A STUDY OF POLYMERIC FLOCCULANTS

by

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SUMMARY

This thesis describes an investigation into the flocculation of colloids by polymers in solution. The results have been interpreted in terms of the theory of colloid stability and the proposed mechanism of polymer bridging between flocculating colloidal particles. Due to the complexity of practical systems and the difficulty of interpretation, model systems were devised where a number of parameters could be controlled and their influence determined. The first of the two types of model systems considered was a non-aqueous one with the colloidal particles dispersed in an organic solvent and a polymer whose end groups could chemically bond to the surface of the particle acting as the flocculant. Many parameters of this system could be controlled, but the electrostatic interaction between the particles could not be controlled and no meaningful results could be obtained. The second model system was an aqueous system using well characterized polystyrene latexes as the colloid and oppositely charged polyelectrolytes of different molecular weights as the flocculant. These experiments showed that the major flocculation mechanism is polymer chain bridging between the particles and not surface electrostatic charge reduction. Certain unusual features of colloid stability with polymer dosages above that required for flocculation were found and an attempt was made to explain them. The flocculation was followed by counting the colloid particles present using an automatic Laser light scattering flow ultramicroscope which was built and developed for the work. The instrument allows small degrees of flocculation when dimers and trimers of particles are formed to be detected, by noting the change in particle concentration.

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CHAPTER 1

INTRODUCTION

Polymeric flocculants are used to facilitate the separation of colloidal suspended solids from water. The size of the dispersed particles commonly ranges from the sub-microscopic (e.g. clay particles down to 0.01 μm), through the micron range (as with bacteria and algae), up to silts and slimes (up to 20 μm), such as those produced by the mineral industry. The conventional separation methods of filtration, settling or centrifugation fail with colloidal suspensions fundamentally because the particles remain separate and discrete; they do not adhere to one another when they collide under the action of Brownian motion. It has long been known that the only practical way of treating colloidal suspensions is first to operate on their surface chemistry in order to induce coagulation and then, when the flocs have grown as large as possible, to separate them by settling or filtration. Recent reviews of this subject have been written by Kitchener[1]; Vincent[2] and Lyklema[3].

It has been known for a long time that high molecular weight natural polymers effect the stability of hydrophobic colloids. Zsigmondy (1901) and others compared the stabilising or protective power of different proteins and gums for different hydrophobic sols. The explanation of this stabilization is obvious enough. As was proved by

Bechhold (1904), the protective agent is adsorbed by the hydrophobic colloid and forms a coating having hydrophilic properties. This was confirmed by measurements of the electrophoretic velocity of colloidal particles. The mobility is changed by addition of protein and, at saturation, becomes virtually identical with the electrophoretic mobility of the protein itself.

The investigation of the stabilising action of the hydrophilic colloids led to the discovery of their ability to flocculate hydrophobic colloids. At that time the phenomenon was named 'sensitisation.' In 1915 Brossa and Freundlich, investigating sensitisation, proved that serum albumin was adsorbed by ferric oxide sol, the isotherm being linear at very low concentrations and reaching a saturation level at relatively high concentrations. Also the adsorption was not readily reversible. Freundlich (1922) suggested that the particles of hydrophilic colloid were attached to the outside of the hydrophobic particles although their size and amount, when causing sensitisation, are insufficient to completely enclose the hydrophobic core.

It was not however, until modern understanding of polymer configuration was applied to the problem that the idea of polymer chains linking or bridging between particles came forward. During the 1930's the only application of polymeric flocculants was the use of starch in coal preparation, following a French patent by

Henry in 1928; but from about 1951 onwards attention was directed to the use of gelatine or glue for treating slurries in the South African uranium extraction industry, and subsequently synthetic polymers were introduced for the mining industry. About the same time, enthusiasm for the proposed application of similar polymers as "soil conditioners" reached a maximum[4]. In the 1950's and early 1960's the pioneering papers of Linke and Booth[5] on flocculation of silica with polyacrylamide polymers, of Ruehrwein and Ward[6] and Michaels and Morelos[7] on the aggregation of clays and of La Mer[8] on studies of the flocculation of phosphate slimes with starch and later synthetic polymer flocculants, all emphasised the concept that polymeric molecules can act as links between small particles.

