0.44)</td>
</tr>
<tr>
<td>11% H$_2$O L''/L</td>
<td>29.53</td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td>(2.33)</td>
<td>(0.9)</td>
</tr>
<tr>
<td>11% H$_2$O H''/H</td>
<td>59.47</td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td>(4.57)</td>
<td>(1.5)</td>
</tr>
</tbody>
</table>
was too great.

Section 4.28 Summary

1) In all cases the values of the $\tau_{298}$ are much larger than those of the water in the zeolite cavities as determined from NMR relaxation measurements. This is a reflection of both the size of the radical c.f. water molecules, and also the fact that the charged radicals will also be subjected to electrostatic forces from either the zeolite framework, or the cations. As stated earlier, no previous work has ever been performed on zeolites using STESR, but in the conventional ESR study by Martini et al. [12] on fully hydrated faujasite zeolites the value of $\tau_{298}$ was found to be approximately 20 ps for all the spin probes used in this study. This value is only 5 ps slower than that for the probes in bulk water, so obviously the effect of dehydrating the zeolites is conclusively seen to significantly reduce the water mobility.

2) In all the zeolites studied the ratio of the high field lines was found the most inaccurate. However, for the case where it was possible to fit that ratio, together with the samples where both the centre and low field ratios could also be fitted, it was possible to see that the centre field ratio measured a faster motional regime than either the low, or high field ratios. This is good evidence for the anisotropic motion of the probe molecule in the cavity of the zeolites as detailed earlier, and has been shown in reference [39].
3) In the case of dealuminated-Y with different water contents it was possible to see that as the water content decreased then the motion of the probe slowed, from the value of the correlation time. Also the activation energy increased with the water content, which could be due to a greater amount of hydrogen bonding as occurs in bulk water.

4) The fact that a lot of the values of activation energy are close to that for bulk water i.e. around 20 kJmol⁻¹ is certainly not due to a large amount of bulk water behaviour by the zeolitic water. The reason is probably due to the extra forces present in the cavities of the zeolite which raise the value of the activation energy.

5) The behaviour of the sample of Y with TempTMA⁺ and 48% H₂O seen in Fig. 4.11 was unique in that at low temperatures the activation energy changed slowly, hence with a low activation energy. At higher temperatures above 273K it was found that the correlation time shortened dramatically, which produced a huge increase in the activation energy. This is a difficult observation to reconcile with the fact that the water in the zeolite definitely does not freeze at 273K.

A similar dependence of correlation time with temperature has been seen by Fajer and Marsh [41] who studied phospholipid spin labels in lipid bilayers. In the lipid bilayer there is a phase transition from an ordered fluid, to a disordered one as the temperature is increased. This is reflected by a slow increase in the correlation time at low temperatures in the ordered region, with an increase
in correlation time after the phase change as the temperature is further increased. This was attributed to the onset of rapid long axis rotation of the spin labelled lipid molecules, since this rotation would modulate the anisotropy of the g tensor in the x-y plane leaving all other tensor values unchanged. This would account for the fact then that only saturation transfer occurs in the central region of the spectrum. This indicates a high degree of discrimination between axial and off-axial
motion. If in the case of [41] there had been motion of the long axis itself then this would have modulated all the spectral anisotropies, giving rise to saturation transfer in the full spectrum.

The large change in the $C/c$ ratio was also checked to make sure that it was due to a change in the correlation time and not to a change in the spin-lattice relaxation time $T_1$, which would also alter the line height ratio. This was done by measuring the amplitude of the $90^\circ$ out-of-phase signal and comparing that of the in-phase signal at a microwave power of 63 mW. This ratio has been shown by Thomas et al. in [30, 44] to be directly proportional to $(\omega T_1)$ where $\omega$ is the modulation frequency of the magnetic field and can be used for detecting changes in $T_1$. In my sample of zeolite Y, with TempTMA$^+$ and 48% H$_2$O, the out-of-phase to in-phase ratio were approximately constant at 11% which, according to the work in [30] is in the range which would have very little effect on the spectral parameters. Hence, it is possible to be fairly certain that the large change in the central line height ratio in my sample around 273K is due to the commencement of a different motional process by the probe molecule.

