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UNIVERSITY OF DURHAM

THE PREPARATION AND DISPERSION OF MAGNETIC FERRITE PARTICLES

submitted by

A. Wooding, B.Sc. (Dunelm)

Thesis submitted to the University of Durham
in candidature for the Degree of
Doctor of Philosophy

October 1987

28 JAN 1988

To my Mother and Father

DECLARATION

The work described in this thesis was carried out at the University of Durham between October 1984 and September 1987. This work has not been submitted for a degree in this or any other University and is the original work of the author except where acknowledged by reference.

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Some aspects of this work have already been accepted for publication.

1. "Proteins and Carbohydrates as Alternative Surfactants for the Preparation of Stable Magnetic Fluids". A. Wooding, M. Kilner and D.B. Lambrick, to be published in IEEE Trans. Magn., 1988.

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ABSTRACT

Magnetic fluids containing magnetite (Fe_3O_4) have been prepared using colloidal size particles, obtained by alkaline treatment of mixed iron(II)/iron(III) chloride solutions. The particles have been dispersed in a variety of carrier liquids employing a wide range of surfactant materials. In non-aqueous carrier liquids, a single layer of surfactant is chemically adsorbed at the particle surface to effect steric stabilization. In aqueous media, a primary layer of chemisorbed surfactant interpenetrates a secondary layer which is physically adsorbed. This arrangement places hydrophilic charged groups at the surfactant/water interface, thereby maintaining a favourable interaction between the two phases.

A wide variety of surfactants, including a range of straight-chain fatty acids, have been evaluated for use in aqueous magnetic fluids. Fluids incorporating up to 32 wt. % magnetite have been prepared. Stability towards dilution, changes in pH and quantity of dispersing agent have all been studied. Charge-stabilized magnetic fluids, in both acidic and alkaline aqueous media, have been investigated.

Control of Fe_3O_4 particle size, between 60Å and 80Å diameter, has been achieved by altering the conditions under which precipitation occurs, namely temperature, reagent concentrations, viscosity and solvent composition. In addition, water was found to be capable of dispersing larger particles than organic carrier liquids.

Particles as small as 30Å diameter have been prepared by *in situ* magnetite precipitation with naturally occurring polymeric surfactants, such as proteins and polysaccharides. Functional groups along the polymer backbone are thought to coordinate to Fe^{2+} ions, thus maximising

the number of particle nucleation sites. Small particles with narrow size distributions result. In this way, magnetic fluids have been prepared, stabilized with low toxicity naturally occurring materials for possible medical applications.

Magnetite particles, too large for use in magnetic fluids, have been made by condensing iron(II) hydroxide with a variety of hydrated iron(III) oxide species. Particle size was dependent upon the size and solubility of the iron(III) precursor. Non-colloidal magnetite particles were also obtained by the aerial oxidation of iron(II) hydroxide suspensions at temperatures > $60^{\circ}C$.

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CHAPTER 1

MAGNETIC FLUIDS - AN INTRODUCTION

A magnetic fluid or ferrofluid is defined as a colloidal suspension containing single domain ferro- or ferri-magnetic particles dispersed in a carrier liquid and stabilized with a surfactant. It will thus have some of the magnetic properties of a magnetic material such as iron, cobalt, nickel or magnetite but will remain liquid at room temperature.

The concept of a magnetic liquid dates back to the late 18th century at which time Wilson[1] was using suspensions of iron filings in water for the preparation of artificial lodestone, but the particles were much too large for true colloidal stability. It was only in the last twenty five years that stable magnetic colloids, which remained liquid in the presence of an applied magnetic field, were considered feasible. Since then, there have been significant developments both in the preparation and understanding of these systems and this has led to a whole range of commercial applications, some of which are still in the process of development.

The combination of the magnetic and hydrodynamic properties of a ferrofluid gives rise to many curious and interesting phenomena. It is no wonder, therefore, that such fluids are continuing to be studied for their hydrodynamic as well as their magnetic properties. Virtually every aspect of hydrodynamics can be considered afresh in the expectation that magnetism will modify fluid properties in remarkable ways.

This sense of intrigue has attracted scientists from many disciplines including chemistry, solid state physics, fluid mechanics and even biology, all of them contributing to what is still a relatively new and expanding area. The work presented here is a contribution by a chemist to a subject area long dominated by physicists and engineers.

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1.1. COMPONENTS OF A MAGNETIC FLUID

There are three components of a simple magnetic fluid, the single domain magnetic particles, the carrier liquid and the surfactant. These interact to create an apparently homogeneous magnetic liquid, a schematic representation of which is given in Figure 1.1.

i) The Magnetic Particles

Particles suitable for magnetic fluid preparations are typically below 150Å (15 nm) in diameter. Larger particles will be subject to increased gravitational pull causing them to settle out. In addition, the forces of attraction between magnetic particles increase as particle size increases and, for particles > 150Å in diameter, this will favour the formation of particle aggregates with consequent settling out. The particle may consist of a ferromagnetic material such as iron,[2] cobalt[3] and nickel,[4] or it may be of a ferrimagnetic oxide such as magnetite (Fe_3O_4),[5] γ-Fe_2O_3 or cobalt ferrite ($CoFe_2O_4$). It has recently been possible to produce particles of mixed metal composition, in particular iron-cobalt alloys.[6]

ii) The Surfactant

Magnetic fluids are lyophobic colloids, i.e. there is no affinity between the particles and the dispersion medium. The function of a surfactant is to act as a bridge between the two phases thus increasing the affinity of one for the other. At one end of the surfactant molecule is an ionizable 'head' group which adsorbs onto the particle surface. This 'head' group is negatively charged for anionic surfactants, and positively charged for cationic surfactants. In some cases the 'head' group is polar rather than ionic and these are called non-ionic surfactants. The remainder of the surfactant molecule consists of a long-chain hydrocarbon tail typically 10-20Å in length. These tails

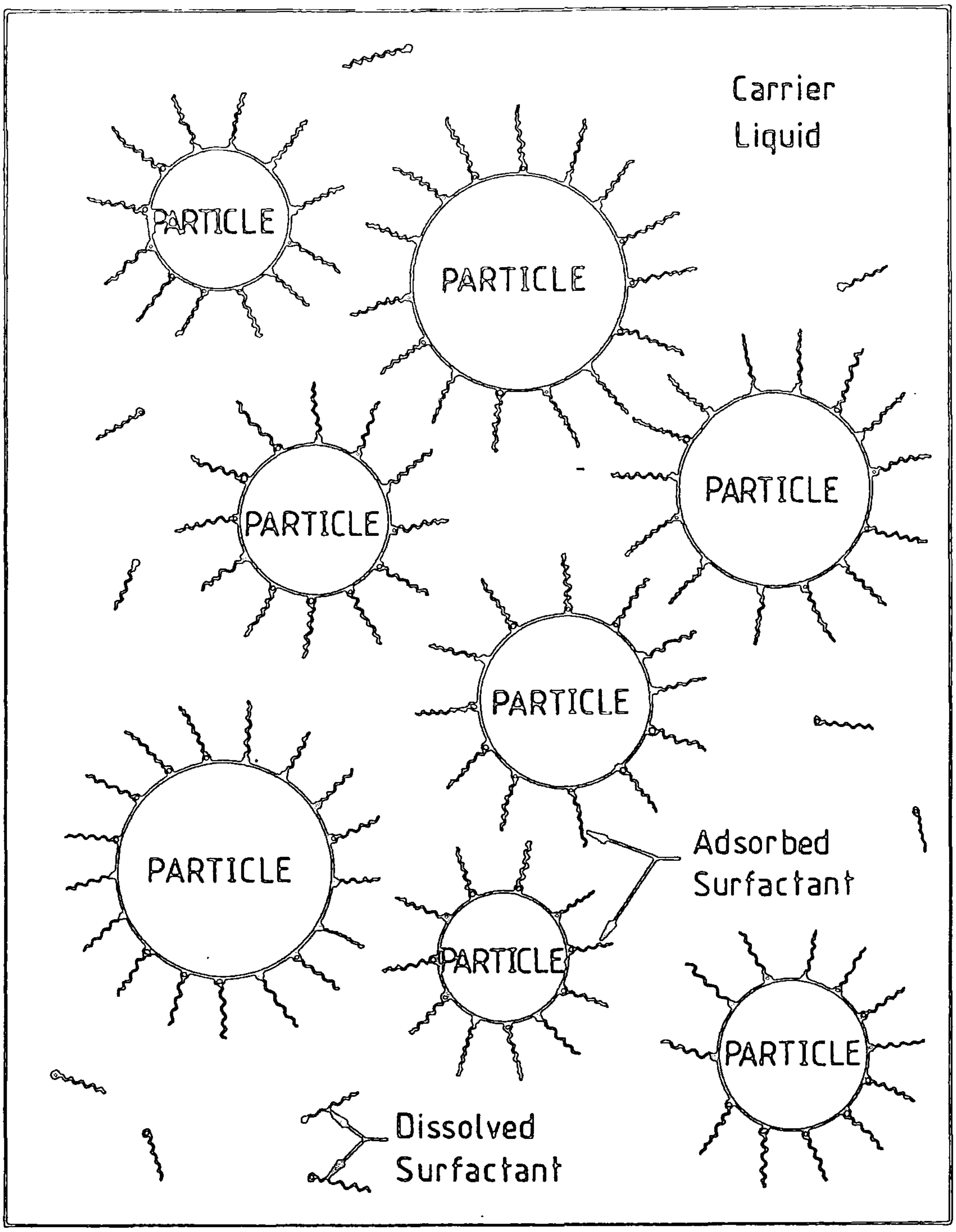


Figure 1.1. The components of a magnetic fluid.

fan out from the particle surface conferring -

i) Compatibility between particle and carrier liquid by ensuring a favourable interaction at the surfactant/solvent interface.

ii) Steric stabilization by cushioning the particle from close approach of other similarly coated particles. If this layer was not present then short range Van Der Waals attractive forces would soon aggregate the particles causing them to settle out as large clumps.

The mechanism of surfactant stabilization in aqueous and non-aqueous media is different and will be discussed elsewhere. A good surfactant for organic-based ferrofluids will have a 'tail' eighteen or more carbon units in length with a double bond or side chain group which provides a kink in the chain and prevents intermolecular association.[7] The 'tail' should not have an affinity for the particle as this will cause it to lie flat on the surface. An example of a good surfactant for the dispersion of magnetic particles in hydrocarbon solvents is oleic acid: $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$.

Water-based magnetic fluids employ surfactants shorter in length and without the need for a double bond. A typical example is decanoic acid: $CH_3(CH_2)_8COOH$.

Polymeric surfactants have polar or ionizable 'head' groups all along their length giving many points of attachment from a single molecule. In this way they coil around the particle until steric stabilization is achieved. In reality however, the bulkiness of these materials has tended to limit their use in magnetic fluid preparation.

Examples of the different types of surfactant available are given in Table 1.1.

TABLE 1.1.

Types of surfactant used for colloidal magnetic particle dispersion

Class	Examples
Anionic	$CH_3(CH_2)_nCOOH$: n = 6-18 ⎤ Aqueous Systems $CH_3(CH_2)_{11}OSO_3^-Na^+$ ⎦ $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ Non-Aqueous Systems
Cationic	$C_{12}H_{25}N^+(CH_3)_3Br^-$ $C_{11}H_{23}NH_2$
Non-Ionic	Synthetic detergents based on polyoxyethylene e.g. $C_{12}H_{25}(OCH_2CH_2)_6OH$: "$C_{12}E_6$"
Polymeric	1) Polyethoxylates: $R(OCH_2CH_2)_nOH$ 2) Acrylic ester copolymers 3) Proteins and polysaccharides e.g. Gelatin ⎤ Poly-glucosamines ⎬ Water Soluble Carboxymethyl Cellulose ⎦

iii) Carrier Liquid

Many solvents have been used as carrier liquids in magnetic fluids, depending upon the particular application. Organic high boiling point liquids such as kerosene and petroleum-ether 200-240^{o}C b.p. are commonly used when the ferrofluid will encounter high temperatures. Aromatic and aliphatic hydrocarbons such as toluene and hexane are also suitable. Water is a common solvent for magnetic oxide-based ferrofluids and has the advantage of producing a low toxicity fluid. Many polar organic solvents such as ethanol and acetone cause particle agglomeration and are therefore unsuitable as carrier liquids. These solvents are often used as flocculating agents prior to redispersion of the particles in an alternative carrier liquid.

1.2. THE THEORY OF MAGNETISM

Ferro/ferrimagnetism occurs because of the motion of electrons within atoms. An electron will have associated with it two types of angular momentum, orbital angular momentum as it travels around the nucleus and spin angular momentum, a purely quantum-mechanical effect. Both types of motion give rise to a magnetic moment and it is a combination of these two which describes the overall moment of an electron. For the whole atom, the total electron spin motion gives rise to a resultant magnetic vector $\vec{S}$, and the total electron orbital motion a vector $\vec{L}$. The sum of these vectors gives the total angular momentum which relates closely to the magnetic moment of the atom. Different types of magnetism are encountered in bulk materials, as discussed below.

1.2.1. Paramagnetism

Paramagnetism is a property associated with atoms or molecules containing unpaired electrons. In the absence of an applied field thermal energy disorders the individual magnetic moments to give random orientations resulting in no net magnetization. With an applied magnetic field the moments tend to become aligned in the field direction. This alignment is opposed by thermal motions, the net result being only partial alignment and a small magnetic moment. When the external field is removed the moments revert to a random configuration with no net magnetization.

1.2.2. Ferromagnetism

In a ferromagnetic material such as iron, cobalt or nickel, there exists between groups of adjacent atoms a quantum-mechanical exchange interaction which spontaneously aligns the individual magnetic moments even in the absence of an applied field. Below a certain temperature, the Curie temperature, each group of atoms is spontaneously magnetized. Above this temperature the high thermal energy within the system overcomes these exchange forces and the material becomes paramagnetic. The Curie temperatures of the ferromagnetic materials, iron, cobalt and nicel, although above room temperature, are well below their melting points (Table 1.2.); this explains the non-existence of single phase liquid ferromagnets.

Parallel alignment of magnetic moments, as described above, leads to the formation of magnetic domains with dimensions of the order of 10^{-2}-10^{-5} cm, each domain being spontaneously magnetized to saturation. Although there is spontaneous alignment within each domain, the overall magnetic moment for a particular domain is randomly orientated, giving rise to zero net magnetization in the bulk material. When a field is applied, those domains orientated with the field grow at the expense of those opposed to it by movement of the domain walls. These walls are

TABLE 1.2.

The melting point and Curie temperatures of some ferro- and ferri-magnetic materials

Material	Melting Point °C	Curie Temperature °C
Iron	1535	770
Cobalt	1495	1134
Nickel	1453	358
Fe_3O_4	1594	585

boundaries a few hundred Angstroms thick, over which the direction of magnetization gradually changes.

Let us consider the simplest case of a two domain particle before and after application of an external field, H.

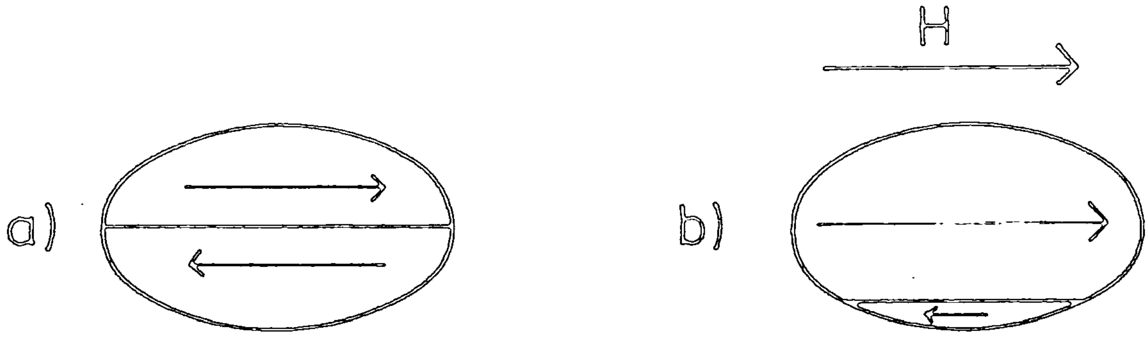


Figure 1.2. A two domain particle a) before and b) after the application of an external magnetic field.

In Figure 1.2.b) the domain wall has migrated to give almost a single domain particle. However, in practice, this is never the case because of imperfections in the wall microstructure which hinders its movement. When the external field is removed these same imperfections ensure that not all domains revert to their original magnitude. Quantitative data on this phenomenon gives us hysteresis loops of the type shown in Figure 1.3. B_r is the remanent magnetization which remains in the sample after the external field has been reduced to zero whilst H_c, the coercivity, is the reverse field required to reduce the magnetization to zero after the sample has been magnetized in the forward direction.

1.2.3. Antiferromagnetism

In an antiferromagnetic material, such as NiO, the individual magnetic moments within each domain are orientated antiparallel giving zero net magnetization even in an applied field. Above the Curie

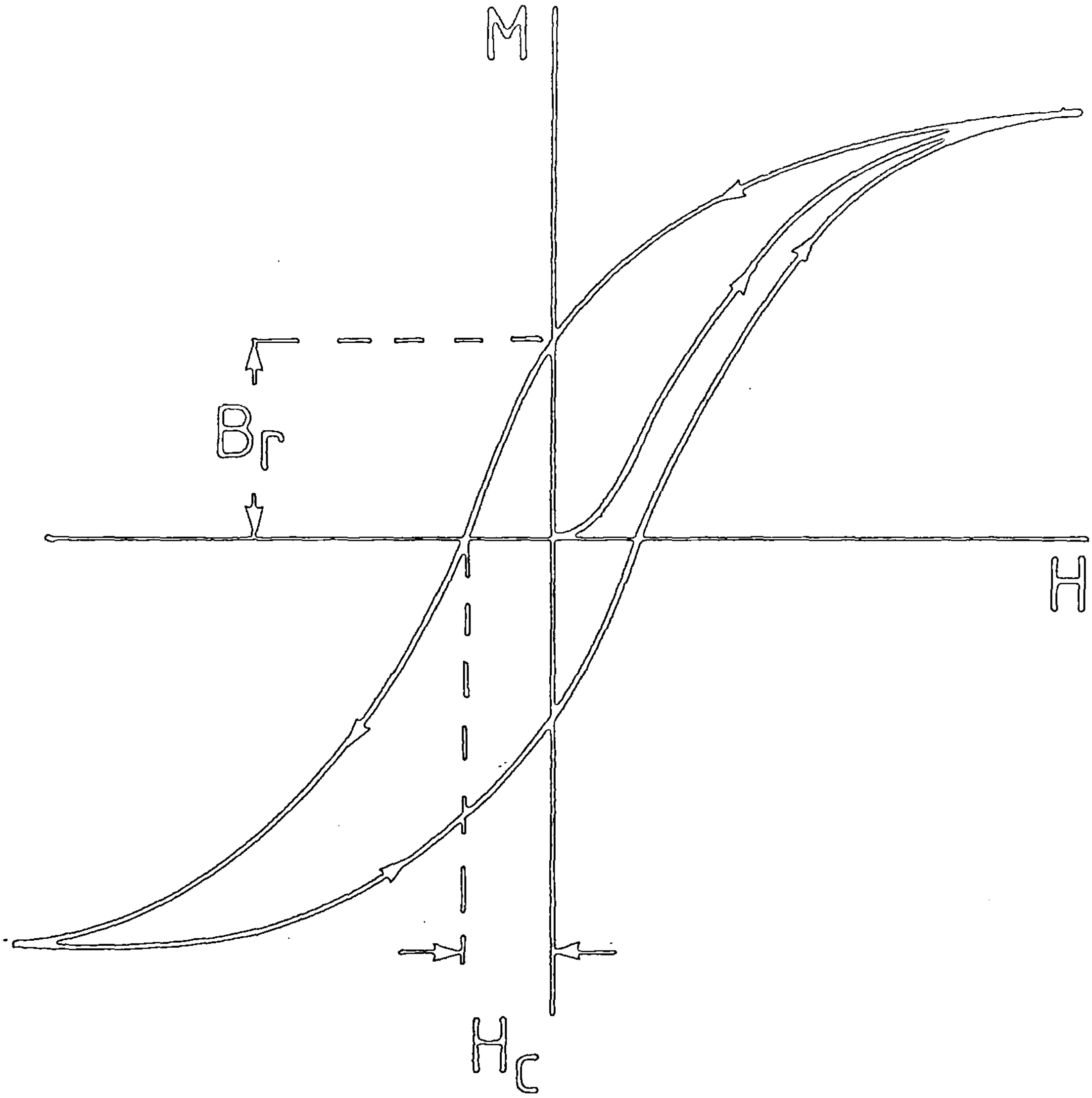


Figure 1.3. The hysteresis loop of a bulk ferromagnetic material exhibiting coercivity and remanence.

temperature (which for antiferromagnetics is termed the Néel temperature) antiparallel alignment is disrupted and we revert to normal paramagnetic behaviour.

1.2.4. Ferrimagnetism

Ferrimagnetism is a property of the magnetic oxides of iron and cobalt which adopt the inverse spinel unit cell structure. It is similar to ferromagnetism in that there are magnetic domains which are spontaneously magnetized giving large positive susceptibilities, but also similar to antiferromagnetism because of antiparallel alignment of the magnetic moments within those domains. Fortunately, one set of magnetic moments is larger than the other, giving a net magnetization.

In spinel ferrites, such as Fe_3O_4, those cations occupying tetrahedral sites within the unit cell, namely $8Fe^{3+}$, are aligned antiparallel to those in octahedral sites, namely $8Fe^{3+}$ and $8Fe^{2+}$. The magnetic moments of Fe^{3+} ions cancel and we are left with a net magnetization due to the $8Fe^{2+}$ ions in octahedral sites. It is believed that electron transfers between O^{2-} and Fe^{2+} ions give rise to reduced exchange forces in spinel ferrites. A diagram of the Fe_3O_4 unit cell illustrating the above features is given in Figure 1.4.

1.2.5. Superparamagnetism

When a magnetic particle is below about 150Å (15 nm) in diameter, it becomes energetically favourable for it to exist as a single domain. This was predicted by Frenkel and Dorfman,[8] and later by Kittel.[9] There are no domain walls as in bulk ferro- or ferri-magnetic materials, and when an external field is applied each particle moment begins to align.[10] This alignment is opposed by thermal motions in a similar way to that for simple paramagnetic systems. Whereas in a paramagnetic sample the atomic or molecular moments are only a few Bohr magnetons in

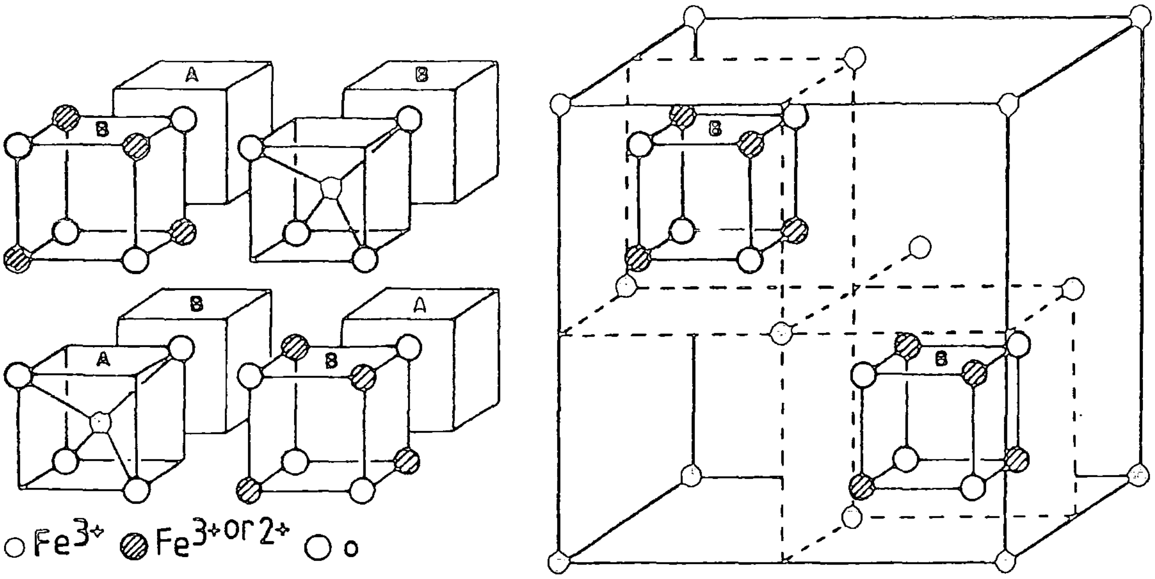


Figure 1.4. The Fe_3O_4 spinel unit cell. The structure can be thought of as eight octants of alternating Fe^{3+} tetrahedra and $(Fe^{3+})_2(Fe^{2+})_2O_4$ cubes as shown in the left-hand diagram. This builds up into a face-centred cubic (fcc) lattice of 32 O^{2-} ions coordinating both tetrahedrally and octahedrally. The four A octants contain $4Fe^{3+}$ ions and the four B octants $8Fe^{3+}$ and $8Fe^{2+}$ ions. The unit cell is completed by an encompassing face-centred cube of tetrahedral Fe^{3+} ions as shown in the right-hand diagram; this is shared with adjacent unit cells and comprises the remaining 4 tetrahedral Fe^{3+} ions in the complete unit cell. The location of two of the $(Fe^{3+})_2(Fe^{2+})_2O_4$ cubes is shown for orientation.

magnitude, a single domain spherical particle of ferro- or ferri-magnetic material containing many atoms may have a moment of the order of 10,000 Bohr magnetons. This behaviour is termed intrinsic superparamagnetism.[11]

1.2.6. Magnetic Relaxation

There exists within a single domain particle certain crystallographic directions along which the magnetization vector will prefer to lie.[12] This magnetic 'anisotropy' provides an energy barrier to rotation of the particle moment between preferred directions or easy axes. Both crystal structure and particle shape contribute to the overall anisotropy, shape anisotropy being discounted for perfectly spherical particles. In reality, particles are invariably elongated in one direction, and for a particle displaying uniaxial symmetry the easy axis becomes the long axis.

At room temperature thermal energy (kT) far exceeds the anisotropy energy and the particle moment will fluctuate between the two 180^{o} opposed directions. This we call Néel rotation and associated with it is a relaxation time T_N.[13] Even if the magnetic dipole is locked into a crystal direction it may also rotate by rotation of the particle itself. This is Brownian rotation with a relaxation time T_B.[13] Magnetic relaxation will occur by whichever mechanism is the faster, and for particles < 100Å diameter $T_N < T_B$. This implies that when the external field is removed from a sample of magnetic fluid the magnetic dipoles will spontaneously randomize by Néel rotation. For this reason coercivity and remanence are not observed in fine particle systems except at very low temperatures (< 4 K) where kT no longer exceeds the anisotropy energy.

1.3. MAGNETIZATION CURVES: THE ESTIMATION OF PARTICLE SIZE AND SIZE DISTRIBUTION

The magnetic behaviour of a paramagnetic sample is described by Langevin's function,

$$L(b) = \coth b - 1/b$$

where $b = \mu_H/kT$, μ being the magnitude of atomic or molecular moments and H the applied field.

The classical expression for paramagnetism may be adapted and applied to superparamagnetic single domain particles assuming they exist as discrete non-interacting units.[14] In this case, the magnetic moment of each particle (m) is expressed in terms of the saturation magnetization of the bulk material (M_b^∞) and the particle diameter (d) by the following relationship.

$$m = \frac{\pi M_b^\infty d^3}{6}$$

We may then derive an equation for the magnetization per unit volume (M_{ff}) of a ferrofluid.[86]

$$M_{ff} = \varepsilon_v M_b^\infty \left[\coth\left(\frac{\pi M_b^\infty H d^3}{6kT} \right) - \frac{6kT}{\pi M_b^\infty H d^3} \right]$$

where ϵ_v is the volume packing fraction of magnetic material within the ferrofluid, and H is the applied field. This relationship allows us to generate theoretical magnetization curves for ferrofluids.

The experimentally obtained curves presented in this study are a measure of σ_{ff} (magnetization per unit mass), in joules per Tesla per kilogram, as a function of applied field B_0 (the induction field measured in Teslas). Curves are generated for both positive and negative values of applied field, passing through the origin and showing no signs of hysteresis (i.e. no coercivity or remanence). At high B_0 the curves flatten out to give a value for M_{ff}^{∞}.

The relationship between ferrofluid magnetization and applied field assumes that particles all have the same diameter, whilst ferrofluids invariably contain a distribution of particle sizes. This will affect the magnetic properties and hence magnetization curves generated for such fluids.

Chantrell et al.[15] have developed a quantitative method for estimating particle sizes and size distributions from magnetization curves assuming a lognormal distribution of particle sizes. The median particle diameter, $\bar{d}_v$, and the lognormal distribution parameter, σ, which is related to the width of the distribution, are given by the following equations.

$$\bar{d}_v = \left[18\,kT / \pi M_b^{\infty} \sqrt{K I^{\circ} / 3 M_{ff}^{\infty}} \right]^{1/3}$$

$$\sigma = 1/3 \sqrt{\ln(3K / M_b^{\infty} I^{\circ})}$$

where K is the initial susceptibility of the ferrofluid and I^0 is the intercept on the $^1/B_0$ axis of the limiting slope of an M_{ff} vs. $^1/B_0$ plot

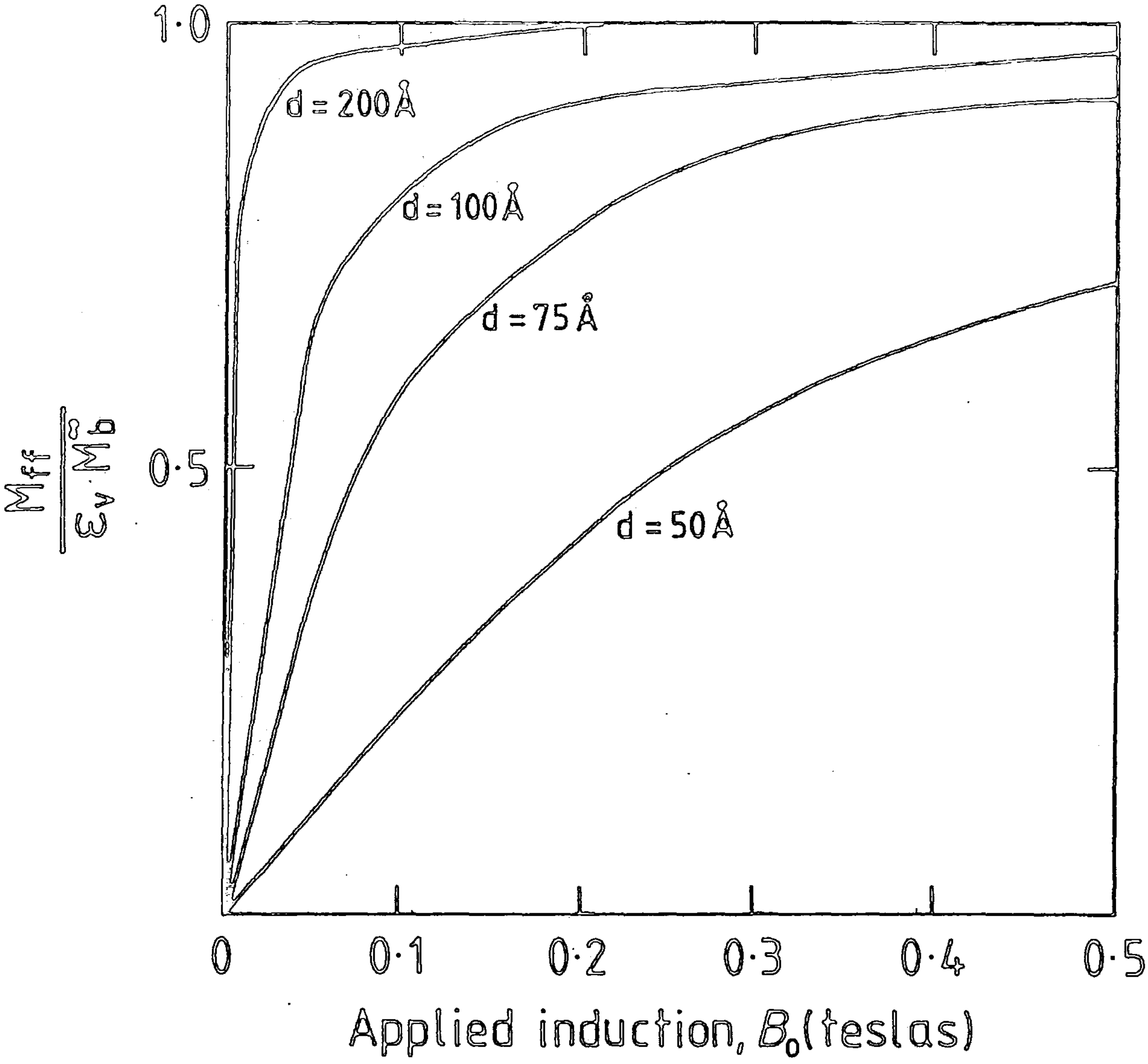


Figure 1.5. Calculated magnetization curves for spherical magnetic particles of varying diameter, at positive values of applied field.

as $B_0 \to \infty$.

Expressed in qualitative terms, the technique permits values for $\bar{d}_v$ and σ to be estimated from the shape of the magnetization curve. This is illustrated for a wide range of sizes in Figure 1.5.[15] Large particles have correspondingly large magnetic moments and reach saturation at lower applied fields than do smaller particles. This is reflected in a steep initial gradient of the magnetization curve. Small particles need a much larger B_0 to reach saturation which, in some instances, can only be attained at low temperatures with the use of a cryostat.

Particle magnetic moments are volume dependent and hence $\bar{d}_v$ is a volume distribution median diameter. Physical size measurements by electron microscopy give mean diameters based on a number distribution. Conversion of $\bar{d}_v$ to a number distribution mean diameter ($\bar{d}_m$) is achieved using the following equation.[16]

$$\bar{d}_m = \bar{d}_v \, e^{-5/2 \, \sigma^2}$$

This allows direct comparison of mean diameters obtained by magnetic and physical methods ($\bar{d}_m$ and $\bar{d}_p$ respectively).

1.4. PHYSICAL VS. MAGNETIC PARTICLE SIZE DETERMINATION

There is often a discrepancy between the mean diameters obtained by physical observation and magnetic analysis. For particles below 50Å diameter, the magnetic sizes are exaggerated on account of the inability of this technique to detect the very smallest particles. Such particles require large applied fields to effect alignment of the magnetic moments.

The opposite effect is observed for particles in excess of 50Å diameter, especially of metallic composition. This is attributed to the existence of non-magnetic 'dead layers'[11] on the surface of particles which contribute to the physical size but are undetectable by magnetic analysis. They may be produced in the following ways.

i) Simple oxidation of surface atoms to non-ferromagnetic products.

ii) Chemical modification of the surface atoms through adsorption of surfactant molecules, e.g. Fe_3O_4 + oleic acid $\longrightarrow$ Iron oleate.

iii) 'Spin pinning' of the surface atom magnetic moments in a way which reduces the net magnetic moment to zero.[17]

1.5. FORCES ACTING IN MAGNETIC FLUIDS

There are conflicting forces, attractive and repulsive, acting within a magnetic fluid. Attractive forces, comprising Van der Waals and magnetic attraction, tend to destabilize a fluid by promoting the formation of particle aggregates which ultimately fall out of suspension. Repulsive forces include contributions from electric and steric repulsion. These forces stabilize a fluid by keeping the individual particles separate from one another.

1.5.1. Van der Waals Attraction

These are powerful but short range forces arising out of the interaction between orbiting electrons in one particle and the oscillating dipoles they induce in another.[18] How this attractive force varies with range between two spherical particles is illustrated in Figure 1.6.[19] The attraction energy between two particles at close quarters far exceeds the thermal energy of the system at room temperature. It is inconceivable therefore that particle aggregates formed in this way could be separated by physical means.

1.5.2. Magnetic Attraction

These forces are less powerful than Van der Waals, yet they act over a longer range. Each and every particle in a magnetic fluid possesses a magnetic dipole moment, and the magnetic forces of attraction arise out of the magnetic affinity of one particle for another by dipolar interaction. The degree of attraction varies with the size of the particle and particle separation.[7] These features are illustrated in Figure 1.7.

The curves illustrate another feature, the effect of an external field on the interaction energy. The energy increases because particle dipoles become aligned thus increasing their magnetic affinity for one another. With reference to Figure 1.7. magnetic attraction tends only to be applicable to particles > 50Å in diameter.

1.5.3. Steric Repulsion

This is imparted by surfactant molecules which adhere to the particle surface thus preventing the close approach of two similarly coated particles. There are both entropic and enthalpic contributions to this kind of repulsion. When two particles come into close contact, interaction between surfactant tails in each protective layer restricts the normal thermal motions of those tails, this being the equivalent to a loss of entropy.[20]

For surfactant chains which have a strong affinity for the carrier liquid, close approach involves the disruption of surfactant chain - solvent interactions, this being energetically unfavourable.[21] The enthalpic effect can, however, work both ways. If the surfactant or solvent molecules prefer to associate with their own kind, then

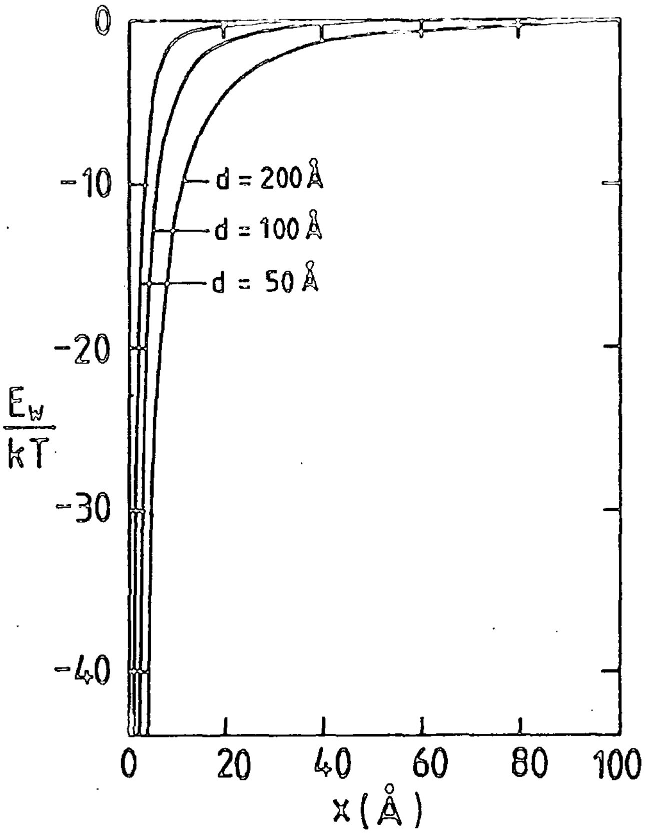


Figure 1.6. Van der Waals attraction energy as a function of of inter-particle separation.

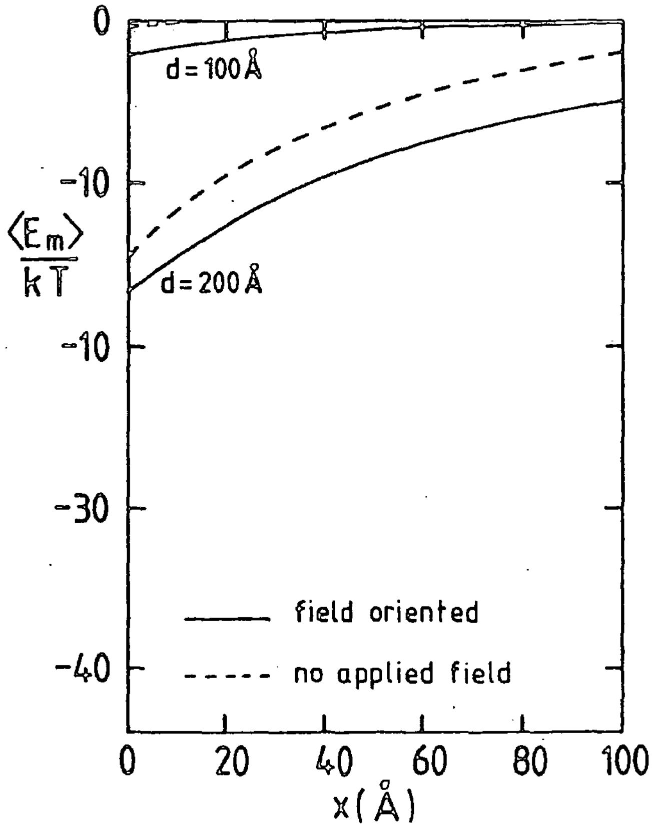


Figure 1.7. Magnetic attraction energy as a function of inter-particle separation.

repulsion is reduced or even changed to attraction. Hence the enthalpic term makes steric stabilization very sensitive to solvent composition and choice of surfactant. Figure 1.7.a) shows how steric repulsion energy varies with interparticle separation, assuming a 20Å surfactant sheath.[21] Curves are computed for different size particles as shown in the Figure.

1.5.4. Electric Repulsion

Magnetic particles are capable of picking up electric charge when placed in a polar medium containing ionic species. The particles can acquire this charge in any of three ways.

i) Surface dissociation to produce ions.
ii) Adsorption of ions formed by the carrier liquid.
iii) Adsorption of ions from species dissolved in the carrier liquid.

The most common form of electric repulsion occurs for particles in aqueous media at high and low pH. They pick up a layer of positive or negative charge depending on whether the solution is acidic or basic.[22] This in turn produces an electric potential at the particle surface and subsequent repulsion of similarly charged particles. At a specific pH, not necessarily 7, the surface charge will become neutralised thereby favouring particle aggregation. The pH at which this occurs is known as the isoelectric point and is ~ 6.5 for Fe_3O_4.[23]

This is an oversimplification because the repulsion described is not simply coulombic in nature. In order to preserve electrical neutrality within the bulk solution there exists a diffuse layer of counter- or gegen-ions which reside further from the particle surface but which are held in place by simple electrostatic interaction with the first adsorbed layer. The charge within the diffuse layer is

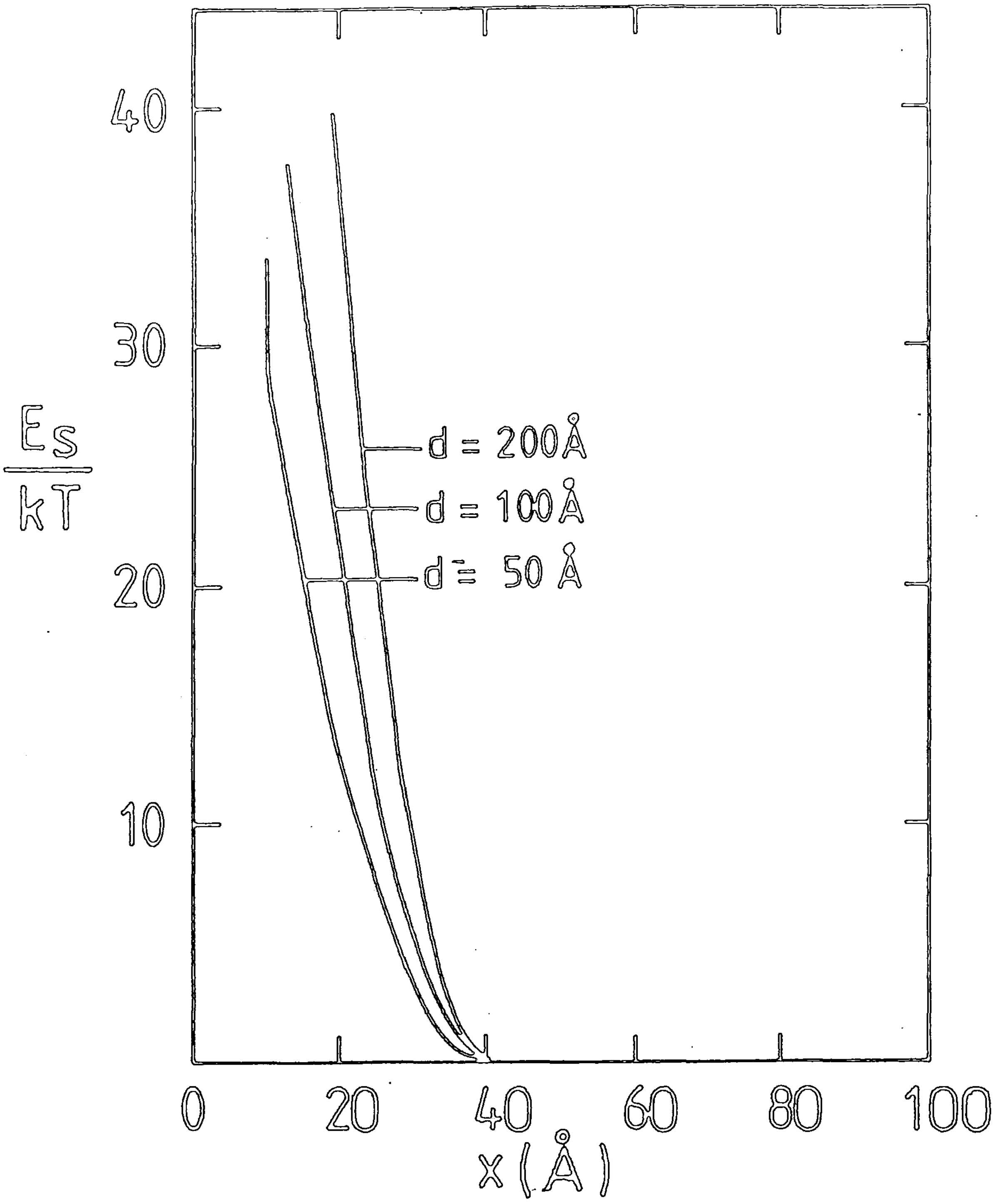


Figure 1.7.A. Steric repulsion energy as a function of inter-particle separation assuming a 20Å surfactant sheath.

insufficient to affect the overall potential which increases with proximity to the particle surface. In this way we define the electric double layer.[24,25]

The double layer theory helps to explain the interaction between surfactant molecules and charged surfaces as illustrated in Figure 1.8.[26] Aqueous ferrofluids are prepared in alkaline media and hence the electric double layer corresponds to an overall negative potential as indicated by curve a).