A great number of polymeric materials have been found to flocculate colloidal suspensions. These can be separated into three groups:-

a) Non-ionic polymers, which are water soluble due to polar functional groups, e.g. Polyacrylamide, Polyethyleneoxide, Polyvinyl alcohol.

b) Anionic polymers, with negative functional groups attached to the polymer backbone, e.g. hydrolysed polyacrylamide, polyacrylic acid, sodium alginate.

c) Cationic polymers, ones with positive functional groups, e.g. Polyethyleninimine, quaternised Polyvinyl pyridine.

Also there are a few amphoteric ones, e.g. Gelatine whose charge is pH dependent.

1.2 Interactions between Colloidal Particles

To understand why a flocculant can bring about the aggregation of an otherwise stable colloid one must first consider why the colloid is stable. It is obvious that there must be a repulsive force between the hydrophobic particles. This force is due to the surface charge these particles have. The surface charge can be the result of one of the following four processes:-

a) Dissociation of Surface Groups

This is the charge determining mechanism for several oxides, e.g. silica can aquire a negative charge by dissociation of surface silanol groups[9]. Also polystyrene lattices are negatively charged due to ionizable catalyst fragments on the surface.

b) Adsorption of Potential-Determining Ions[10]

A familiar example being the adsorption of Ag^+ and I^- ions on AgI, rendering the AgI particles positive or negative respectively.

c) Adsorption of Ionized Surfactants

Carbon Black dispersions, for example, can become negatively charged by adsorption of anionic surface active substances.

d) Isomorphic Substitution

This particularly applies to clay minerals. The charge is due to the fact that inside the solid lattice a (say) Si^{4+} ion is isomorphically replaced by an Al^{3+} ion, resulting in a deficit of positive charge on the particle.

It is important to note that in some of the above cases the surface charge can be controlled by predetermining the concentration of the relevant ionic or adsorbing species in the solution. The pH for silica in case (a), the pAg and pI in case (b) and the surfactant concentration in case (c). The surface charge can be reduced to zero and the dispersion will be unstable.

The fact that a hydrophobic colloid particle bears a nett surface charge is not yet a sufficient condition for stability because electroneutrality demands that the particle plus its immediate surroundings bear no nett charge. In other words, the surface charge must be compensated by an equal but opposite countercharge, so that surface charge and countercharge together form an electrical double layer. It is of crucial importance how this countercharge is distributed. If the countercharge is very diffusely distributed and extends far from the particle, the countercharges around two equally charged particles that are approaching each other due to Brownian motion already start to interpenetrate when the particles are far apart, thus giving rise to electrostatic repulsion. When on the other hand the double layer is

compressed (in the extreme case all counter ions are on the surface) the particles can approach each other very closely before repulsion is felt and finally the Van der Waals attraction becomes so strong that aggregation occurs.

A quantitative theory therefore requires the formulation of the charge (or potential) distribution around colloidal particles. Deryaguin and Landu[12] and independently, Verwey and Overbeek[13] formulated a general and quantitative theory. This theory, currently known as D.L.V.O. theory, is nowadays almost generally accepted as the basic theory of colloidal stability because it appears to be in sufficient general agreement with many experimental facts.