Section 4.29 STESR in the presence of an Electric Field

It was found only to be possible to perform STESR with one of the zeolites as the reduced sensitivity using the electric field cell (described in the NMR chapter) proved to be too great to observe the spectra accurately enough in
most of my samples. The one sample that did have a strong
enough signal to be accurately observable using the electric
field cell was that of H-ZSM-5, with Tempyo\textsuperscript{-}, and 17\% H\textsubscript{2}O. The results obtained with this sample are shown in Table 4.13.

Table 4.13

<table>
<thead>
<tr>
<th>Electric Field kVmm\textsuperscript{-1}</th>
<th>$\tau_\text{c from } C'/C \times 10^{-8}$ s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.75</td>
</tr>
<tr>
<td>0.33</td>
<td>2.83</td>
</tr>
<tr>
<td>0.67</td>
<td>2.95</td>
</tr>
<tr>
<td>1.33</td>
<td>3.13</td>
</tr>
<tr>
<td>2</td>
<td>3.01</td>
</tr>
<tr>
<td>0</td>
<td>3.01</td>
</tr>
<tr>
<td>2</td>
<td>3.01</td>
</tr>
<tr>
<td>3</td>
<td>3.13</td>
</tr>
<tr>
<td>left for one hour</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.75</td>
</tr>
<tr>
<td>3</td>
<td>2.83</td>
</tr>
<tr>
<td>0</td>
<td>2.75</td>
</tr>
</tbody>
</table>

It must be borne in mind that these are just preliminary
measurements, but there does seem to be the indication that
it may be possible to measure motional changes inside
zeolite particles using STESR in the presence of an electric
field. The changes in the correlation time are smaller than
those seen using conventional ESR, but in this case the
water content of the zeolite is much reduced, so the probe
motion is much slower to begin with. A typical STESR spectrum from a zeolite sample in the electric field cell is shown in Fig. 4.12.

Further experiments on this type of system will need to be carried out to ensure that these initial observations are both real, and reproducible, as the correlation times calculated are at the extreme of the region covered by the STESR experiment.
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CHAPTER 5 CONCLUSIONS

Section 5.1. Structure of Chapter

This chapter will firstly consider the conclusions that have been drawn from the various techniques used in this study, which are directly relevant to the CI effect. Then a review of the various models for the CI effect will be made with the aim of identifying the essential features from our results that are inherent in the EP mechanism.

Section 5.2. Conclusions from the EP Yield Rig

1) The smaller the particle size of the solid, the larger is the EP effect. For the lithium polymethacrylate,

2) There does not appear to be much correlation between the current and the yield of the samples, with a linear relationship probably giving the closest fit, but this is still in doubt.

3) The activating fluids which give the largest EP effect are those with a high dielectric constant such as water and formamide, which are better than aurinol.

4) The most conductive solutions give the best EP effect such as LiI and NaI, which were found to be better than those with lower conductivities such as MgO. This was in agreement with the work by Marshall [1] who also found that the CI effect depends on the presence of ions, since these systems have a polarisation effect due to ionic migration, which will be discussed in more detail later.

5) Protonated resins, in particular those with quite a low number of cations i.e. silicate resins e.g. mordenite and ZSM-5, have a low electrical conductivity and a larger EP
Section 5.1 Structure of Chapter

This chapter will firstly consider the conclusions that have been drawn from the various techniques used in this study, which are directly relevant to the ER effect. Then a review of the various models for the ER effect will be made with the aim of identifying the essential features from my results that are inherent in the ER mechanism.

Section 5.2 Conclusions from Static Yield Rig

1) The smaller the particle size of the solid then the larger is the ER effect for the lithium polymethacrylate.

2) There does not appear to be much correlation between the current and the yield stress in the majority of the samples, with a linear relationship probably giving the closest fit, but this is still in doubt.

3) The activating fluids which give the largest ER effect are those with a high dielectric constant such as water and formamide, which are better than methanol.

4) The most conductive cations give the best ER effect such as Li\(^+\), and Na\(^+\), which were found to be better than those ions with lower conductivities such as Mg\(^{2+}\). This was in agreement with the work by Marshall [1] who also found that the ER effect depends on the presence of ions, since these systems have a polarisation mechanism due to ionic migration, which will be discussed in more detail later.