An anionic surfactant can penetrate the diffuse layer of positive charge, its closest approach being the locus of the centres of charge of the first adsorbed layer, or inner Helmholz plane.[27] The negative 'head' group is now sufficiently close to the particle surface for chemical adsorption to occur. The surfactant layer provides steric stabilization whilst the electric potential within the double layer is augmented, Figure 1.8. curve b), thereby increasing charge stabilization as well. Because chemisorption is irreversible, dilution will not affect fluid stability.

A cationic surfactant, with a positively charged head group, will encounter electrostatic repulsion as it approaches the diffuse layer. The point of closest approach is known as the outer Helmholz plane,[27] where the surfactant becomes physically and reversibly adsorbed. Charge reversal has taken place and the double layer now corresponds to an overall positive charge (Figure 1.8 curve c)). Upon dilution of the magnetic fluid, adsorption of surfactant will be lowered because of decreased concentration in the bulk solution. Charge reversal will therefore be diminished. At a critical dilution, the charge on the outer Helmholz plane will become nullified and the quantity of surfactant left will be insufficient to cushion the particles. The loss

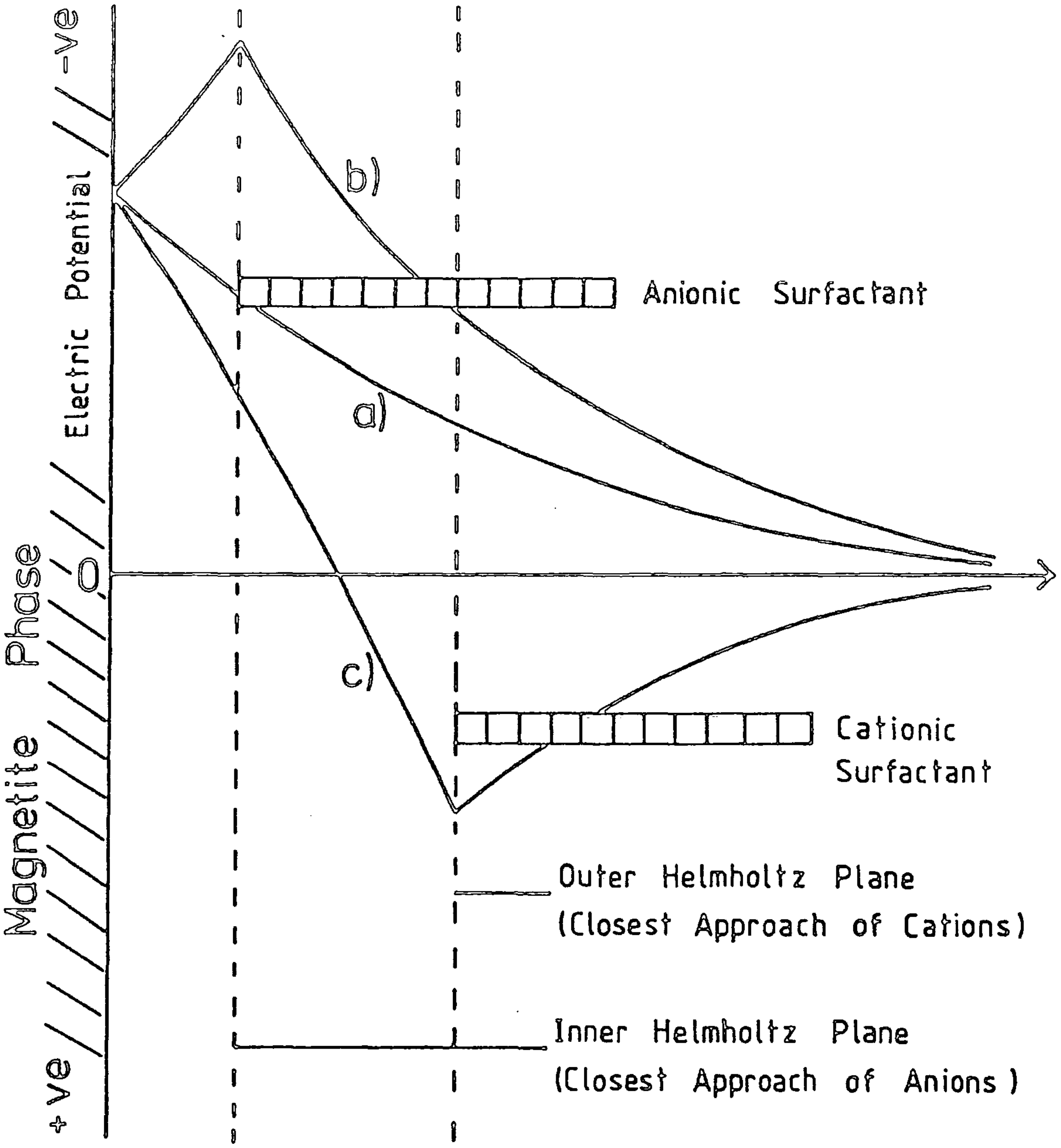


Figure 1.8. Potential profiles of the electric double layer on magnetite at the negative branch of the electrocapillary curve.

of both electrostatic (charge) and steric stabilization will cause the particles to aggregate.

Charge stabilization without the use of a surfactant is possible in both acidic and alkaline aqueous media so long as the counter-ions, which make up the diffuse part of the double layer, are of sufficiently low polarizability to ensure a maximum possible positive or negative potential at the particle surface.[28]

Much emphasis has been placed on electrostatic considerations because the work described in this thesis is concerned mainly with the dispersion of Fe_3O_4 in aqueous media.

1.5.5. Net Potential Energy Curves

The stability of a magnetic fluid depends on a balance of all the interparticle forces hitherto discussed. Consideration of all these forces gives potential energy curves for different size particles, as shown in Figure 1.9. for 100Å and 200Å particles.[13]

For 100Å particles in the absence of an applied field the potential energy minimum corresponds to 0.4 kT, hence thermal energy will be sufficient to keep the particles separate. When a field is applied the potential well deepens and exceeds kT thereby favouring aggregation. For 200Å particles the well is much deeper and will favour particle aggregation both in and out of an external field. An interparticle distance of ~ 40Å will be maintained as indicated in the Figure. Closer approach is inconceivable on account of repulsive forces indicated by a steep slope to the left of the potential energy minimum.

1.6. THE MAGNETIC AND MECHANICAL PROPERTIES OF FERROFLUIDS

The force acting on a colloidal magnetic particle is proportional to the product of the absolute value of the particle magnetic moment and

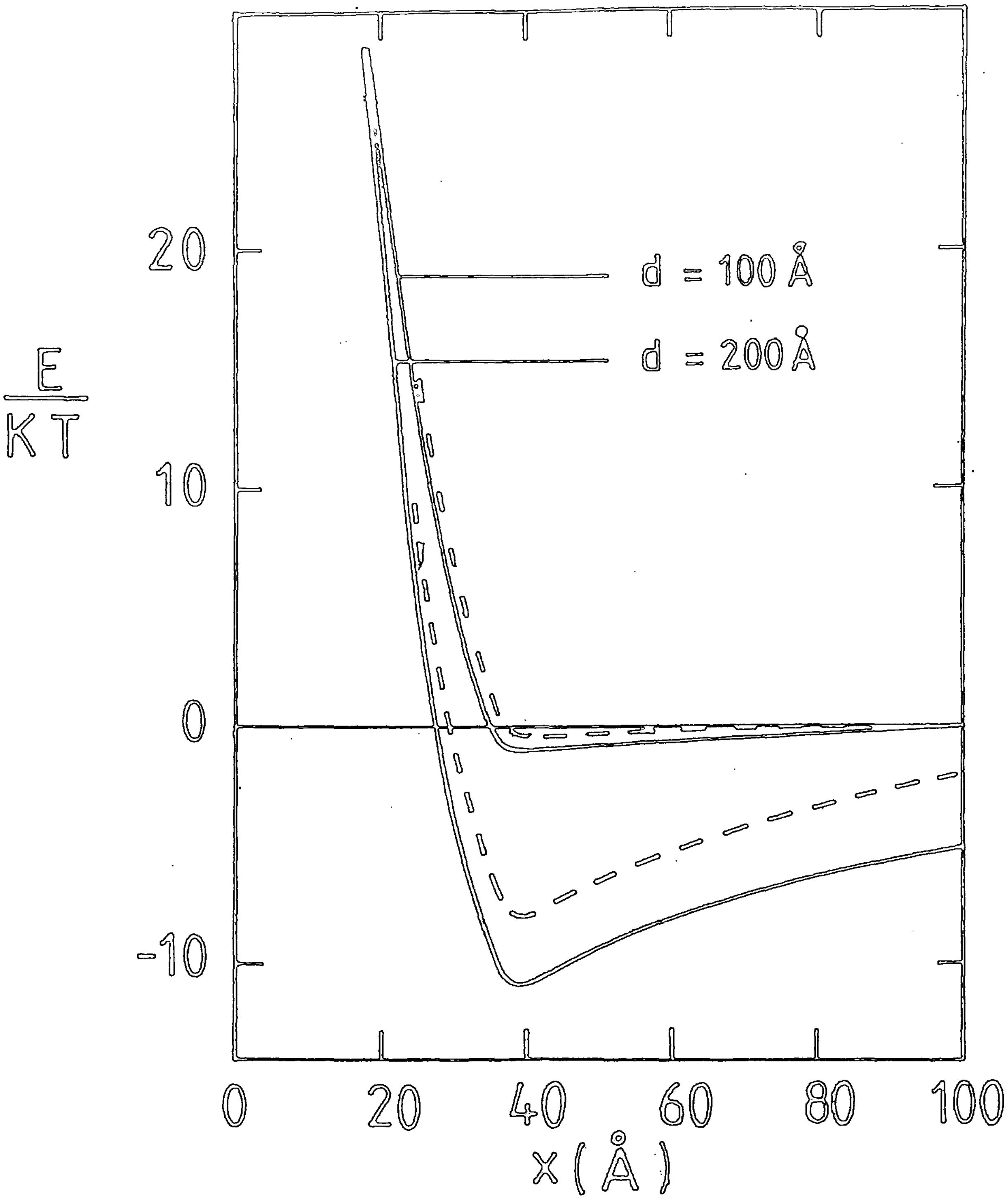


Figure 1.9. Net potential energy curves for inter-particle forces as a function of particle separation.

the magnitude of the applied field. When a magnetic field is applied to a ferrofluid a body force is developed within the liquid throughout its total volume due to the forces on the magnetic particles.[29] When a permanent magnet is placed near a quantity of ferrofluid, the magnetic particles are drawn towards the magnet. As drag is imparted upon them by the carrier liquid, the fluid as a whole is seen to move.

A better demonstration of the magnetic body force is seen when a metal rod is placed vertically in a shallow pool of ferrofluid. If a magnetic field is imposed, by passing a steady electric current through the rod, the fluid leaps up and surrounds the rod forming a symmetrical concave meniscus wide at the base and tapering at the top. This is explained with reference to the Bernoulli equation which states that, within a ferrofluid, the sum of the four forms of inherent energy; pressure, kinetic, gravitational and magnetic energy, is constant. In the above example the pressure and kinetic energy are constant. The magnetic energy varies inversely with field strength hence, to maintain constant energy, the fluid nearest the rod (having the least magnetic energy) must have the most gravitational energy and therefore climb the highest.

If a spherical non-magnetic object, of higher density than a ferrofluid, is placed in that fluid, it sinks. However, if the fluid is then placed between the like poles of two identical magnets, the object rises to the centre of the fluid and stays there until the field is removed.[30] This is the phenomenon of magnetic levitation which relies upon the interaction of pressure and magnetic energy. The field at the centre of the fluid is zero and increases towards the edges. It follows that the pressure must also be at its lowest in the centre of the fluid, this being the driving force behind levitation.

The most interesting feature of magnetic fluids is that of surface instability. If a magnetic field is orientated perpendicular to a pool of ferrofluid, at a critical intensity the flat surface breaks up into a hexagonal pattern of spikes. Small random waves that are always present on the fluid[31] surface become amplified because they focus the magnetic field and with it the magnetic stress to which they themselves are subjected. When the magnetic force exceeds the restoring forces of surface tension and gravity, numerous small peaks begin to appear on the surface. The peaks that grow fastest tend to suppress their neighbours, so that the surviving peaks are uniformly spaced at the maximum possible distance. The spacing is most efficiently accommodated into a hexagonal pattern. For surface instability to be observed, the fluid must contain at least 20% by weight of magnetic material.

Magnetic particles in a ferrofluid often form random clusters which regroup into long chains when an external field is applied, the chains being orientated parallel to the field direction.[3] The degree of clustering or chaining is greater for iron than for Fe_3O_4 because of the greater saturation magnetization of iron. Chaining occurs in an applied field because the particles function as individual bar magnets which line up end to end, thereby minimizing the energy of the system. This rigid alignment is responsible for a significant increase in viscosity. However, a true magnetic fluid will still exhibit Newtonian flow even in an applied field.

Viscosity can be related to particle diameter and magnetic volume fraction in a quantitative manner.[32] These results show that highly concentrated (high saturation magnetization) ferrofluids of greatest possible fluidity are favoured by particles of small surfactant coating thickness, large particle radius and spherical shape. These desired trends are opposite to the requirements for stabilization as a colloid, so compromises must obviously be made.

1.7. APPLICATIONS OF MAGNETIC FLUIDS

1.7.1. Technical Applications Preferring Hydrocarbon-Based Ferrofluids

It was in 1968 that the newly formed Ferrofluidics corporation of Nashua, New Hampshire, U.S.A., pioneered the first commercial use of a magnetic fluid, in rotating shaft seals. The gap that is always present between a rotating shaft and its supporting structure was plugged with a few drops of ferrofluid and surrounded by a permanent magnet. The fluid creates an impermeable ring around the shaft while allowing it to rotate with negligible friction. These seals are particularly useful in differential pressure systems but have also been used in gas lasers, motors and, more recently, in computer disc memory units. Fluids of low vapour pressure and high thermal conductivity are used since temperatures of 100°C and shaft speeds of 5000 rpm are frequently encountered.[33]

A sample of ferrofluid used to fill the gap between voice coil and permanent magnet in a loudspeaker serves to dissipate heat and helps remove unwanted resonances in the signal output.[34] Once again, the emphasis is on ferrofluids dispersed in low vapour pressure carrier liquids.

Ferrofluids have been employed as engine shaft seals[35] where there is axial (linear) motion of a piston. Loss of fluid from the seal region is prevented by a field gradient which exerts a restoring force upon the fluid. Lubrication, being the main function of the seal, necessitates small particles to avoid abrasion and wear on the shaft.

Ferrofluids have been used to detect cracks in oil pipelines. If a magnetic field is applied to an iron sphere then the field is accentuated around any surface imperfections which may contain straight lines. Magnetic fluid can be made to congregate around such imperfections to facilitate their detection.

Acicular magnetic particles are used in magnetic ink-jet printing.[36,37] The jet of ink is steered in flight by either an electric or a magnetic field. The particles, which exhibit remanent magnetizations, form printed characters which can be read by a magnetic reader.

A prototype magnetocaloric engine, utilizing a magnetic fluid, has been designed with the intention of producing low voltage high current electricity with improved efficiency.[20,38] The layout is illustrated in Figure 1.10. As a magnetic fluid, containing ferro- or ferri-magnetic particles, is heated, its magnetization decreases until the Curie temperature is reached where it becomes paramagnetic. Cold ferrofluid is attracted to a region of magnetic flux where it is heated. The fluid's magnetization diminishes and it is expelled from the field by cooler fluid arriving from below. A heat sink then cools the magnetic fluid to its original temperature in preparation for another cycle. The constant flow could be used to drive a turbine or pass through a magnetohydrodynamic generator for direct production of electricity.

1.7.2. Specific to Water-Based Magnetite Ferrofluids

Since much of the work in this study is concerned with aqueous magnetite dispersions it is relevant to mention in greater detail two specialist applications for such systems.

Magnetic levitation of solid bodies placed in a ferrofluid is utilized in the separation of non-magnetic ores according to density.

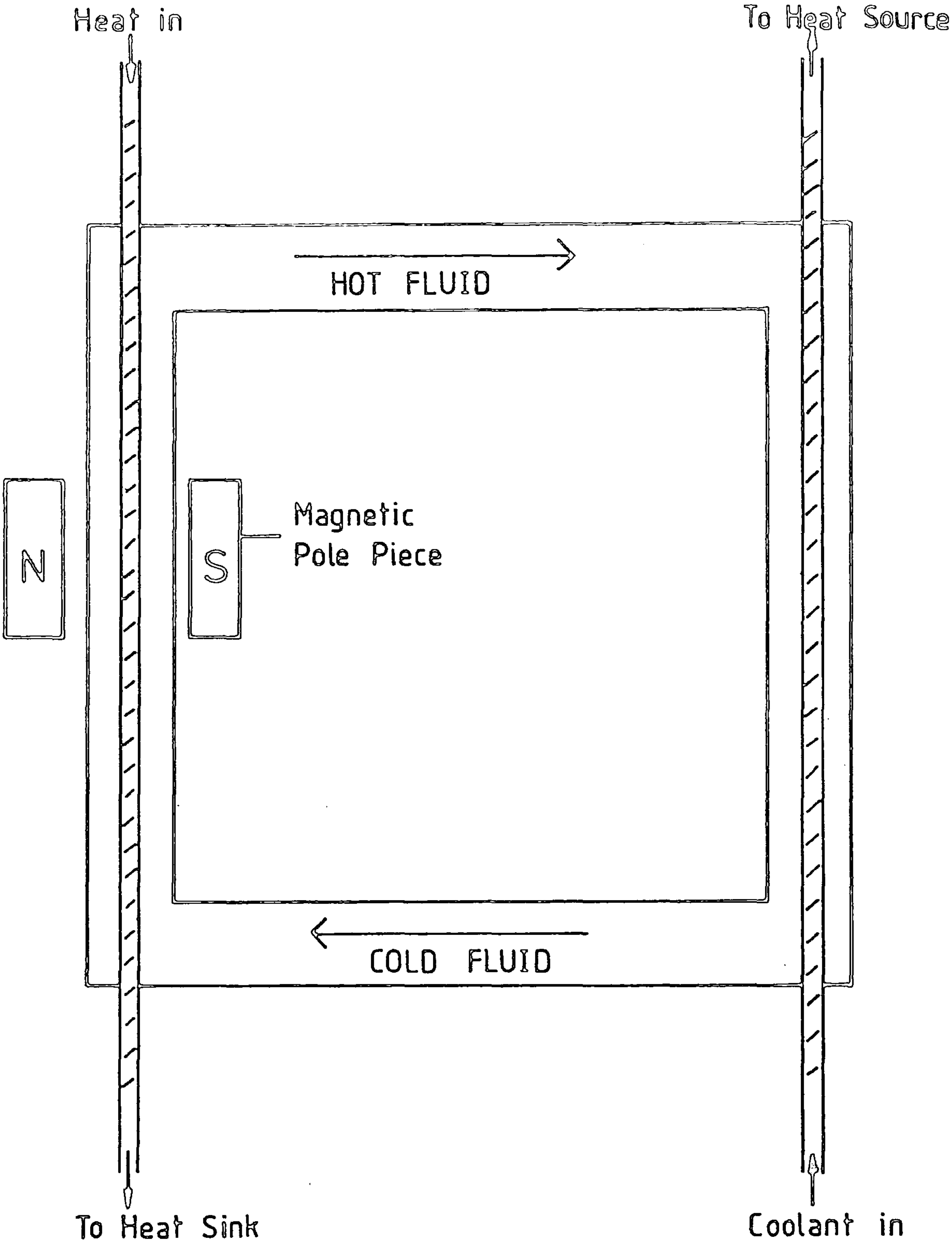


Figure 1.10. The working components of a magnetocaloric energy conversion system utilizing a magnetic fluid.

In a magnetic field gradient the ores rise within the fluid in order of increasing density.[39]

The separated ores are smeared with magnetic fluid which must be retrieved to leave the recovered metal free from contamination, and also for reasons of cost effectiveness. If the fluid was organic based it could be washed off with the appropriate solvent, but this would dilute the fluid with comparatively expensive solvent and an energy consuming process of evaporation would be required. In practice, water-based ferrofluids are used for two reasons.

i) The solvent is cheap, hence suitable for the high volume requirement of this application.

ii) Wasted ferrofluid is recovered by washing the ore with water. The diluted fluid is then acidified to flocculate the magnetic particles. These are magnetically decanted, washed with water and resuspended in the required quantity of water, with the addition of dilute alkali, to effect 99.8% recovery of magnetic fluid in its original concentration.[39]

The use of magnetic particles has created a great deal of interest in clinical medicine and biomedical research.[41] Widder et al.[40] first suggested that magnetic particles might be utilized as drug carriers for site-specific drug delivery. Clinical trials were carried out in humans using micron-sized magnetic particles surrounded by and stabilized with a protein/drug complex, the whole unit being known as a microsphere. These microspheres were drawn into the appropriate region of the body using a focussed magnetic field. Subsequent field modulation shook the drug free of the magnetic particles which were then destroyed in the liver.

The treatment of malignant tumours is not so much restricted by the range of drugs available, but more so by the difficulty of transporting them to a region of limited blood flow. For this reason small colloidal particles will have an advantage over their micron-sized counterparts. The greater surface area/volume ratio of the former will enable more drug to become attached per unit mass of Fe_3O_4.

Emphasis must be placed on low toxicity and compatibility with body tissue. For this reason, water-based ferrofluids employing Fe_3O_4 as the magnetic material are used. In this thesis, a range of naturally occurring proteins and polysaccharides will be evaluated as non-toxic surfactant materials. The very small particles, stabilized by natural materials, are at the stage of development for treating cancers by an intriguing new method.

The body produces tumour specific antibodies to counter the invasion of foreign cells and these ′monoclonal′ antibodies, which are basically proteins, can be isolated outside the body. There are points of attachment on the antibody both for drug and magnetic particle (via the protein's functional groups). Once injected back into the body the antibody-drug-particle complex will, given time, locate the tumour region of its own accord where it is ingested and enzymically destroyed with release of the drug. A focussed magnetic field, directed towards the malignant region, will supplement the natural homing instinct of the antibody-drug-particle complex and thus hasten delivery of the drug.

CHAPTER 2

MAGNETIC FLUID SYNTHESIS

INTRODUCTION

This section may be conveniently subdivided into metallic and non-metallic ferrofluids. Although the two types of fluid are similar both in appearance and magnetic properties, the mode of preparation is quite different.

2.1. BACKGROUND TO FERROFLUID PREPARATION

Historically, the development of magnetic fluids owes much to the work of Elmore[42] who fabricated magnetic colloids for use in the Bitter pattern technique[43] for the observation of magnetic domains in ferromagnetic materials; and to Luborsky who pioneered the development of elongated single-domain (E.S.D.) magnets.[44] As mentioned in chapter 1, the first known publication of a magnetic liquid preparation occurred when Wilson reported Gowan Knight's synthesis of artificial lodestone[1] (magnetite), the precursor of which was a magnetic suspension of iron filings in linseed oil. Neither this, nor Rabinow's synthetic clutch fluids[45] are regarded as true magnetic colloids because of their instability towards sedimentation over short time periods. We must not of course confuse ferrofluids with single phase 'liquid ferromagnets', theoretically predicted by Handrich and Kobe (1970),[46] but not as yet observed.

The first ferrofluid bearing any resemblance of colloidal stability was prepared by Papell[47] in 1965, by ball-milling a sample of coarse Fe_3O_4 for an extended period using oleic acid as a 'grinding agent', to produce particles $< 1000Å$ in diameter. He then suggested that a stable magnetic fluid, employing rocket propellant as the dispersing medium, could be used to ensure the continuous flow of propellant in zero-gravity conditions, an artificial gravity condition being imposed by magnetic fields.

Later, Rosensweig and various co-workers produced sub-200Å particles for dispersion in a variety of solvents including water, aliphatic and aromatic hydrocarbons,[20,48] thus establishing magnetic fluids as a totally separate research area.

2.2. NON-METALLIC FERROFLUIDS

These consist mainly of magnetite (Fe_3O_4) or other magnetic ferrites where some or all of the Fe^{2+} in octahedral sites is replaced by Co^{2+} or Ni^{2+}. Occasionally, complete substitution by other transition metal ions, as in manganese-zinc ferrite ($Mn_{0.5}Zn_{0.5}O.Fe_2O_3$), maintains a permanent magnetic moment within the crystal. γ-Fe_2O_3, which also adopts the spinel structure, is ferrimagnetic but generally unsuitable for magnetic fluids on account of the large and acicular nature of particles prepared by conventional methods. Fe_3O_4, having the largest saturation magnetization of the magnetic oxides (91 JT^{-1} kg^{-1}), is usually the preferred material.

2.2.1. Size Reduction by Grinding or Ball-Milling

This method starts with coarse magnetic oxide and, by a process of grinding, reduces the particle size to that required for colloidal stability. The technique was pioneered by Papell,[47] as mentioned previously. The slurry, consisting of Fe_3O_4, surfactant (oleic acid) and grinding agent in an appropriate carrier liquid, was placed in a cylindrical ball-mill containing $^1/2$ inch diameter steel balls and ground for a period of several days. The stable colloid was occasionally decanted, and milling continued with further grinding agent and carrier liquid. The final product was centifuged to remove entrained non-colloidal particles.

The technique was further investigated in 1965 by Rosensweig et al.[20] They found that an average particle size of 100Å is automatically generated in the process, but size distribution was substantial, sizes varying between 20 and 200Å. They also developed the concept of the monolayer surfactant coating, principles for selection of a dispersant, definitive measurement of particle size and factors affecting the maximum concentration of solid magnetic material. Near-quantitative conversion of the original solids to colloidal size particles was possible, although the net rate of production was increased by earlier removal of oversize solids and starting a new run. In 1967, the same author further developed the process and succeeded in dispersing magnetic particles of Fe_3O_4 and Mn-Zn ferrite in a variety of solvents using carboxylic acids, amines and succinic acid derivatives as surfactants.[48] The first application-specific ferrofluid was developed using Mn-Zn ferrite, which has a highly temperature-dependent magnetization, for use in heat exchange systems (see chapter 1).

A flow diagram of the basic grinding process for production of a magnetic fluid is illustrated in Figure 2.1.

An understanding of the dispersion process allowed Rosensweig to substitute one ferrofluid solvent for another.[49] When a polar organic solvent, such as ethanol or acetone, is added to a ferrofluid the particles flocculate. The flocculating agent makes the surfactant molecules less compatible with their fluid environment, this now comprising a mixture of polar and non-polar organic solvent or, alternatively, polar organic solvent and water. The surfactant 'tails' are repelled by the solvent combination, tending to fold back on themselves toward the surface of the particles. Thus, the depth of coating is effectively reduced. The flocculated particles may then be

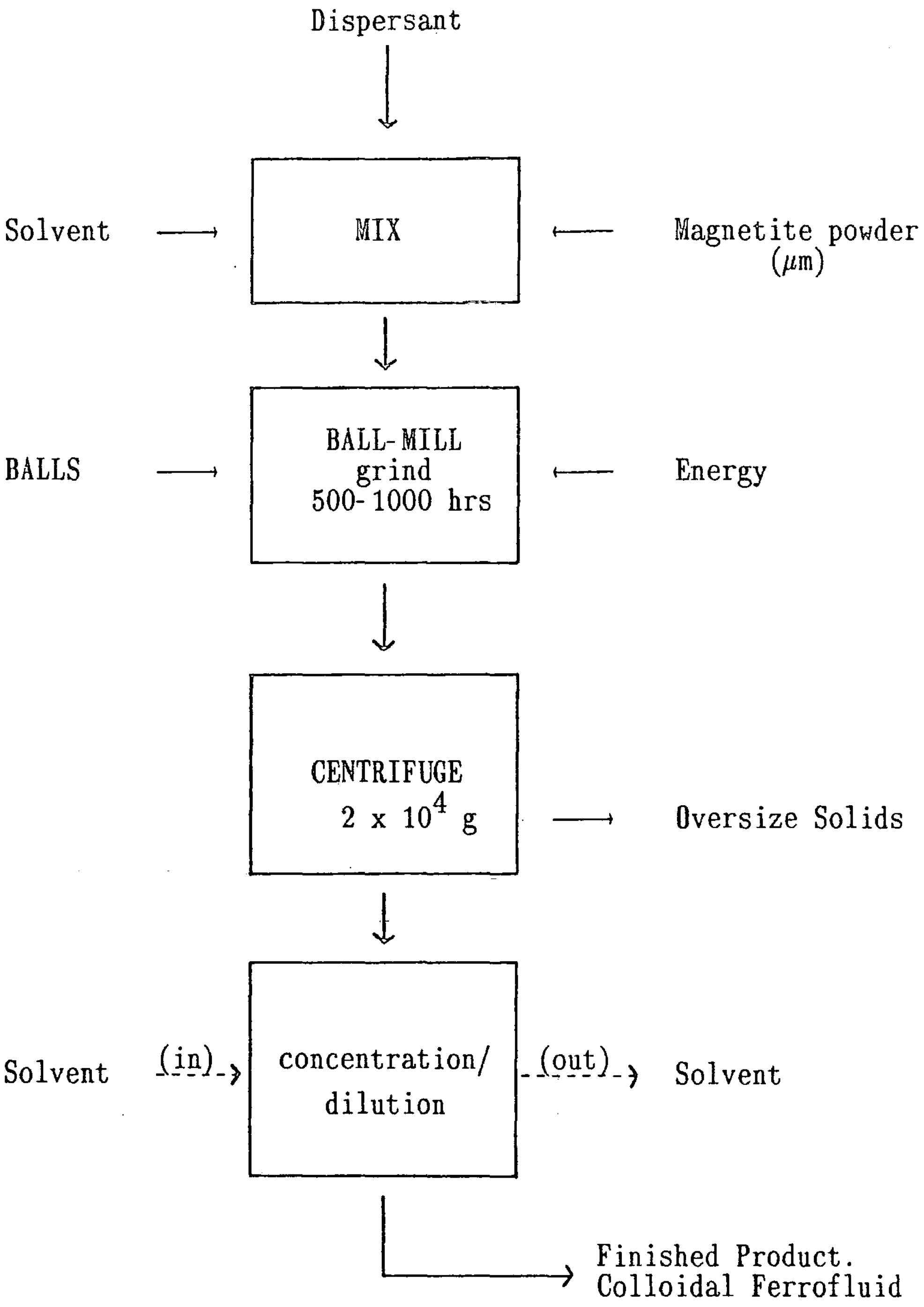


Figure 2.1. Flow diagram of the Ball-milling process for production of a magnetic fluid.

isolated and resuspended in an alternative carrier liquid. The entrained flocculating agent appears not to affect fluid stability.

This development was particularly useful since it allowed grinding to proceed in a low viscosity solvent (maximum grinding efficiency), which was then substituted for a more viscous carrier liquid with greater dispersing qualities.

A variation of this method came in 1975 from the same author,[50] who claimed to have irreversibly flocculated aqueous magnetic fluids, produced by ball-milling, with polar organic solvents. When the flocculating agent was removed the particles were not redispersable in water. This is, in fact, a consequence of the surfactant double layer in aqueous magnetite ferrofluids which maintains compatibility between surfactant sheath and solvent (see chapter 4). Ethanol or acetone just removes the second absorbed layer, the chemically adsorbed monolayer being unaffected. This explains why the particles were redispersable in organic solvents without the need for additional surfactant, but not in aqueous media.

Another variation on the same theme involved ball-milling a non-magnetic precursor compound to produce a stable colloid, and then converting the dispersed phase to a ferro- or ferri-magnetic form.[51] This process allows grinding to be accomplished without complications arising from interparticle magnetic attraction. Micron sized haematite (α-Fe_2O_3) particles were reduced to wustite (FeO) at 650°C using a 3:1 CO_2/CO mixture, whilst maintaining particle size and shape. The wustite, in its metastable form, was then ball-milled with kerosene and oleic acid after which, heating at 275°C caused the wustite to disproportionate into metallic iron and magnetite.

$$4FeO \rightleftharpoons Fe + Fe_3O_4$$

2.2.2. Precipitation from Mixed Fe^{3+}/Fe^{2+} Aqueous Solution

Alkaline hydrolysis of an aqueous solution containing Fe^{3+} and Fe^{2+} salts in the molar ratio 2:1 precipitates the black magnetic oxide, Fe_3O_4. This process is far less time consuming than ball-milling, the fundamental difference being that colloidal particles are generated by the growth of very small nuclei rather than size reduction of extremely large particles.

The first successful ferrofluid preparation using this technique involved room temperature precipitation of Fe_3O_4 in the way described above, using excess ammonium hydroxide as base.[52] Oleic acid was immediately introduced and the mixture heated to 95^{0}C with stirring. The newly formed ammonium oleate adsorbed at the particle surface before being decomposed to the parent acid with evolution of ammonia. Kerosene, or a similar organic solvent, was introduced and oleic acid coated particles partitioned into the organic phase leaving a clear aqueous layer containing dissolved ammonium salts. The organic fluid was decanted, and heated to remove any traces of water.

Ammonia was employed as the base because ammonium salts are subject to degradation at temperatures > 70^{0}C. Sodium hydroxide may also be used to precipitate Fe_3O_4 but needs to be removed prior to introduction of surfactant to avoid formation of the temperature stable sodium salt. Alternatively, oleate may be converted to the parent acid by quenching the suspension with hydrochloric acid.

Another modification involves isolating (usually by magnetic decantation) the gum-like solids of oleic acid coated magnetite prior to addition of kerosene. Washing the solids with acetone or ethanol not only removes excess water but also excess unadsorbed surfactant, surplus to requirements in organic-based dispersions.

Fe_3O_4 magnetic fluids prepared via the precipitation method and employing a variety of carrier liquids and surfactants are reported. These include silicone oil-based fluids with organosilicone surfactants, the fluids having low temperature dependent viscosities;[53] fluorocarbon-based fluids with an emphasis on high thermal stability;[54] and low vapour-pressure polyphenyl ether-based fluids for use in differential pressure seals.[55]

There are also reports of Fe_3O_4 precipitation in the presence of a surfactant,[56] though the significance of this variation is unclear.

Subsequent workers[25,57] discovered that a molar ratio of 3:2, Fe^{3+}:Fe^{2+} resulted in greater purity with respect to Fe_3O_4. The reaction proceeds via formation of iron(II) hydroxide and hydrated ferric oxide complexes. Air oxidation of iron(II) species occurs, especially at the high temperatures often employed (80-90°C). An excess of iron(II) over that required for stoichiometric conversion to Fe_3O_4 compensates for this, thus avoiding contamination of the product with non-ferromagnetic impurities. The main drawback is that wide size distributions are observed in the product.

Aqueous magnetite dispersions may be prepared using the precipitation method followed by addition of an appropriate surfactant. Khalafalla and Reimers[26] used a range of fatty acids (anionic surfactants) and fatty amines (cationic surfactants) and evaluated the fluids in terms of stability towards dilution, excess base and quantity of dispersing agent. Kelley[58] also prepared aqueous ferrofluids using petroleum surfactants. Shimoiizaka[59] prepared aqueous ferrofluids by separating the oleic acid coated particles, as obtained by Rosensweig, and dispersing them in an aqueous solution of short chain anionic or non-ionic surfactant which is more compatible with the solvent. This technique was also reported by Buske and Sonntag in 1984.[60]

The preparation of instant water-based magnetic fluid was now possible simply by adding base to a solution of iron(II) and iron(III) chloride containing the appropriate surfactant. The interaction of surfactant with the magnetic particles was understood in terms of the electric double layer effect (as explained in chapter 1) and its application to aqueous magnetic fluids.

The preparation of charge-stabilized magnetic fluids by precipitation methods, and without the need for a surfactant, was pioneered by Massart in 1981.[28] This will be discussed in more detail in chapter 5.

The precipitation method gives particles with narrow size distributions compared with the ball-milling technique. By altering the reaction conditions namely temperature, concentration of reagents, medium viscosity and doping the reaction medium with alcohol or added electrolytes, the mean particle size can be controlled between ~ 50Å and 100Å by changing the relative rates of nucleation and crystal growth. By choosing different iron(III) oxide precursors (with different solubility characteristics) particles as large as 1000Å may be prepared. These particles, although spherical, are obviously too big for colloidal stability.

2.3. METALLIC FERROFLUIDS

This section deals with the various ways in which fine metallic particles of the ferromagnetic elements may be prepared, and their dispersion in a suitable carrier liquid.

2.3.1. Evaporation Techniques

Fine metal particles typically $< 10^4$Å in diameter may be prepared by evaporation of bulk metal in the atmosphere of an inert gas such as nitrogen, argon or helium.[61,62] The metal is heated in an evaporation chamber by a variety of methods including electric arc, RF induction and laser beam heating. The vaporized metal atoms collide with cooler gas atoms causing metal condensation (nucleation). Particle size is dependent on the nature of the gas used, the gas pressure and the temperature at which metal is evaporated. Maintaining constant temperature and pressure, the particle size was found to increase in the order helium, argon, xenon. An increase in either temperature or pressure results in larger particles being produced. Gas pressure ranges between 0.1 and 300 mm Hg. At 3 mm Hg, using argon gas, 150Å particles of iron or cobalt are obtained. These particles have a narrow size distribution and are particularly stable towards oxidation.

Using mixed-metal alloys it is possible to obtain fine particles of similar constitution to the starting material. Iron-cobalt,[63] iron-nickel[64] and iron-cobalt-nickel[65] alloy particles have all been prepared in this way. Shepherd et al.[66] have produced a rare-earth gadolinium ferrofluid by evaporation onto a mercury surface agitated by a stream of argon. This arrangement helps to suppress the growth of particle nuclei.

2.3.2. Electrodeposition

This is a convenient way of producing small single-domain ferromagnetic metal particles and incorporating them into a liquid-metal carrier, in particular mercury, or a low melting point alloy containing such metals as cerium, tin, indium and bismuth. Salts of the ferromagnetic metals dissolved in water or alcohol are used, with the liquid-metal carrier as cathode in an electrolytic cell. Agitation of the carrier, for example under a stream of argon, promotes the formation of small spherical particles. Iron, nickel, cobalt and their alloys[67,68] have all been deposited into mercury and its alloys by this technique, the composition of the particles being governed by the ratio of metal salts in the original solution. The growth of particles, both during and after deposition, may be suppressed by doping the mercury cathode with tin or sodium metal to form an amalgam.[69,70] In this way particles as small as 40Å have been observed.

These mercury based systems cannot be regarded as true ferrofluids because Van der Waals forces will eventually aggregate the particles, even when formed in the presence of tin or sodium. These fluids will presumably have an advantage in applications requiring high thermal or electrical conductivity, but their usefulness is further restricted by the high viscosity imparted by even low concentrations of ferromagnetic material. This effect has been studied for iron fluids by Hoon et al[71] and found to be dependent on particle size. For a particle size of 40Å, the iron concentration at which the fluid becomes a slurry is ~ 0.8 weight %.

2.3.3. Spark Erosion

Spark erosion results from maintaining an electric discharge between two electrodes immersed in a dielectric medium. The heat generated causes micron size molten droplets and vaporized material to be ejected from one or both electrodes. The vaporized material then condenses into colloidal size particles when cooled by the surrounding fluid.[72,73]

If the electrodes are composed of a ferromagnetic metal or its alloys, then the resulting particles will be suitable for magnetic fluid preparations.

The spark discharge also causes polymerization of the dielectric liquid, typically an aromatic or aliphatic hydrocarbon, into a fibrous solid form. This enmeshes the magnetic particles in the same way as a polymeric surfactant would. The encapsulated metallic particles are then isolated magnetically and resuspended in a suitable carrier liquid by ultrasonication. Large micron size particles fall out of suspension leaving an upper layer of stable ferrofluid.

In this way it is possible to prepare magnetic fluids containing up to 5% magnetic material with mean particle diameters in the range 25Å-100Å.

2.3.4. Chemical Reduction

Chemical reduction of aqueous solutions of ferromagnetic metal salts, using sodium borohydride[74] or sodium hypophosphite[75] as reducing agent, has been used to prepare fine magnetic particles of sub-micron size. The system can be doped with a palladium chloride catalyst. This is reduced to palladium metal in particulate form which then acts as seed crystals for the growth of ferromagnetic particles.[76] The addition of water-soluble viscosity increasing agents such as gelatine or carboxymethyl cellulose can help to limit the particle size.[77] However, particles are generally acicular and of dimensions too large for use in magnetic fluids.

2.3.5. Decomposition of Organometallic Compounds

This is the most frequently used route to metallic fine particle magnetic fluids, and involves the thermal or ultraviolet decomposition of zerovalent ferromagnetic metal compounds, in particular metal carbonyls. Cyclopentadienyl complexes may also be used with the added requirement of a reducing agent such as molecular hydrogen.

Early work in this area was dominated by the production of fine metallic cobalt in the thermal decomposition of dicobalt octacarbonyl

$[Co_2(CO)_8]$ by refluxing in toluene for several hours.[3] The particles obtained were ~ 1000Å in diameter and particularly unstable towards oxidation.

Sub-100Å single domain cobalt particles, with a face-centred cubic (fcc) crystal structure, were obtained by performing the same reaction in solutions containing high molecular weight polymeric materials such as methyl metacrylate/ethyl acrylate copolymer.[78,79] The polymer, comprising a hydrocarbon chain with at least one polar adsorptive group every 200 backbone atoms, has three functions.

i) It controls particle size by altering the relative rates of nucleation and crystal growth.

ii) In sub-100Å particles, the polar groups adhere to the metal surface leaving the bulk of the polymer to form a thick protective layer around the particle.

iii) This coating helps prevent oxidation of the particle surface layers.

A range of mean particle sizes between 10Å and 200Å, with narrow size distributions, have been obtained by varying the type (molecular weight) and concentration of dissolved polymer. Evaluation of several such polymers as possible surfactant materials has been undertaken by Hess and Parker.[3]

Non-polymer dispersants such as Sarkosyl-'O' and Aerosol O.T.[80,15] have recently been added to the list of size controlling surfactants, to give stable cobalt magnetic fluids with saturation magnetizations up to 35 $J/T^{-1}/kg^{-1}$ and a viscosity of a few centipoise.

Typical carrier liquids for the thermolysis of the carbonyl include aromatic, aliphatic and halogenated hydrocarbons as well as ethers.