5) Protonated zeolites, in particular those with quite a low number of cations i.e. siliceous zeolites eg. mordenite, and ZSM-5, have a low electrical conductivity, and a larger ER
6) For zeolites with no cations, i.e., those with very little aluminium in the framework, the ER effect is much reduced.

7) For the polymer, low water contents lower the ER effect and the current. For the zeolite samples if the water content is too high then the ER effect is reduced due to internal heating.

Section 5.3 Conclusions from the Electroviscometer

1) Response time of the ER effect was shown to be in the millisecond time scale.

2) The shear stress is roughly proportional to the \((\text{Electric field})^2\) initially, and then becomes linear. This is strong evidence for the presence of mobile ions, since if these were not present the polarisation would be proportional to the square of the electric field the whole time.

3) The starting value of the electric field for a significant increase in the apparent viscosity increases as the temperature is lowered. Those samples with low conductivity need particularly large electric fields to begin the effect. Whether there is a lower limit of the electric field for the onset of the ER effect had received very little attention previously.

4) The effective viscosity was found to be proportional to the square of the distance between the particles for the polymer based fluids, in agreement with the pioneering work of Klass and Martinek [2] who used this relationship as
evidence of the double layer mechanism for the effect.

5) All the fluids were found to be shear thinning at and above ambient temperatures. It has been shown by Hoffman [3] that in suspensions with a strong yield stress that exhibit shear thinning there is a three-dimensional lattice structure formed by electrostatic repulsion forces between particles in quiescent colloidal dispersions. The effect of shear on this structure is to order the particles into a lamellar structure, with the layers parallel to the planes of constant shear. Increasing the shear rate brought a deterioration of this two dimensional packing first into lines of spheres followed by a total loss of order. The shear stress versus shear rate characteristics are dependent on several factors including solid concentration, shape and dimension, as well as temperature and electrical charge which combined together lead to a huge amount of theoretical possibilities.

6) The ER effect in the majority of samples decreased above and also slightly below, room temperature. One theory that has been proposed in the past to account for the reduction in the yield stress on increasing the temperature was that water was forced to contact sites between the particles by the increased temperature. The water will have increased rotational, and diffusional mobility at high temperatures, but whether this will force the water to contact sites is still open to debate. Of course increased temperatures will increase the Brownian motion of the ions in the water, and decrease the value of the dielectric constant, which leads
to an increase in the current, and a lowering of the ER effect respectively. The work of Deinega et al. [4] also looked at temperature effects on ER fluids in the range 0 to 45°C, and found a maximum effect in the range of 20 to 30°C as I found with my fluids.

7) The small number of surfactants that were tested were found not to affect the performance or the conductivity of the zeolite samples of low conductivity. For the polymer fluids there was a tremendous increase in conduction with the same surfactants, which resulted in a much reduced ER effect due to heating by the current.

Section 5.4 Conclusions from NMR Experiments

1) The motion of the protons in the protonated zeolites is much slower than that of the water, while all zeolites whether protonated or not contain hydroxyl groups formed during the dehydration process.

2) The water motion is significantly faster in zeolite ZSM-5 than in faujasite zeolites, with zeolite A having the slowest water motion. This trend also follows a decrease in the ER effect.

3) The water motion in mordenite zeolite was not appreciably affected by exchanging Na⁺ for a less conductive cation such as Mg²⁺, but the ER effect was reduced.

4) The mobility of the Li⁺ ion is greatest in ZSM-5, followed by mordenite and then the faujasites, with zeolite A having the least ion mobility.

5) The water mobility in the polymer samples is much reduced
in comparison with that in any of the zeolite samples, whilst the ER effect of the polymer is larger than that observed for some of the zeolites.

6) The mobility of the Li\(^+\) ions in the polymer is on a par with that in zeolite A.

7) The polymer was found to lose water from the solid into the supporting oil which might lead one to expect that this would lead to some level of bulk ionic conductance, but this was not observed. None of the ions were found in the supporting oil as detected by NMR, whilst in the zeolite samples, neither water nor lithium cations were detectable in the silicone oil.