More recently, preparation of metallic iron ferrofluids was achieved via the thermal decomposition of either iron pentacarbonyl,[81,82] diiron nonacarbonyl or triiron dodecacarbonyl[83] in organic-based solutions of a functional polymer or non-polymeric surfactant. In the former case, the polymer served as a catalyst for the decomposition of $Fe(CO)_5$ and induced particle nucleation in its vicinity. Thermolysis proceeded at 150°C under a blanket of argon using decalin, xylene, dichlorobenzene or chlorobenzene as the organic solvent. Mean particle size, in the range 50Å-200Å, varied according to the polymer/solvent system chosen and the iron:polymer weight ratio. Particles below 80Å were spherical and amorphous in nature, whilst those above 80Å adopted definite crystallographic shapes giving rise to sharp electron diffraction lines typical of the α-iron body-centred cubic (bcc) crystal lattice. Surface oxidation gave rise to a 30Å thick layer of γ-Fe_2O_3 which subsequently picked up moisture to give a non-magnetic β-FeOOH 'dead layer'.

Nickel magnetic fluids have been prepared by the thermal decomposition of nickel tetracarbonyl in benzene[84] and, more recently, by ultraviolet decomposition of the same nickel compound in toluene and also by hydrogen reduction of less toxic nickelocene.[85] Particles with diameters ~ 50Å with an fcc crystal structure were observed.

The first preparation of a mixed-metal particle ferrofluid by the organometallic decomposition route was achieved by Mason et al, in 1985.[6] A 1:1 iron-cobalt alloy fluid was prepared by the thermal decomposition of a mixed metal carbonyl precursor ($(\pi$-$C_5H_5)Fe(CO)_2Co(CO)_4$) in toluene based surfactant solution. Particles in the range 50-80Å were physically observed whilst electron diffraction revealed them to have an ordered "superlattice" bcc crystal structure.

Alloy particle magnetic fluids are particularly attractive as they permit some control over such parameters as Curie temperature, saturation magnetization and crystalline anisotropy. For instance, iron-cobalt alloys in the range $0 < x < 60$ wt. % cobalt have higher saturation magnetizations than straightforward iron particles.

Other ordered phase single-domain bimetallic particles have been prepared by Mason[86] using heteronuclear metal-metal bonded dinuclear complexes as the non-magnetic precursors. These materials were synthesized in the laboratory prior to decomposition. Co_3Fe and Ni_3Fe alloy particles were prepared, their overall composition being established by energy dispersive analysis of X-rays using an electron microscope. With the possible exception of cobalt, preparation of alloy magnetic particles has proved significantly easier than their single metal counterparts.

CHAPTER 3

REAGENTS, TECHNIQUES AND INSTRUMENTATION

3.1. STARTING MATERIALS

i) Iron Salts

Hydrated iron(II) and iron(III) chloride were obtained as 99.9% pure products from BDH Chemicals. The iron(II) salt was stored under nitrogen to avoid oxidation, whilst iron(III) chloride was kept dry with a sachet of silica gel desiccant.

ii) Surfactants

A wide range of fatty-acids were employed as surface-active materials. Some were low melting point solids, e.g. stearic and lauric acid, whilst others were liquid at room temperature, e.g. oleic and octanoic acid. A full list of the surfactants employed in these studies and selected characteristics are given in Table 3.1. In cases where water solubility was required, salts were prepared prior to use. The polymeric surfactants used are described more fully in chapter 7.

iii) Solvents

Water was the most widely used carrier liquid, distilled water being used on all occasions. Hydrocarbon solvents, where applicable, were used as supplied by the manufacturer.

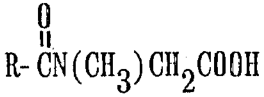
3.2. EXPERIMENTAL TECHNIQUES

Although magnetite once formed is fairly stable to atmospheric oxidation, air must be eliminated immediately prior to precipitation so that the stoichiometric ratio of iron(III):iron(II) is retained. If the precipitation is undertaken in air, compensation for oxidation of iron(II) to iron(III) is made by using a molar ratio of 3:2, iron(III):iron(II), but this gives a much wider particle size distribution.

In all our studies Fe_3O_4 was precipitated from mixed

TABLE 3.1.

Surfactants used in this Study

Name	Class	Formula	Supplier
Sarkosyl-'0'	Anionic	 $R-\overset{O}{\overset{\parallel}{C}}N(CH_3)CH_2COOH$	Ciba-Geigy
Oleic acid	Anionic	$R-COOH$	B.D.H.
Stearic acid	Anionic	$CH_3(CH_2)_{16}COOH$	Koch-Light
Myristic acid	Anionic	$CH_3(CH_2)_{12}COOH$	B.D.H.
Lauric acid	Anionic	$CH_3(CH_2)_{10}COOH$	Aldrich
Decanoic acid	Anionic	$CH_3(CH_2)_8COOH$	Aldrich
Octanoic acid	Anionic	$CH_3(CH_2)_6COOH$	B.D.H.
Dispex GA 40	Polymeric/Anionic	*	Allied Colloids
Gelatin	Polymeric/Amphoteric	*	B.D.H.
Polygalacturonic acid	Polymeric/Anionic	*	Fluka
Carboxymethyl Cellulose	Polymeric/Anionic	*	Sigma

* See chapter 7.

$R = CH_3(CH_2)_7CH{=}CH(CH_2)_7$

iron(III)/iron(II) chloride solutions (molar ratio 2:1) prepared using deaerated water. Precipitation was facilitated by rapid mechanical stirring whilst maintaining a steady flow of nitrogen until the reaction was complete. Temperature was carefully controlled by isomantles fitted with thermostats.

In most cases the particles were surfactant stabilized before aggregation could occur. In some instances, especially with the shorter fatty-acid surfactants or with large (> 100Å) particles, an IKA-WERK high shear mixing device was used to separate the particles. If this was unsuccessful, the particles were dispersed using a Dawe Instruments ultrasonic cell disrupter consisting of a titanium alloy probe vibrating at 20,000 Hz.

The pH of fluids and reaction mixtures was measured using an EIL direct reading pH meter with combined glass and silver/silver chloride electrode. The instrument was periodically calibrated with pH 5 or 9 buffer solutions, depending on whether readings were to be taken in acidic or alkaline media.

3.3. INSTRUMENTATION

The following specialist analytical techniques were used to study the materials prepared in this work.

3.3.1. Electron Microscopy

A transmission electron microscope was used for obtaining particle shape and size data. Using a Philips EM 400 T instrument, shadow electron micrographs at magnifications ranging from 100,000 to 360,000 revealed discrete particles of sufficient clarity for size determination.

In many instances fluids were sufficiently weak for electron microscope study without further dilution. Other fluids were simply diluted with the appropriate carrier liquid.

A drop of fluid was placed on a specially prepared 3 mm copper grid coated with a composite layer of carbon and formvar. The sample was bombarded with high energy electrons under an accelerating voltage of 100 kV and the images preserved on Kodak 83 mm electron microscope film.

3.3.2. The Automated Electro-Optic Image Size Analyser

This instrument was used to obtain physical sizes and size distributions for the particles observed by electron microscopy. The electron micrograph negatives were printed onto Kodak lightweight projection paper. The print was then placed on a flat raised transparent surface through which was projected a narrow beam of light, the diameter of which could be adjusted using an iris. The beam diameter was made to coincide with each particle in turn and the data recorded by a BBC microcomputer. A pen automatically marked each particle as it was analysed thereby preventing duplication. The microcomputer gathered all the particle size data and converted it to particle diameters. The data were then 'binned' and displayed as a histogram with a calculated mean diameter and standard deviation, the latter being a measure of size distribution. Normally 300-500 data points were required to give reasonable distributions with good statistics. The instrumentation package is described in more detail by Hoon et al.[87]

3.3.3. Magnetic Analysis: The Vibrating Sample Magnetometer (VSM)

This instrument was used to generate magnetization curves for magnetic fluids and solid magnetic material. A schematic diagram of the VSM is given in Figure 3.1. The magnetic fluid was weighed into a small glass bulb and positioned between the poles of a variable electromagnet.

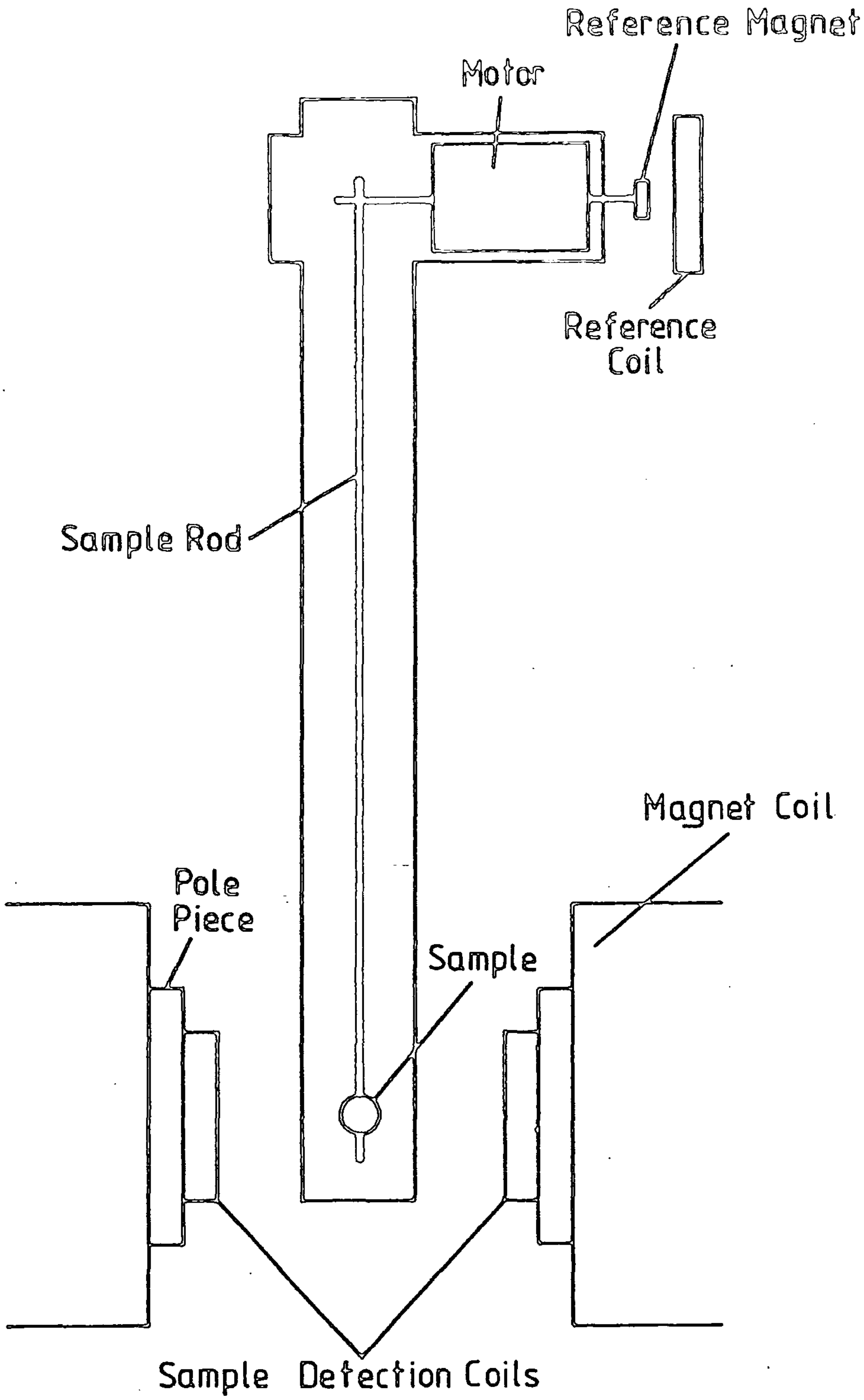


Figure 3.1. An illustrative representation of the vibrating sample magnetometer.

The sample was vibrated in a direction perpendicular to the applied field, thus inducing an e.m.f. in the detection coils located on the magnetic pole pieces. The range of applied field, +1.2 to -1.2 Tesla, was scanned at intervals of 0.01 Tesla whilst the sample was vibrating. An A.C. voltage was thus generated in the detection coils. Simultaneously, a cobalt permanent magnet used as a reference sample was made to vibrate between a pair of reference coils inducing another A.C. voltage. The signal to noise ratio of both outputs was improved by feeding them into a phase sensitive detector. The output (a D.C. voltage) was proportional to the magnetic moment of the sample, which was obtained after calibration of the instrument with a nickel standard.

Room temperature magnetization curves were kindly recorded by D.B. Lambrick in the Department of Physics. σ_{ff} (the magnetization per unit mass) is plotted against B_0 (the applied field). The saturation magnetization value for each fluid was obtained either directly or by extrapolation, and gave a measure of fluid strength in terms of magnetic material concentration. From this value and from the data obtained in generating the curve, mean particle sizes and size distributions were derived as indicated in chapter 1, section 3.

3.3.4. Magnetic Analysis: The Gouy Magnetometer

The Gouy method was particularly useful for estimating particle diameters in weak ferrofluids. The method is less time consuming than the VSM technique. It was used in preliminary investigations and where comparisons rather than exact values were required.

Using a Johnson Matthey magnetic susceptibility balance, values for the mass susceptibility (χ_g) of ferrofluids were obtained. The sample, contained in a narrow cylinder, was placed between the poles of a permanent magnet. The enrgy of the ferromagnetic sample is lowered when in the magnetic field and is attracted to it. The instrument is essentially a balance which measures this force on the sample. χ_g was substituted into the following equation to generate upper limits for mean particle size.[88]

$$d_{upper} = \sqrt{\frac{18\,kT\,\rho_{Fe_3O_4}\;\chi_{ff}}{\pi\,(M_b^{\infty})^2\;\varepsilon_m}}$$

where $\rho_{Fe_3O_4}$ (density of Fe_3O_4) = 5240 kg m^{-3}

$M^{\infty}_{Fe_3O_4}$ (saturation magnetization of Fe_3O_4 per unit volume) = 4.77 x 10^5 $JT^{-1}kg^{-1}$

$\chi_{ff} = \chi_g$ (c.g.s.) x 10^4 in $JT^{-1}kg^{-1}$

ϵ_m = mass fraction of Fe_3O_4 in ferrofluid.

3.3.5. Atomic Absorption Analysis

Iron analyses of ferrofluids and solid samples were measured using a Perkin-Elmer 5000 atomic absorption spectrophotometer. A small sample was weighed and dissolved in concentrated nitric acid. The solution was diluted with water to a total concentration of ~ 3-5 ppm iron, this being the region where the instrument functions with maximum accuracy. The spectrophotometer was calibrated with standard iron(III) nitrate solution prior to analysis, and again after estimation of the unknown sample.

3.3.6. X-Ray Powder Diffraction

This technique was used to determine the composition of the oxide material. Different oxides have different crystal structures and hence give recognizable diffraction patterns when irradiated with X-ray photons. The sample may be a solid or a concentrated ferrofluid, packed into a 0.5 mm capillary tube which is mounted in a special camera.

A molybdenum source was used to generate Kα and Kβ radiation. The Kβ was removed by a thin zirconium window placed in the X-ray beam. A working voltage of 35 Kv and current of 30 mA were used, and under these conditions, 3-4 hours was sufficient to generate good diffraction patterns.

The X-rays are scattered by the rotating sample, giving a series of concentric rings on Kodak 'DEF-392' 35 mm direct exposure film. From the diameters of these rings the d-spacings for the crystal were calculated. Identification of the oxide or oxides present was made by comparison with literature values.

3.3.7. Infra-Red Spectroscopy

Infra-red spectra in the frequency range 300-4000 wavenumbers (cm^{-1}) were recorded using Perkin-Elmer 577 and 580 grating spectrometers and, more recently, on a Mattson 'Polaris' Fourier-transform infra-red spectrometer. Solid samples were mounted as nujol mulls between KBr or NaCl plates. A single scan speed of 13 minutes gave adequate resolution of the low frequency iron oxide peaks.

CHAPTER 4

PREPARATION AND CHARACTERIZATION OF SURFACTANT DISPERSED Fe_3O_4 MAGNETIC FLUIDS

INTRODUCTION

Significant interactions between the different components of magnetic fluids occur both during and after the preparative stage because of the very nature of colloidal systems. The surfactant molecule is required to form a bridge between magnetic particles and the carrier liquid, by a process of adsorption. The following interactions must therefore be considered:

i) Surfactant-particle interaction

Prior to adsorption, the surfactant interacts strongly with the carrier liquid in which it is dissolved. For adsorption to occur, one end of the surfactant molecule (the 'head group') interacts more favourably with the particle surface than with the solvent.

ii) Surfactant-carrier liquid interaction

Once adsorption has taken place, the rest of the surfactant molecule must remain compatible with the carrier liquid so as to effect steric stabilization.

These factors will be influenced by the nature of both the surfactant and the carrier liquid. Bearing this in mind, it is possible to draw distinctions between aqueous and non-aqueous magnetic fluids in terms of preparative techniques, choice of surfactant and the nature of stabilization.

4.1. NON-AQUEOUS MAGNETIC FLUIDS

Choice of surfactant is vitally important in the preparation of stable magnetic fluids. Essential features include a polar 'head' group capable of adhering to the particle surface, and an organic 'tail' which interacts favourably with organic solvents. This organic 'tail' must satisfy the following criteria for stability in hydrocarbon solvents.

i) It must be sufficiently hydrophobic so as to be compatible with the carrier liquid. A minimum hydrocarbon chain length of eighteen carbon units (C_{18}) fulfills this requirement.

ii) It must contain, along its length, a double bond (as in oleic acid or Sarkosyl-'O'). This produces a kink in the chain and helps prevent interaction between surfactant sheaths on neighbouring particles. Such interaction may not only reduce the distance between particles (loss of steric stabilization) but may also induce crystallization of the surfactant.[7] To illustrate this effect, stearic acid (oleic acid without the double bond) is incapable of dispersing Fe_3O_4 in organic media.

4.1.1. Fluid Preparation

Initial attempts to create stable dispersions involved mixing together, by means of ultrasonication, finely divided magnetite powder with a solution of oleic acid in toluene. Even at high temperatures only very weak dispersions could be obtained in this way, probably due to a combination of two factors:

i) By first drying the magnetite, particle aggregates may have formed. Because of the strong attractive forces between particles, they will be difficult to separate even with ultrasonic bombardment.

ii) The surfactant 'head' group in its unionized form will have a greater affinity for the carrier liquid than for the particle surface. Under these conditions adsorption will be unfavourable.

The preparation of Reimers et al,[52] with selected modifications, overcomes both these problems. The idea is to precipitate Fe_3O_4 with an excess of aqueous ammonia which places a layer of negative charge around the newly formed particles and hinders aggregation. Oleic acid is introduced and is immediately converted to partially soluble ammonium oleate. Because of the nature of the electric double layer at the particle surface (see chapter 1), the oleate anion is attracted to and chemically adsorbed at the inner Helmholz plane. Furthermore, the limited solubility of ammonium oleate in water means that the loss of hydration energy associated with adsorption will be minimized.

The adsorbed ammonium oleate is decomposed at 90°C to form oleic acid coated particles which are then dispersed in organic solvents.

Procedure

Fe_3O_4 (10 grams) was precipitated from a mixed iron(III)/iron(II) chloride (molar ratio 2:1) solution in deaerated water at 80°C using an excess of 33% aqueous ammonia. Oleic acid (1 gram:1 gram Fe_3O_4) was immediately added and the suspension stirred at 90°C for 30 mins. or until a black gum-like solid formed. This solid was isolated and quenched with 2 molar aqueous perchloric acid ($HClO_4$) to ensure complete conversion to oleic acid. Washing with water then removed excess $HClO_4$ along with any unwanted ammonium chloride. Excess oleic acid was removed by washing with warm ethanol[50] and twice with acetone. The chosen organic solvent (40 ml) was added. Subsequent heating removed any residual acetone and resulted in an organic based magnetic fluid. The fluid was placed over a permanent magnet and a small quantity of entrained particles removed by decantation. The stable fluid was evaporated to maximum magnetite concentration.

The same experiment was performed using Sarkosyl-'O' instead of oleic acid.

4.1.2. Analysis and Discussion

Four organic based ferrofluids were prepared in the way described. The carrier liquid and surfactant employed in each are set out in Table 4.1. along with the maximum Fe_3O_4 content, obtained by atomic absorption

TABLE 4.1

Maximum magnetic weightings in organic-based ferrofluids

Fluid	Carrier Liquid	Surfactant	Weight % Fe_3O_4
4.1.1.	Petroleum-ether 200-240°C	Oleic acid	33.8
4.1.2.	Petroleum-ether 100-120°C	Oleic acid	22.8
4.1.3.	Petroleum-ether 30-40°C	Oleic acid	16.4
4.1.4.	Petroleum-ether 200-240°C	Sarkosyl-'O'	24

analysis. Electron micrographs of Fluids 4.1.1. and 4.1.4., having been diluted with petroleum ether, were taken at x220,000 magnification and then analysed for particle size. This revealed diameters of 67Å and 61Å respectively. An electron micrograph of Fluid 4.1.1. (after dilution) is displayed as Figure 4.1. This is typical of the organic-based dispersions prepared in the study.

Referring to Table 4.1., oleic acid is seen to disperse more Fe_3O_4 than Sarkosyl-'O'. This is also reflected in the particle sizes of the two fluids. It appears that oleic acid will disperse larger particles than Sarkosyl-'O'. A more extensive study of this phenomenon is included in chapter 7. For a series of petroleum carrier liquids consisting mainly of saturated hydrocarbons between C_5 and C_{15}, Fe_3O_4 content of a ferrofluid is seen to increase with increasing chain length and hence boiling point of the solvent. The C_{18} surfactant chains seem more compatible with the higher molecular weight hydrocarbons, but there may also be a contribution from the high solvent viscosity which effectively slows down the rate of sedimentation.

4.1.3. Flocculation and Redispersion in Other Organic Solvents

As mentioned in the preparation, oleic acid coated particles may be washed with a polar organic solvent, such as ethanol or acetone, to remove excess surfactant but to retain that which is adsorbed onto the particle surface. This is confirmed by the redispersion of such particles in a non-polar organic solvent to give a stable magnetic fluid. In fact, particles washed in this way gave rise to more concentrated fluids than if the washing stage had been omitted. It appears therefore that excess surfactant, which presumably becomes dissolved in the bulk carrier liquid, impairs stability.

The remainder of Fluid 4.1.1. was flocculated by mixing with an

Fig.4.1 Electron micrograph of Fluid 4.1.1 (×200,000)

equal quantity of acetone. After magnetic decantation, followed by extensive washing with ethanol and acetone, portions of the slurry were resuspended in various different carrier liquids to test for their ability to disperse the particles. Success, or otherwise, is indicated in Table 4.2. Of the non-polar organic solvents, all except 1-methyl naphthalene and mineral oil gave stable fluids. These two exceptions are by far the most viscous solvents being studied. The bulkiness of their molecules may impede the interaction of surfactant and carrier liquid. As a result the surfactant chains will interact with themselves giving rise to flocculation.

Polar organic solvents, both protic and aprotic, cause flocculation of magnetic fluids.[49] They have a far greater affinity for themselves than for the alkyl chains of surfactant molecules. This causes the chains to fold inwards and subsequent loss of steric stabilization produces flocculation.

As the homologous series of alcohols is ascended, interaction between the alkyl chains of surfactant and carrier liquid becomes increasingly favourable. As a result, alcohols below C_8 (octanol) caused flocculation whilst C_8 and above gave progressively more Fe_3O_4 in the fluids.

4.2. AQUEOUS MAGNETIC FLUIDS

The preparation of Khalafalla and Reimers in 1980[26] is typical of that used in the production of aqueous magnetic fluids. It involves heating an aqueous suspension of magnetite at 80°C in the presence of ammonium dodecanoate to give an instant water-based fluid.

Our own efforts to reproduce this experiment resulted, on each occasion, in semi-stable dispersions which quickly settled out in a

TABLE 4.2

Magnetic fluid stability as a function of carrier liquid

Carrier-Liquid	Dispersion Characteristics
Petroleum-ether 200-240°C	√
Petroleum-ether 100-120°C	√
Petroleum-ether 30-40°C	√
Hexane	√
Decane	√
Cyclohexane	√
Xylene	√
Toluene	√
Decalin	√
1-methyl naphthalene	X
Mineral oil	X
n-pentanol	X
n-octanol	P
n-decanol	√
n-butyl acetate	X
Diethylamine	√
Dimethyl Sulfoxide	X

√ = complete dispersion
P = partial dispersion
X = flocculation

directional magnetic field. It was this kind of inconsistency which first suggested that preparation of water-based fluids would not be quite so straightforward as their non-aqueous counterparts.

The results and conclusions presented in this study illustrate the complex and often temperamental nature of aqueous magnetic fluid preparations. There have indeed been many failures along the way.

4.2.1. Fluid Preparation

The range of surfactants suitable for aqueous systems is large compared with non-aqueous systems. Straight chain fatty acids ranging from eight to eighteen carbon atoms in length, (C_8-C_{18}), all show signs of surface activity. In addition, oleic acid and Sarkosyl-'O' are equally suitable in aqueous as well as non-aqueous media.

A general purpose fluid preparation is described below, followed by additional comments on the relative abilities of each surfactant to disperse magnetic particles.

i) Procedure

Fe_3O_4 (1 gram) was precipitated from a mixed iron(III)/iron(II) chloride solution (molar ratio 2:1) in deaerated water (100 ml) at 80^oC, with excess 33% aqueous ammonia. 1 gram neat surfactant was immediately added and stirred in at 90^oC for 30 minutes. The suspension/dispersion was cooled and to it was added 2 molar perchloric acid (30 ml). Immediately a black gum-like solid formed which was settled out over a magnet leaving a clear supernatant liquid with a thick surface scum (excess surfactant). The black solid was washed several times with distilled water and then resuspended in water (20 ml) at 80^oC containing a few drops of aqueous ammonia.

ii) Results and Discussion

The fluids were analysed by atomic absorption analysis for weight %

iron, and hence Fe_3O_4. The results are displayed in Table 4.3. Of the straight chain fatty acids, all except hexanoic acid (C_6) were capable of surfactant activity. It appears that the C_6 alkyl chain provides inadequate cushioning of the magnetic particles and longer chains are required for dispersion. With reference to the electron-micrographs of Figure 4.2. stearic acid based fluids have discrete, well separated particles whilst for the lower molecular weight acids the formation of clumps occurs. On the other hand, stearic and myristic acids could not effect complete dispersion of the sample of magnetite used indicating perhaps that some material was not being coated with surfactant. Interestingly, when the C_{18} chain contains a kink, complete dispersion was once again achieved.

If the addition of perchoric acid was omitted from the preparation then only three of the surfactants gave instant water-based fluids, namely, octanoic acid (C_8), decanoic acid (C_{10}) and Sarkosyl-'O' (C_{18}).

If, instead of adding the unionized fatty acid to an ammoniacal Fe_3O_4 suspension, surfactant in the form of its ammonium salt was added to a neutral Fe_3O_4 suspension, instant dispersions failed to form. This gives us insight into the mechanism of surfactant adsorption. The particles are first surrounded by a layer of negative charge (OH^- ions); conversion of unionized surfactant to its ammonium salt thereby takes place at the particle surface and is accompanied by chemical surface adsorption.

4.2.2. Micelle Formation in Surfactant Solutions

The longer the alkyl chain of a fatty acid, the more hydrophobic it becomes. When ammonium salts of the larger fatty acids are dissolved in water, the hydrocarbon 'tails' try as best they can to avoid contact

TABLE 4.3

Relative abilities of different surfactants to disperse Fe_3O_4 by procedure of section 4.2.1

Surfactant	Chain Length	Nature of Chain	Weight % Fe_3O_4
Sarkosyl-'O'	C_{18}	Crooked	4.73
Oleic acid	C_{18}	Crooked	4.7
Stearic acid	C_{18}	Straight	1.6
Myristic acid	C_{14}	Straight	2.83
Dodecanoic acid	C_{12}	Straight	4.71
Decanoic acid	C_{10}	Straight	4.74
Octanoic acid	C_8	Straight	4.71
Hexanoic acid	C_6	Straight	0

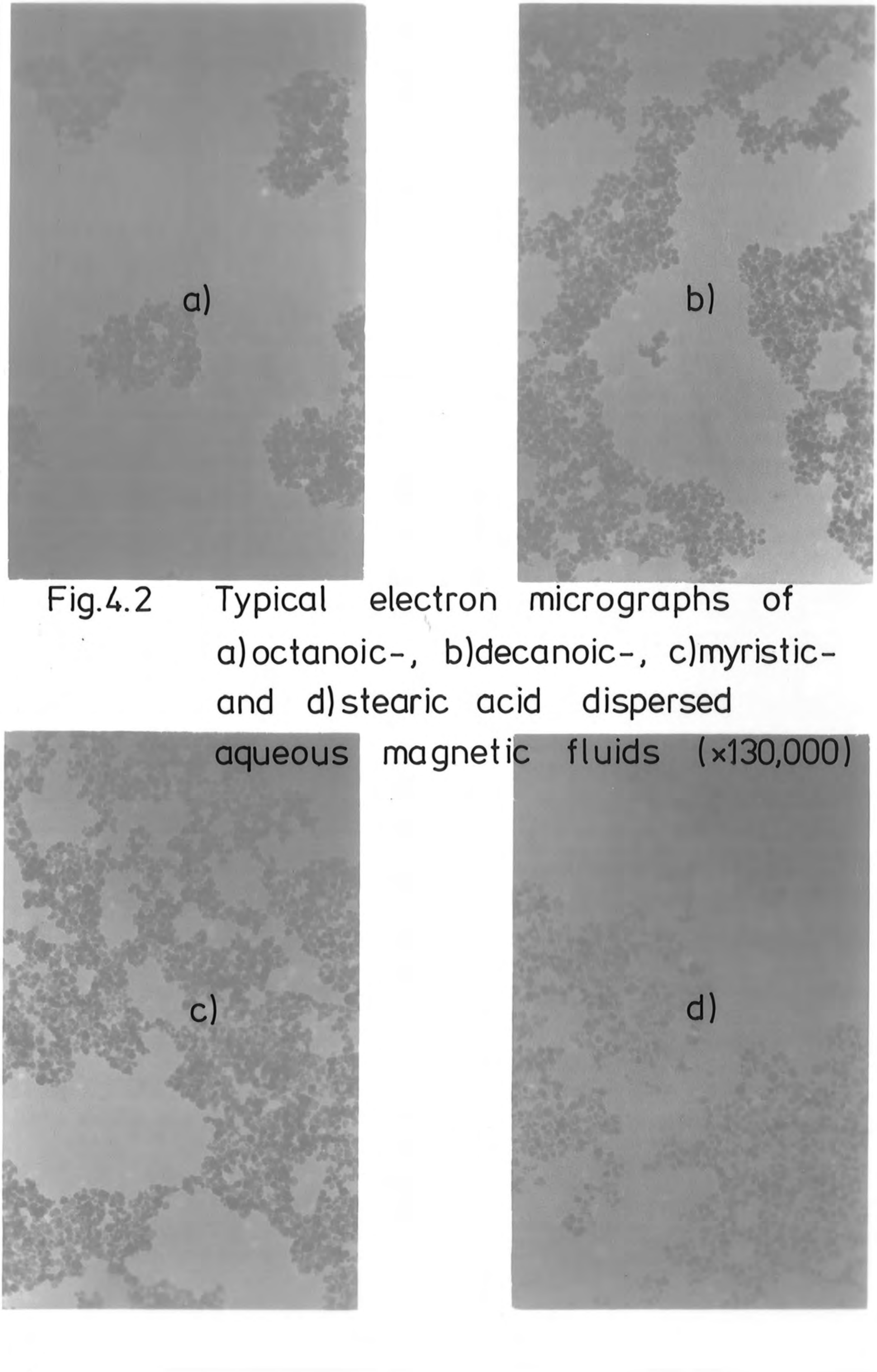


Fig.4.2 Typical electron micrographs of a) octanoic-, b) decanoic-, c) myristic- and d) stearic acid dispersed aqueous magnetic fluids (×130,000)

with the solvent. They do this by interacting with one another to form micelles.[6] The hydrophilic charged 'head' groups occupy the surface of the micelle whilst the hydrophobic 'tails' penetrate the interior. These large, often spherical units are responsible for the opaqueness of concentrated surfactant solutions.

There exists a critical concentration, which varies with surfactant, above which micelle formation becomes appreciable. The critical micelle concentrations for a variety of straight-chain fatty acids, along with the surfactant concentrations used in fluid preparations, are displayed in Table 4.4.

TABLE 4.4

Critical micelle concentrations for various straight-chain surfactants

Surfactant	[Surfactant] in fluid prep. (mol/dm^{-3})	Critical micelle[90] concentration (mol/dm^{-3})
Stearic acid (C_{18})	3.5×10^{-2}	4.4×10^{-4}
Myristic acid (C_{14})	4.4×10^{-2}	4.8×10^{-3}
Dodecanoic acid (C_{12})	5×10^{-2}	2.58×10^{-2}
Decanoic acid (C_{10})	6×10^{-2}	7.1×10^{-2}
Octanoic acid (C_8)	7×10^{-2}	0.36

From this data we observe that for C_{18}, C_{14} and C_{12} fatty acids, the experimental surfactant concentration exceeds the critical micelle concentration and therefore micelles occur in the solutions used. Micellar formation will reduce the quantity of surfactant available for particle stabilization. This explains why complete dispersion was not achieved using stearic and myristic acids. Furthermore, these observations demonstrate that micelle formation is a significantly more rapid process than surface adsorption.

Figure 4.3. shows an excellent example of micelle formation in a myristic acid-based fluid, containing a large excess of surfactant. The particles are chemically adsorbed at the surface of the micelle which contains the polar 'head' groups. The photograph illustrates just how much surfactant is not taking part in the stabilization process.

Both oleic acid and Sarkosyl-'O' gave rise to complete dispersion despite having C_{18} alkyl chains and in view of what has already been said. It is likely that micelle formation is hampered by the crooked nature of the surfactant 'tails'. Indeed, concentrated solutions of ammonium Sarkosyl showed no signs of turbidity. Unfortunately, values for the critical micelle concentration of these surfactants were not traceable in the literature.

To test the micelle hypothesis the following experiment was devised.

Procedure

Four separate fluid preparations were performed using the procedure of section 4.2.1. and myristic acid as the surfactant. The same overall quantity of surfactant was introduced but in stages, the number of which differed with each preparation. The results are summarized in Table 4.5.

The greater the number of separate additions, the lower will be the concentration of surfactant present at any one time, thereby diminishing the likelihood of micellar formation. This is reflected in the amount of Fe_3O_4 incorporated in each case. With ten separate additions of 0.1

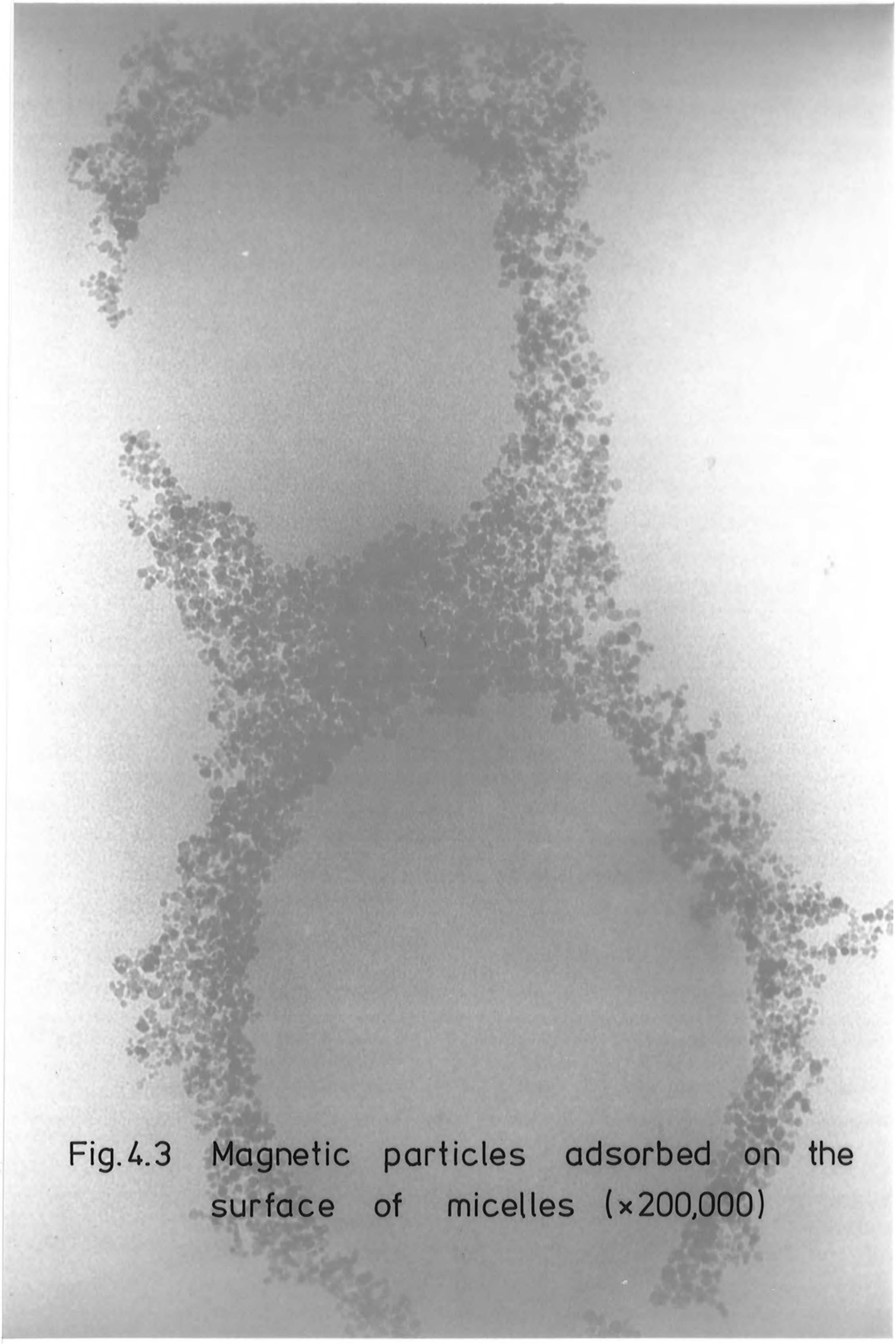


Fig. 4.3 Magnetic particles adsorbed on the surface of micelles (×200,000)

TABLE 4.5

The effect of stagewise myristic acid addition on the dispersion of Fe_3O_4

Expt.	Number of Additions	Quantity of Addition (grams)	Total Reaction Time	Weight % Fe_3O_4
1	1	1	30 mins.	2.83
2	2	0.5	30 mins.	3.17
3	3	0.33	30 mins.	3.8
4	6	0.17	30 mins.	4.52
5	10	0.1	30 mins.	4.68

gram surfactant, almost all the magnetic material was dispersed.

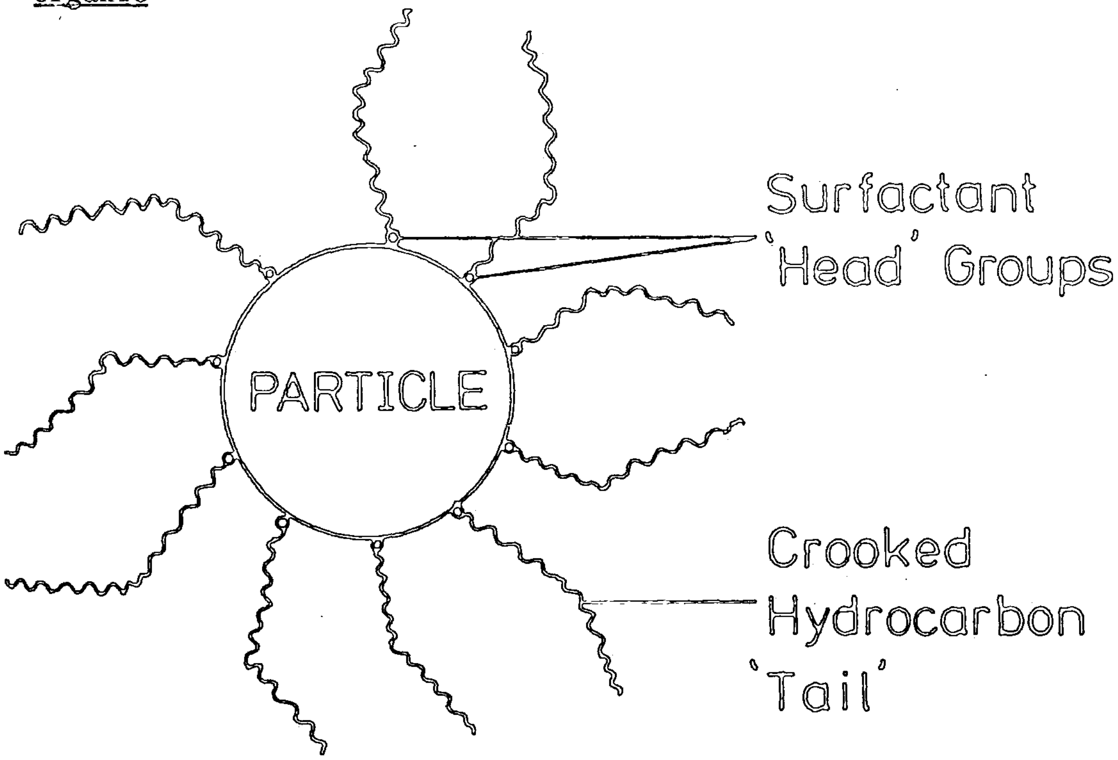
4.2.3. The Surfactant Double Layer

An aqueous magnetic fluid was prepared with Sarkosyl-'O' as the surfactant. The fluid was then flocculated by addition of acetone followed by washing with warm ethanol and acetone to remove excess surfactant. A portion of the suspension was then dispersed in toluene at 110^{0}C to give a stable magnetic fluid. Another portion was washed with water, suspended in a further 20 ml water and heated to 80^{0}C with a few drops of aqueous ammonia in an attempt to create a water-based magnetic fluid. This proved unsuccessful.

It appears that the excess surfactant, whilst being superfluous in organic dispersions, is essential for the stabilization of particles in aqueous media. This observation may be correlated with the interaction between surfactant and carrier liquid. In organic-based fluids the surfactant 'tails' are fully compatible with the solvent and stabilization is achieved by monolayer adsorption at the particle surface (Figure 4.4.i). In aqueous systems, the hydrophobic nature of the alkyl chains requires that a subsequent layer of surfactant interacts with and penetrates that already adsorbed, as illustrated in Figure 4.4.ii). This minimizes the contact between surfactant 'tails' and carrier liquid whilst, at the same time, placing hydrophilic charged groups at the surfactant-water interface.[59] The whole scenario is not unlike that of micelle formation as previously described. As well as steric stabilization there is now an element of charge stabilization causing the particles to repel one another.