8) After electrical breakdown the zeolite recovers the initial mobility of both the water molecules, and the lithium ions, with the ER effect unchanged. The polymer meanwhile has much more mobile water molecules after breakdown, while the lithium ions also remain slightly more mobile. The ER effect of the polymer based fluids are reduced after the fluid has broken down.

Section 5.5 Conclusions from ESR Experiments

1) The probe molecules showed that there are different environments in the zeolites by using different water contents.

2) In an applied electric field, highly hydrated zeolites showed appreciable slowing of the water motion for those with a large ER effect. The only zeolites that did not fit the trend of reduced water mobility for a large ER effect
were the protonated zeolites which only showed a small reduction in water motion not in line with their ER effect.

3) With the use of STESR it may be tentatively suggested that there is also slowing of the small amount of water present in partially dehydrated zeolites.

Section 5.6 Viscoelastic Properties

The interparticle forces of a dispersion increase the resistance to both flow and deformation which, if the diffusion time of the particles is in the same region of the experimental time scale, can give a viscoelastic response.

This property of the LiPMA based fluids was investigated by Brooks et al. [5] who found a maximum in the storage modulus as the electric field ves increased. The voltage at which the maximum occurred moved to higher voltages as the volume fraction of the solid particles decreased. A theoretical model for the results was suggested in which the number of nearest neighbours in contact with one particle increases from 3 for volume fractions in the range 9 to 14%, up to 4 for volume fractions in the range 18 to 22%. These were the number of nearest neighbours which gave the best fit but the model was still not too convincing. The particle flexibility determined by its elasticity can affect the dynamics of the fluid by increasing the length of the particle, which should increase the response time of the fluid to the application of the electric field.
Section 5.7 Particle Size and Structure Formation

As I have shown in the results from the polymer samples it appears that to obtain a larger ER effect it is preferable to have a solid content made from smaller particles. An upper limit for particle size has been specified by Stangroom [6] which is the particle maximum size is one tenth of the electrode spacing. Some lower level for the particle size must also exist as Brownian motion will begin at a certain level, which will overcome the ER effect. The use of irregular shaped particles and sharp edges will increase the zero field viscosity of a dispersion, as will the use of charged particles due to the electroviscous effect.

The formation of strings of particles to form fibres in quiescent ER fluids in an electric field at a low solid volume fraction was thought by Block and Kelly [7] not to be a sufficient explanation for the shear stress of the fluid when in flow. It was not implied that there was no aggregation during flow, merely that it was difficult to envisage a complete span of the chains between electrodes during flow. The importance of aggregation of the solid particles in the ER effect is still open to interpretation, however other workers have also investigated this area.

Chains of solid particles do dramatically increase the effective viscosity in a dilute suspension, and even if the chains do not span the electrode gap the effective viscosity could still increase. It has been shown by Batchelor [8] that the fractional increase of the effective viscosity due
to chain formation is given by,

\[ 1 + k c N^2 \]  

(1)

where \( c \) is the volume concentration of the solid, \( k \) is a constant, and \( N \) is the number of particles in the chain. The yield strength is a strong function of volume fraction, with the dependence being linear for concentrations of solids of less than 15%, which is as would be expected if chains were responsible for the yield strength. For higher concentrations the notion of a chain is no longer applicable, and the number of connections between particles increases. This explains the faster than linear rise in yield strength for the higher concentrations.

Klass and Martinek [2] suggested that the idea of particle migration by Winslow in [9], with the chain formation as the origin of the ER effect was unlikely, as the time required for such a restructuring is excessive when compared with the response times of the systems being studied. In fact Brooks et al. [5] observed optically a time scale for chain formation of the solid particles of the order of 20 s, which of course is much longer than the actual millisecond response time of the effect.