The additional stability conferred by this arrangement may well explain why low molecular weight straight chain fatty acids are suitable for aqueous dispersions whilst giving rise to flocculation in organic

i) <u>Organic</u>



ii) <u>Aqueous</u>

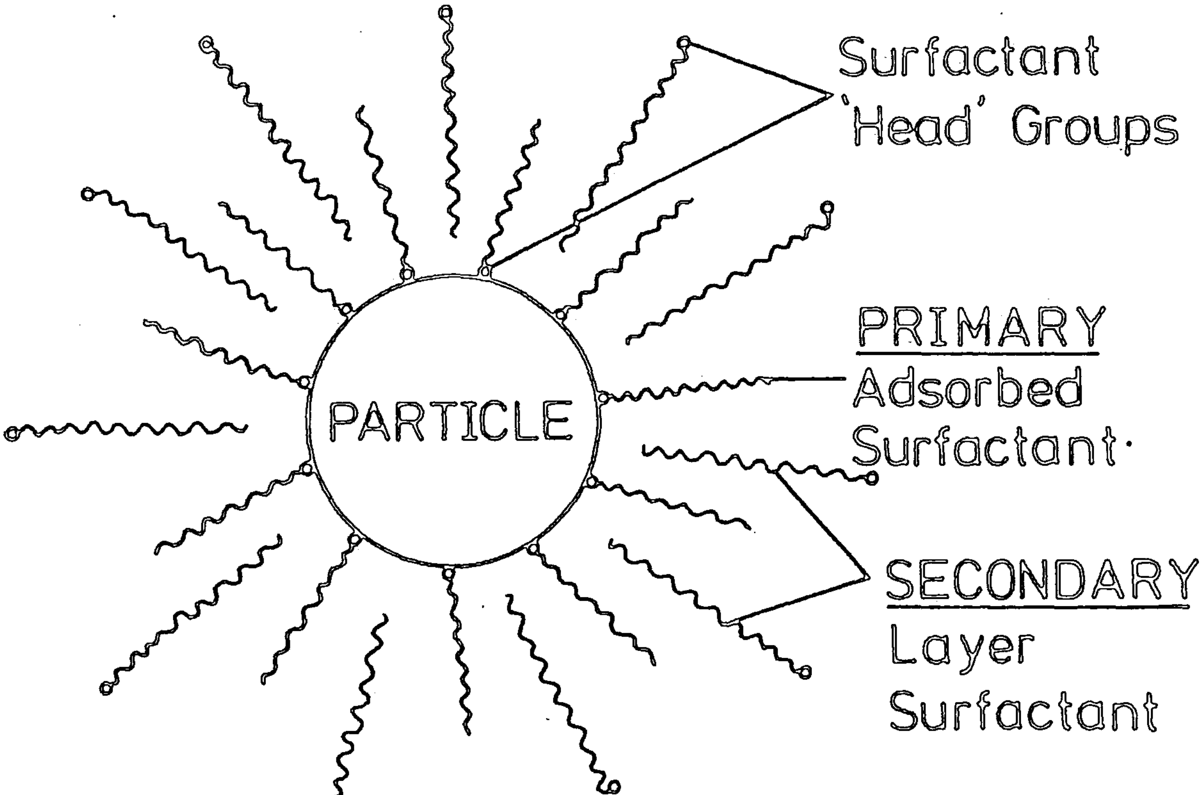


Figure 4.4. Surfactant/particle interactions in organic and water-based magnetic fluids.

media.

The significance of perchloric acid addition prior to redispersion becomes apparent. As surfactant in the form of its ammonium salt is converted exclusively to the parent acid so the hydrocarbon 'tails' will interact in the way described. This ensures that each and every particle is surrounded by a double layer surfactant sheath prior to redispersion. The fluid reforms when surface carboxyl groups are converted to their ionic form by addition of base thereby setting up a favourable interaction between surfactant and aqueous carrier liquid.

4.2.4. Revised Fluid Preparation

To ascertain exactly what quantity of surfactant is required to stabilize a magnetic particle and to understand better the interactions involved, the following experiment was devised.

i) Procedure

A series of Fe_3O_4 suspensions were prepared by base precipitation from mixed iron(II)/iron(III) chloride solution at 70°C using 33% aqueous ammonia, to give 5 grams of material in 200 ml water. 5 grams neat surfactant was added slowly to the ammoniacal suspension over a period of 30 mins. and stirred at 90°C for a further 30 mins. The fluid/suspension was cooled and flocculated by addition of an equivalent volume of acetone. The particles were washed with warm ethanol and acetone, and a very small portion of the solid was dried for subsequent atomic absorption analysis. Each preparation was undertaken in an identical way, the only difference being the surfactant used.

From the weight % Fe_3O_4 in these samples, a value was obtained for the total weight of surfactant which is chemically and irreversibly adsorbed at the particle surface (PRIMARY LAYER). Using a value of 70Å for the mean size of the particles, the number of molecules of surfactant on each particle, and hence the area occupied by each molecule, were calculated. It was assumed that particles were spherical.

The remaining particles were suspended in water (50 ml). Ten suspensions were prepared in this way, two for each of the five surfactants mentioned in Table 4.6.

Solutions of ammonium and monomethylammonium salts of the same five surfactants were prepared in water (50 ml) using 5 grams surfactant. The final pH was 8.

Each solution in turn was added via a burette to an Fe_3O_4 suspension (50 ml), stabilized using the same adsorbed surfactant, at 80^oC and with vigorous stirring until first signs of fluid formation were observed. Addition in 0.5 ml amounts was continued (cooling after each addition) until there was no visible settling out when placed over a permanent magnet for a period not less than two minutes.

In some instances a fluid did not form, in which case a large excess of freshly made surfactant solution was finally added to confirm the observation. For the fluids which did form, the total weight of added surfactant was calculated. This is regarded as the quantity required to interact with the primary layer hence shielding the alkyl chains from their aqueous environment. It will be regarded as the SECONDARY LAYER.

All the results, along with observations are summarized in Table 4.6.

ii) <u>Discussion</u>

Inspection of Table 4.6. raises many points worthy of consideration, the first being that the secondary surfactant layer

TABLE 4.6

The quantity of surfactant material required for the stabilization of magnetic particles in aqueous media

		PRIMARY LAYER			SECONDARY LAYER		
Surfactant	% Fe_3O_4	wt surfactant per gm Fe_3O_4 (gms)	No. molecules on each particle	Surface area per molecule	NH_4^+ surfactant per gm Fe_3O_4 (gms)	No. molecules at each particle	$MeNH_3^+$ surfactant per gm Fe_3O_4 (gms)
Sarkosyl-'O'	81.3	0.23	412	37Å^2	-	-	-
Oleic acid	84.76	0.18	402	38Å^2	0.36	804	0.37
Myristic acid	80.65	0.24	657	23Å^2	0.27	739	0.27
Decanoic acid	83.19	0.20	734	21Å^2	0.31	1138	-
Octanoic acid	88.53	0.13	569	27Å^2	0.95	4158	-

contains the greater proportion of overall surfactant. This was predicted on the basis of spherical surface area and packing considerations.

The smaller the surfactant molecule the greater the number adsorbed at the particle surface, presumably because there is less steric hindrance between neighbouring molecules. Anomalous behaviour is observed with octanoic acid, for which the greater affinity of surfactant for carrier liquid and the correspondingly larger solvation energy make it less favourable for adsorption to occur with accompanying loss of hydration.

TABLE 4.7.

Percentage of total surfactant in each layer

Surfactant	% of Whole	
	1^0 layer	2^0 layer
Oleic Acid	33	67
Myristic Acid	47	53
Decanoic Acid	39	61
Octanoic Acid	12	88

With reference to the above table and working downwards, an initial decrease in the 2^0 layer contribution is explained by the less hydrophobic alkyl chains requiring a smaller degree of protection from their environment. With decanoic acid and in particular octanoic acid, having short hydrocarbon tails, interaction between 1^0 and 2^0 layers will be reduced compared with oleic acid. That the fluids remain stable indicates a sufficiently thick cushion of surfactant must still be present to sterically stabilize the particles. This may be explained in terms of additional surfactant entering the 2^o layer, allowed by the lower steric repulsion between smaller molecules.

The driving force behind these double layer interactions is illustrated by the choice of cation in aqueous surfactant solutions (Table 4.6.). Ammonium salts are prone to decomposition at temperatures $> 80^oC$ to yield the parent acid (with evolution of ammonia). This does not occur with monomethylammonium (MMA) salts. Complete dispersion was achieved using both forms of oleic and myristic acids, indicating that the surfactant molecules are sufficiently hydrophobic for interaction to occur in their ionized form. Conversely, with salts of decanoic and octanoic acid, for interaction to be favoured there must be prior conversion to the parent acid (unionized form); hence no fluid was obtained with MMA salts of these surfactants.

The behaviour of Sarkosyl-'O' suggests that double layer interactions in the vicinity of the particle are unfavourable under all circumstances. This can only be attributed to the additional amide function which is present in Sarkosyl-'O' but not in oleic acid. On the other hand, if excess Sarkosyl-'O' was added to an ammoniocal suspension of Fe_3O_4, as in section 4.2.1., an instant water-based fluid resulted. It is suggested that interaction between surfactant molecules themselves occurs in the bulk solution prior to adsorption and that molecular clusters, similar to but smaller than micelles, are adsorbed as discrete units.

4.2.5. Magnetic Fluids of Commercial Concentration

On the basis of features established here, one can now envisage a single aqueous ferrofluid stabilized by two different surfactants: one as the primary layer, the other as the secondary layer.

The following experiments are designed to investigate these systems in terms of the interactions already discussed. In addition, a measure of the maximum possible Fe_3O_4 incorporation will help to further evaluate the relative abilities of the different surfactants to disperse magnetic particles.

i) Procedure

The procedure of section 4.2.4. was followed exactly, employing a variety of fatty acid surfactants both as primary and secondary layers. In cases where a stable magnetic fluid resulted, solvent was evaporated by boiling the fluid until first signs of settling out were observed. The formation of gum-like solids was commonplace especially with the higher molecular weight surfactants. Addition of a few drops of aqueous ammonia appeared to be a remedy. After magnetic removal of entrained particles the fluids were collected for analysis.

ii) Analysis

In many cases the aqueous fluids were sufficiently concentrated to produce the phenomenon of surface instability when subjected to an applied magnetic field. All the fluids were subjected to VSM magnetic analysis and the results are summarized in Table 4.8. As a general rule, fluids with over 20% Fe_3O_4 exhibited surface instability. The importance of using ammonium salts, especially of Sarkosyl-'O', octanoic and decanoic acids, further illustrates the driving force behind surfactant interactions within the double layer. In cases where stability was not cation dependent, we observed equal concentrations of Fe_3O_4 using NH_4^+ and $MeNH_3^+$ salts of the same surfactant.

The ability, or otherwise, of Sarkosyl-'O' and oleic acid to

<u>TABLE 4.8</u>

The ability of different surfactants, both as primary and secondary layer, to disperse magnetic particles in water

		SECONDARY SURFACTANT LAYER									
		Sarkosyl-'0'		Oleic acid		Myristic acid		Decanoic acid		Octanoic acid	
		$MeNH_3^+$	NH_4^+	$MeNH_3^+$	NH_4^+	$MeNH_3^+$	NH_4^+	$MeNH_3^+$	NH_4^+	$MeNH_3^+$	NH_4^+
Primary Layers	Sarkosyl-'0'	X	X	X	27.2	X	24.5	X	24.9	X	9.2
	Oleic acid	X	X	19.1	19.7	√	21.9	27.2	26.9	X	24.3
	Myristic acid	X	X	X	X	√	24.8	√	18.6	X	26.4
	Decanoic acid	X	X	X	X	√	14	X	21.5	X	31.9
	Octanoic acid	X	X	X	X	√	25.2	X	26.7	X	4.6

√ = Stable fluid (but no analysis performed)
X = No fluid

N.B. Numbers refer to maximum weight % Fe_3O_4.

interact with the straight-chain surfactants is worthy of mention. There is bound to be some strain associated with such an interaction for steric reasons alone. This is best alleviated when Sarkosyl-'0' is employed as the primary adsorbed layer. With reference to Table 4.6., this makes for less congestion at the particle surface, allowing the straight-chain surfactant tails to penetrate. If the roles are reversed then there is higher packing within the primary layer and penetration, especially by Sarkosyl-'0' and oleic acid, is significantly more difficult. As indicated by the results, this arrangement inhibits the formation of stable fluids.

The data for maximum Fe_3O_4 incorporation reveals no obvious trends. So long as there is a positive interaction with consequent steric stabilization then the nature of the surfactant, be it as primary or secondary layer, appears to be immaterial. It is interesting to note that the fluid prepared exclusively from octanoic acid and that using an octanoic acid/Sarkosyl-'0' combination are noticeably weak. Both surfactants are comparatively hydrophilic in nature thereby reducing tail interactions. Furthermore, in the former case, the surfactant sheath may be insufficient in thickness to adequately cushion the particles.

The magnetization curves generated for fluids employing octanoic acid as the secondary layer are illustrated in Figure 4.5.

4.2.6. Fluid Stability

Aqueous fluids prepared according to section 4.2.5. could be diluted by a factor of 64 without the formation of any residue. Boiling the fluids for several hours, with periodic additions of water, gave the same result.

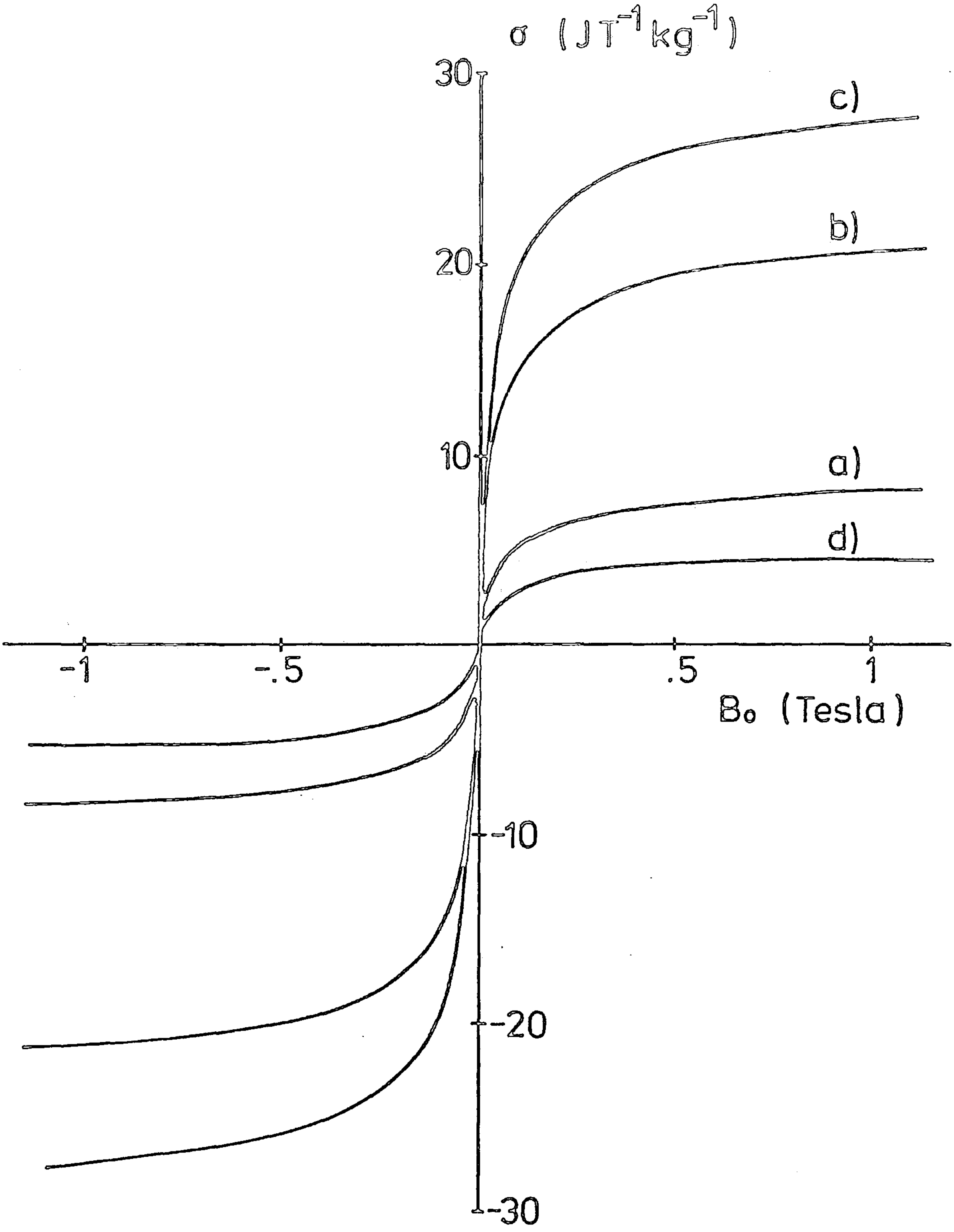


Figure 4.5. Magnetization curves for aqueous fluids employing a) Sarkosyl-'O', b) Oleic acid, c) Decanoic acid and d) octanoic acid as the primary adsorbed layer, and octanoic acid as the secondary layer in all cases.

When the fluids were acidified to pH 5, flocculation was accompanied by the formation of a black gum. This is simply a reversal of the dispersion process by which a stable fluid was first obtained. Addition of alkali gave rise to progressive flocculation as indicated in the experiment described below.

i) Procedure

To an oleic acid-based fluid prepared as in section 4.2.4., and containing 2.7 grams oleic acid in total, was added 2 molar perchloric acid to effect flocculation. After washing several times with water the solids were resuspended in water (100 ml) and heated to 80°C. Portions of a 30% tetramethylammonium hydroxide (TMAH) solution were successively added to the suspension which was stirred at 80°C for 5 mins. A fluid began to form. After each addition, a small sample was removed for atomic absorption analysis.

ii) Results and Discussion

The Fe_3O_4 content of each fluid is plotted against the total added quantity of TMAH (in moles) in Figure 4.6.

With addition of TMAH, progressive ionization of carboxyl groups at the surfactant/water interface occurs until maximum dispersion is achieved. With further addition, stability is at first maintained but swiftly gives way to flocculation in the presence of excess base and a consequent rise in pH.

Considering only that portion of surfactant adsorbed as secondary layer, complete dispersion is first achieved when 66% has been ionized by TMAH. This is obviously sufficient to ensure a favourable interaction at the above interface. Further addition of base causes extensive ionization whilst, as expected, maintaining fluid stability. With excess base, the increased solubility of oleic acid in the bulk

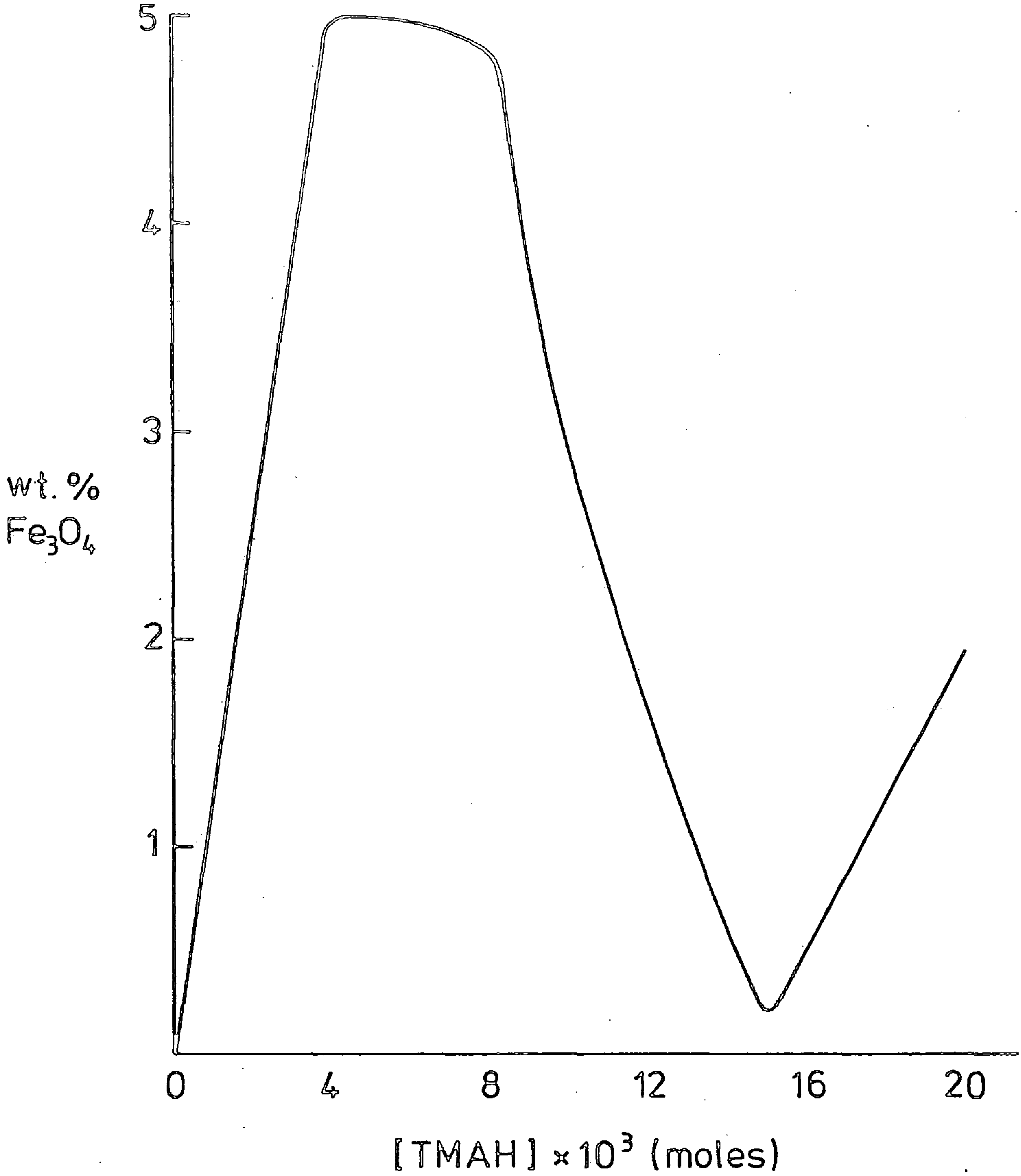


Figure 4.6. The dispersing effect of different tetramethyl ammonium hydroxide concentrations upon a surfactant stabilized aqueous magnetic fluid.

carrier liquid favours separation of the hydrocarbon chains as surfactant passes into solution. Flocculation is inevitable. At even higher pH however, the fluid reforms. This is unusual and best explained with reference to the following observations.

a) A parallel experiment was performed using aqueous ammonia as base. Flocculation occurred as with TMAH but in contrast, the solids were not redispersable at high pH.

b) A portion of the original flocculate was washed with water and acetone. The dried material, by atomic absorption analysis, contained only 85% Fe_3O_4 indicating the continued presence of a chemisorbed surfactant monolayer.

c) To a suspension of the product from part b), having been washed thoroughly with water, was added TMAH solution (20 ml). Complete dispersion was achieved.

Redispersion both in part c) above, and as observed in the initial experiment is brought about by adsorption of hydroxide ions at the surfactant/water interface and subsequent charge stabilization of the magnetic particles. Low polarizability of the tetramethylammonium cation promotes stability whilst the highly polar ammonium cation gives rise to flocculation. A more detailed investigation of this phenomenon is the subject of the next chapter.

4.2.7. Poly-Acrylic Acid

'Dispex' is the trade name for a range of low molecular weight, anionic, water soluble polymers based on acrylic acid. These materials are supplied in the form of their ammonium salts by Allied Colloids.

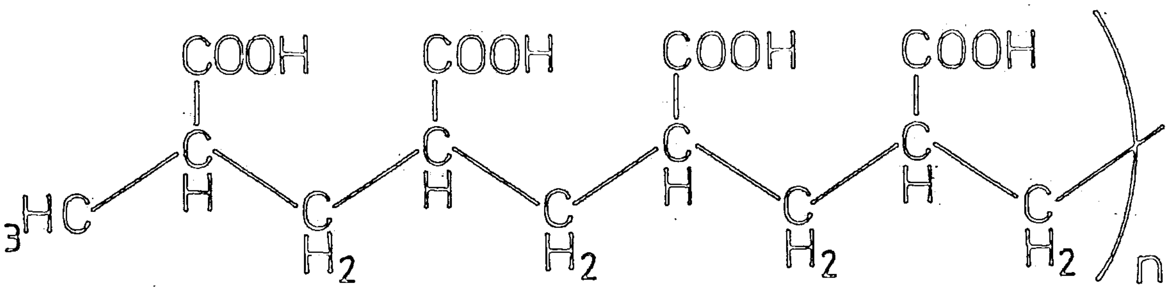


Figure 4.7. Poly-acrylic acid.

The basic material is illustrated in Figure 4.7. Also available was a related product in which an unspecified number of acrylate groups had been esterified, but insufficient to affect its water solubility. Both materials were evaluated as possible surfactants in magnetic fluid preparations.

i) Fluid Preparation

The preparative procedure was identical to that described in section 4.2.1., using 1 gram Dispex:1 gram Fe_3O_4. The coated particles were flocculated with 2 molar perchloric acid and resuspended in water using a few drops of aqueous ammonia. Dispersion could not be achieved using the ammonium salt of poly-acrylic acid, whereas the partially esterified material gave rise to a stable magnetic fluid.

The material was again flocculated with 2 molar perchloric acid and washed with warm ethanol and acetone to remove excess surfactant. A portion was dried and retained for atomic absorption analysis. Surprisingly, the particles formed an instant water-based fluid on addition of ammonia.

ii) Analysis and Discussion

Atomic absorption analysis revealed only 62% Fe_3O_4 in the dried solid, hence a considerable amount of surfactant remained even after washing with ethanol and acetone.

A modified version of the surfactant double layer theory may be used to satisfactorily explain the results of this study. Surfactant interactions in the vicinity of the particle serve to minimize the contact between any hydrophobic elements and the solvent itself. The former are absent in the ammonium salt of poly-acrylic acid and, although chemisorption will occur, this monolayer will be insufficient to adequately cushion the particles. Moreover, any hydrogen bonding which could occur between surfactant molecules, thus increasing the thickness of the sheath, will be offset by similar interactions between surfactant and carrier liquid.

Partial esterification provides an element of hydrophobic character as previously mentioned. Protection of these groups from their aqueous environment will now provide the impetus behind surfactant interactions at the particle surface. The polymer chains will wrap themselves around one another until the desired thickness has been achieved. Unesterified carboxyl groups will be orientated towards the surface as with previous systems.

The inability of polar organic solvents to overcome such interactions, and hence remove secondary surfactant layers, suggests that, ironically, there is extensive hydrogen bonding between polymer chains within the cushioning layer. This is in obvious contrast to aqueous magnetic fluids prepared using the straight-chain fatty acids.

4.3. SUMMARY

The stabilization of magnetite particles in both aqueous and non-aqueous media using appropriate surfactants has been described. In each case, the mechanism of surfactant activity has been explained with relation to intermolecular surfactant interactions, and interactions between surfactant and carrier liquid. By careful choice of surfactant in the appropriate concentrations, magnetic fluids have been prepared, equal in concentration to those used in many commercial applications.[29] Much emphasis has been placed on aqueous dispersions with which the chapters to follow are mainly concerned.

CHAPTER 5

IONIC FERROFLUIDS

INTRODUCTION

The ability to disperse magnetic particles in aqueous media without the use of a surfactant has been investigated by Massart.[28]

Stabilization is achieved through a layer of charge which is adsorbed at the particle surface and which causes similarly charged particles to repel one another. The sign of the charge depends on whether the medium is acidic or alkaline.[22] Surrounding this first adsorbed layer is a diffuse layer of counter- or 'gegen'-ions which are held in place by the attraction between charges of opposite sign. The electric double layer is thus defined, as mentioned in chapter 1.

The 'gegen' ions are nevertheless insufficient to restore electrical neutrality within the double layer as a whole, so that in alkaline media there is an overall negative potential which increases with proximity to the particle surface, whilst in acidic conditions the potential is positive.

The magnitude of this potential is strongly dependent upon the nature of the counter-ions. Small highly polarizable ions will be strongly attracted to the surface, thereby reducing the net potential and hence inter-particle repulsion. Low polarizing counter-ions will reside further away from the particle surface so that charge stabilization of magnetic particles is maintained[28].

To illustrate these effects, stable magnetic fluids are obtained at low pH using an acid with a low polarizing anion. Perchloric acid ($HClO_4$) is especially suitable. On the other hand, sulphuric acid with its highly polarizable SO_4^{2-} anion gives rise to flocculation.

Similarly, bases with low polarizing cations, such as tetramethylammonium hydroxide, give instant water-based magnetic fluids at high pH whilst ammonia and the alkali-metal hydroxides give rise to flocculation.

Although these concepts are well established[28], little work has been done, from a quantitative standpoint, on the stability characteristics of these fluids at different pH values, and in the presence of added electrolytes.

5.1. ACID STABILIZATION

In the following preparations perchloric acid is employed as an ionic dispersing agent. Limited success was also obtained using hydrochloric acid, but conversion of the magnetic oxide into soluble iron chlorides, especially at pH < 2, was deemed unacceptable.

5.1.1. Fluid Preparation

Fe_3O_4 was precipitated from mixed iron(II)/iron(III) chloride solution using an excess of 33% aqueous ammonia. The suspension at pH 11 was swiftly quenched with 2 molar perchloric acid to attain a pH of 2. The Fe_3O_4 precipitate was isolated by magnetic decantation, and a stable ferrofluid was obtained simply by addition of water to the magnetic particles. The fluid had a pH of 2.3. A portion was diluted with water, which incidently had no effect upon stability, prior to examination by electron microscopy. An electron micrograph at x400,000 magnification is shown in Figure 5.1.a).

5.1.2. Discussion

Further addition of perchloric acid to the stable colloid caused immediate flocculation at pH 2.2. Thus a lower limit of pH for the formation of an acidic fluid is established.

It is essential that a high initial pH in the original suspension is attained prior to quenching with perchloric acid. If the suspension was first neutralized to pH 7 and left to stand, or even washed with

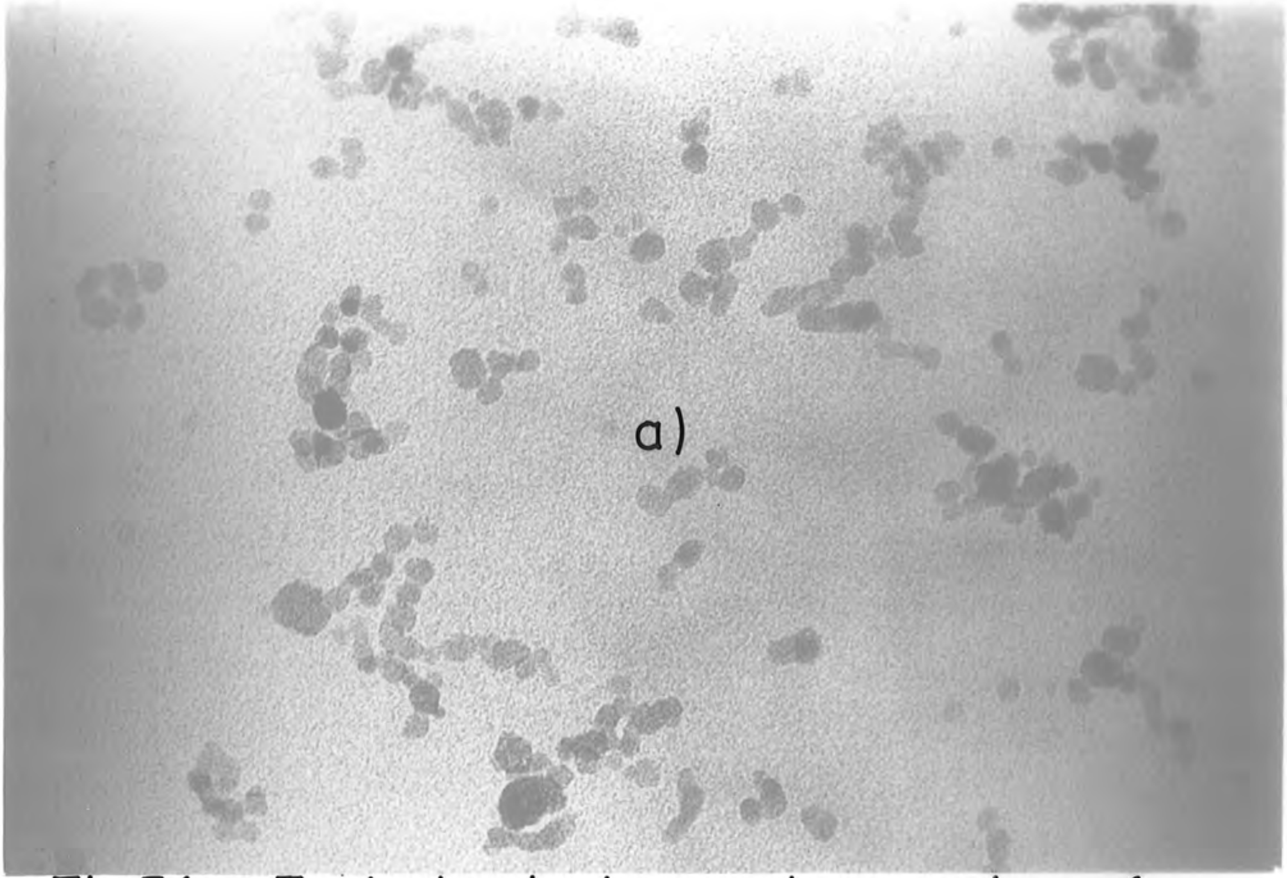
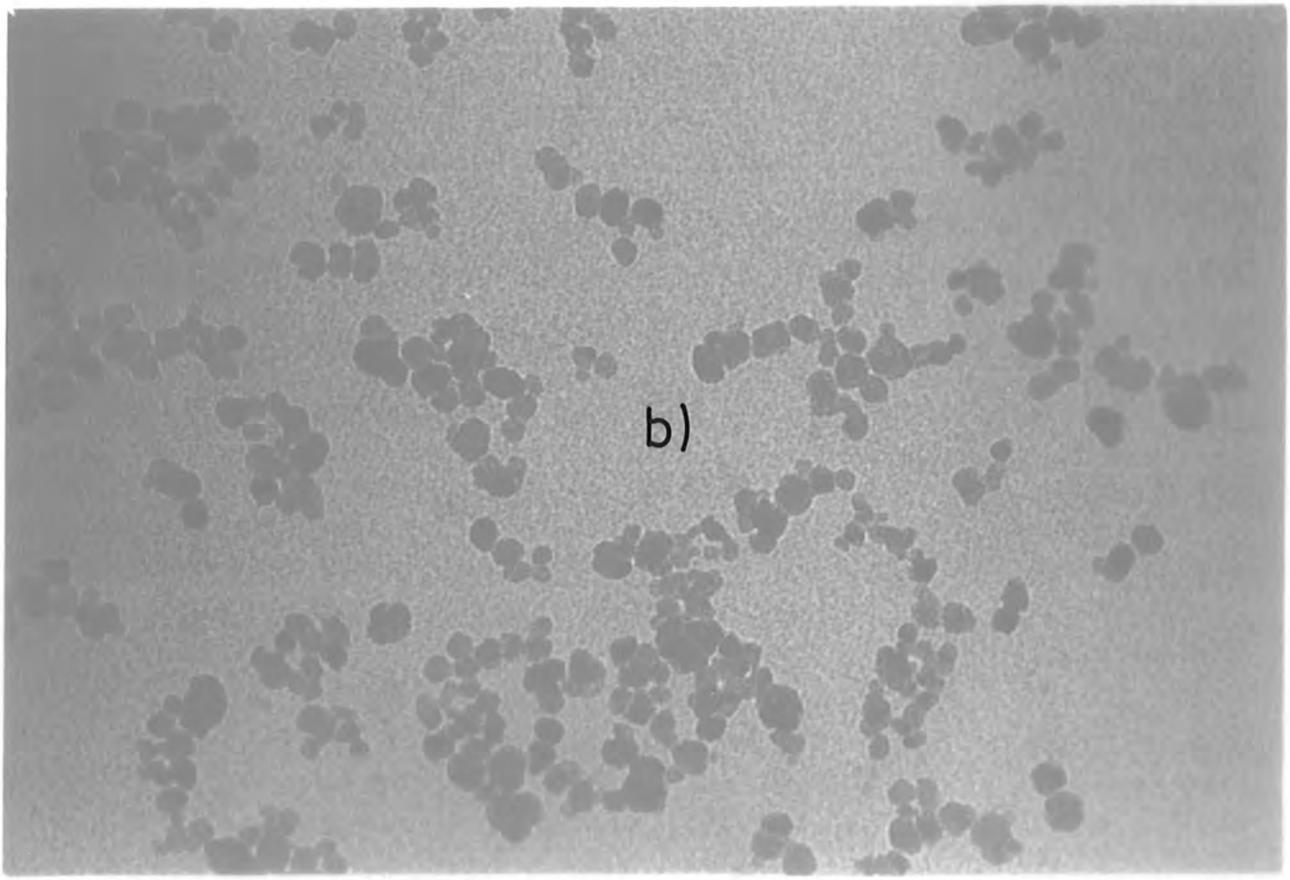


Fig.5.1 Typical electron micrographs of a)acidic and b)alkaline charge-stabilized magnetic fluids (×400,000)



water, then redispersion in acid was rendered impossible. It is envisaged that, in alkaline suspension, the particles are to some extent charge separated. If $HClO_4$ addition is sufficiently swift then an electric potential, be it negative or positive, will be maintained at the particle surface. If the suspension is allowed to stand at neutral pH for any length of time aggregation of uncharged particles, through Van der Waals and magnetic attraction, will quickly occur. The aggregation is irreversible as far as redispersion in acid is concerned.

Addition of pH 7 ammonium perchlorate solution to an acidic fluid caused precipitation. This highlights the need to first flocculate the particles at a pH below 2.2 in the initial preparation, so as to remove dissolved electrolytes prior to redispersion.

5.1.3. Dilution Studies

An acidic ferrofluid at pH 2.5 was successively diluted by a factor of two. After each dilution a portion was removed for atomic absorption analysis. From this data the total weight of Fe_3O_4 retained by the fluid was calculated, and a dilution curve was thus generated (Figure 5.2.).

Although there is at first a slight loss of material, the curve soon flattens out indicating stability to dilution. In fact, the fluid remained stable at a dilution factor of 130. By the sheer nature of these fluids, stability will depend strongly upon pH. Dilution is accompanied by a rise in pH up to a value of 4.6 at a dilution factor of 130. Addition of dilute ammonia to the above fluid gave complete flocculation at pH 4.8, whilst addition of more concentrated ammonia to the original fluid produced flocculation at pH 3.15. This confirms the influence of dissolved ammonium perchlorate on fluid stability.

By treating the diluted and undiluted fluids with tetramethyl-

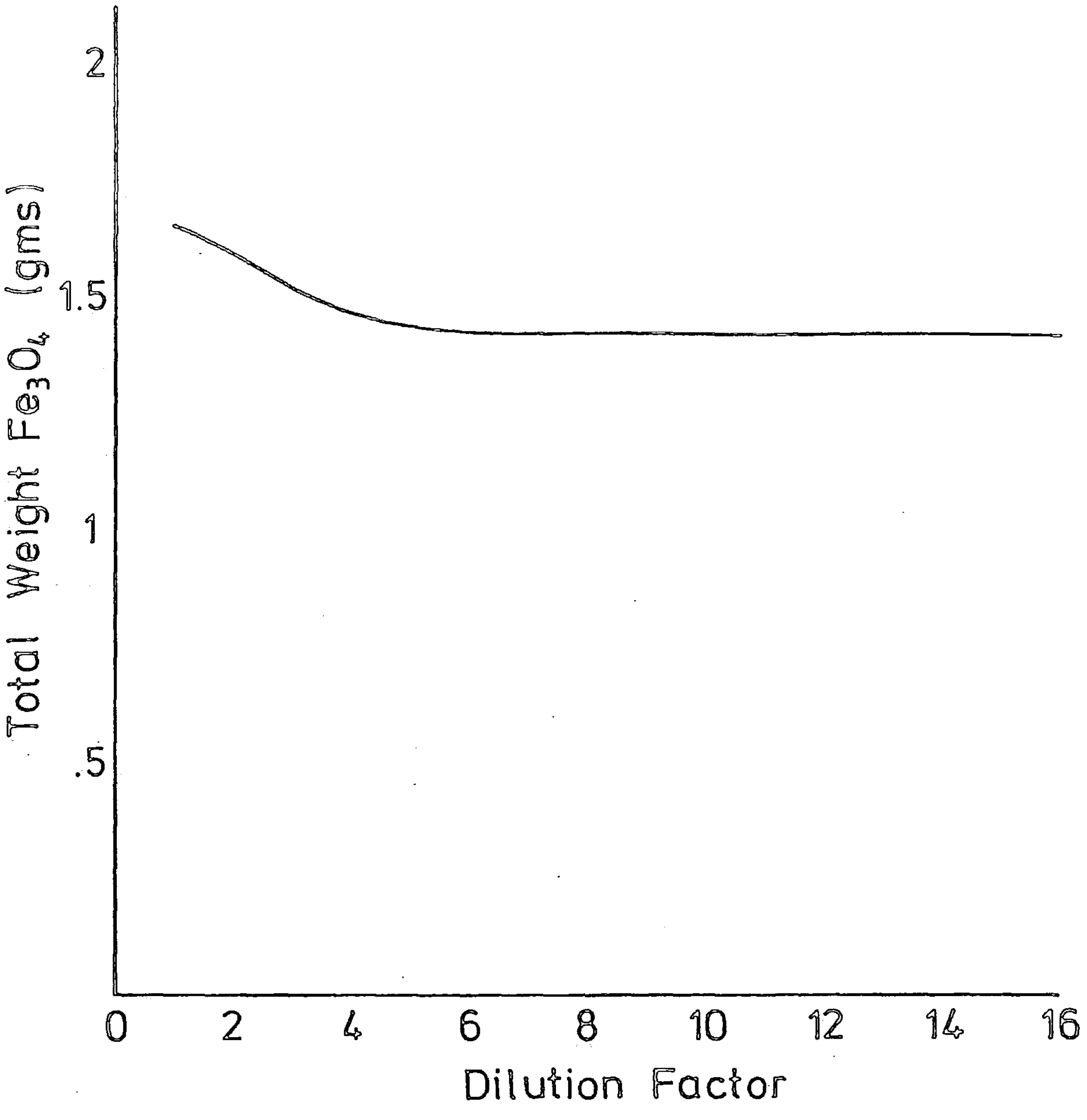


Figure 5.2. Dilution curve for a perchloric acid dispersed ionic ferrofluid.

ammonium hydroxide instead of ammonia, stability was maintained up to pH's of 6.5 and 5.8 respectively. Not only may we now define an upper pH limit for colloidal stability, but we may also conclude that the tetramethylammonium cation is a far weaker flocculating agent than the ammonium cation, despite the fact that $(CH_3)_4NOH$ is the stronger base and hence a better provider of OH^- ions. This is an unusual observation in acidic media since the particles are already positively charged and will hence repel other positively charged species, in particular the highly polar ammonium cation. The overall potential within the electric double layer should remain unaffected but, for reasons not fully understood, this does not appear to be the case.

The pH of an acidic ferrofluid rises if it is agitated for several minutes. On standing, it falls back again to its original value. This effect is more pronounced in the weaker fluids. We thus conclude that agitation causes the particles to pick up extra hydrogen ions from the bulk solution which then desorb when the fluid is laid to rest. This implies an equilibrium being set up between adsorbed hydrogen ions and those in solution.

5.2. ALKALI STABILIZATION

In the same way that the formation of an acidic fluid requires the initial suspension to be alkaline, so dispersion of magnetic particles in alkaline media requires prior acidification of the precipitate. As mentioned in the introduction, the base must incorporate a low polarizing cation such as tetraethylammonium, tetramethylammonium or triethanolammonium cation. The following procedure is standard.

5.2.1. Fluid Preparation

To a freshly prepared Fe_3O_4 suspension containing excess ammonia was added 2 molar perchloric acid to a pH of 2. The solids were isolated by decantation, thus removing dissolved ammonium ions which would doubtless cause flocculation at a later stage. 30% tetramethylammonium hydroxide (TMAH) solution was swiftly added thereby forming an instant alkaline ferrofluid with a pH of 11. A portion was diluted with water prior to examination by electron microscopy. An electron micrograph at x400,000 magnification is shown in Figure 5.1.b).

5.2.2. Discussion

The fluid was stable to addition of perchloric acid down to pH 8.5 whilst, at the other extreme, virtual saturation with solid TMAH had little or no effect upon stability. A portion of the original fluid was diluted by a factor of 64 and retained all its magnetic material. As expected, if aqueous ammonia is added to the stable fluid it quickly flocculates as the $(CH_3)_4N^+$ cation is exchanged for the ammonium cation in the diffuse part of the double layer.

It is possible to convert a stable acidic fluid to an alkaline one simply by adding TMAH solution to pH 11. The fluid is, as predicted, unaffected by the large excess of tetramethylammonium perchlorate thus generated.

5.3. SUMMARY

Aqueous magnetic fluids have been prepared without the use of a surfactant by charge stabilization of the magnetic particles in both acidic and alkaline media. Stability towards dilution has been demonstrated and the constraints of pH defined in each case. The effect of dissolved electrolytes has been established along with the nature of the electric double layer at both high and low pH.