A microscopic investigation by Sprecher et al. [10] was carried out on dilute ER fluids based on silica as the solid particles. In a static fluid under the application of an electric field a swirling motion in the fluid was occasionally observed, this was thought to be an electrohydrodynamic effect as this swirling did not occur continuously, nor throughout the fluid. At \( \dot{\gamma} < 1 \text{ s}^{-1} \) the
fibres of solid particles deformed uniformly, but after a few minutes a zone without fibres developed in the centre of the gap, and shearing occurred for the most part in this region. At higher shear rates of $\dot{\gamma} > 1 \text{ s}^{-1}$ the fluid was more turbulent and this frequently destroyed the fibrated structure throughout the sample.

The theory for the ER effect will now be considered in more detail.

**Section 5.8 Charge Oscillation and Conductivity**

Matsepuro [11] showed that individual particles of ER fluids oscillate between the electrodes, and upon touching them accumulate charge. The charge accumulated was said to be the same as that by a sphere of platinum of the same dimensions i.e. like a conducting particle. In this particular article the conductivity of an ER fluid was thought to be linearly related to the interparticle bond strength. The ER effect is known to be quite similar for both dc electric fields, and also for alternating fields up to a frequency of 60 Hz, but the effect rapidly decreases in the range of 100 to 10,000 Hz.

The work of Block and Kelly [7] has led them to doubt whether the current that accompanies the ER effect is due to the effect itself, or else due to other causes related to the nature of the fluid. A similar comment was made by Sasada et al. [12] on the basis that a polarisation mechanism for the ER effect only requires an electric field, with no current being necessary, although the proviso was
included that in any practical ER fluid sufficient conducting species exist to produce a current.

A different view of conductivity of ER fluids has been presented by Makatun et al. [13] which depends on the mobility and number of the charge carriers, while conditions and chemical nature of the material determines which of the above parameters is the limiting one.

In some fluids it has been found that the current generated by an ER fluid is proportional to the rise in the yield stress, which is consistent with the idea of chains as both the yield stress and the current would be proportional to the number of chain connections. As mentioned earlier I did not find that the conductivity in the majority of my samples obeyed any particular power law with the yield stress, although the closest fit was probably linear. This result was also found by Brooks et al. [5] who also studied the electrophoretic mobility (u) of polymer based ER fluids. Using the equation derived by Hückel [14] as shown below it was possible to derive an electro-kinetic potential ($\zeta$).

$$\zeta = 3 u \frac{\eta_o \varepsilon}{2}$$

In this case $\varepsilon$ is the dielectric constant of the supporting oil, and $\eta_o$ is the oil viscosity. A value of 0.045 V was found for $\zeta$ which corresponded to a surface charge of $1.35 \times 10^{10}$ proton charges per particle. The value of $\zeta$ was found to decrease at volume fractions above 20% down to 0.03 V. It was found that the data best fitted a model for the conductivity which was primarily due to the counter ions
associated with the particles rather than the volume fraction of the highly conducting particles. For the current to be transmitted through the solid particles ionic species would have to soluble in both the water inside the particle, and also in the supporting oil, and transferring across the water/oil interface. The authors believe that there is no ionic flux across the interface, hence in terms of suspension conductivity the solid particles behave as non-conductors, and may be treated as perfectly polarisable dielectrics which will assume a constant surface potential in an electric field. The potential around one particle also depends on the number and position of the neighbouring particles, as well as the surface potential.

The effect of temperature on the conductivity of the LiPMA based fluids was found to be that approximately a 5°C increase in temperature caused an increase in the current of a factor of 2, whilst for the zeolite fluids this factor was reduced to around 1.5.

Section 5.9 Polarisation Mechanisms for the ER Effect

It has been shown by Deinega and Shilov [15] that classical polarisation underestimates the ER effect by an order of magnitude and, in the case of electronic polarisation the time scale is incorrect for the ER effect. One argument against the simple polarisation mechanism is that not all conducting substances, like metallic particles will give the ER effect. The commonly agreed ER phenomenon has a basis in some form of induced polarisation originating.
in or around the particle. There is less of an agreement of what then subsequently occurs to induce the ER effect.

Block and Kelly [7] showed that there is a high level of low frequency polarisation of fluids, as a consequence of charge migration, rather than dipolar orientation. The precise region for charge migration was said to vary from system to system e.g. bulk, surface, or within a double layer. For interfacial polarisation the only prerequisite is that there should be mobile charges present in the system.

The work of Bullough and Peel [16] considered four possible polarisation effects. 1) optical 2) atomic 3) orientational and 4) interfacial. The time dependence data of the ER effect tended to favour interfacial polarisation, which was enhanced by the high value of the dielectric constant for water, but significantly other effects were not excluded.

According to Marshall [1] the ER effect was thought to arise from induced dipole/induced dipole interactions in the suspensions based on water containing particles, due to ionic migration. The pair interaction force depends on both the separation of particles, and the angle between the external field and the line of centres of the particles. Considering these parameters Vlodavets et al. [17] calculated the pair interaction force from the effect of mutual polarisation. This forms the theoretical basis that particles in ER fluids form chains. This has been assessed electrically and is theoretically possible from the
consideration of the dielectric properties of the dispersion as found by Davis [18]. It was concluded that the particles in an ER fluid have two spherically mutually attractive zones at each end in a direction parallel to the field, and a repulsion zone at their centre perpendicular to the field.

The magnitude of the ER effect was seen to decrease as the temperature increased which, in part, is a reflection of the decrease in the dielectric constant which is critically involved in the mechanism for the effect. Block and Kelly [7] have shown that shearing of the fluid definitely influences the dielectric response of the fluid as the shearing causes the particles to spin, and the principle axis for polarisation has to change within the particle. The dielectric constant was seen to have a loss peak at frequencies in the range 100 to 10,000 Hz for all ER fluids, which implicates a time dependence of the polarisation in the effect. A common fact in both moist, and dehydrated systems is that polarisation takes place on the same time scale. The results from my ESR experiments suggest that there is an effect on the water throughout the solid particles by the electric field, although of course the actual centre for polarisation could be at the surface where the charge congregates. At this stage there is no definite evidence that the ER effect involves a particular form of polarisation, only conjecture and implication.

The understanding of dielectric phenomena extends only to systems of low concentration, whilst systems of high solid concentration where multi-body interactions dominate.
are poorly understood. The work of Dukhin et al. [19] showed that the water in the solid particles of an ER fluid increases the low frequency dielectric constant of a dispersion by two to three orders of magnitude, and there exists a water content when the dielectric constant is a maximum.

The dielectric constant of the LiPMA based fluids have been monitored by Brookes [20] using a Wayne-Kerr bridge. The value of the dielectric constant increased from 6 to 9 for LiPMA with water contents from 0 to 30%, and then from 9 to 25 for water contents for water contents of 30 to 50%. For one particular water content in the polymer the dielectric constant increases linearly with volume fraction, with the rate of increase becoming larger as the water content of the solid increases. Also for LiPMA the dielectric constant decreases with the increase of the frequency of the electric field with a loss peak at approximately 150 Hz.

Since the dielectric constant of water is approximately 80 it is tempting to assume ER behaviour is due to the dielectric properties alone, but estimates for yield stress assuming a dielectric response only to the electric field are too small by several orders of magnitude. This points to an electric effect that dominates the dielectric response, with the obvious next step being to look at the role of the ions in these systems.
Section 5.10 Proton Transfer Mechanism

The basic contribution to the polarisation of particles carrying an adsorbed protogenic activator was summed up by Shulman et al. [21] as being provided by the directional diffusion of the protons in the adsorbed layer at the interphase boundary. The importance of the role of proton transfer was also acknowledged by Brooks [20] who stated that hydroxyl groups linked by hydrogen bonds play a large part in particle polarisation, with protons migrating along such chains to produce high polarisability. The generation of an electric current due to the proton jumping mechanism was suggested by Fournié [22], who considered that in solution there will be an attractive unoccupied orbital on an adjacent water molecule only a short distance from a $\text{H}_3\text{O}^+$ ion. If the proton then transfers, or jumps, from the ion to the water molecule then the neutrality is disturbed, and there appears to be a movement of charge. When this process takes place in an applied electric field then a conduction mechanism is evolved. The orientation for the proton transfer from $\text{H}_3\text{O}^+$ to the water molecule is automatically set up by the ion as it possesses a Coulombic field which orients the water molecule, which is a dipole, into the correct position for proton transfer.