CHAPTER 6

FACTORS AFFECTING PARTICLE SIZE IN MAGNETIC FLUIDS

INTRODUCTION

The mean particle size in a colloidal Fe_3O_4 dispersion depends primarily upon the reaction conditions at the time of particle formation. If conditions favour a high initial degree of nucleation then many small particles will be formed; but if nucleation is suppressed then new material will be available for the crystal growth of existing nuclei[91]. This situation will create fewer but larger particles.

Precipitation of Fe_3O_4 from mixed Fe^{II}/Fe^{III} salt solutions is believed to proceed via the formation of ferrous hydroxide and a hydrated ferric oxide complex which is commonly, but incorrectly, referred to as $Fe(OH)_3$. When these two condense to form a magnetic particle, the size of that particle may be influenced by several factors including temperature, concentration of reagents and solubility in the reaction medium. This study will deal with those variables and try to evaluate to what extent particle size may be influenced by careful choice of reaction conditions.

6.1. TEMPERATURE AND CONCENTRATION EFFECTS

A series of magnetite samples were prepared varying both the temperature of formation (T_F^o) and the concentration of reagents. Aqeuous magnetic fluids were prepared from these samples in the way described below.

6.1.1. Experimental Procedure

Samples of Fe_3O_4 were prepared by base (aqueous ammonia) precipitation from mixed iron(III)/iron(II) chloride solution in the molar ratio 2:1, and 100 ml total volume. Reactions to give 2 grams Fe_3O_4 proceeded at temperatures between 30^oC and 95^oC. In addition, reagent concentration was varied so as to give 0.5, 1 and 5 grams Fe_3O_4 at 60°C. Immediately after particle formation an appropriate amount of Sarkosyl-'O' was added (0.75 grams:1 gram Fe_3O_4) and the mixture stirred at 85°C for 30 mins. A portion of the dispersion was flocculated with 2 molar perchloric acid, the magnetite washed with water and resuspended in water at 80°C using a few drops aqueous ammonia. This gave stable aqueous magnetic fluids in all cases.

6.1.2. Particle Size Analysis

Portions of each fluid were diluted and examined by electron microscopy. Particle size analysis generated the curves as seen in Figure 6.1. and 6.2.

Increasing the temperature of preparation should not affect the relative rates of nucleation and crystal growth. Nucleation will increase as encounters between iron(II) and iron(III) species become more likely but, at the same time, diffusion of material to the surface of newly formed particles (i.e. crystal growth) will also be more favoured. The observed decrease in particle size as temperature approaches 80°C is undoubtedly a result of increased solubility and hence dissolution rate of both $Fe(OH)_2$ and $Fe(OH)_3$. If either or both of these are required to be in the dissolved phase prior to condensation, it follows that the nucleation rate of Fe_3O_4 particles will rise with increased solubility of iron(II) and/or iron(III) hydroxide.

The observed particle size increase above 80°C is interesting in that it introduces another aspect of colloid formation. The formation of a solid Fe_3O_4 nucleus will only occur if the concentration of Fe_3O_4 in solution is in excess of the solubility product, otherwise it will spontaneously redissolve. Because of the extremely low solubility

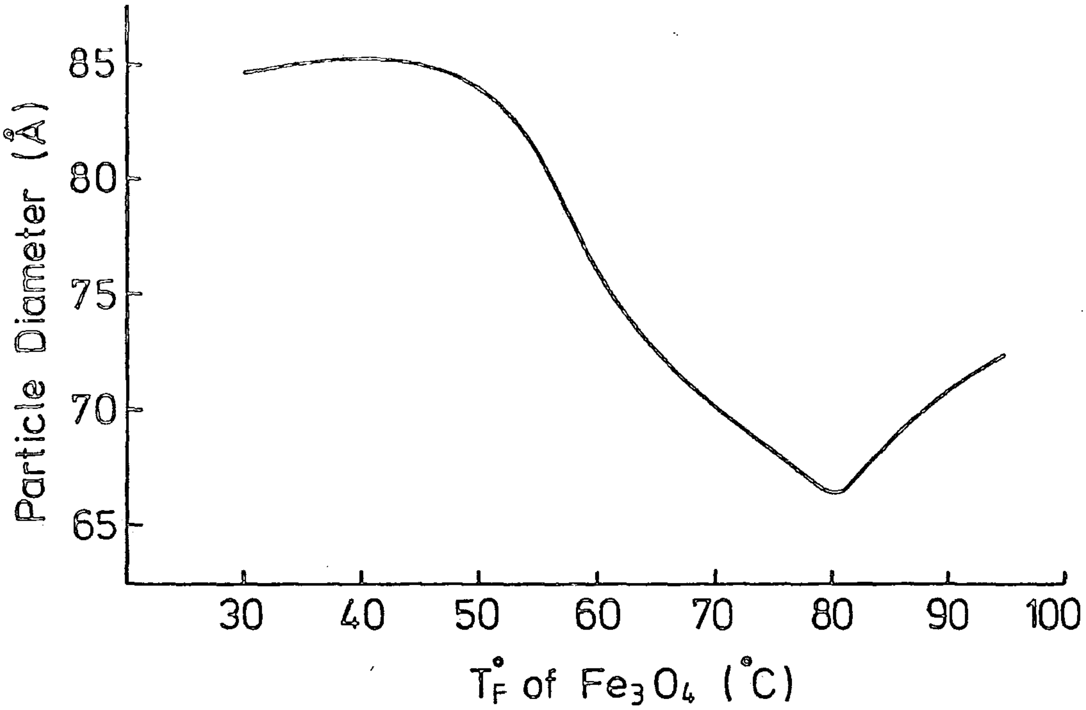


Figure 6.1. Particle size as a function of temperature in the precipitation of Fe_3O_4 (2 gms Fe_3O_4 in 100 cm^3 total volume).

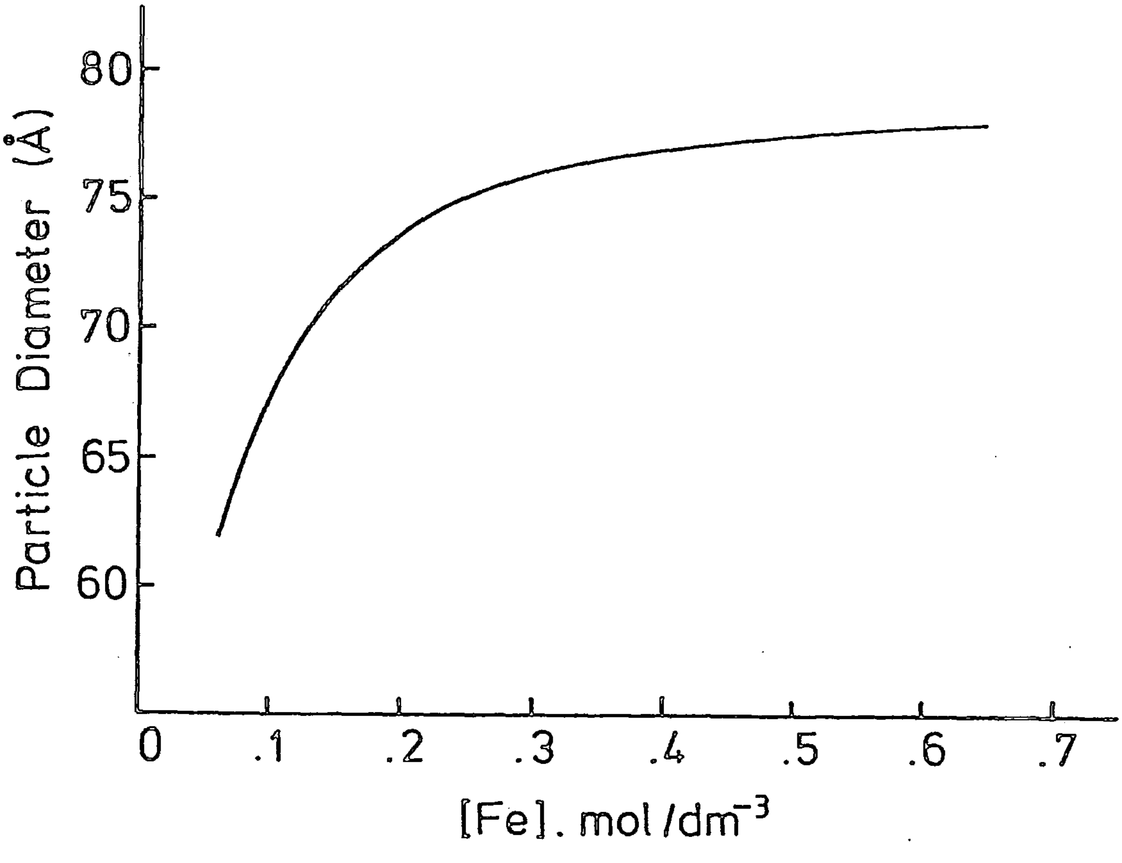


Figure 6.2. Particle size as a function of iron chloride concentration in the precipitation of Fe_3O_4 at 60°C.

product of Fe_3O_4, the effect is usually of no consequence. It is likely that the increase in solubility associated with very high temperatures is sufficient to dissolve some of the smallest particles which then recrystallize on the larger ones.

The curve in Figure 6.2. illustrates more features of colloid formation. As concentration increases, nucleation rate stays more or less constant whilst there becomes more material available for crystal growth. We shall therefore see a curve where particle radius $\sim \sqrt[3]{3x/4\pi}$ where x is the total weight of Fe_3O_4 available. The gradient should, and indeed does become progressively more shallow. The actual curve is seen to flatten out at high concentrations; this could be a result of high viscosity in the reaction medium restricting the diffusion of further material to the particle surface and hence slowing down crystal growth.

6.2. SOLVENT EFFECTS

Pursuing the idea that increased solubility of $Fe(OH)_2$ and $Fe(OH)_3$ favours smaller particles, it was decided to employ ethanol/water mixtures as the reaction medium. $Fe(OH)_2$ is soluble in cold absolute alcohol to the extent of 30 g in 100 ml solvent and hence solubility will increase as the proportion of alcohol increases.

6.2.1. Fluid Preparation

The procedure was essentially the same as in section 6.1.1. using alcohol/water mixtures of varying composition and a temperature of $60^{o}C$. The alcohol must be removed before a magnetic fluid can be prepared, as it strips the particles of vital surfactant, causing flocculation. The suspension was therefore magnetically decanted and washed several times with water before the surfactant (Decanoic acid, 0.75 grams:1 gram

Fe_3O_4) was added. Aqueous fluid preparation was then as before.

6.2.2. Particle Size Analysis

Particle sizes have once again been obtained via electron microscopy. Figure 6.3. shows the effect of doping the system with alcohol. Curves a) and b) represent 1 gram and 2 grams respectively of Fe_3O_4 precipitated in 100 ml total volume of reaction mixture.

No size decrease is observed below 70% alcohol content for curve a), whilst curve b) represents a continuous decrease over the entire range of solvent composition. In both cases it is probable that increased solubility of $Fe(OH)_2$ in the reaction medium is causing a decrease in Fe_3O_4 particle size. The effect is enhanced at higher reagent concentrations whilst one might expect, on the basis of previous results, for the opposite to be true. This result is not fully understood but is likely to be related to the higher initial nucleation rates associated with increased solubility of iron(II) hydroxide.

6.3. ADDITION OF ELECTROLYTES

To give credence to the findings of section 6.2. it was decided to precipitate Fe_3O_4 in an aqueous medium containing various amounts of dissolved salts. Iron(II) hydroxide is soluble in concentrated ammonium chloride solution because of the formation of chloro-hydroxy complexes but, perhaps more importantly, because the overall solution becomes moderately acidic. The more concentrated the solution is with respect to ammonium chloride, the more soluble the iron(II) hydroxide will be. Further samples of Fe_3O_4 were precipitated from aqueous solution containing dissolved sodium chloride. This salt does not affect the overall pH which will remain at ~ pH 9. We would therefore expect iron(II) hydroxide to be less soluble in sodium chloride than in

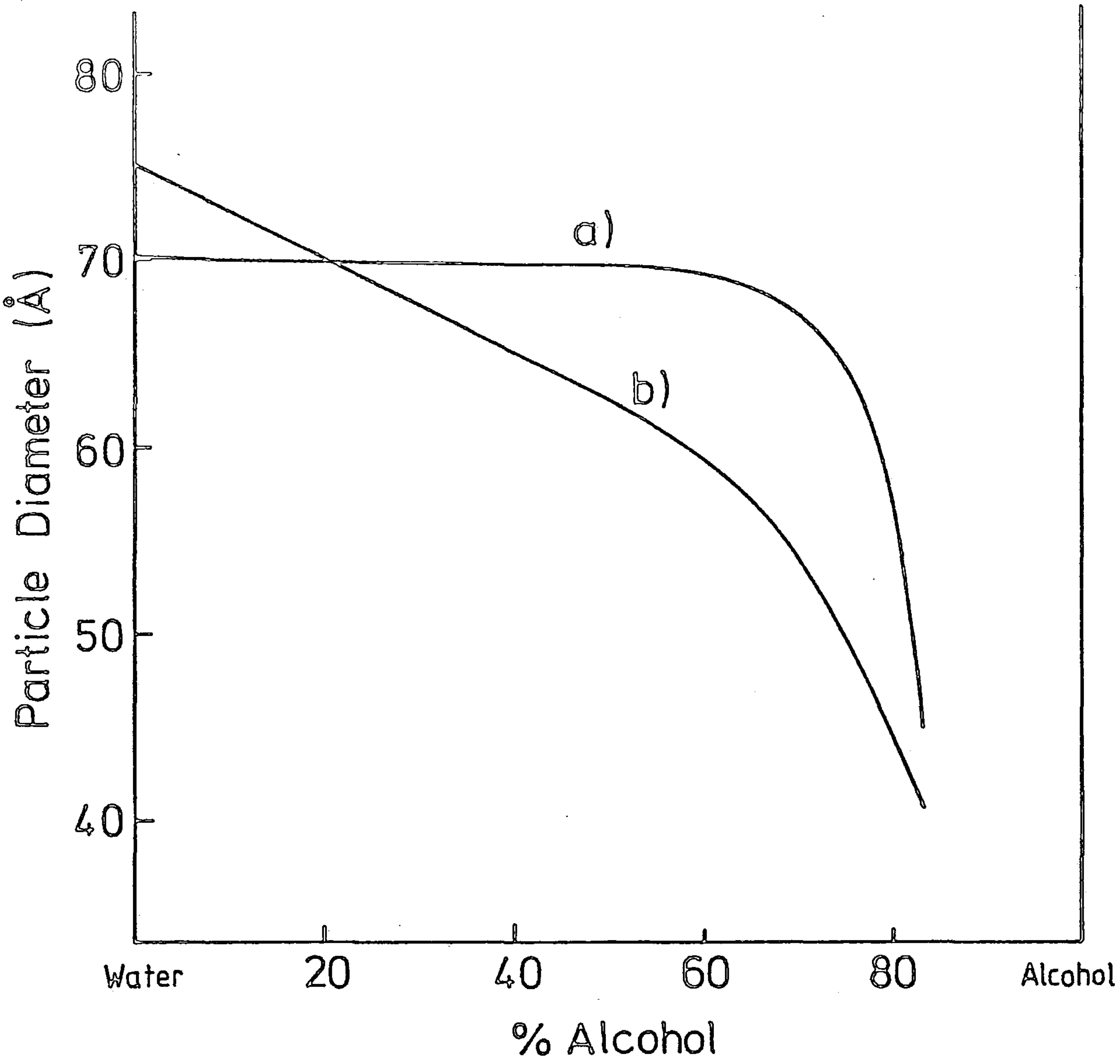


Figure 6.3. The effect of solvent composition on Fe_3O_4 particle size

ammonium chloride solutions.

6.3.1. Particle Size Analysis

Aqueous magnetic fluids, prepared in the usual way, were again the subject of electron microscopic examination. The results form curves a) and b) in Figure 6.4. That for NaCl (curve b)) shows a small but definite size decrease with increasing salt concentration. This effect has been observed by several workers investigating other colloidal systems, whereby adsorption of electrolyte at the particle surface inhibits crystal growth[92]. The drop in size with dissolved NH_4Cl is much more pronounced and can now be assigned, with some confidence, to the increased solubility of $Fe(OH)_2$ therein.

6.4. VISCOSITY EFFECTS

High viscosity media have the effect of inhibiting the crystal growth of particle nuclei by slowing down the rate of diffusion of new material to the particle surface. In the following experiments, Fe_3O_4 was precipitated from mixed salt solutions in the presence of polyethylene glycol (PEG), a non-surface active viscosity increasing agent. Two solid forms of the above material were used - molecular weight 20,000 (high viscosity solutions in water), and molecular weight 4,000 (low viscosity solutions).

6.4.1. Fluid Preparation

Fe_3O_4 (2 grams) was formed by base (aqueous ammonia) precipitation from mixed iron(II)/iron(III) chloride solutions (total volume 100 ml) at 60°C, containing different concentrations of PEG 20,000 and PEG 4,000 dissolved therein. The Fe_3O_4 was settled out over a magnet and washed several times with water to remove PEG. The oxide was resuspended in water, ammoniated and heated to 80°C. Decanoic acid (1.4 grams) was

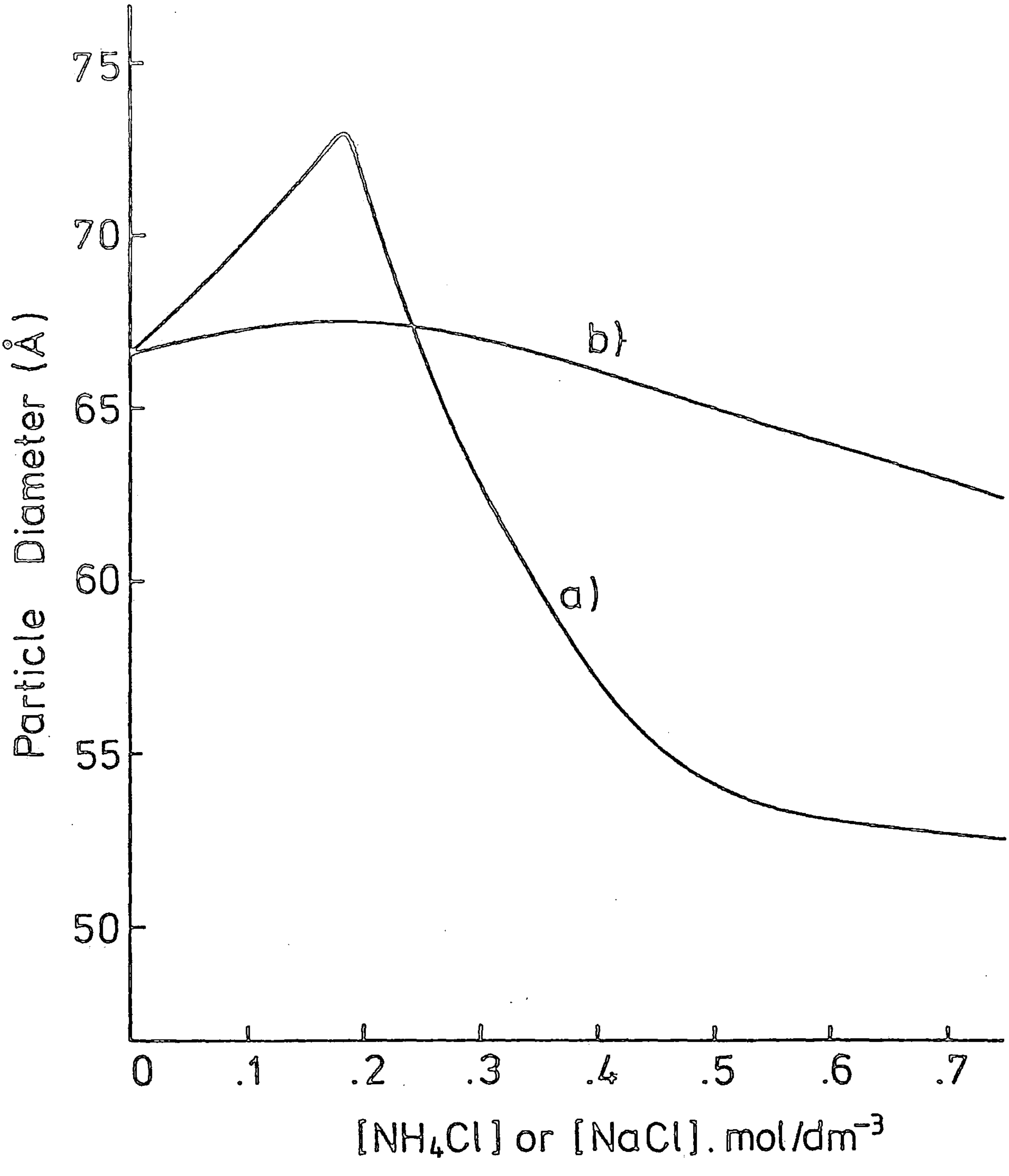


Figure 6.4. The effect of dissolved a) NH_4Cl and b) NaCl on Fe_3O_4 particle size.

added with stirring. After 5 mins. at 80°C the semi-stable dispersion was cooled and flocculated with 2 molar perchloric acid. A black gum formed which, after washing with water, was resuspended in water at 90°C with 5 drops 33% aqueous ammonia to give a stable magnetic fluid.

6.4.2. Particle Size Analysis

Electron micrographs were taken at x220,000 magnification and analysed in the usual way. The results are presented in graphic form (Figure 6.5.).

Mean sizes in the 65-85Å range were observed but, more importantly, the results are indicative of the effect viscosity has on the formation of colloidal particles.

Both curves go through a trough and a peak before falling away again, at which point viscosity is extremely high and tends to hinder effective mixing of reagents. Both curves show the same trends, but that for the lower molecular weight material is displaced towards higher concentrations as expected. The trough is also more pronounced with PEG 4,000 and better reflects the suppression of crystal growth which gives rise to smaller particles in viscous media. The subsequent peak is not fully understood but it may be that, at such high viscosities, nucleation is also being inhibited thereby encouraging deposition of material on existing nuclei.

6.5. PHYSICAL METHODS

The following experiments involve variations in the mixing of reagents to effect precipitation of Fe_3O_4. It was hoped to alter the relative rates of nucleation and crystal growth and hence particle size.

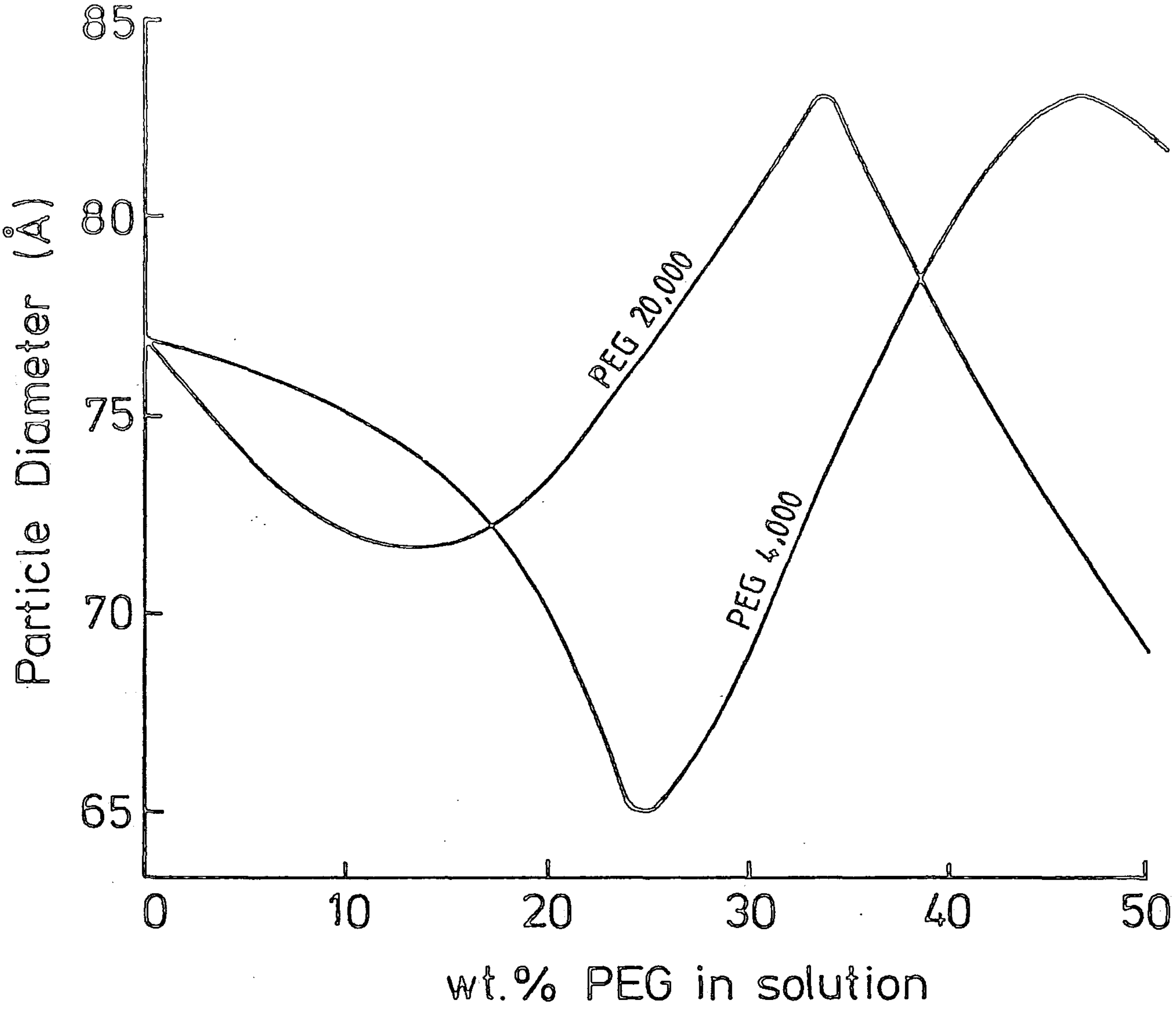


Figure 6.5. Mean particle sizes of Fe_3O_4 formed in the presence of polyethylene glycol.

6.5.1. Experimental

i) Preliminary experiments revealed that magnetite formation begins at $\sim$ pH 5.5. A mixed iron(II)/iron(III) chloride solution was swiftly quenched to pH 5.5 with 5% aqueous ammonia. The mixture was heated to 70°C. Further ammonia was then added dropwise to pH 8 over a period of $\sim$ 2 hrs. An aqueous fluid was then prepared in the usual way, employing Sarkosyl-'O' as the surfactant - Fluid 6.5.1.

ii) An equal quantity of iron(II)/iron(III) chloride solution was utilized in the following experiment.

To a small volume of 1% aqueous ammonia was added a quantity of the above salt solution to pH 8. 5% aqueous ammonia and mixed iron(II)/iron(III) chloride solution were then simultaneously added dropwise to this pre-prepared solution over a period of 2 hrs., maintaining a pH of 8 ± 0.2. An aqueous fluid was then prepared in the usual way, with Sarkosyl-'O' as the surfactant - Fluid 6.5.2.

6.5.2. Particle Size Analysis

The fluids were analysed for particle size by means of electron microscopy. Typical electron micrographs of these two fluids are displayed in Figure 6.6. Sizes were obtained manually for Fluid 6.5.1., and using the Image Size Analyser for Fluid 6.5.2.

The mean particle sizes were 340Å and 119Å respectively.

6.5.3. Discussion

Both samples have mean sizes significantly larger than anything yet prepared. Those particles in Fluid 6.5.1., although appearing well dispersed, were too large for true colloidal stability and indeed may no longer be superparamagnetic.

To ascertain why such noticeable size differences have occurred,

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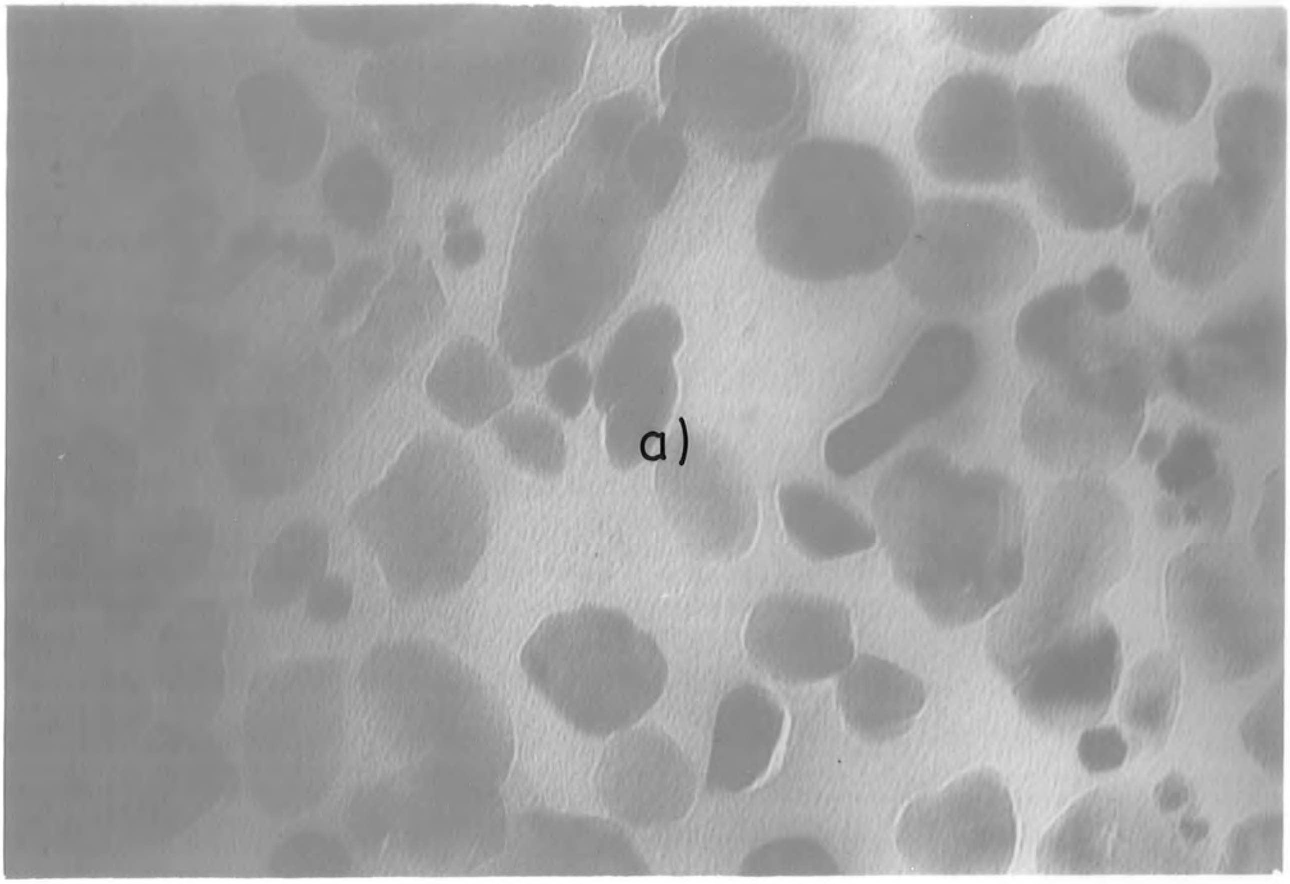
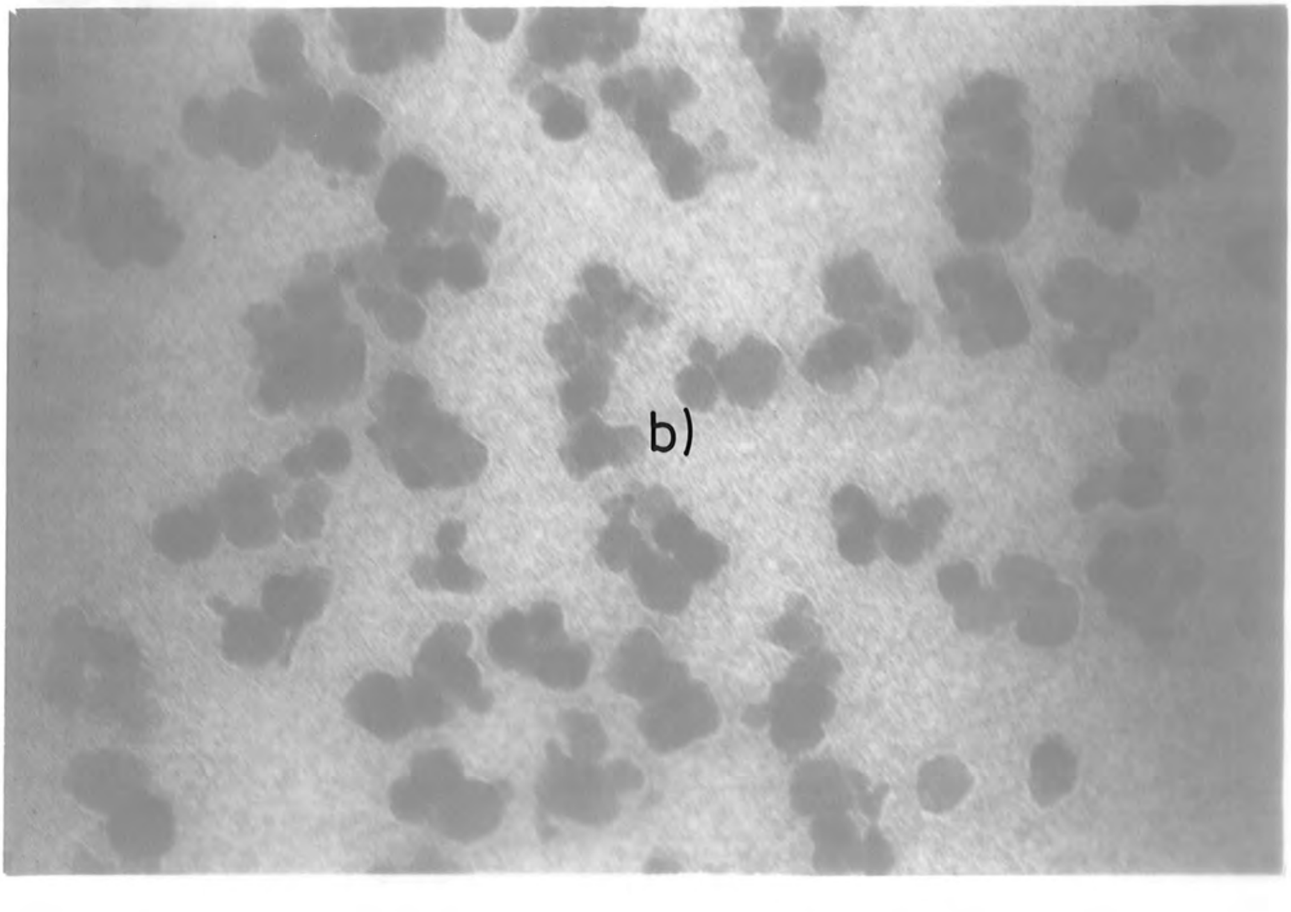


Fig.6.6 Electron micrographs of a)fluid 6.5.1 and b)fluid 6.5.2 (×400,000)



let us consider both mixtures in the early stages of precipitation when only a small quantity of Fe_3O_4 particles have been formed. In the first preparation (Fluid 6.5.1.) such particles exist in a medium containing predominantly Fe^{2+} and Fe^{3+}. For insoluble magnetite, crystal growth is most likely to occur by, first reaction and then subsequent deposition of material at the surface of existing nuclei. Whilst these nuclei are surrounded by a Fe^{2+}/Fe^{3+} mixture there is a definite possibility of this occurring.

In the second preparation, the first few magnetite crystals find themselves in an almost neutral aqueous medium containing few Fe^{2+} or Fe^{3+} ions. Formation of new material is therefore more likely to occur away from the surface of existing nuclei, thus creating more nuclei and a smaller mean particle size.

Considering both experiments as a whole it appears that, for precipitation reactions, particle size is strongly influenced by the order in which reagents are mixed and the time factor involved.

6.6. ORGANIC VERSUS AQUEOUS FLUIDS

It has been noticed that when aqueous and organic-based magnetic fluids are prepared from the same sample of Fe_3O_4, the aqueous fluid is often the more stable even though the same surfactant has been used in both cases. The following experiments are designed to probe these systems, with a view to understanding why such instabilities should arise.

6.6.1. Experimental Procedure

i) Fe_3O_4 (10 grams) was precipitated at 60°C in 100 ml H_2O. Oleic acid (10 grams) was then added and the heating continued at 85°C until gum-like solids formed. These were isolated and washed several times with water.

a) A portion was resuspended in water at 80°C with a few drops aqueous ammonia to create a stable magnetic fluid - Fluid 6.6.1.

b) A portion was washed with hot ethanol, acetone and suspended in toluene at 110°C. The fluid was placed over a magnet to remove entrained particles - Fluid 6.6.2.

c) The residue from part b) was washed with acetone and water, then resuspended in water at 80°C with ammonium laurate. The dispersion was flocculated with 2 molar perchloric acid, washed with water and resuspended in water/ammonia at 80°C - Fluid 6.6.3.

d) A portion of the original solid was washed with hot ethanol, acetone and resuspended in paraffin at 110°C. The fluid was placed over a magnet to remove entrained particles - Fluid 6.6.4.

e) The residue from part d) was washed with acetone and water then made into an aqueous fluid as in part c) - Fluid 6.6.5.

ii) Same as i) except using Sarkosyl-'O' instead of oleic acid. Fluids were prepared as in i) a), b) and c) to yield Fluids 6.6.6., 6.6.7. and 6.6.8.

All the fluids prepared were stable to both gravitational fields (having been allowed to stand for several days without sedimentation), and magnetic fields (no sedimentation when placed over a magnet for a period not less than five minutes).

6.6.2. Particle Size Analysis and Discussion

Electron microscopy and VSM magnetic measurements were both used to examine the fluids for particle size and size distribution. These

TABLE 6.1.

Particle size data for aqueous and non-aqueous fluids (section 6.6.)

Fluid	Nature of Particles	Surfactant	Carrier Liquid	TEM(Å)		Magnetic Chantrell (Å)	
				D_p	σ	D_m	σ
6.6.1.	Original Fe_3O_4	Oleic Acid	Water	75	24	56.4	24.8
6.6.2.	Original Fe_3O_4	Oleic Acid	Toluene	72	23.3	51.1	24
6.6.3.	Residue from 6.6.2.	Oleic Acid	Water	121	42.1	112.9	36.8
6.6.4.	Original Fe_3O_4	Oleic Acid	Paraffin	66.	20.5	47.6	23.3
6.6.5.	Residue from 6.6.4.	Oleic Acid	Water	138	44.4	78.8	36.1
6.6.6.	Original Fe_3O_4	Sarkosyl-'O'	Water	74	24	50.1	24.1
6.6.7.	Original Fe_3O_4	Sarkosyl-'O'	Toluene	62	16.4	47.7	21.8
6.6.8.	Residue from 6.6.7.	Sarkosyl-'O'	Water	84	21.4	50.4	25

results, along with other preparative details, are displayed in Table 6.1.

The first thing to notice is that mean particle sizes for organic-based fluids are consistently 5-10Å smaller than aqueous fluids prepared from the same samples. The residue which settles out from organic dispersions, be it only a small quantity, has particle sizes typically > 100Å. It appears that water will disperse particles of all sizes whereas organic solvents select only the small particles, depositing larger ones. TEM and magnetic analyses revealed the same trends, the latter being 10-20Å smaller in both organic and aqueous fluids. This can be attributed to non-magnetic 'dead' layers caused by oxidation, the extent of which appears to be independent of the carrier liquid.

Substituting Sarkosyl-'0' for oleic acid caused visibly more material to settle out. The mean particle size in organic-based dispersions fell from 72Å to 62Å, whilst that of the residual material also fell from 120Å to 85Å. All this indicates that the size threshold for stable organic dispersions is less using Sarkosyl-'0' which must therefore be deemed a worse surfactant than oleic acid.

It would be experimentally useful to be able to define a particle size cut off point below which particles were dispersable in both aqueous and organic media, and above which only in aqueous media. Because of the practical difficulties in separating the residue from the dispersion however, diameter distributions of the relevant fluids do tend to overlap. Water can accommodate much larger particles than any of the non-aqueous solvents. This probably reflects the mechanism of surfactant stabilization, as discussed in chapter 4, whereby two layers of surfactant are used to stabilize each magnetic particle and the overall quantity of surfactant surrounding each particle is greater than for organic-based fluids.

6.7. SUMMARY

Several factors including temperature, reagent concentrations, viscosity and even the nature of the carrier liquid have been found to affect the size of colloidal magnetite particles. Von Weimarn,[93] concerned with the variation of particle size in barium sulphate precipitates with changes in temperature and reagent concentration, observed similar trends to those obtained in this study. It would appear, therefore, that many of the principles involved in magnetite size control can also be applied to colloidal systems in general.

Particles as small as 50Å and as large as 350Å in diameter have been obtained simply by changing the environment in which precipitation occurs. It is generally accepted that the smaller the particle the more stable it is towards precipitation and, to this end, it was considered desirable to produce particles even smaller than 50Å with even narrower size distributions. Such particles would have a high surface area:volume ratio for the attachment of other molecules such as anti-cancer drugs. The next chapter will describe how serendipity played a part in creating sub-50Å particles and why they could have very important medical applications.

CHAPTER 7

POLYMER DISPERSED MAGNETIC FLUIDS

INTRODUCTION

One of the advantages of using metal oxides as the magnetic material in ferrofluids is that they may be dispersed in aqueous media, something which has not been achieved using metallic fine particles because of problems with oxidation. Compared with the ferromagnetic elements, Fe_3O_4 is relatively non-toxic and indeed, occurs naturally in many animals and organisms. If a suitably non-toxic dispersing agent can be found, a magnetic fluid capable of being tolerated by living tissue may be produced. It may then be used for medicinal purposes as described in chapter 1.

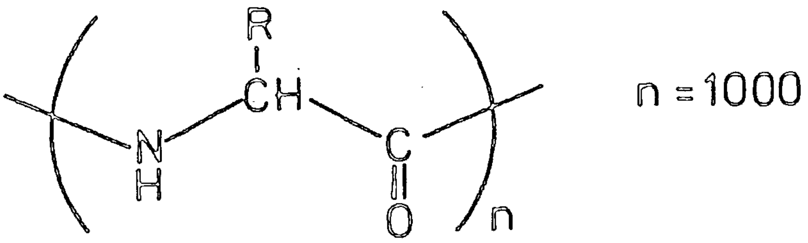
Fortunately, suitable dispersing agents do exist in the form of naturally occurring polymers such as proteins and polysaccharides. These are long chain molecules which have, along their length, many functional groups capable of adhering to the particle surface. Some examples of these are illustrated in Figure 7.1.

Little work has been done previously in this area on account of the bulkiness of these natural materials giving rise to two serious drawbacks in the resulting magnetic fluids. Firstly, only limited quantities of magnetic material can be dispersed (6% as opposed to 40% using conventional surfactants e.g. oleic acid). Secondly, because of the ability of these materials to form intermolecular hydrogen bonds the fluids gel below $300^{o}K$ at polymer concentrations $> 0.5\%$.

In the proposed medical applications, gelation is no longer a problem at $310^{o}K$ body temperatures, whilst concentrated fluids are undesirable anyway. Good stability towards dilution must be achieved and stability studies have been performed on all the fluids prepared.

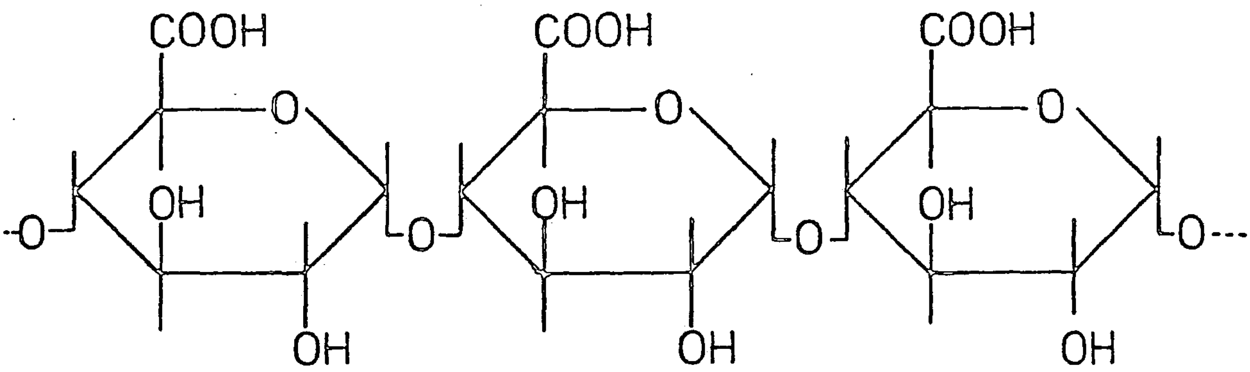
The colloidal systems prepared in this work have many potential advantages over the micron sized magnetic particles presently used,[42]

GELATIN

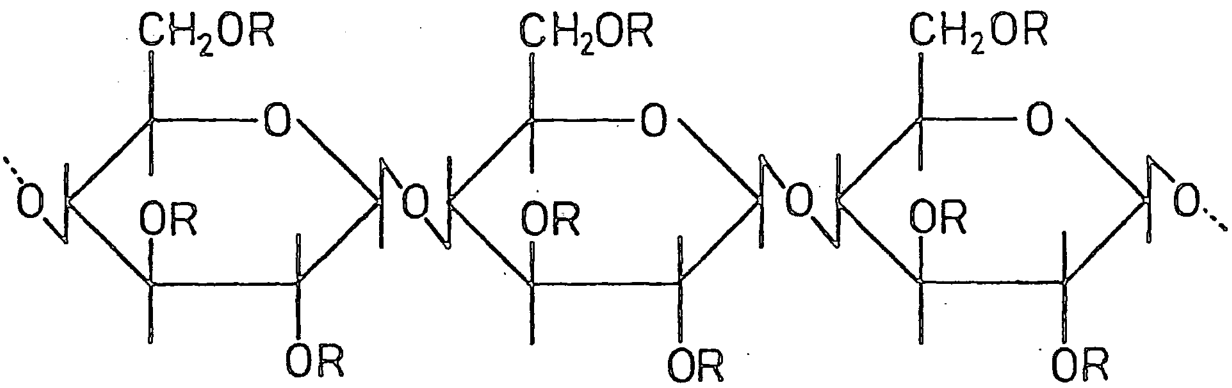


R contains	$-COOH$,	10%.	eg. aspartic acid.
	$-NH_2$,	8%.	eg. arginine + lysine.
	$-OH$,	17%.	eg. hydroxyproline.
	H, OR ALKYL GROUP,	65%.	eg. alanine + glysine.

POLYGALACTURONIC ACID



CARBOXYMETHYL CELLULOSE



R = CH_2COOH

Figure 7.1. Some proteins and polysaccharides used as polymeric dispersing agents.

not only in terms of increased mobility and penetration but also because, being smaller, there is a greater surface area per unit mass for the attachment of drugs etc. to the particle surface.

7.1. GELATIN AND ITS DERIVATIVES

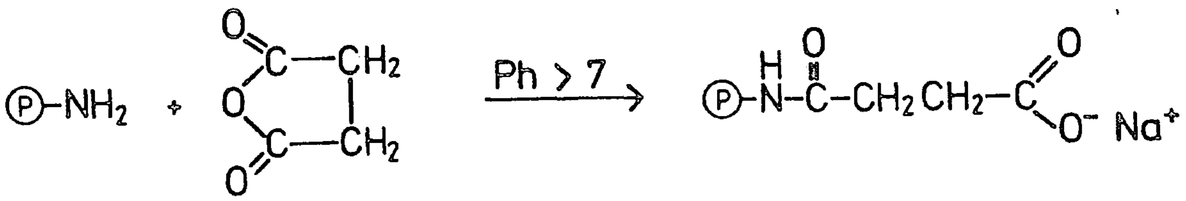
Gelatin is a fibrous protein comprising long chain molecules typically 1,000 amino-acid residues in length.[94] It is derived from collagen with which it shares the same chemical composition, the latter being an insoluble protein consisting of gelatin molecules folded into a triple helix via covalent, electrostatic and hydrogen bonds between individual chains.[95,96] On hydrolysis the protein chains are freed from one another and pass into solution as more random coils.

The gelatin molecule contains many different amino acids[94] the more important of which are indicated in Figure 7.1. Many of them have side chains containing functional groups and, because of the wide variety of such groups, solubility in both acid and alkaline conditions is achieved via ionization of the appropriate function. Gelatin forms solutions of high viscosity in water and at concentrations > 0.5% will set to a gel on cooling.

7.1.1. Surfactant modifications

i) Succinylated gelatin (SG)[97]

This modification replaces side-chain amino- with amide- and carboxyl-functions, placing excess negative charge on the protein molecule, thus rendering it insoluble under acidic conditions. Existing carboxyl groups are unaffected.

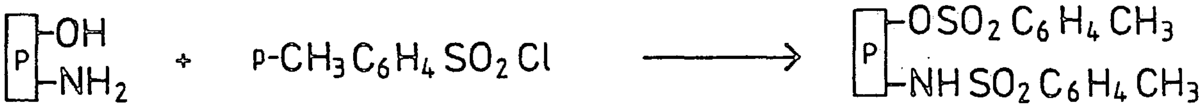


Procedure[98]

To a solution of gelatin in water (~ 5%) at room temperature was added an equivalent mass of succinic anhydride in small aliquots over a period of 1 hour, maintaining a pH of 7-10 by occasional additions of concentrated sodium hydroxide solution. Stirring was continued for a further half hour. 10% Acetic acid was then added to the solution until precipitation occurred at ~ pH 3. The precipitate (SG) was isolated, washed several times with cold water and resuspended in water at pH 7 to give a solution less viscous than that of the parent gelatin and which did not gel on cooling.

ii) Para-toluenesulphonylated gelatin (TSG)[99]

This modification replaces side chain amino- and hydroxyl-groups with non-ionizable 'tosyl' groups, once again rendering the molecule insoluble under acidic conditions. Carboxyl groups are unaffected.



$$\boxed{P}\begin{cases}-OH\\-NH_2\end{cases} + p\text{-}CH_3C_6H_4SO_2Cl \longrightarrow \boxed{P}\begin{cases}-OSO_2C_6H_4CH_3\\-NHSO_2C_6H_4CH_3\end{cases}$$

Procedure

The same procedure was employed as with succinylation, substituting succinic anhydride with para-toluenesulphonyl chloride (one third gelatin mass equivalent of reagent). The gelatinous product was resuspended in water at pH 7 to give a solution, once again, of lower viscosity than the parent gelatin.

7.1.2. Magnetic Fluid Preparation

To a solution of iron(II) chloride tetrahydrate (0.85 grams) in deaerated water (10 ml) was added a solution of gelatin or modified gelatin (x grams in 60 ml water, where x varies between 0.5 and 8), and the mixture heated to 80^{0}C with stirring under a steady flow of nitrogen. 33% Aqueous ammonia (2 ml) was then added to precipitate iron(II) hydroxide.

Meanwhile, a suspension of iron(III) hydroxide was prepared by adding 33% aqueous ammonia (12 ml) to iron(III) chloride (2.33 grams) dissolved in deaerated water (20 ml) at 80^{0}C.

The iron(III) hydroxide suspension at 80^{0}C was now added to the iron(II) hydroxide/surfactant mixture at 80^{0}C with stirring to precipitate the black magnetic oxide (1 gram). After 5 minutes at 80^{0}C the suspension was swiftly cooled to room temperature. Portions were removed and agitated for 10 minutes by means of an ultrasonic probe. This disperses the particle agglomerates and produces a stable magnetic fluid.

In the cases where the gelatin:Fe_3O_4 mass ratio $\leq$ 1:1, additional surfactant must be added immediately after particle formation to ensure complete dispersal. The anionic surfactant Sarkosyl-'0' may be used for this purpose.

7.1.3. Particle Size Analysis

Electron micrographs of all the prepared fluids were taken at appropriate magnifications (220,000-360,000x). These were analysed in the usual way to give particle sizes and size distributions.

Room temperature magnetization curves have been obtained for the same fluids and used to generate magnetic sizes and the corresponding size distributions. For gelatin and its derivatives both sets of data are displayed in Table 7.1.

Initial observations reveal a wide range of sizes and distributions, varying with the amount of polymer used in the fluid preparation. The TEM data for gelatin-based fluids points to a minimum

TABLE 7.1

Particle size data for gelatin and modified gelatin dispersed magnetic fluids

Surfactant	Mass Ratio Surfactant:Fe_3O_4 Used in Preparation	TEM (Å)		Magnetic Chantrell (Å)	
		D_p	σ	D_m	σ
Gelatin	8	57.8	21.1	62.4	22
Gelatin	5	52.4	8.7	51.3	15.7
Gelatin	3.5	57.4	13	45.9	18.9
Gelatin	2	61.2	22.1	46.7	27.3
Gelatin	1	76	17.5	49.6	23.3
Gelatin	0.5	79.2	23	46.4	24.4
Succinylated Gelatin	5	61.1	20	44	22
Succinylated Gelatin	2	44.9	13.4	42	16.4
Succinylated Gelatin	1	71.1	18.2	53.6	21.2
Tosylated Gelatin	5	54.1	10.8	50.8	13
Tosylated Gelatin	2	60.3	15.8	48.2	21.4
No Surfactant	0	67	22.1	60.9	25.4

size of 52Å at a gelatin:Fe_3O_4 ratio of 5:1. As the polymer concentration decreases the particle size steadily increases and then drops back to ~ 67Å. With increasing particle size comes an increase in size distribution also. This is borne out in both the TEM and magnetic data. Electron micrographs and the corresponding diameter distributions are set out in Figure 7.2. and 7.3. respectively.

By succinylating gelatin, and after corrections have been made for the consequent increase in relative molecular mass, particles as small as 45Å in diameter have been observed at lower surfactant concentration than for parent gelatin, whilst either side of this concentration value the same trends are observed. These results indicate that size differences might be, in some way, related to side-chain carboxyl groups. This explanation is reinforced by the results for para-toluenesulphonylated gelatin which are comparable with those for gelatin itself, even though most, if not all, of the amino-acid and hydroxyl side-chain functions were removed.

7.1.4. Fluid Stability

Magnetic fluids stable to precipitation in both gravitational and magnetic fields can be prepared using all the surfactants mentioned previously. Heating at 90°C for a period of several hours had no effect on stability. The effect, or otherwise, of various external influences on the fluids is discussed in the following paragraphs.

i) Dilution Studies

Experiments have shown that, for complete incorporation of magnetic material, ~ 1 gram gelatin is required to disperse 1 gram Fe_3O_4. Good dispersion is also dependent on the quantity of carrier liquid and the maximum Fe_3O_4 weighting of 6% quickly decreases when insufficient water is present.

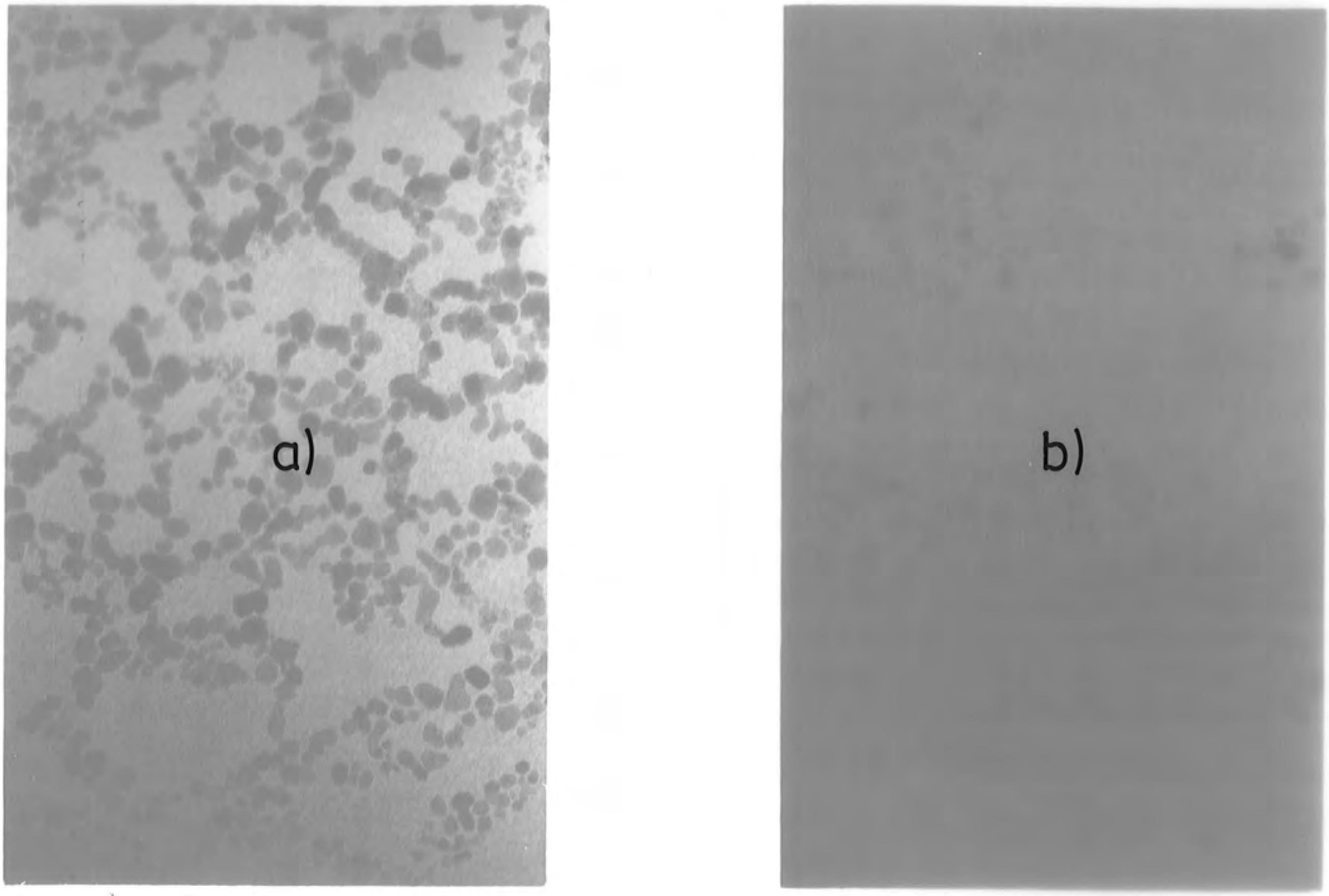
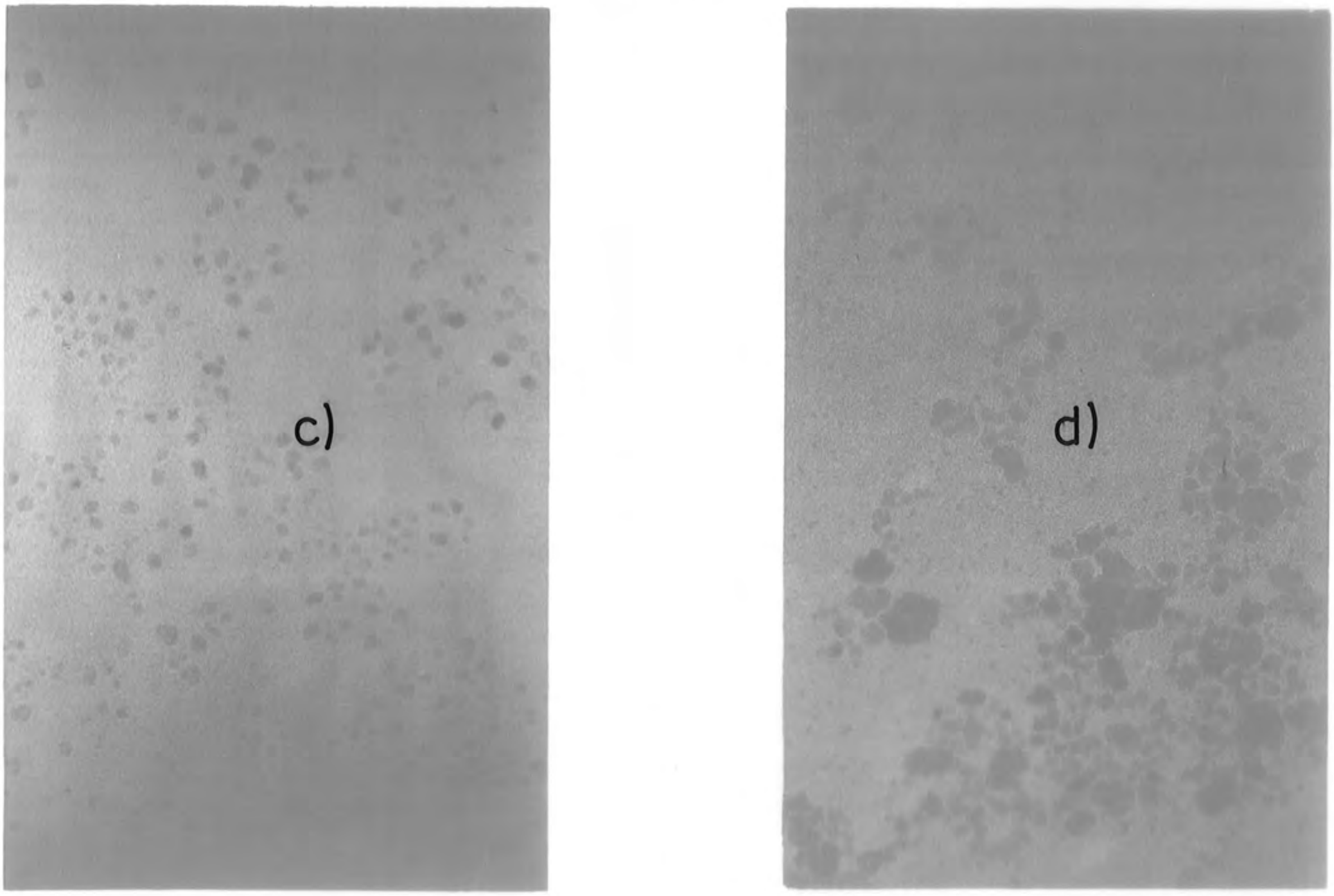


Fig.7.2 Electron micrographs of fluids containing a)8, b)5, c)2 and d)1 gram gelatin (×220,000)



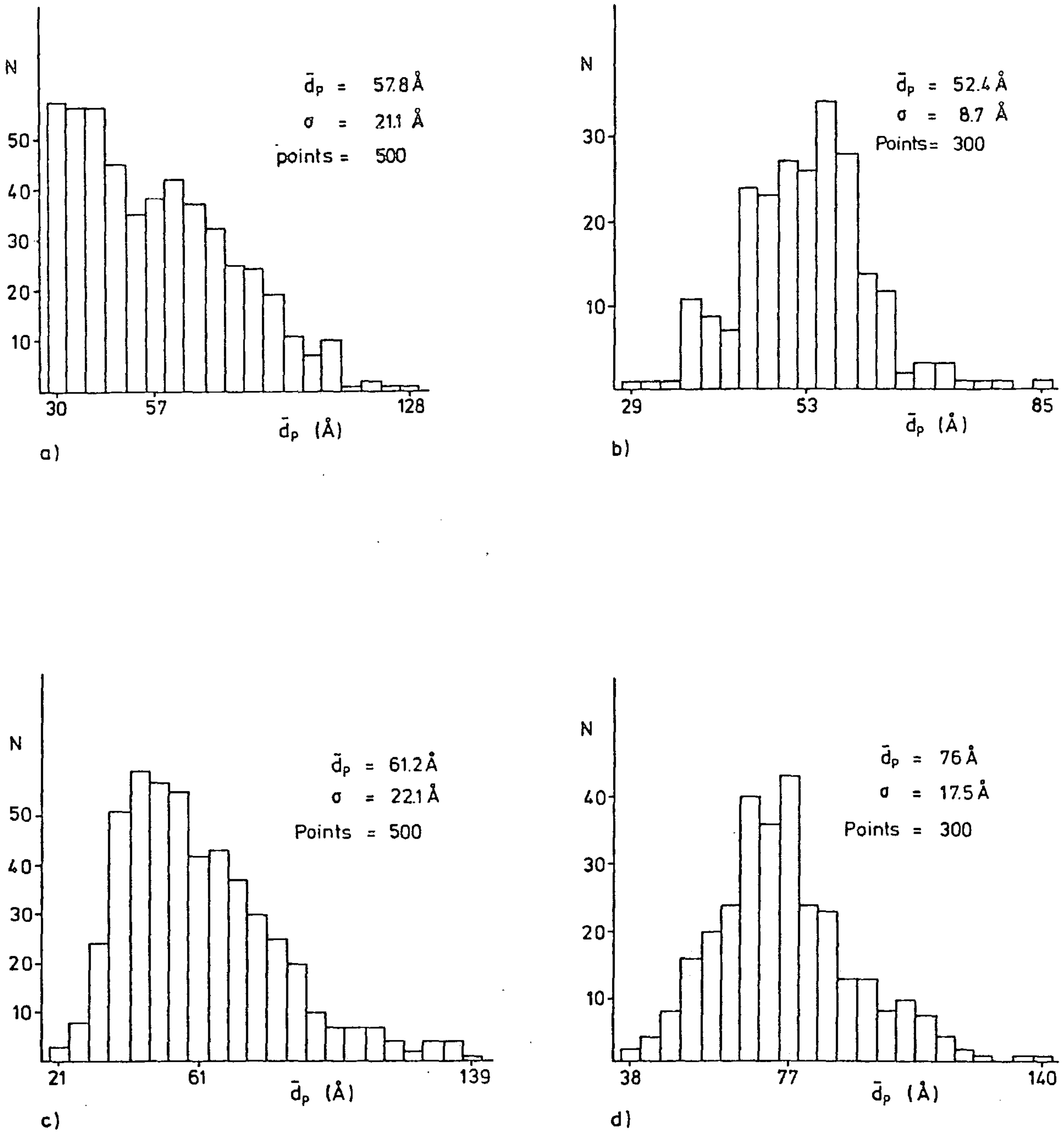


Figure 7.3. Diameter distributions of fluids containing a) 8 gms, b) 5 gms, c) 2 gms and d) 1 gm gelatin.

A fluid was prepared by the usual procedure with 8 grams gelatin to disperse 8 grams Fe_3O_4. The overall volume of liquid was 100 ml. Portions were removed and diluted prior to ultrasonication. The resulting fluids were centrifuged at 2400 rpm to remove entrained particles. Figure 7.4. shows the quantity of Fe_3O_4 dispersed in each fluid as a whole (8 grams max) after adjustments had been made for the dilution factor involved.

Quantity of carrier liquid is the limiting factor in the original preparation, and the curve rises sharply to a maximum as the fluid is diluted by a factor of 1.5 (Fluid 1.4.A.). At this stage all the magnetic material is dispersed, corresponding to 5.3% by weight Fe_3O_4. As the fluid is further diluted progressively more Fe_3O_4 settles out until, at a dilution factor of x32, only half the original quantity remains dispersed.

Viscosity effects become negligible as the fluid is diluted and hence may be ruled out as a possible cause for such instability which is, more likely, due to desorption of gelatin from the particle surface into the bulk solution.

Mean particle size values for the diluted fluids, obtained from magnetic data determined by the Gouy method, are also displayed in Figure 7.4. These indicate that the larger particles settle out first on dilution.

ii) <u>Viscosity effects</u>

At high surfactant concentrations viscosity may serve to retain, in the fluid, particles which are not truly dispersed. To test this aspect, equal portions of the viscous gelatin ferrofluids 1.4.A. and 1.4.B. were first centrifuged at 2400 rpm at different temperatures for 10 minutes. The results then obtained are displayed in Figure 7.4.A.

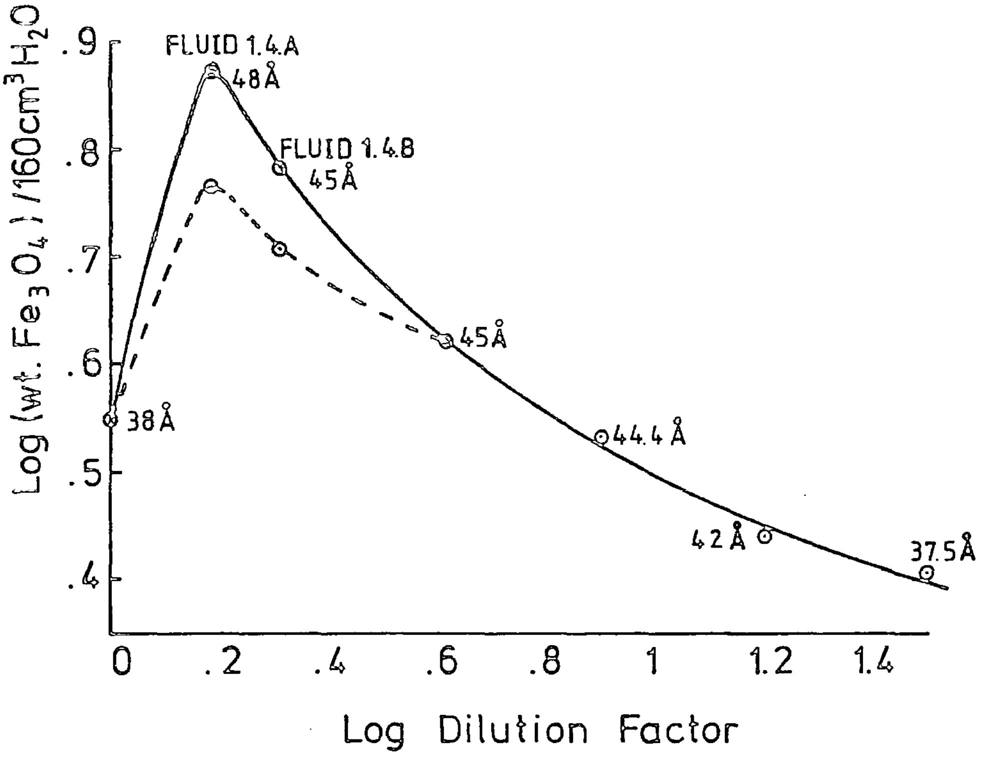


Figure 7.4. Dilution curve for a gelatin-dispersed ferrofluid.

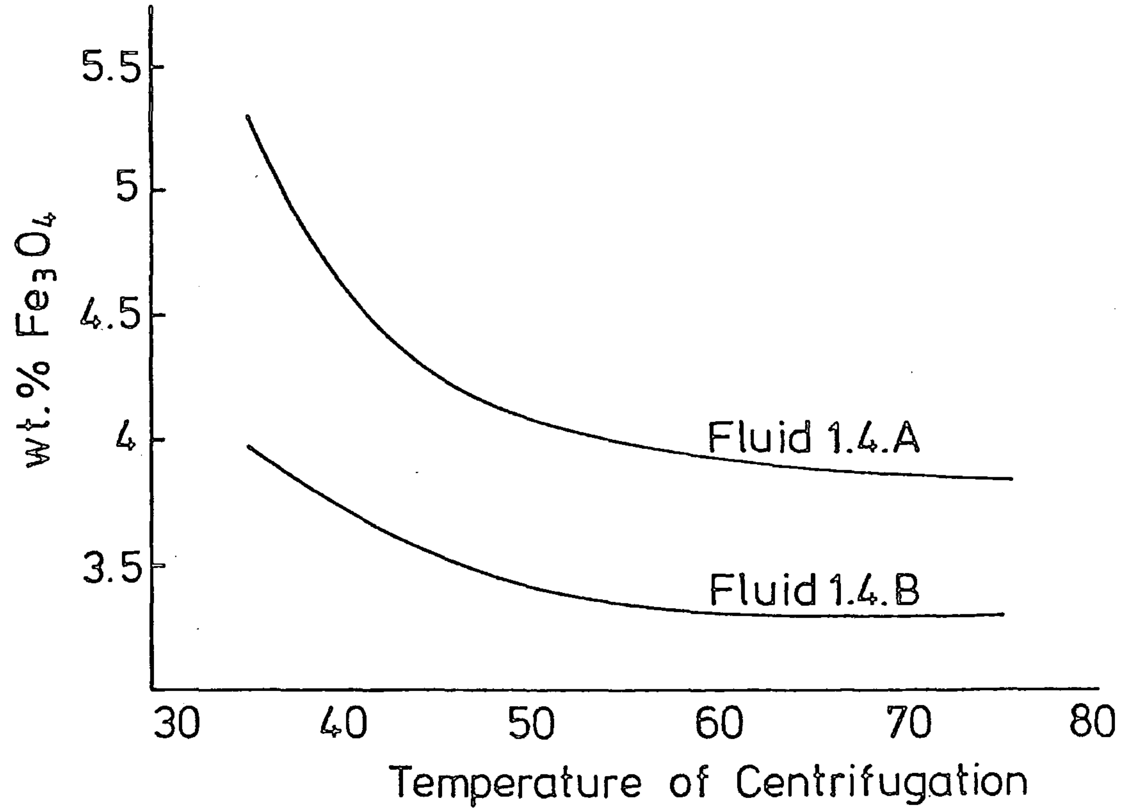


Figure 7.4.A. The effect of temperature and hence viscosity on the retention of Fe_3O_4 in a gelatin-dispersed ferrofluid.

The graphs indicate that viscosity has a marked effect upon retention of material. Having corrected these fluids for viscosity effects, a new curve is generated (Figure 7.4. broken line) which represents the true dilution curve for a gelatin magnetic fluid.

iii) pH Studies

The peptide linkages of gelatin are particularly susceptible to base hydrolysis.[100] This occurs in the presence of concentrated sodium hydroxide at pH > 12.5 and room temperature, and also at elevated temperatures above pH 9. The bonds between certain amino-acids are, however, resistant to this hydrolysis even after boiling for several hours.[94] Denaturation at high pH will therefore split the gelatin molecule into many low molecular weight peptide fragments. When a gelatin ferrofluid is heated to 80°C with concentrated sodium hydroxide, the fluid quickly flocculates leaving a clear yellow supernatant liquid containing these fragments.

The magnetic particles form a gelatinous sludge which, after washing, still shows signs of entrained gelatin. A portion was washed with water and dried under vacuum. Atomic absorption analysis revealed it to contain only 76% Fe_3O_4, indicating that a significant proportion of the denatured gelatin is still particle bound. This is likely to be in the form of small peptide units still adsorbed but of insufficient length to confer stability by steric means. Hydrolysis occurs to a much lesser extent in acid solutions,[94] insufficient to affect fluid stability.

In all magnetic fluid preparations ammonia solution is used in preference to sodium hydroxide for the precipitation of Fe_3O_4. Gelatin appears to tolerate ammonia at high temperatures despite a pH value of up to 11.5.

iv) Oxidation

Surface oxidation of magnetic particles, giving rise to non-magnetic 'dead' layers, is a problem in both metallic and oxide systems. Magnetite ferrofluids often turn brown if exposed to the air for periods longer than one week. Gelatin appears to inhibit this visible oxidation. Atomic absorption analysis on the total iron content and VSM magnetic analysis on the proportion of iron present as the black magnetic oxide were both performed on a gelatin ferrofluid aged in air for a period of one month. The two results coincide in terms of total iron content, indicating that gelatin actually suppresses oxidation. Referring to Table 7.1., magnetic particle diameters are consistently lower than their TEM determined counterparts. Compatibility between the two sets of data increases with gelatin concentration and lends further support to the theory that gelatin suppresses the formation of non-magnetic 'dead' layers. More detailed comparison of the two analyses is included at the end of the chapter.

The initial preparation of Fe_3O_4 uses a 2:1 molar ratio of $Fe^{3+}:Fe^{2+}$. This is the correct stoichiometric ratio for Fe_3O_4 formation. In practice, a 3:2 ratio has been used by many workers because of the ease of oxidation of Fe^{2+} species. The presence of gelatin appears to suppress this oxidation also, allowing a 2:1 ratio to be used.

7.1.5. Partition into Organic Solvents

Attempts to partition gelatin coated magnetic particles into organic solvents by introducing a second surfactant more compatible with the new solvent have met with no success. However, by first denaturing the gelatin with base, oleic acid may be introduced to create stable organic based dispersions.

Procedure

An aqueous gelatin ferrofluid was denatured by boiling in concentrated sodium hydroxide for 30 minutes. The solution was then removed by decantation from magnetically held particles. The residue was washed with water, dilute hydrochloric acid (to remove excess sodium hydroxide), then again with water. The suspension was mixed with ammonia and heated to 80°C with stirring. Oleic acid was added (1 g oleic acid:1 g Fe_3O_4) then the mixture heated at 80°C to decompose the ammonium oleate until a black gum formed. The supernatant liquid was decanted from the gum which was washed with the following reagents in sequence, each solution being decanted from the magnetite whilst the latter was held using a magnet: one washing with dilute hydrochloric acid, one washing with distilled water, two washings with hot ethanol (removes excess oleic acid) and one washing with acetone. Toluene was added and the mixture heated to 110°C to remove acetone and create a stable ferrofluid. The solvent was finally removed in vacuo to produce a fluid of the desired concentration.

In this way, dilution stable organic-based fluids were made, incorporating up to 30% magnetic material. Figure 7.5. shows an electron micrograph of one such fluid after dilution with toluene. The particles are ~ 50Å diameter with a narrow size distribution, indicative of the fact that gelatin was used in the initial preparation.

Discussion

Following denaturation of the gelatin surfactant, there are unlikely to be many vacant sites at the particle surface onto which oleic acid can adsorb, on account of the residual peptide fragments still present. The preparation of fluids in toluene using oleic acid is probably a result of electrostatic interactions between oleate anion and

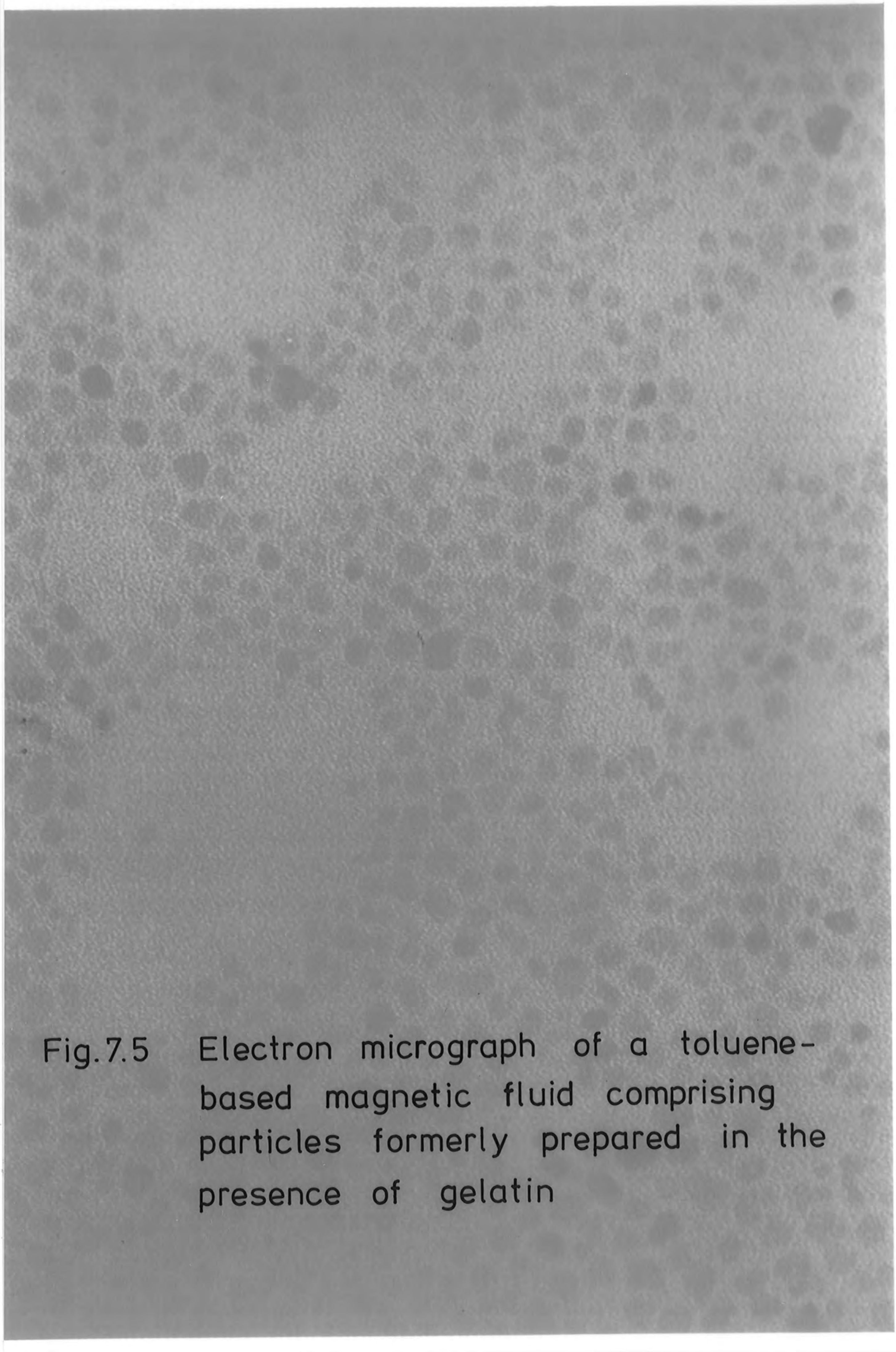
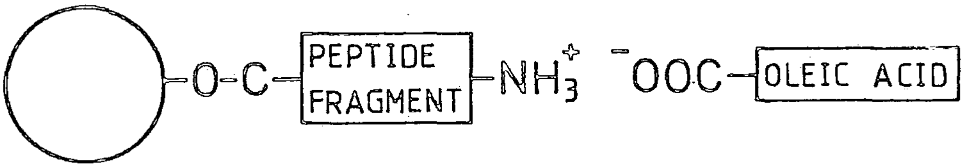


Fig. 7.5 Electron micrograph of a toluene-based magnetic fluid comprising particles formerly prepared in the presence of gelatin

the many basic residues created by hydrolysis of the peptide.



In the above representation the protein component functions as a bridge between oleic acid and the particle surface.

7.1.6. Control of Gelation

Magnetic fluids containing > 1% gelatin readily form gels at temperatures below 300°K. Addition of urea or guanidine hydrochloride will suppress gelation by interfering with the intermolecular hydrogen bonds responsible in the main for these rigid structures.[101] They must, however, be present in very large concentrations such that, if aqueous carrier liquid is lost by evaporation, crystals will form within the fluid which seriously affect its flow characteristics.

Succinylated gelatin-based fluids will tolerate up to 4% surfactant concentration before gelation occurs. This larger concentration compared with that for gelatin is most likely due to the reduced electrostatic interactions between oppositely charged groups in the modified protein. By doping these fluids with alcohol it has been possible to suppress gelation without affecting fluid stability. By extending this work, a modified gelatin-based ferrofluid in 100% ethanol has been produced.

i) Doping with ethanol

The effect of adding ethanol to a gelatin magnetic fluid is to lower the viscosity and suppress gelation. At the same time it dehydrates the peptide chains giving rise to varying degrees of flocculation when the ethanol content exceeds 50%. These results only apply at pH 4-8. At more extreme pH values, up to 80% alcohol content can be tolerated, stabilization being achieved by a layer of charge at the gelatin/solvent interface causing particles to repel one another.[103]

A series of fluids was prepared employing 60:40 alcohol/water mixtures and a gelatin:Fe_3O_4 weight ratio 1:1. By changing the pH, 5% concentrations of surfactant and Fe_3O_4 were obtainable without flocculation or gelation occurring. The results are summarized in Figure 7.6. The main point to be deduced from the work is that to incorporate higher and higher gelatin, and hence Fe_3O_4, concentrations into stable alcohol/water-based magnetic fluids, the more extreme has to be the acidity or alkalinity of the fluid.

ii) Gelatin Lauryl Sulfate[104,105]

Amino-groups on the protein react with sodium lauryl sulfate: $C_{11}H_{25}OSO_3Na$, to give a fully substituted product which is soluble in 100% ethanol.

Fluid Preparation

A previously made gelatin dispersed aqueous magnetic fluid was adjusted to pH 4. Sodium lauryl sulfate solution, also at pH 4, was added with stirring until flocculation occurred. The flocculate was isolated, by decantation, washed with water and resuspended in 100% ethanol to give a stable magnetic fluid.

Discussion

Lauryl sulfate anions bind electrostatically to basic groups on the gelatin. The C_{11} alkyl chains fan out causing the particle/surfactant combination to become hydrophobic. The magnetic particles are redispersable in polar organic solvents but, surprisingly, not in non-polar organic solvents.

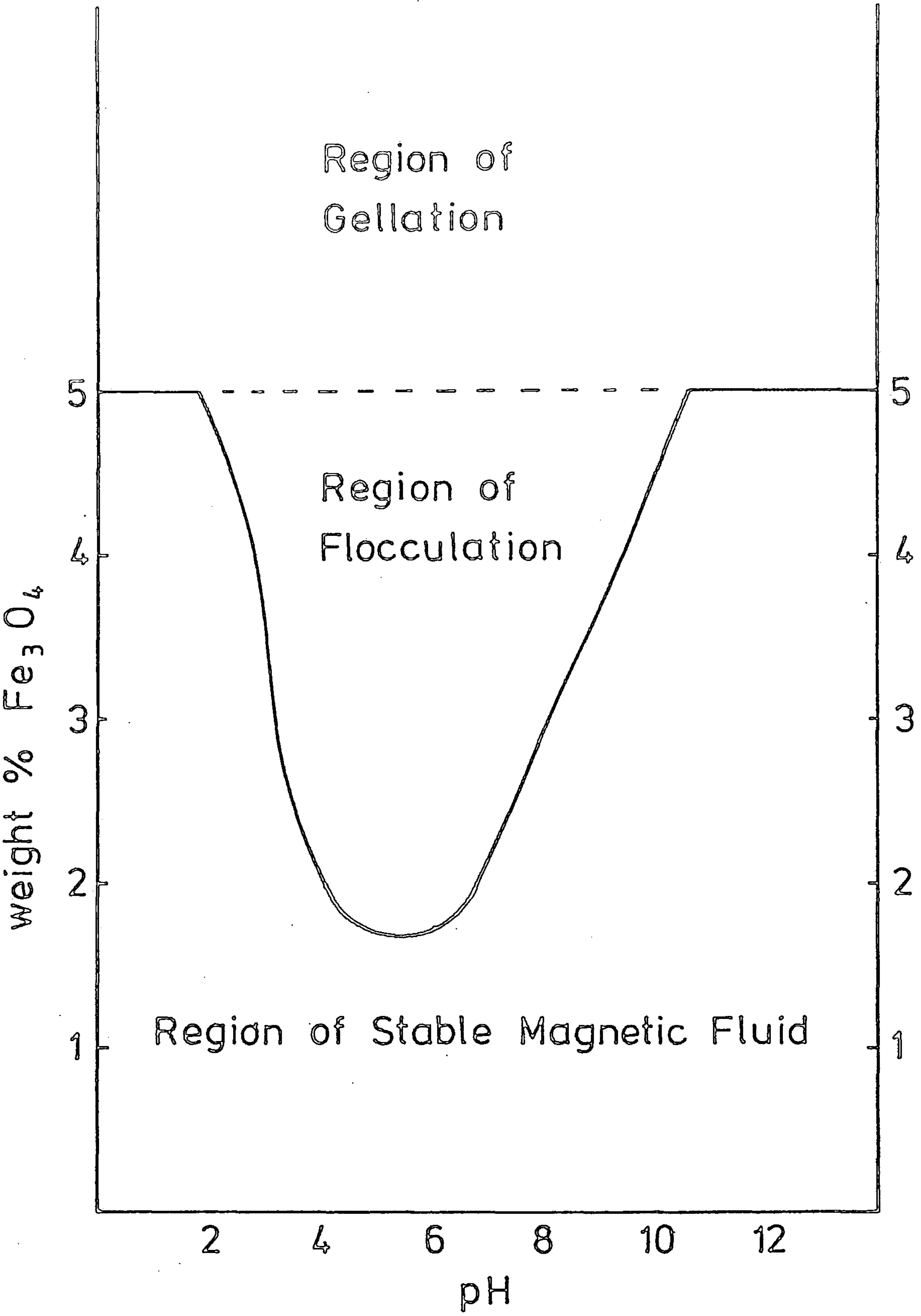


Figure 7.6. Effect of pH on the stability of a gelatin magnetic fluid dispersed in a 60:40 alcohol/water mixture.