Since all ER activating species are able to form hydrogen bonds, it seems to indicate that the proton transfer mechanism may be the limiting factor for charge transfer. The work of Shulman and Matsepuro [23] involved the study of ER fluids with aluminium dihydrotriphosphate.
dihydrate (Al \(\text{H}_2\text{P}_3\text{O}_{10}\cdot2\text{H}_2\text{O}\)) as the solid component. This compound has a layer structure, and it is thought that the phosphohydryl groups dissociate between the layers enabling proton transfer to water molecules, leading to an equilibrium formation of \(\text{H}_3\text{O}^+\) ions by the process shown below.

\[
P\text{–OH} + \text{H}_2\text{O} \leftrightarrow P\text{–O}^- + \text{H}_3\text{O}^+ \quad (3)
\]

In this compound the intracrystalline water is firmly bound to the lattice, therefore the proton transfer must be by a carrier mechanism. This is a very similar situation to the one encountered in partially dehydrated zeolites, in which most of the water is firmly bound to the lattice: all zeolites also contain hydroxyl groups. The density of the oxonium ions was found by Lapko et al. [24] to increase by a factor of five in the temperature range from 293 to 423 K using broad line proton NMR, with an activation energy of 8.4 kJmol\(^{-1}\). At the same time another process was found to occur connected with the fact that some of the water molecules, and oxonium ions acquire rotational, and diffusional mobility which had an activation energy for diffusion of approximately 63 kJmol\(^{-1}\), comparable to that measured in this study in zeolite fluids, but larger than that in polymer based ER fluids.

The narrowing of the NMR line and the increase in the conductivity of this type of sample were found to coincide in the same temperature range by Makatun et al. [25], which suggests that the basic contribution to particle polarisation by proton transfer is provided by their
mobility. Further evidence for this theory is that the activation energy for the increase in conductivity is $71.1 \text{ kJmol}^{-1}$, which is similar to the value for the diffusional mobility of the water molecules. It was also suggested by Makatun et al. [25] that it is sufficient for proton transfer involving the relay mechanism for there to only be a small amount of water in the interlayer space, with a marked reduction in mobility being observed only after intense dehydration. In fact Shulman and Matsepuro [23] went so far as to state "the search for new disperse phases for ER fluids should be amongst compounds that contain protogenic groups that have controlled transfer paths for proton transfer".

Section 5.11 Water Bridge Mechanism

The idea that the forces in ER fluids, with a solid component containing an activator, are due to water bridges formed between the particles is probably the simplest mechanism to consider, but it has a number of major faults. Since it was first shown that moist glass beads in poly(butadiene) form chains held together by the force of water bridges on the surface of the solid some workers have tried to apply this scheme to explain the ER effect. However, there are a number of problems associated with this mechanism, such as why is the conductivity of ER fluids in the order of $10 \mu \text{Acm}^{-2}$ if a continuous network of water exists. Also although the quantity of water appears sufficient for bridges with solid particles, why should it
happen with porous particles. Finally, if the water goes in and out of the solid then it would have to do this at \( \text{ac} \) field frequencies for those experiments in which an \( \text{ac} \) field has been used. In the past frequencies of up to 2 kHz have been used which appears difficult to reconcile with the mobility of the water in and out of the solid.

Section 5.12 Electro-osmosis Mechanism

The idea of electro-osmosis as a possible mechanism for the ER effect has a number of points in its favour. In this mechanism an electric dipole is induced by movement of the water molecules within the solid particles, which for a zeta potential \( (\zeta) \) of 0.1 V corresponds to a response time for the effect of 1 ms, which is in the range of that measured. Also the electric field required to produce this effect will be of the order of the \( \zeta \) potential divided by the length of the particle which corresponds to a value of approximately 1 kV mm\(^{-1}\) with a dielectric constant of water of 80. When the field is removed the imbalance of the charge leads to a large force to take the water to its original equilibrium position, with the time scale for this process also being in the millisecond region.

Section 5.13 Conduction Model

In this mechanism ions are considered to move inside the particle under the influence of the electric field, so as to make the electric field vanish within the particle as there are equal and opposite charges at either end of the
particle. The relaxation time for this mechanism should be larger than the conduction time by the ratio of the particle dimension : gap between particle charges, which is equal to $10^{-6}/10^{-9} = 10^3$. This means that since the conduction time is in the $\mu$s region, then the relaxation time should be in the millisecond time scale, as observed. If the electric field is kept below the value necessary for electrical discharge then the system will return to its original state when the electric field is removed. When electrical discharge does occur the net charge of the particles may change so that when the field is removed some charged particles will remain, which would continue to increase the effective viscosity for a time. The characteristic time scale for this model is independent of the strength of the applied electric field but would be very sensitive to the concentration of particles. The surface of the particles would also change the time scale of the effect if it were changed by the addition of surfactants to the fluid.

For the fluids which I have studied in this work there has always been a certain amount of water needed to produce a reasonable ER effect, as well as the presence of ions in the system.

Section 5.14 Summary

1) It would seem that firstly the water is influenced by the electric field, as seen in the ESR results. This could be a sign of organisation, or aggregation of the water to induce a dipole within the zeolite particles which is similar to
the mechanism proposed by Deinega et al. [26]. The degree of organisation of water in unprotonated zeolites would seem to be an indication of the efficiency of that solid in an ER fluid.

2) The proton transfer mechanism would seem to provide the low conductivity pathway to account for the protonated zeolite samples whilst, in those zeolites with a significant number of metal cations, they also contribute to the conductivity so increasing the final value.

3) In the polymer samples the conductivity again would seem to have contributions both from the water, and the lithium ions so producing currents similar to those for the unprotonated zeolites. Of course the NMR results have shown that the water in the zeolites is much more mobile than that in the polymer, so the zeolite requires much less water than the polymer to have the same conductivity.

4) The force between the particles produced by the activating fluid seems to be greatest for those fluids with the highest value of dielectric constant such as water, and formamide, which are most polarisable.

Finally, it would seem that the actual ER mechanism is very complicated, being a function of several different contributory factors. However, the results of this study seem to point in some quite definite directions to those factors of most consequence to the ER effect.

Section 5.15 Suggestions for Future Work

The possible studies of zeolites by magnetic resonance
techniques is obviously very wide and varied. In this study only a very small number of zeolites have been tried so there remains a very wide range of both naturally occurring and synthetic zeolites on which to draw on using the information gained in this work. One possible new NMR experiment would be to examine the reaction of adsorbed Xe in zeolite cavities upon the application of an electric field. Also different activating compounds besides water could be studied using NMR of various zeolites.

The ESR experiments could also be extended to study other zeolite structures under the conditions required to produce the ER effect using the techniques described in this work. Also it would be interesting to carry out an investigation of the interior cation sites in zeolite based ER fluids using various paramagnetic transition metal ions such as copper or manganese, both with and without the application of an electric field.

The area of the use of surfactants in ER fluids requires a much more detailed survey, with also the possibility of the use of magnetic resonance to study the action of surfactants in ER fluids. The most efficient surfactants need to be researched for each type of ER fluid.

It would also be of great use to carry out a more detailed accurate study of the conductivity of ER fluids in order to glean further information in this poorly understood area. If possible the study of the dielectric constants of the zeolite based ER fluids would be worth studying as they have never been investigated before for these fluids. It
would be of interest to find the variation of the dielectric constant with both temperature, as well as shear rate for these fluids.

The mechanical testing of ER fluids could be extended over both a wider temperature, and shear rate range using the electroviscometer. It would be useful to study the variation with volume fraction of the ER effect for all the zeolite based fluids, as only zeolite X has been studied so far.

In the hope of not having to rely on water based ER fluids it is essential that thorough investigations are carried out into the non-water containing fluids described by Inoue [27] and Fujii et al. [28]. These fluids should also allow study by magnetic resonance techniques so that the ER mechanism for this type of fluid may be ascertained at a molecular level.

It must be remembered that there is a branch of fluids that represent the magnetic equivalent of ER fluids based on ferromagnetic dispersions which may prove useful to study in order to reveal similarities with the ER effect.

One fact that is certain about ER fluids is that there remains much work still to be carried out on the subject, with the eventual likelihood of an enormous amount of commercial applications for some types of fluid.
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