7.2. CARBOHYDRATES

Stable magnetic fluids may be prepared using a variety of long chain polysaccharides (M.W. 50,000-100,000) as alternative surfactants.[106] Their structures are illustrated in Figure 7.1., the common factor being that each individual sugar unit has at least one functional group capable of adhering to a magnetic particle. In this study emphasis is placed on polygalacturonic acid (PGA)[107] and carboxymethyl cellulose (CMC),[108] comparisons being made with the gelatin systems.

7.2.1 Fluid Preparation

Experimental procedure was identical to that described for gelatin. Solutions of PGA and CMC were adjusted to pH 6 prior to use, so as to ensure that the carboxyl groups were fully ionized. Surfactant:Fe_3O_4 weight ratios between 0.5 and 8 were once again employed. Complete dispersion was achieved over the whole range without the need to employ additional surfactant (c.f. gelatin). Indeed, 1 gram PGA was capable of dispersing 2 grams Fe_3O_4.

7.2.2. Particle Size Analysis

Electron microscopy (TEM) and VSM magnetic analyses have both been used to obtain particle sizes and size distributions. The results are displayed in tabular form in Table 7.2. The same effects are observed as for gelatin, the particle size and spread steadily decreasing as the concentration of surfactant is increased. TEM data for PGA fluids reveal particles as small as 30Å and for CMC fluids 40Å, sizes which are much smaller than previously obtained.

The magnetic sizes reflect the same trends, but are consistently 5-10Å larger than their TEM counterparts. This may be due to the inability of the former technique to recognize the very smallest

TABLE 7.2

Particle size data for gelatin and modified gelatin dispersed magnetic fluids

Surfactant	Mass Ratio Surfactant:Fe_3O_4 Used in Preparation	TEM (Å)		Magnetic Chantrell (Å)	
		D_p	σ	D_m	σ
Polygalacturonic Acid	8	30.1	7.8	40.7	13
Polygalacturonic Acid	5	35.3	8.2	49.2	14.3
Polygalacturonic Acid	2	37.7	10.8	44	18.5
Polygalacturonic Acid	1	45.4	12.7	52.3	19.7
Carboxymethyl Cellulose	4	49.6	15	61.2	19.6
Carboxymethyl Cellulose	2	40.2	10.1	52.5	20
Carboxymethyl Cellulose	1	46.8	14.5	50.5	20.2

particles.

Whether 30Å is the smallest size obtainable using PGA is a matter for speculation. The situation is more clear cut with CMC, as with gelatin. Changing the concentration of surfactant on either side of that producing the minimum particle size, causes the formation of larger particles. This ideal concentration is 2 grams per gram Fe_3O_4 with CMC, as opposed to 5 grams per gram Fe_3O_4 with gelatin.

Diameter distributions for four PGA based fluids are illustrated in histogram form as Figure 7.7. The sizes are more or less normally distributed around the mean throughout the range of surfactant concentrations. This is in contrast to gelatin where the mean is often displaced towards the larger particles. Magnetization curves for the same four fluids are also presented (Figure 7.8.). Differences in the gradients of these curves prior to saturation reflect the different particle sizes involved.

Typical electron micrographs of PGA and CMC based magnetic fluids are displayed in Figure 7.9. The particles appear to be better dispersed using CMC. This is not reflected in the maximum Fe_3O_4 content of such fluids which, by magnetic analysis, is ~ 4.5% by weight using either surfactant. This is slightly less than in the more viscous gelatin fluids, possibly because higher viscosity will itself inhibit sedimentation of material.

7.2.3. Fluid Stability

The problems encountered with gelatin have not recurred using PGA or CMC. Both systems have been diluted up to 32x original volume without any loss of stability. Figure 7.10. shows the dilution curve for a PGA dispersed magnetic fluid.

Both systems also appear to tolerate extremes of pH. Subjecting

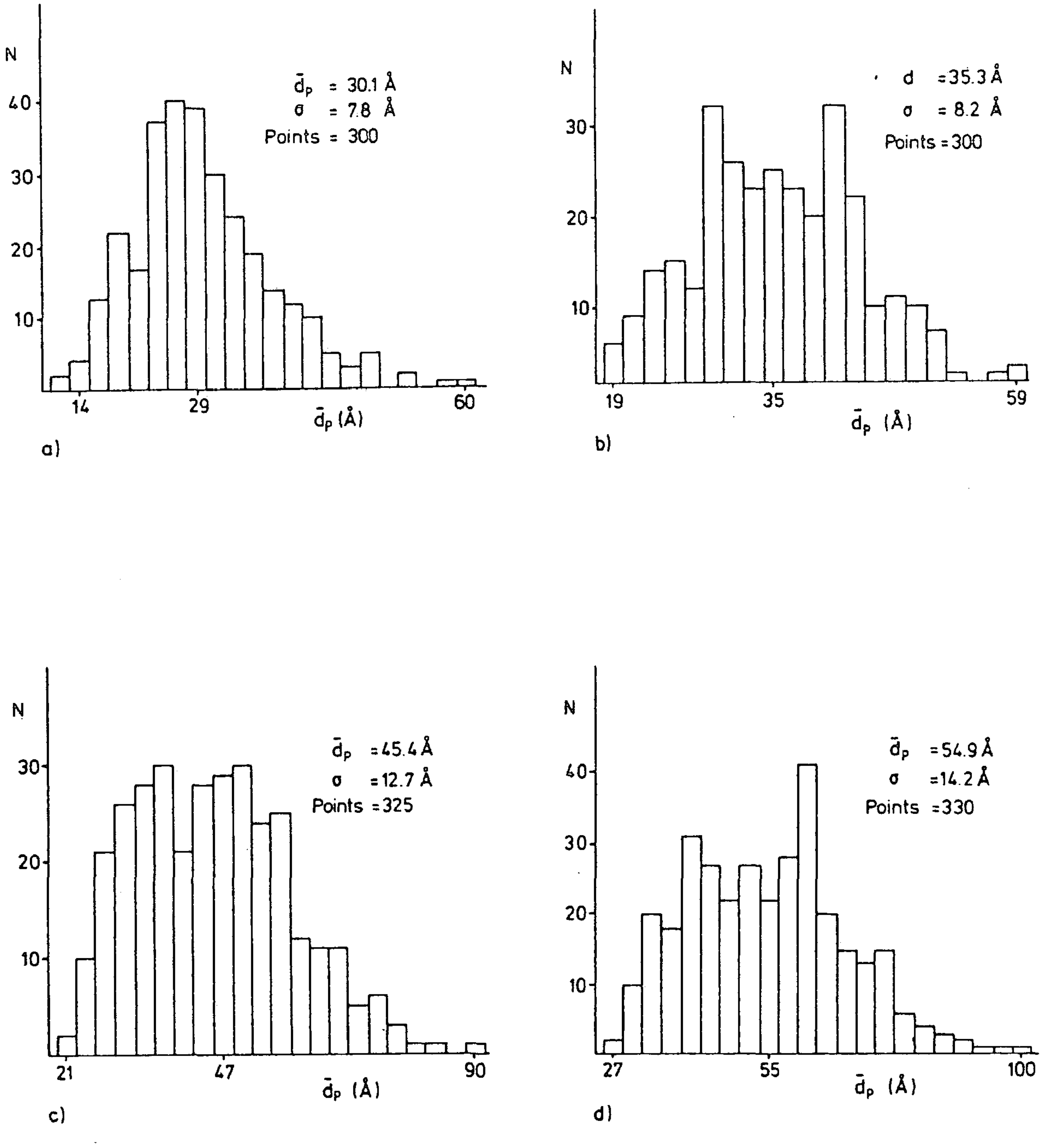


Figure 7.7. Diameter distributions of fluids containing a) 8 gms, b) 5 gms, c) 1 gm and d) 0.5 gms polygalacturonic acid.

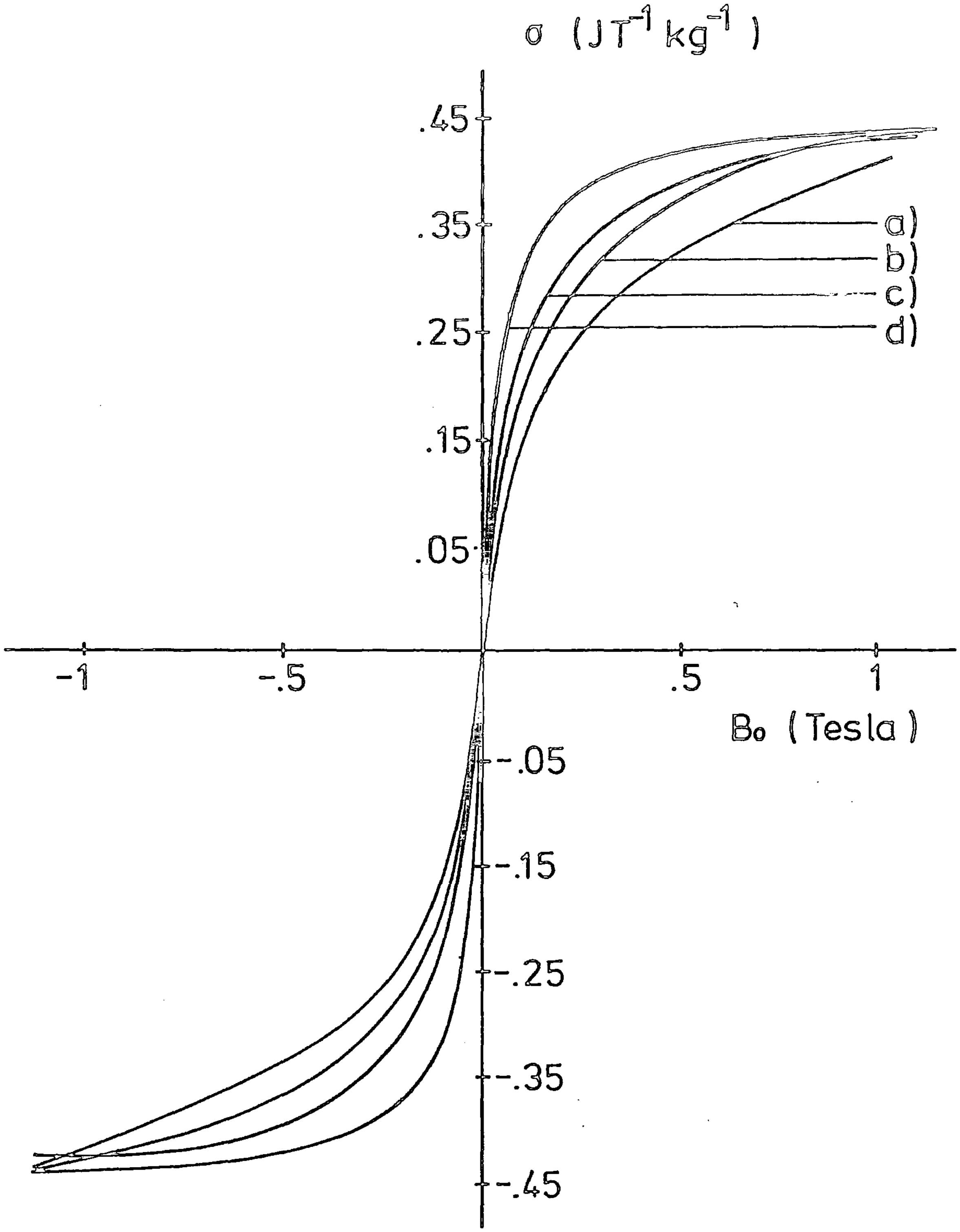


Figure 7.8. Room temperature magnetization curves of fluids containing a) 8 gms, b) 5 gms, c) 1 gm and d) 0.5 gms polygalacturonic acid.

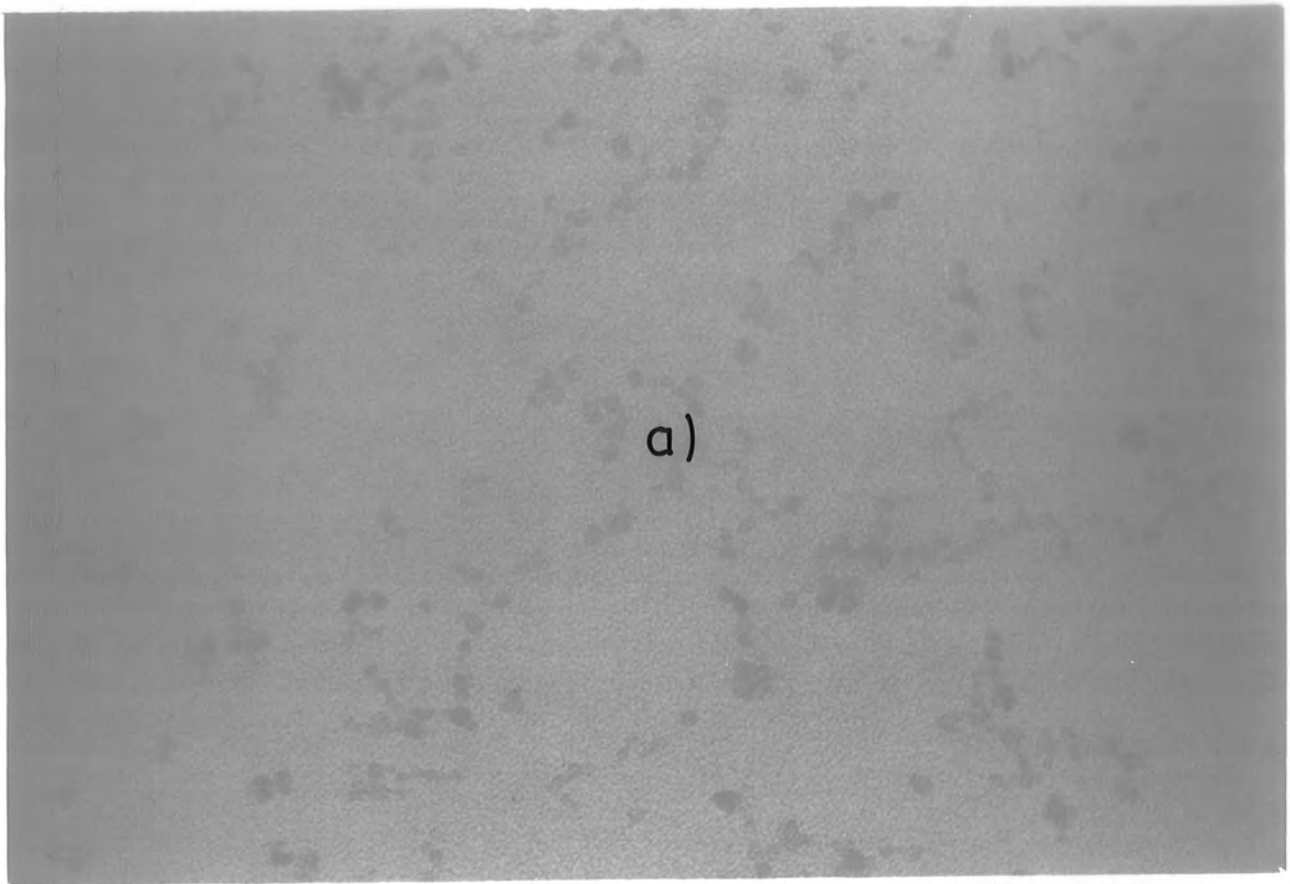
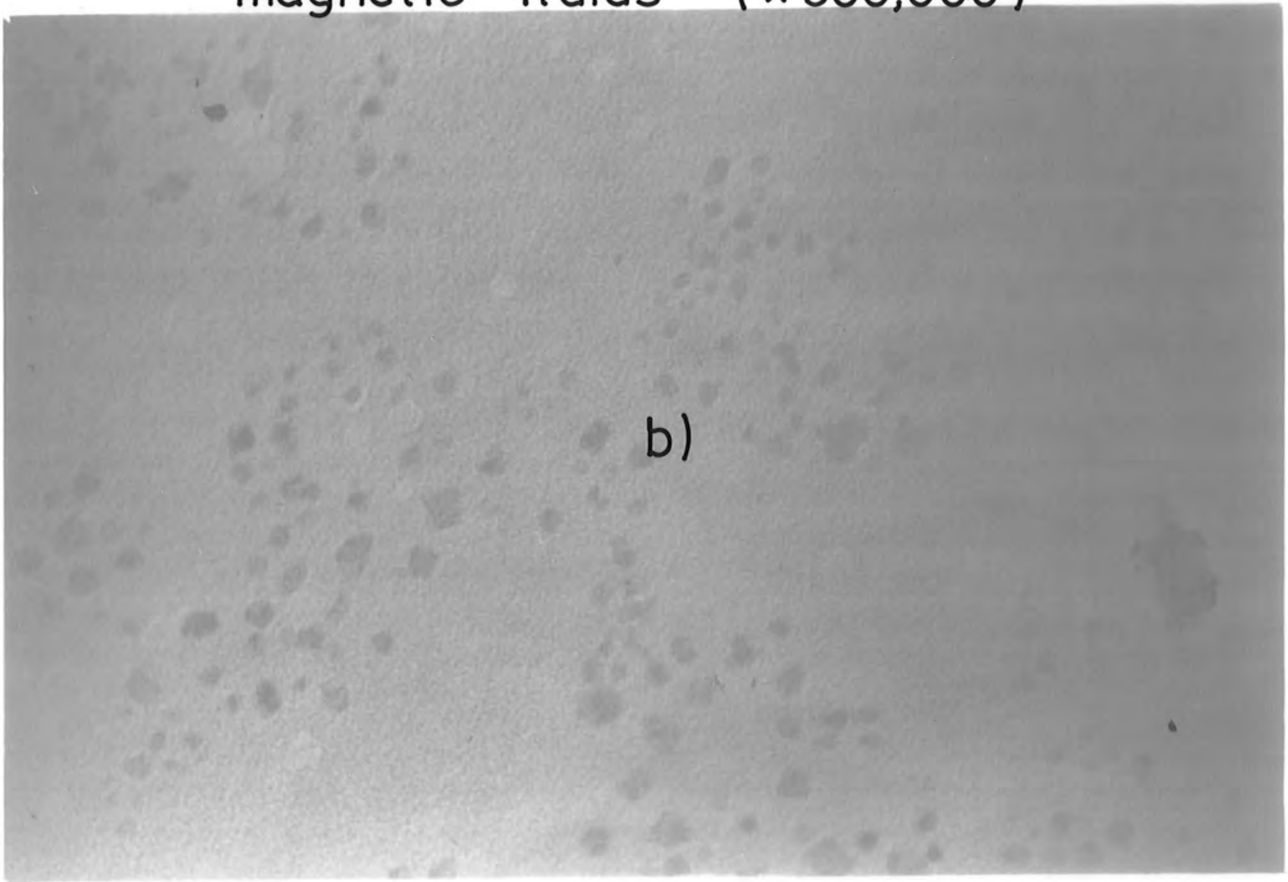


Fig.7.9 Typical electron micrographs of a) PGA and b) CMC dispersed magnetic fluids (× 500,000)



either fluid to pH 1 (perchloric acid) or pH 13 (sodium hydroxide) for several hours at 90-100^{0}C had no appreciable effect on stability. Indeed, glycosidic linkages are reported as being more resistant to hydrolysis than peptide linkages.[108] Fluids aged in air for several weeks were then subjected to atomic absorption and VSM magnetic analysis. Results were comparable with the corresponding experiment on a gelatin ferrofluid (section 7.1.4.iv)), indicating the same resistance to oxidation.

7.3. OTHER SURFACTANTS

Several other proteins have been evaluated as possible substitutes for gelatin. These include albumin from various sources, and IgG, a mixture of human antibody proteins. They have been found to possess only very limited dispersive qualities. The folded nature of these so called 'globular' proteins[102] makes for a greatly reduced surface area for attachement to a magnetic particle. Gelatin, on the other hand, contains a greater than average proportion of hydrophilic side chain groups which ensures a smaller degree of folding when exposed to aqueous media.

Chitosan (a poly-D-glucosamine)[109] will disperse Fe_3O_4 in aqueous media to a limited degree, presumably by attachment of basic amino-groups to the particle surface. Insolubility at $pH > 7$ severely limits its usefulness however.

'Dispex' is the trade name for a range of low molecular weight polymeric dispersants based on acrylic acid: CH_2=CHCOOH. The sodium and ammonium salts of these polycarboxylic acids are soluble over a wide range of pH. Initial experiments involving the precipitation of Fe_3O_4 in the presence of 'Dispex' solutions seem to indicate the formation of

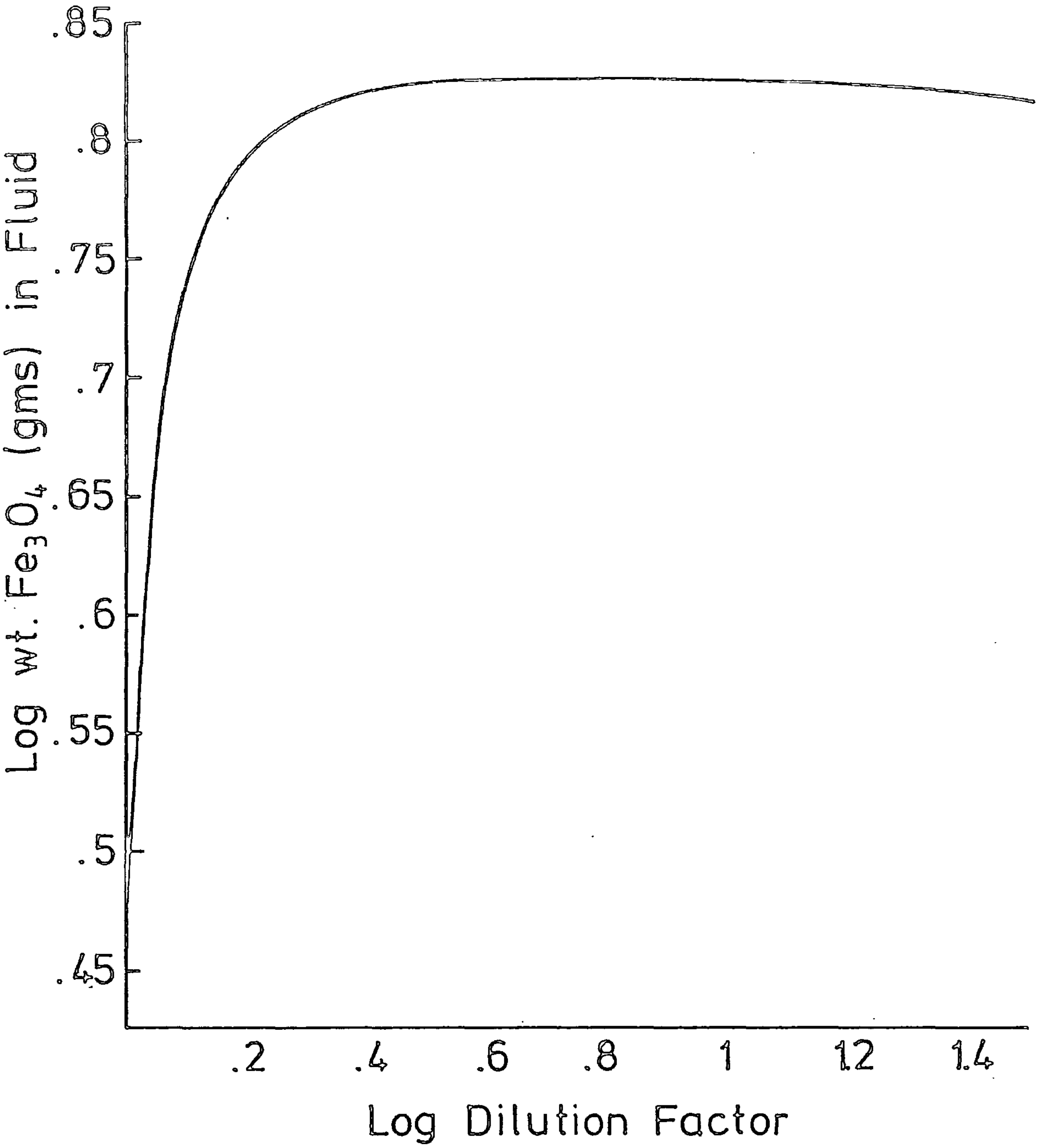


Figure 7.10. Dilution curve for a PGA dispersed ferrofluid.

sub-30Å particles. Unfortunately they are not easily discernible using electron microscopy due to the formation of large aggregates.

Room temperature magnetic analysis was performed on 'Dispex' dispersed ferrofluids two weeks after preparation. A typical magnetization curve is displayed in Figure 7.11. Saturation magnetization was not reached (the curves did not flatten out) and hence a magnetic particle size was unobtainable. The above observation indicates either that the Fe_3O_4 particles are extremely small or that they are not ferrimagnetic, i.e. hydrated iron(III) oxides formed by oxidation. The fluids themselves were red in appearance suggesting the latter possibility but the curve does show signs of some magnetic material being present; this could be Fe_3O_4 or γ-Fe_2O_3.

On the basis of this evidence alone, and without any diffraction data to refer to, it is likely that oxidation has occured in the surface layers of the magnetite particle leaving a ferrimagnetic core surrounded by paramagnetic hydrated ferric oxide (FeOOH).

7.4. A MECHANISM FOR CRYSTAL GROWTH

The formation of soluble complexes of gelatin and transition metal ions (in particular Fe^{2+} and Fe^{3+}) is well documented.[110,111] The process is believed to occur via proton loss from the side-chain carboxyl groups (i.e. glutamic or aspartic amino-acid residues) along the polymer chain and subsequent complexation with the metal ion.[112] This ionization is almost complete at pH 5 whereas iron(II) hydroxide does not begin to form below pH 6-7. Hence a situation may be envisaged whereby, as the pH of a gelatin/iron(II) chloride solution is increased from pH 2 upwards, the gelatin/iron(II) complexes will form before

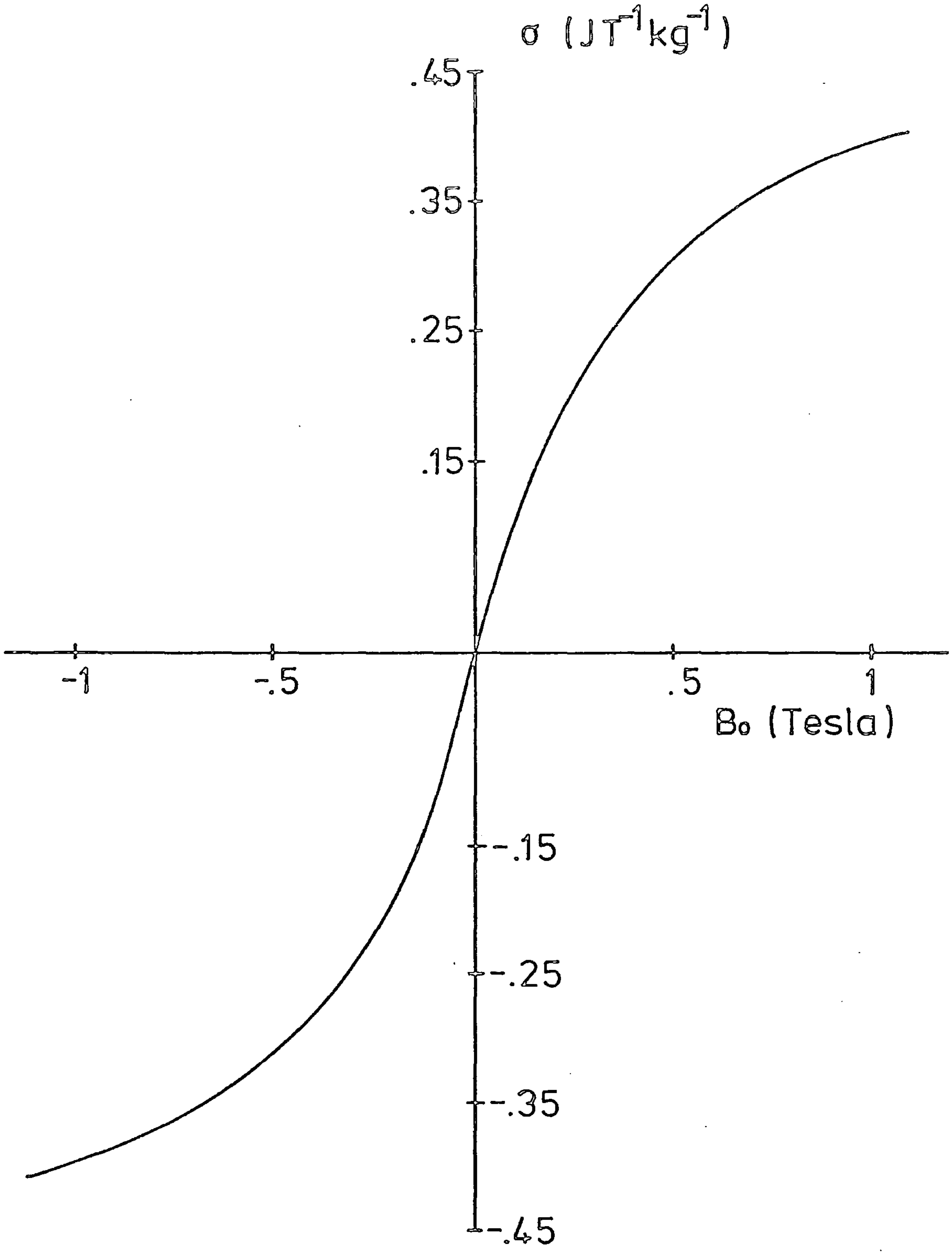


Figure 7.11. Room temperature magnetization curve of a 'Dispex' dispersed magnetic fluid.

iron(II) hydroxide. This is likely to have two effects.

i) It creates the maximum amount of nucleation sites, since iron(II) hydroxide forms whilst Fe^{2+} ions are coordinated individually to sites on the gelatin, prior to formation of the mixed valent oxide.

ii) Formation of particles of a fairly uniform size, i.e. 52Å using a gelatin:Fe_3O_4 weight ratio of 5:1. Interestingly, the carboxyl groups on gelatin are regularly spaced about 10 amino-acid residues or 50Å apart. Since the particles are also 50Å in diameter, this may imply uniform crystal growth while the particle is still attached to a particular coordination site along the gelatin backbone. It is conceivable that growth will continue until it is sterically hindered by other particles growing on neighbouring groups. Thus particle size control here may be a direct consequence of the chemical and structural features of the protein used.

Size uniformity is observed at a surfactant:Fe_3O_4 weight ratio of 5:1. If all the acidic functions were available for complexation then such a ratio corresponds to one acid group for every Fe^{2+} species. This situation would indeed maximize the degree of nucleation but would imply that no material was available for crystal growth. Perhaps some of these nuclei then detach and combine with others along the protein chain to effect such growth. A more likely explanation is that many active sites are buried as a result of protein conformation. Nucleation then occurs to a lesser extent, and these nuclei grow by the deposition of new material. This, of course, implies that such growth is preferred to the formation of other nuclei independent of the protein chains.

As the surfactant:Fe_3O_4 ratio decreases from 5:1, thereby reducing the number of carboxyl groups available for coordination, the average particle size increases and, more significantly, the standard deviation also increases (Table 7.1 and Figure 7.3.c) and 7.3.d)). These figures may be interpreted in terms of insufficient nucleation sites to maintain growth only on gelatin coordinated particles. Some magnetite therefore forms independently of the protein and subsequent crystal growth is consequently unimpaired. Larger particles are found in such samples, and the results overall give credance to this possible explanation.

When the system contains a large excess of gelatin over iron(II) then, according to the above model, both small and large particles should grow along the polymer chain; particle size being governed by the extent to which they are allowed to grow before encountering another particle. It is found experimentally that at high gelatin concentration (8:1 weight ratio) 58Å particles with a very wide size distribution are formed (see Figure 7.2.a) and 7.3.a)).

The viscosity effect, as discussed in chapter 6, may also have a role to play in these systems, especially at weight ratios > 2:1. Viscosity cannot however be held responsible for particle sizes below 65Å as observed in these studies.

The number of potential coordination sites on the gelatin may be increased by treating it with succinic anhydride, which attaches succinyl groups to the side-chain amino-groups. Use of succinylated gelatin in the magnetic preparation was expected, on the basis of the previous model, to lead to smaller particle sizes than with the parent molecule. Indeed at an optimum weight ratio of 2:1 (SG:Fe_3O_4) smaller particles (45Å) having a narrow size distribution were obtained. Again, ratios either side of this ideal concentration gave increases in particle size and standard deviation.

The use of para-toluenesulphonylated gelatin gave results comparable with gelatin itself. Modification of protein amino-groups has been accomplished without affecting the overall carboxyl content of the molecule. The above model predicts that particle size should not therefore be affected. The results not only confirm this but they also indicate strongly that amino groups have no major part to play in the dispersion of magnetic particles by gelatin and its derivatives, despite the fact that nitrogen containing groups do possess high coordinating abilities.

The magnetic particle sizes for magnetic fluids based on gelatin and its derivatives are consistently smaller than their TEM counterparts and do not appear to reflect the same trends. Lack of agreement is more pronounced at low surfactant concentrations. These differences serve to illustrate the following effects:

i) Even at low surfactant concentrations increased viscosity within the reaction medium is significant. This will suppress the rate of molecular collisions between iron(II) and iron(III) species and hence particle formation. Oxidation of iron(II) hydroxide in the interim period upsets the stoichiometric ratio of iron(II) and iron(III) required for Fe_3O_4 formation. The excess of iron(III) shows up as non-ferrimagnetic 'dead layers' on the surface of particles, undetected by magnetic analysis but included in TEM size determinations.

ii) The method of Chantrell[15] tends to overlook very small particles because of the large applied fields required to align their magnetic moments. Mean sizes obtained by magnetic analysis for samples containing very small particles will thus be exaggerated.

iii) Suppression of oxidation by polymeric surfactants encourages agreement between the two sets of analyses at high surfactant concentrations.

The first effect will predominate in gelatin based fluids (particle size 50Å-80Å) especially at low and intermediate surfactant concentrations where the viscosity is still significant, but there is insufficient gelatin to suppress atmospheric oxidation. As the concentration increases the third effect makes a significant contribution and encourages agreement between the two sets of data. The second effect takes over in PGA and CMC based fluids (particle size 30Å-50Å) and explains why magnetic sizes are larger than those physically observed.

Polygalacturonic acid and carboxymethyl cellulose are both linear polysaccharides with at least one carboxyl group per glycoside unit.[107] This places such groups no more than 10Å apart and, as such, magnetic particles of a similar dimension might be expected. However, particles no smaller than 30Å have been observed. The following explanations have been considered.

i) Clumps rather than individual particles were being observed by electron microscopy, but were treated in the particle size measurements as discrete units because of the lack of resolution at the high magnifications used (360,000).

ii) At the high polymer concentrations used, extensive hydrogen bonding exists between polymer chains which serves to block a proportion of the carboxyl groups from complexing with iron(II) ions.

It is suspected that a combination of factors is preventing sub-30Å particles from being observed. Comparing the data for these two systems with that for gelatin reveals the same trends of particle size and size distribution. For PGA and CMC dispersed fluids, much less surfactant is required to effect the same degree of size reduction. This is probably due to the unfolded nature of the polymer chains relative to gelatin, which effectively provides more carboxyl groups onto which particles can nucleate and grow. This structural feature is also reflected in the much lower viscosities of PGA and CMC dispersed magnetic fluids.

7.5. SUMMARY

Magnetic fluids, stable to both gravitational and magnetic fields, have been prepared using a variety of non-toxic polymers as dispersing agents. The low magnetic weightings of these fluids do seriously restrict their applications but their low toxicity, stability towards dilution (especially with PGA and CMC) and the small uniform size of the particles thus dispersed does indicate usefulness as potential drug carriers. Only a representative selection of naturally occurring materials have been used here as dispersing agents, and I feel that the success of this work now permits the tailoring of the surfactant for specific uses in medicine. There are a wide variety of other naturally occurring materials which may be used to stabilize magnetic particles for use in drug delivery, targetting, focussing, marking, mapping etc.

CHAPTER 8

ALTERNATIVE ROUTES TO MAGNETITE FORMATION

INTRODUCTION

Samples of magnetite have been prepared having a variety of sizes and shapes, sometimes for specific uses such as in magnetic inks, sometimes as precursors to other oxides of iron, such as γ-Fe_2O_3 for magnetic recording purposes. Most 'wet' synthetic routes to Fe_3O_4 involve the condensation of an amorphous iron(II) hydroxide particle with an iron(III) oxide or oxohydroxide species. This results in spherical or cubic Fe_3O_4 particles whose size depends on the reaction conditions and, in particular, on the solubilities of the two reagents. Other 'dry' preparations include the selective reduction of iron(III) oxide particles to give acicular Fe_3O_4[113].

In this study we will concentrate again on precipitation techniques and, in particular, on the way in which particle size is influenced by the different reagents and modes of preparation involved.

8.1. IRON(III) OXIDES AND OXOHYDROXIDES

The mean particle size of a magnetite sample depends primarily upon the nucleation rate of those particles. Steck[114] suggests that this in turn is dependent on the solubility properties and hence the rate of dissolution of the reagents at the given reaction conditions. As the solubility product of $Fe(OH)_2$ is at least one hundred times greater than that of any iron(III) hydroxo-species over the entire range of pH, then it follows that the nucleation rate will depend on the solubility of the latter. In this study a range of hydrous ferric oxides have been prepared, varying both in size and composition. These were subsequently used to prepare Fe_3O_4, particle sizes of which were analysed using electron microscopy.

8.1.1. Experimental

i) Preparation of β-FeOOH[115]

A solution containing iron(III) chloride (27 grams), ammonium chloride (13.5 grams) and urea (30 grams) was prepared in water (500 ml). The mixture was refluxed for two hours then cooled, filtered under vacuum and the residue washed with water and methanol. The yellow product was dried in a vacuum desiccator.

ii) Preparation of α-FeOOH[116]

Iron(II) sulphate (25 gms) was dissolved in water (175 ml) and added to a solution of sodium hydroxide (50 gms) in water (200 ml). The suspension was stirred and shaken before leaving to age for 24 hrs.

The supernatant liquid was removed and further water added to give a total volume of 400 ml. The pH was adjusted to 13.5 and compressed air blown through the suspension for 3 hrs. at 40°C. The orange suspension was filtered under vacuum, washed with water and methanol and dried in a vacuum desiccator. The product will be known as α-FeOOH 1.

iii) Preparation of larger α-FeOOH particles[117]

Iron(II) sulphate (31 gms) was dissolved in water (70 ml). Hydrogen peroxide (25 ml, 10%) was added over a period of 5 mins., producing an orange solution. To this was added sodium hydroxide (11.25 gms) in water (70 ml), to which was added 1 gram of previously prepared α-FeOOH 1.

The brown suspension was heated at 90°C for 13 hrs. with mechanical stirring, after which time the suspension had turned orange. The mixture was cooled, filtered under vacuum, the residue washed with water and methanol and dried in a vacuum desiccator. The product will be known as α-FeOOH 2.

iv) Preparation of Fe_3O_4[118]

α or β-FeOOH (2.1 gms), previously prepared, was suspended in deaerated water (80 ml) in a 250 cm^3 round-bottomed flask fitted with a mechanical stirrer. Iron(II) chloride (2.26 gms) dissolved in water (20 ml) was added to the suspension. The temperature was raised to 65^0C (or 35^0C), 33% aqueous ammonia (12 ml) was then added with stirring. The time taken for the suspension to turn jet black varied according to the nature of the iron(III) precursor used and the temperature of preparation. The reaction temperature was maintained for a further 30 mins. after this. Oleic acid (2 ml) was added and stirred in at 90^0C until black gum-like solids formed. These were isolated, washed with water, hot ethanol and acetone, before attempts were made to form fluids in 30 ml toluene at 110^0C.

Stable colloidal dispersions were unobtainable even after extensive ultrasonication. The unstable fluids were diluted with toluene before being inspected using the electron microscope.

8.1.2. Particle Size Analysis

Stable aqueous dispersions of the non-ferromagnetic iron(III) precursors were prepared without the aid of surfactants. These, along with the unstable magnetite dispersions were then subject to TEM analysis.

Typical electron micrographs of the iron(III) hydroxo-species are displayed in Figure 8.1. The axial dimensions have been measured by hand and form part of Table 8.1. Inspection of Figure 8.1.c) reveals cubic and hexagonal as well as the usual acicular particles. These may indeed be the same particles viewed longitudinally rather than in transverse section. The amorphous-like material also present will be the subject of further study in the section on infra-red spectroscopy.

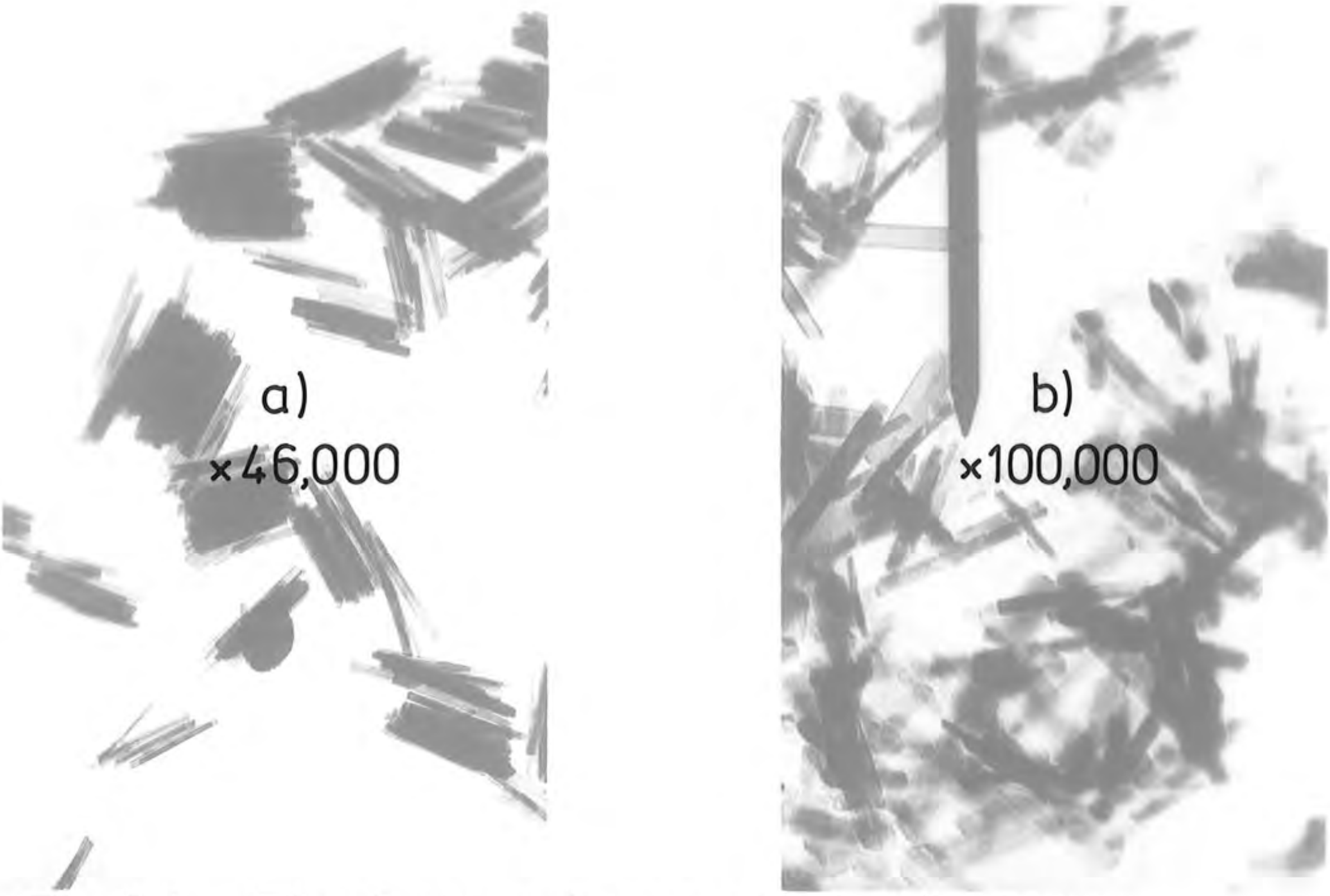
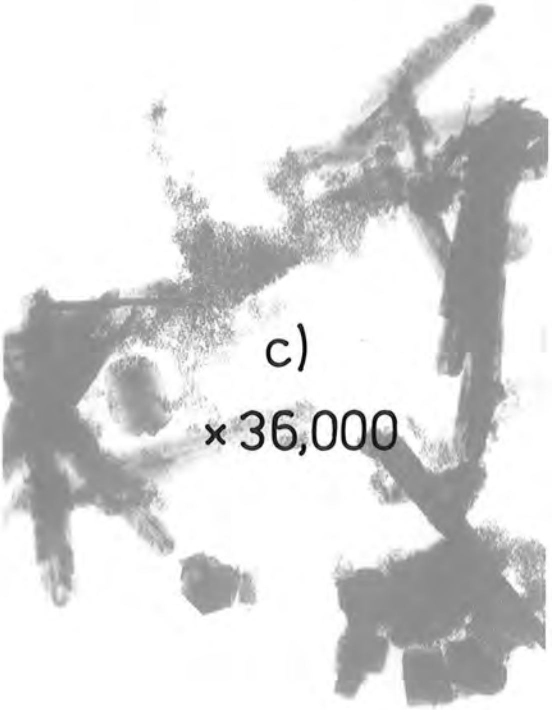


Fig.8.1 Electron micrographs of some hydrated iron(III) oxide species: a)β-FeOOH, b)α-FeOOH.1, c)α-FeOOH.2



Electron micrographs of Fe_3O_4 particles prepared from the above materials are also displayed (Figure 8.2.). Their diameters were also measured manually and are set out in Table 8.1. Lowering T_F^o of Fe_3O_4 using both α and β-FeOOH causes an increase in particle size as would be expected from the decreased solubility of the former material at lower temperatures.

α-FeOOH 1 are smaller than β-FeOOH particles, and thus have a greater surface area from which material can pass into solution. However, by inspection of Figure 8.3., β-FeOOH is by far the more soluble of the two materials. This factor obviously outweighs the surface-area effect and β-FeOOH yields smaller Fe_3O_4 particles.

Comparing the effect of different size particles of the same material, namely α-FeOOH 1 and 2, we observe that the smaller α-FeOOH 1 particles give rise to smaller Fe_3O_4 particles, the larger surface area which aids solution of the material being the deciding factor in this case.

In all these preparations a useful indication of the ensuing particle size is the time taken for black Fe_3O_4 to form. This ranges from 30 seconds in the case of the smallest particles to 1 hour (Table 8.1.). At temperatures < 35°C this could be extended to several hours after which time the product had a definite green tinge. It was decided to investigate the composition of all the prepared materials by infra-red spectroscopy.

8.1.3. Infra-Red Spectroscopy

Infra-red spectra have been obtained for β-FeOOH, α-FeOOH 1 and 2, and the Fe_3O_4 condensed from these oxides with $Fe(OH)_2$ at different temperatures. The results of this study are included in Table 8.2. along with band frequencies previously assigned to these compounds and

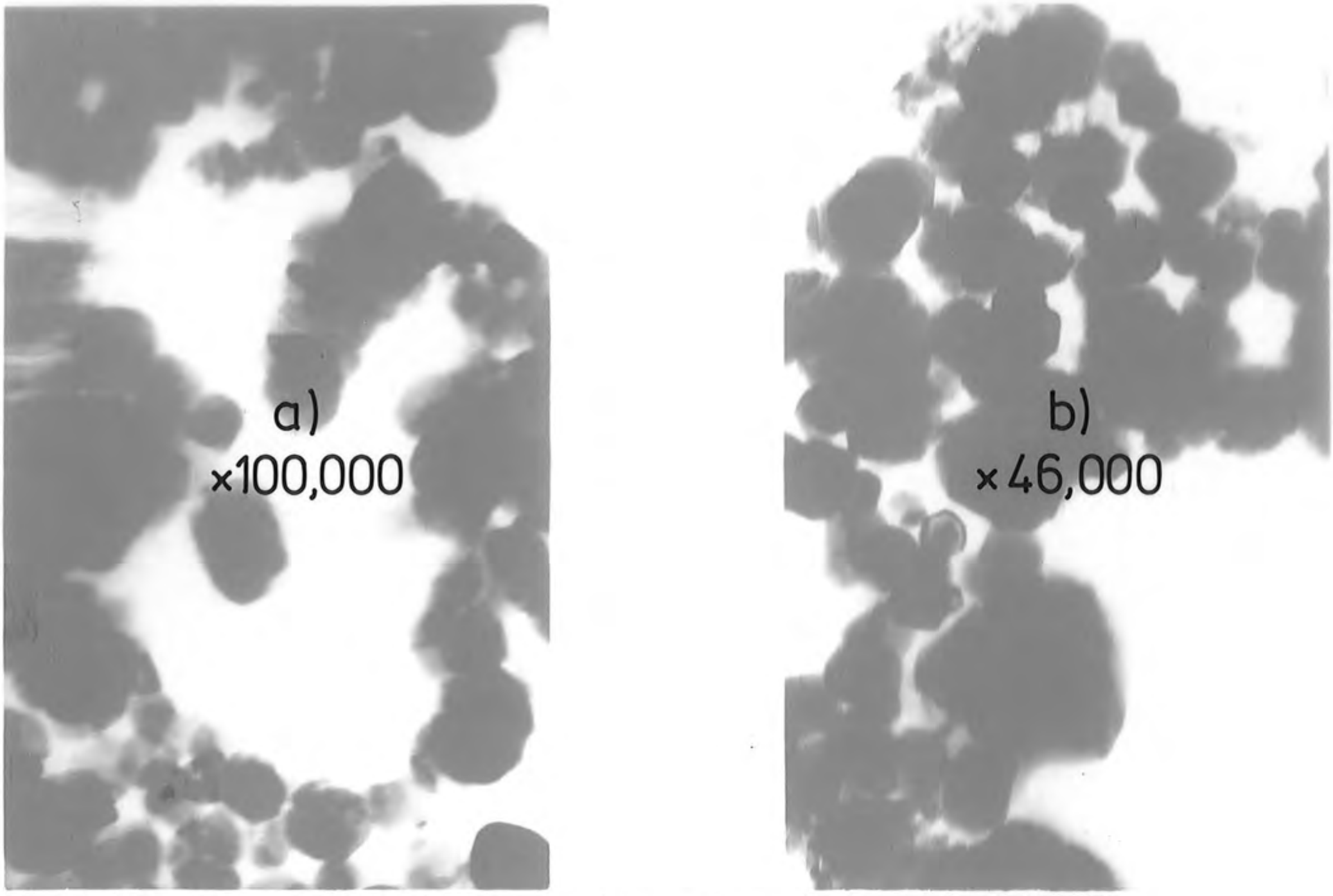


Fig.8.2 Electron micrographs of Fe_3O_4 prepared from - a)β-FeOOH at 65°C, b)α-FeOOH.1 at 65°C, c)α-FeOOH.1 at 35°C and d)α-FeOOH.2 at 65°C

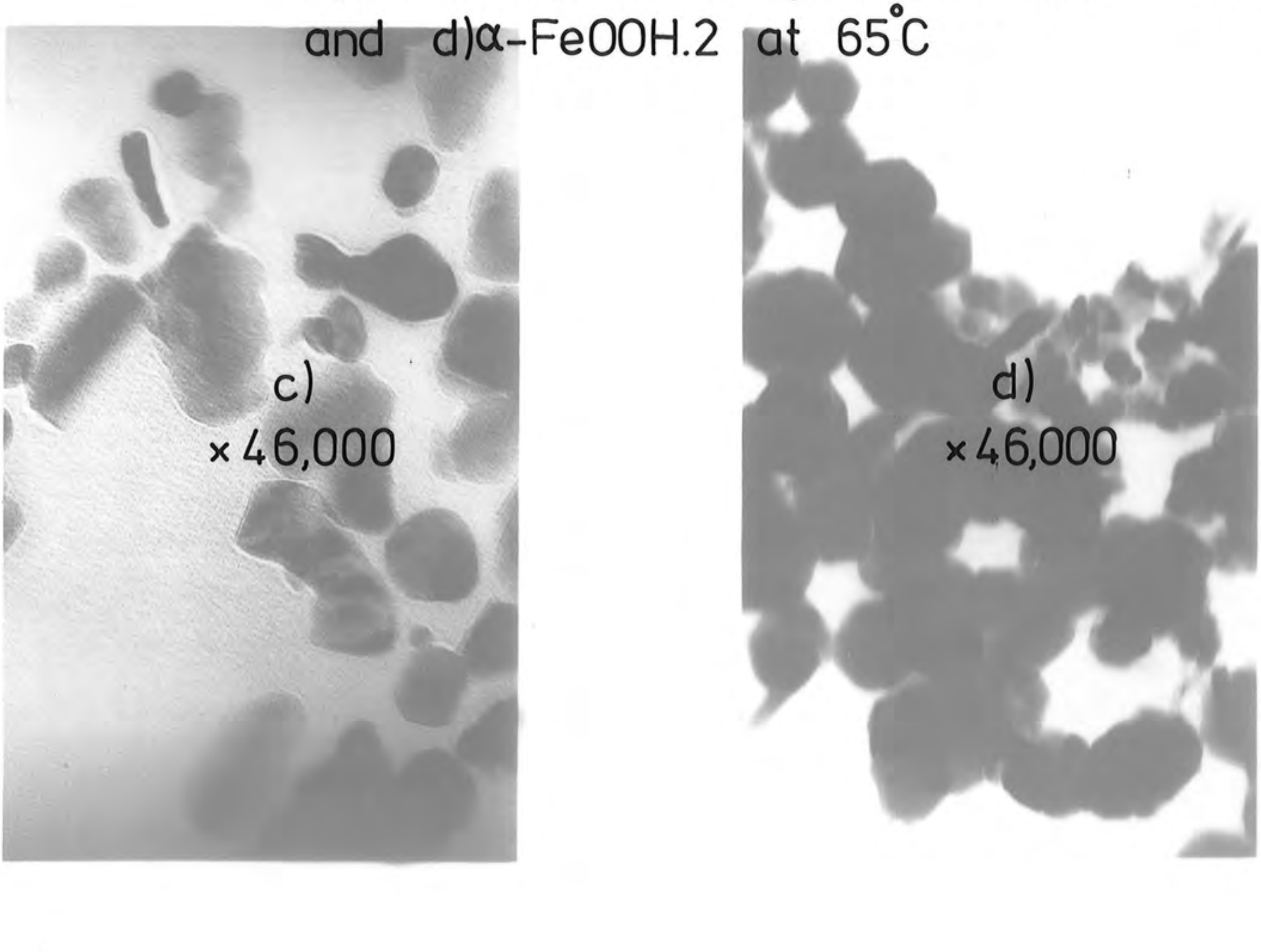


TABLE 8.1.

Reaction conditions and particle sizes obtained for FeOOH and subsequent Fe_3O_4

Iron(III) precursor	Axial dimensions (μm)	Temperature of Fe_3O_4 Formation (T_F^o)	Fe_3O_4 Diameter (μm)	Time of Formation
β-FeOOH	0.23	65°C	~ 0.05	30 secs.
β-FeOOH	0.23	35°C	~ 0.06	3 mins.
α-FeOOH 1	0.15	65°C	~ 0.12	30 mins.
α-FeOOH 1	0.15	35°C	~ 0.17	50 mins.
α-FeOOH 2	0.68	65°C	~ 0.17	1 hour

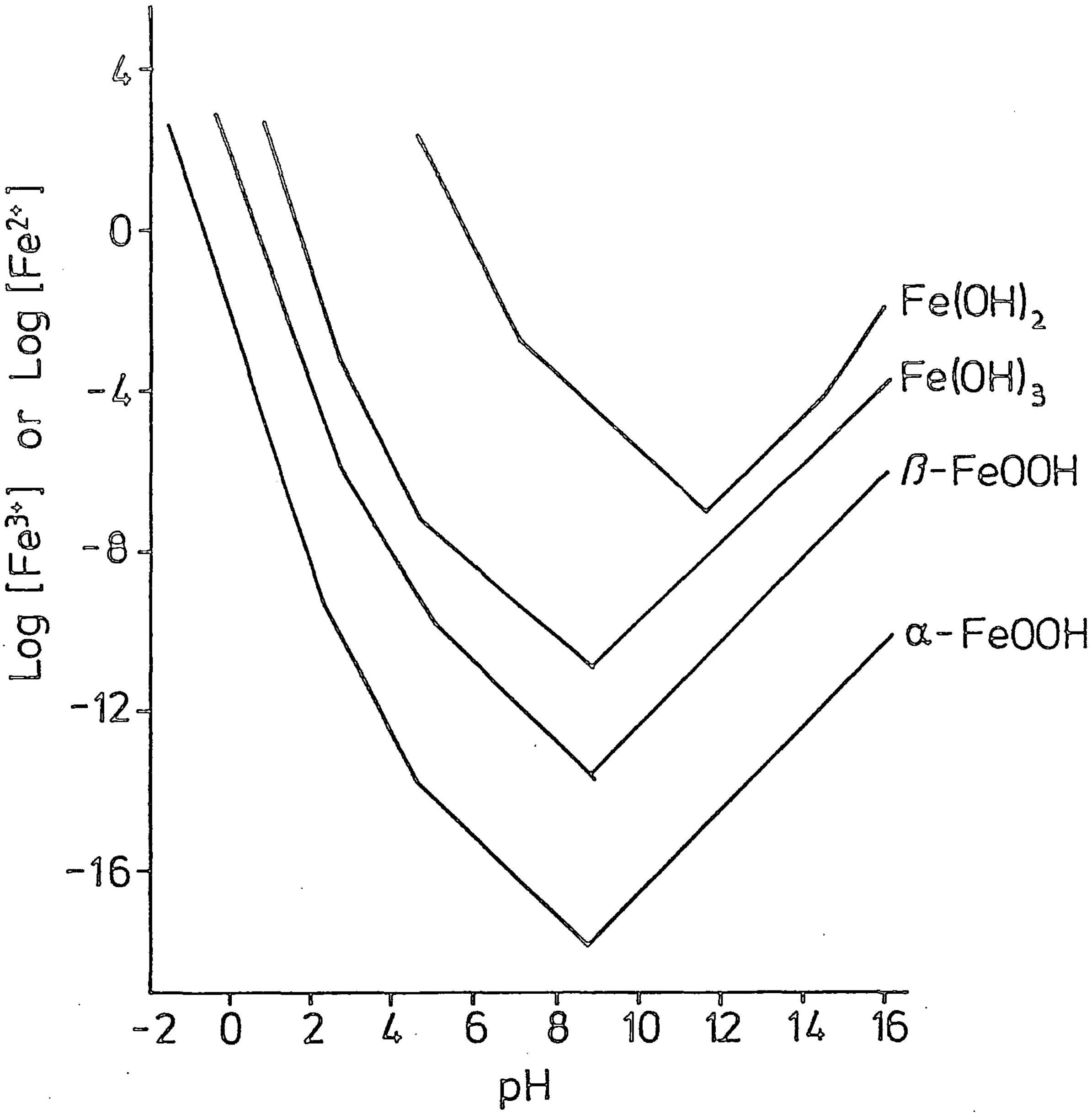


Figure 8.3. The solubilities of hydrated iron oxides at different pH values.

collected from literature sources[119].

The two iron(III) compounds are identifiable by their characteristic absorption bands except that α-FeOOH 2 appears to contain some γ-FeOOH as an impurity. When α-FeOOH 2 is condensed to Fe_3O_4 at 65°C many of these γ-FeOOH bands weaken but persist indicating significant impurities in the product. α-FeOOH 1 and β-FeOOH give reasonably pure Fe_3O_4 at 65°C, the band at 575 cm^{-1} being predominant in the spectrum. Condensation at 35°C leaves definite traces of impurity in the ferrimagnetic product indicated by several absorption bands in the spectrum due to iron(III) hydroxo-species. These absorption bands may be due to starting material or, more likely, $Fe(OH)_2$ oxidation products formed within minutes at low temperature.

Reaction of β-FeOOH at 20°C gives a mixture of Fe_3O_4,α,β and γ-FeOOH in the final product, which also had a green tinge not previously observed. This coincides with the appearance of an intense broad band at ~ 950 cm^{-1}.

This last product was reduced in alkaline solution at 90°C with hydrazine (N_2H_4). The reducing potential is just sufficient to convert iron(III) species to Fe_3O_4 without further reduction to lower valent oxides or even the metal itself.[120] The dried product was still green in appearance, but only two bands persisted in the infra-red spectrum - at 575 cm^{-1} (Fe_3O_4), and the mystery band at 950 cm^{-1}. Kiyama[121] obtained a stable green product by the partial air oxidation of $Fe(OH)_2$ suspensions at temperatures > 60°C and he suggested these to be stable Fe(II) solid complexes. The fact that our green impurity was resistant to reduction gives credence to the suggestion that it may be the same material.

TABLE 8.2.

Infra-red band frequencies for Iron oxides and oxohydroxides

		-OH stretch 3400 cm^{-1}	-OH stretch 3100 cm^{-1}	γ-FeOOH 1600 cm^{-1}	α-FeOOH 1300 cm^{-1}	γ-FeOOH 1150 cm^{-1}	β-FeOOH 950 cm^{-1}	α-FeOOH 900 cm^{-1}	α-FeOOH 800 cm^{-1}	β-FeOOH α-FeOOH 625 cm^{-1}	Fe_3O_4 575 cm^{-1}
PREPARED OXIDES	α-FeOOH 1		B		W	W		S	S	B	
	α-FeOOH 2	B	B	W	W	I		S	S	B	
	β-FeOOH	B,I					W			B	
	Fe_3O_4 (β, 65°)										B
	Fe_3O_4 (β, 35°)					W					B
	Fe_3O_4 (α1, 55°)							W			B
	Fe_3O_4 (α1, 35°)				W			W,S	W,S	W,B	B
	Fe_3O_4 (α2, 65°)	W				W		W	W	W,B	B
	Fe_3O_4 (β, 20°)	W	W		W	W	B,I			B	B

B = Broad   S = Sharp
I = Intense   W = Weak

8.1.4. X-Ray Powder Diffraction

Because of the differences in crystal structure of the various oxides of iron, it was decided to study the X-ray diffraction patterns generated by two magnetite samples, namely Fe_3O_4 from β-FeOOH at 65°C, and Fe_3O_4 from α-FeOOH 2 at 65°C.

The samples were bombarded with Molybdenum $K\alpha$ X-rays for a period of several hours. The X-rays were deflected to varying degrees and produced a series of concentric rings on Kodak film. The diffraction patterns are illustrated in Figure 8.4.

Ring diameters provided d-spacings (dA) whilst relative intensities (1) were estimated visibly. Both sets of data together with the relevant literature values[122] are set out in Table 8.3.

The results clearly show that the product from β-FeOOH is almost exclusively Fe_3O_4, with only two faint lines indicating the presence of FeOOH impurities. Fe_3O_4 from α-FeOOH 2 however contains significant amounts of starting material which manifests itself in the extra diffraction lines.

8.1.5. Conclusions

TEM analysis has confirmed that Fe_3O_4 particle size is strongly dependent on the size and solubility of the iron(III) precursor. Referring to Figure 8.3., this concept may be extended to include $Fe(OH)_3$ which is by far the most soluble of the hydrous ferric oxide species and which condenses with $Fe(OH)_2$ to give the small colloidal size particles suitable for use in magnetic fluids.

8.2. OXIDATION OF IRON(II) HYDROXIDE

The air oxidation of iron(II) hydroxide at temperatures in excess of 65°C gives black Fe_3O_4.[121,123] Below this temperature a significant

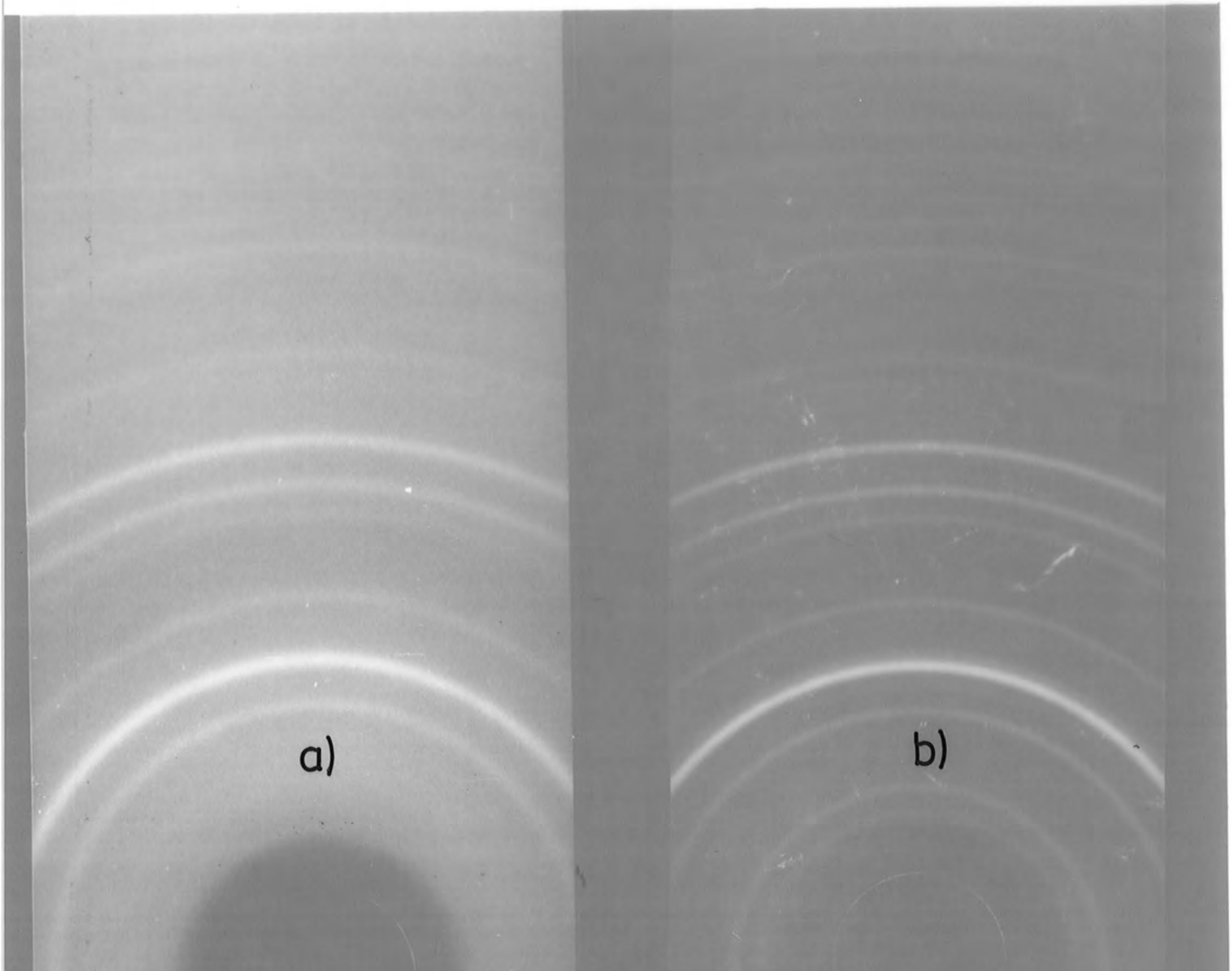


Fig.8.4 X-ray powder diffraction patterns for Fe_3O_4 prepared from -
a)β-FeOOH at 65°C, b)α-FeOOH.2 at 65°C

TABLE 8.3.

X-ray diffraction data for magnetite samples prepared from FeOOH

Fe_3O_4 (β, 65^0)		Fe_3O_4 ($\alpha 2$, 65^0)		Literature[122]		Literature[122]
dA	I (0-100)	dA	I (0-100)	dA	I (0-100)	Assignment
4.876	8	4.876	30	4.97	60	α-FeOOH
		4.242	35	4.18	100	α-FeOOH
		3.382	3	3.36	60	α-FeOOH
2.987	40	2.982	40	2.967	30	Fe_3O_4
		2.702	10	2.69	70	α-FeOOH
2.527	100	2.535	100	2.532	100	Fe_3O_4
		2.402	35	2.44	80	α-FeOOH
2.096	30	2.102	35	2.099	20	Fe_3O_4
		1.912	2	1.92	40	α-FeOOH
		1.80	2	1.80	50	α-FeOOH
1.714	15	1.718	30	1.715	10	Fe_3O_4
1.612	50	1.613	50	1.616	30	Fe_3O_4
		1.565	7	1.56	65	α-FeOOH
1.484	65	1.484	70	1.485	40	Fe_3O_4
		1.426	1	1.42	50	α-FeOOH
1.322	7	1.316	10	1.32	60	α-FeOOH

amount of FeOOH is formed in addition. Oxidation is complete after ~ 1 hour and, on the basis of this, we may expect large particles of Fe_3O_4 to form.

8.2.1. Experimental

i) Iron(II) sulphate (7.2 grams) was dissolved in deaerated water (400 ml) and placed in a 1 litre four-necked round-bottomed flask fitted with thermometer, reflux condenser and pH electrode. Aqueous ammonia (33%) was added to pH 10 and the $Fe(OH)_2$ suspension heated to 80^oC whilst being purged with nitrogen. Compressed air was bubbled through the suspension at 80^oC for $2^1/2$ hrs. by which time the suspension was jet-black and the pH had fallen to 3.8. A small portion of the mixture was removed, mixed with oleic acid and heated at 80^oC until the usual gum-like solids formed. This was washed in the usual way and suspended in toluene at 110^oC to give a magnetic fluid of sufficient stability to be examined for particle size using electron microscopy (Fluid 8.2.1.).

To the remaining suspension was added further iron(II) sulphate (7.2 grams), the pH raised to 10 and oxidation continued for a further $2^1/2$ hrs. After this period, oleic acid (5 grams) was stirred in at 90^oC for 30 mins. and a toluene based fluid was prepared as before (Fluid 8.2.2.).

ii) This method was identical to the above procedure except that the $Fe(OH)_2$ suspension, prior to oxidation, contained 1 gram of Fe_3O_4 seed crystals (previously prepared by simple precipitation from iron(II)/iron(III) chloride solution at 60^oC). Reaction proceeded in two stages as before and a toluene-based magnetic fluid was prepared from the resulting particles (Fluid 8.2.3.).

A toluene-based fluid was also prepared from the seed crystals alone and is designated Fluid 8.2.4.

8.2.2. Particle Size Analysis

The fluids, after dilution with toluene, were examined using electron microscopy in the usual way. This revealed fairly well dispersed particles with noticeable size differences. The results of particle size analysis are displayed below.

Fluid	D_p(Å)	σ(Å)
8.2.1.	94	17.5
8.2.2.	110	20
8.2.3.	97	24
8.2.4.	88	20

Figure 8.5. TEM particle size data for Fluids 8.2.1.,2,3, and 4.

By inspection of Fluids 8.2.1. and 8.2.2. it appears that, after particles have been formed by oxidation, subsequent reaction takes place at the surface of existing particles causing them to increase in size.

This is not however the case when attempts were made to deposit new growth layers on foreign seed crystals (Fluid 8.2.3.). Particle size was seen to be intermediate between the foreign material (88Å) and that formed by oxidation (110Å). The introduction of seed crystals also produced a subsequent increase in size distribution indicating the presence of particles derived from more than one origin.

8.2.3. Discussion

The above observations might suggest that growth of existing Fe_3O_4 nuclei by deposition of new material depends on the surface of those nuclei being in the right condition to accept further growth layers.

Surface topology and/or composition are likely to be factors involved here.

The formation of an Fe_3O_4 particle by the oxidation of $Fe(OH)_2$ is believed to occur via the initial formation, by oxidation, of an insoluble iron(III) hydroxo-complex. This complex then reacts with a soluble iron(II) species (possibly $Fe(OH)^+$) by adsorption of the latter onto the solid surface and condensation into the magnetic oxide. As further iron(II) is adsorbed at the surface, oxidation will occur and create a layer of iron(III) which then resumes the cycle. Particle growth will continue until all the iron(II) is exhausted[121].

At any given stage of the cycle there will always be some iron(III) present at the particle surface. Adsorption of an iron(II) species now will be enhanced by the exothermic nature of the subsequent condensation reaction. It follows then that adsorption onto a pure Fe_3O_4 surface (viz. a magnetite seed crystal) will be unfavourable in comparison since it does not involve any release of energy. This would explain why the presence of seed crystals did not influence the course of reaction and hence the particle size.

Lowering the iron(II) hydroxide concentration in the reaction mixture should suppress crystal growth by limiting the availability of material, and hence sub-90Å particles might be expected. In practice however, such conditions yielded brown solids which, by infra-red spectroscopy, contained a mixture of Fe_3O_4, α, β and γ-FeOOH. It appears therefore that adsorption of $Fe(OH)_2$ onto a solid FeOOH surface to give Fe_3O_4 is inhibited, probably by reduced frequency of collision between the two species brought about by low concentrations of material. Oxidation to iron(III) hydroxo-complexes is now the dominant reaction and will be responsible for the majority of product.

8.3. SUMMARY

Control of particle size, if only to a limited degree, has been achieved without the need for surfactants or electrolytes to be added prior to precipitation. Particles no smaller than 90Å have been obtained making them generally unsuitable for the preparation of stable magnetic fluids.

Chapter 6 dealt with control of particle size by changing the solubility of the iron(II) hydroxide component with the aid of added electrolytes and alternative solvents. This chapter gives evidence that formation of Fe_3O_4 may depend upon the solubility of either iron(II) or iron(III) species. Firstly, the aerial oxidation of iron(II) hydroxide to give Fe_3O_4 involves the migration of soluble iron(II) species to a particle surface containing iron(III) ions, stressing the importance on solubility of iron(II). On the other hand, studies have also shown that size and solubility of an iron(III) component (hydroxo-complex) can be responsible for differences in Fe_3O_4 particle size.

Solubility of both iron(II) and iron(III) species appears to be of crucial importance in the formation of Fe_3O_4, and this suggests that condensation into a magnetic particle nucleus may well occur whilst both iron(II) and iron(III) are in the dissolved phase.

APPENDIX

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:

a) all research colloquia, research seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

b) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out;

c) details of the postgraduate induction course.

a).1. DURHAM UNIVERSITY CHEMISTRY DEPARTMENT LECTURES - 1984-1987

1984

19 October	Dr. A. Germain (Languedoc, Montpellier) "Anodic Oxidation of Perfluoro Organic Compounds in Perfluoroalkane Sulphonic Acids".
24 October	Prof. R.K. Harris (Durham) "N.M.R. of Solid Polymers".
28 October	Dr. R. Snaith (Strathclyde) "Exploring Lithium Chemistry: Novel Structures, Bonding and Reagents".
7 November	Prof. W.W. Porterfield (Hampden-Sydney College, U.S.A.) "There is no Borane Chemistry (only Geometry)".
7 November	Dr. H.S. Munro (Durham) "New Information from ESCA Data".

21 November	Mr. N. Everall (Durham) "Picosecond Pulsed Laser Raman Spectroscopy".
27 November	Dr. W.J. Feast (Durham) "A Plain Man's Guide to Polymeric Organic Metals".
28 November	Dr. T.A. Stephenson (Edinburgh) "Some recent studies in Platinum Metal Chemistry".
12 December	Dr. K.B. Dillon (Durham) "^{31}P N.M.R. Studies of some Anionic Phosphorus Complexes".
1985	
11 January	Emeritus Prof. H. Suschitsky (Salford) Fruitful Fissions of Benzofuroxanes and Isobenzimic Azoles (umpolung of o-phenylenediamine)".
13 February	Dr. G.W.J. Fleet (Oxford) "Synthesis of some Alkaloids from Carbohydrates".
19 February	Dr. D.J. Mincher (Durham) "Stereoselective Synthesis of some Novel Anthracyclinones Related to the Anti-Cancer Drug Adriamy and to the Steffimycin Antibiotics".
27 February	Dr. R. Mulvey (Durham) "Some Unusual Lithium Complexes".
6 March	Dr. P.J. Kocienski (Leeds) "Some Synthetic Applications of Silicon-Mediated Annulation Reactions".
7 March	Dr. P.J. Rodgers (I.C.I. plc Agricultural Division, Billingham) "Industrial Polymers from Bacteria".

12 March	Prof. K.J. Packer (B.P. Ltd./East Anglia) "N.M.R. Investigations of the Structure of Solid Polymers".
14 March	Dr. M. Poliakoff (Nottingham) "New Methods for Detecting Organometallic Intermediates in Solution".
28 March	Prof. H. Ringsdorf (Mainz) "Polymeric Liposomes as Models for Biomembranes and Cells?".
24 April	Dr. M.C. Grossel (Bedford College, London) "Hydroxypyridone Dyes - Bleachable One-dimensional Metals?".
25 April	Major S.A. Shackelford (U.S. Air Force) "In situ Mechanistic Studies on Condensed Phase Thermochemical Reaction Processes: Deuterium Isotope Effects in HMX Decomposition, Explosives and Combustion".
1 May	Dr. D. Parker (I.C.I. plc Petrochemical and Plastics Division, Wilton) "Applications of Radioisotopes in Industrial Research".
7 May	Prof. G.E. Coates (formerly of University of Wyoming, U.S.A.) "Chemical Education in England and America: Successes and Deficiencies".
8 May	Prof. G. Williams (U.C.W. Aberystwyth) "Liquid Crystalline Polymers".
9 May	Prof. R.K. Harris (Durham) "Chemistry in a Spin: Nuclear Magnetic Resonance".

14 May	Prof. J. Passmore (New Brunswick, U.S.A.) "The Synthesis and Characterization of some Novel Selenium-Iodine Cations, Aided by Se N.M.R. Spectroscopy".
15 May	Dr. J.E. Packer (Auckland, New Zealand) "Studies of Free Radical Reactions in Aqueous Solution using Ionizing Radiation".
17 May	Prof. I.D. Brown (McMaster University, Canada) "Bond Valence as a Model for Inorganic Chemistry".
21 May	Dr. D.L.H. Williams (Durham) "Chemistry in Colour".
22 May	Dr. M. Hudlicky (Blacksburg, U.S.A.) "Preferential Elimination of Hydrogen Fluoride from Vicinal Bromofluorocompounds".
22 May	Dr. S. Grimmett (Otago, New Zealand) "Some Aspects of Nucleophilic Substitution in Imidazoles".
4 June	Dr. P.S. Belton (Food Research Institute, Norwich) "Analytical Photoacoustic Spectroscopy".
13 June	Dr. D. Woolins (Imperial College, London) "Metal-Sulphur-Nitrogen Complexes".
14 June	Prof. Z. Rappoport (Hebrew University, Jerusalem) "The Rich Mechanistic World of Nucleophilic Cinylic Substitution".
19 June	Dr. R.N. Mitchell (Dortmund) "Some Synthetic and N.M.R.-Spectroscopic Studies of Organotin Compounds".

26 June	Prof. G. Shaw (Bradford) "Synthetic Studies on Imidazole Nucleosides and the Antibiotic Coformycin".
13 September	Dr. V.S. Parmar (University of Delhi) "Enzyme Assisted ERC Synthesis".
30 October	Dr. S.N. Whittleton (Durham) "An Investigation of a Reaction Window".
5 November	Prof. M.J. O'Donnell (Indiana-Purdue University) "New Methodology for the Synthesis of Amino-Acids".
20 November	Dr. J.A.H. MacBride (Sunderland Polytechnic) "A Heterocyclic Tour on a Distorted Tricycle-Biphenylene".
28 November	Prof. D.J. Waddington (York) "Resources for the Chemistry Teacher".

1986

15 January	Prof. N. Sheppard (U.E.A.) "Vibrational and Spectroscopic Determinations of the Structures of Molecules Chemisorbed on Metal Surfaces".
29 January	Dr. J.H. Clark (York) "Novel Fluoride Ion Reagents".
12 February	Prof. O.S. Tee (Concordia University, Montreal) "Bromination of Phenols".
12 February	Dr. J. Yarwood (Durham) "The Structure of Water in Liquid Crystals".
19 February	Prof. G. Procter (Salford) "Approaches to the Synthesis of some Natural Products".

26 February	Miss C. Till (Durham) "ESCA and Optical Emission Studies of the Plasma Polymerization of Perfluoroaromatics".
5 March	Dr. D. Hathway (Durham) "Herbicide Selectivity".
5 March	Dr. M. Schroder (Edinburgh) "Studies on Macrocycle Complexes".
12 March	Dr. J.M. Brown (Oxford) "Chelate Control in Homogeneous Catalysis".
14 May	Dr. P.R.R. Langridge-Smith (Edinburgh) "Naked Metal Clusters - Synthesis, Characterization and Chemistry".
9 June	Prof. R. Schmutzler (University of Braunschweig) "Mixed Valence Diphosphorous Compounds".
23 June	Prof. R.E. Wilde (Texas Technical University) "Molecular Dynamic Processes from Vibrational Bandshapes".
29 October	Prof. E.H. Wong (University of New Hampshire, U.S.A.) "Coordination Chemistry of P-O-P Ligands".
5 November	Prof. D. Döpp (University of Duisburg) "Cyclo-Additions and Cyclo-Reversions Involving Captodative Alkenes".
26 November	Dr. N.D.S. Canning (Durham) "Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis".
3 December	Dr. J. Miller (Dupont Central Research, U.S.A.) "Molecular Ferromagnets; Chemistry and Physical Properties".

8 December	Prof. T. Dorfmüller (University of Bielefield) "Rotational Dynamics in Liquids and Polymers".

1987

28 January	Dr. W. Clegg (Newcastle-upon-Tyne) "Carboxylate Complexes of Zinc; Charting a Structural Jungle".
4 February	Prof. A. Thomson (U.E.A.) "Metalloproteins and Magnetooptics".
11 February	Dr. T. Shepherd (Durham) "Pteridine Natural Products; Synthesis and Use in Chemotherapy".
17 February	Prof. E.H. Wong (University of New Hampshire, U.S.A.) "Symmetrical Shapes from Molecules to Art and Nature".
4 March	Dr. R. Newman (Oxford) "Change and Decay: A Carbon-13 CP/MAS N.M.R. Study of Humification and Coalification Processes".
9 March	Prof. F.G. Bordwell (Northeastern University, U.S.A.) "Carbon Anions, Radicals, Radical Anions and Radical Cations".
11 March	Dr. R.D. Cannon (U.E.A.) "Electron Transfer in Polynuclear Complexes".
17 March	Prof. R.F. Hudson (Kent) "Aspects of Organophosphorous Chemistry".
18 March	Prof. R.F. Hudson (Kent) "Homolytic Rearrangements of Free Radical Stability".
6 May	Dr. R. Bartsch (Sussex) "Low Co-ordinated Phosphorous Compounds".

7 May Dr. M. Harmer (I.C.I. Chemicals and Polymer Group)
"The Role of Organometallics in Advanced Materials".

11 May Prof. S. Pasynkiewicz (Technical University, Warsaw)
"Thermal Decomposition of Methyl Copper and its Reactions with Trialkylalluminium".

27 May Dr. M. Blackburn (Sheffield)
"Phosphonates as Analogues of Biological Phosphate Esters".

24 June Prof. S.M. Roberts (Exeter)
"Synthesis of Novel Antiviral Agents".

26 June Dr. C. Krespan (E.I. Dupont de Nemours)
"Nickel(0) and Iron(0) as Reagents in Organofluorine Chemistry".

a).2. DURHAM UNIVERSITY CHEMICAL SOCIETY LECTURES 1984-1987

1984

18 October Dr. N. Logan (Nottingham)
"N_2O_4 and Rocket Fuels".

23 October Dr. W.J. Feast (Durham)
"Synthesis of Conjugated Polymers. How and Why?".

8 November Prof. B.J. Aylett (Queen Mary College, London)
"Silicon - Dead Common or Refined".

15 November Prof. B.T. Golding (Newcastle-upon-Tyne)
"The Vitamin B_{12} Mystery".

22 November	Prof. D.T. Clark (I.C.I. New Science Group) "Structure, Bonding, Reactivity and Synthesis as Revealed by ESCA". (R.S.C. Tilden Lecture)
6 December	Prof. R.D. Chambers (Durham) "The Unusual World of Fluorine".

1985

24 January	Dr. A.K. Covington (Newcastle-upon-Tyne) "Chemistry with Chips".
31 January	Dr. M.L.H Green (Oxford) "Naked Atoms and Negligee Ligands".
7 February	Prof. A. Ledwith (Pilkington Bros.) "Glass as a High Technology Material".
14 February	Dr. J.A. Salthouse (Manchester) "Son et Lumière".
21 February	Prof. P.M. Maitlis, F.R.S. (Sheffield) "What Use is Rhodium?".
7 March	Dr. P.W. Atkins (Oxford) "Magnetic Reactions".
17 October	Dr. C.J. Ludman (Durham) "Some Thermochemical Aspects of Explosions". (A Demonstration Lecture)
24 October	Dr. J. Dewing (U.M.I.S.T.) "Zeolites - Small Holes, Big Opportunities".
31 October	Dr. P.L. Timms (Bristol) "Some Chemistry of Fireworks". (A Demonstration Lecture)

7 November	Prof. G. Ertl (University of Munich) "Heterogeneous Catalysis". (R.S.C. Centenary Lecture)
14 November	Dr. S.G. Davies (Oxford) "Chirality Control and Molecular Recognition".
21 November	Prof. K.H. Jack, F.R.S. (Newcastle-upon-Tyne) "Chemistry of Si-Al-O-N Engineering Ceramics".
28 November	Dr. B.A.J. Clark (Research Division, Kodak Ltd.) "Chemistry and Principles of Colour Photography".

1986

23 January	Prof. Sir Jack Lewis, F.R.S. (Cambridge) "Some More Recent Aspects in the Cluster Chemistry of Ruthenium and Osmium Carbonyls". (The Waddington Memorial Lecture)
30 January	Dr. N.J. Phillips (University of Technology, Loughborough) "Laser Holography".
13 February	Prof. R. Grigg (Queen's University, Belfast) "Thermal Generation of 1,3-Dipoles". (R.S.C. Tilden Lecture)
20 February	Dr. C.J.F. Barnard (Johnson Matthey Group Research) "Platinum Anti-Cancer Drug Development - From Serendipity to Science".
27 February	Prof. R.K. Harris (Durham) "The Magic of Solid State N.M.R.".

6 March	Dr. B. Iddon (Salford) "The Magic of Chemistry". (A Demonstration Lecture)
16 October	Prof. N.N. Greenwood (Leeds) "Glorious Gaffes in Chemistry".
23 October	Prof. H.W. Kroto (Sussex) "Chemistry in Stars, between Stars and in the Laboratory".
6 November	Dr. R.M. Scrowston (Hull) "From Myth and Magic to Modern Medicine".
13 November	Prof. G. Allen (Unilever Research) "Biotechnology and the Future of the Chemical Industry".
20 November	Dr. A. Milne and Mr. S. Christie (International Paints) "Chemical Serendipity - A Real Life Case Study".
27 November	Prof. R.L. Williams (Metropolitan Police Forensic Science Department) "Science and Crime".
1987	
22 January	Prof. R.H. Ottewill (Bristol) "Colloid Science a Challenging Subject".
5 February	Dr. P. Hubbersteg (Nottingham) "Various Aspects of Alkali Metal Chemistry". (A Demonstration Lecture)
12 February	Dr. P.J. Rodgers (I.C.I. Billingham) "Industrial Polymers from Bacteria".
19 February	Dr. M. Jarman (Institute of Cancer Research) "The Design of Anti-Cancer Drugs".

5 March	Prof. S.V. Ley (Imperial College) "Fact and Fantasy in Organic Synthesis".
12 March	Dr. E.M. Goodger (Cranfield Institute of Technology) "Alternative Fuels for Transport".

b) RESEARCH CONFERENCES ATTENDED

April 1985, Graduate Symposium, Durham University.

April 1986, Graduate Symposium, Durham University.

April 1987, Graduate Symposium, Durham University.

September 13-16, 1987, Second European Magnetic Materials and Applications Conference, Salford University. Poster presented.

c) POSTGRADUATE INDUCTION COURSE

A series of one hour lectures explaining the various services available in the Department of Chemistry.

1. Departmental organization.
2. Safety matters.
3. Electrical appliances and infrared spectroscopy.
4. Chromatography and microanalysis.
5. Atomic absorption and inorganic analysis.
6. Library facilities.
7. Mass spectroscopy.
8. Nuclear magnetic resonance spectroscopy.
9. Glassblowing techniques.

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