In the D.L.V.O. model the distribution in a diffused double layer is assumed to obey the Poisson-Boltzmann distribution, as formulated by Gouy[14] and Chapman[15]. In this treatment the surface charge on the particle and space charge in the solution are considered as smeared out. Ions are considered as point charges, their distribution being determined only by their valency and not by their volume, shape or polarizability. The solvent is considered as homogeneous and continuous, affecting the ionic distribution only through its dielectric constant, ε_r. The basic equation for the potential distribution reads:

$$\mathrm{div}(-\varepsilon \ \mathrm{grad}\ \psi) = \sum_i z_i e n_i \exp\frac{-z\ e\ \psi}{kT} \qquad (1.1)$$

where $\psi = \psi(x)$ is the potential at a distance from the surface, z_i is the valency of ion i, sign included, e the elementary charge, n_i the number of ion i per unit volume in the bulk of the solution, ε is the permittivity of the medium and is related to the permittivity of a vacuum ε_0 by its dielectric constant ($\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$), k is Boltzmann's constant and T the absolute temperature. It can be seen that the R.H.S. of equation (1) contains a summation over all ionic species: the potential distribution depends in a complex way on the ionic composition of the solution. This fact is the basis for the influence of salts on sol stability.

In the further elaboration of eq. (1.1) it is usually assumed that ε is independent of x. For aqueous systems this is a good approximation except in the inner part of the double layer (very close to the surface). In this case eq.(1) changes into

$$\nabla^2\psi = \frac{-1}{\varepsilon} \sum_i z_i e\, n_i \exp \frac{-z_i e \psi}{kT} \qquad (1.2)$$

where ∇ is the Nabla operator (∇^2 = Laplician operator)

Eqn.(1.2) can be solved analytically only in special cases. Important in this respect are the following parameters:

a) the value of the potential at the surface (ψ_o) because this governs the possibility of expanding the exponentials retaining only a few terms;

b) the radius of curvature of the surface, because this determines the shape of $\nabla^2\psi$

For flat surfaces, eqn. (1.2) can be solved analytically for any ψ_o, provided $Z_+ = Z_-$ or $Z_+ = 2Z_-$ or $Z_- = 2Z_+$. This case will apply when the particle radius a is large as compared to the double layer thickness. The Laplacian of the potential now simplifies to $\frac{d^2\psi}{dx^2}$ and after two integrations the following result is obtained for the case of a symmetrical (Z-Z) valent electrolyte:

$$\psi = \frac{2kT}{Ze} \ln \frac{1 + \gamma \exp[-Kx]}{1 - \gamma \exp[-Kx]} \qquad (1.3)$$

where $$\gamma = \frac{\exp[Ze\psi_o/2kT] - 1}{\exp[Ze\psi_o/2kT] + 1} \qquad (1.4)$$

and $$K = \left(\frac{2e^2 n_o Z^2}{\varepsilon kT}\right)^{\frac{1}{2}} = \left(\frac{2e^2 N_A c Z^2}{\varepsilon kT}\right)^{\frac{1}{2}} \qquad (1.5)$$

where N_A is Avogadro's number and c is the concentration of electrolyte.

If $Ze\psi_o/2kT \ll 1$ ($kT/e = 25.6$ mV at 25°C), the Debye-Huckel approximation can be made

$$\left(\exp\left[\frac{Ze\psi_o}{2kT}\right] \simeq 1 + \frac{Ze\psi_o}{2kT} \right)$$

and equations (1.3) and (1.4) simplify to

$$\psi = \psi_o \exp[-Kx] \qquad (1.6)$$

showing that at low potentials the potential decreases exponentially with distance from the charged surface and how the rate of decay is controlled by K.

The theory also gives the surface charge σ_o as a function of the surface potential. For one symmetrical (Z-Z) valent electrolyte this relation reads

$$\sigma_o = (8\varepsilon nkT)^{\frac{1}{2}} \operatorname{Sinh} \left(\frac{Ze\psi_o}{2kT}\right) \qquad (1.7)$$

which at low potentials reduces to

$$\sigma_o = \varepsilon K \psi_o \qquad (1.8)$$

From eq. (1.8) it can be seen that, at low potential a diffused double layer has the same capacity as a parallel plate condenser with a distance 1/K between the plates. It is customary to refer to 1/K (the distance over which the potential decreases by an exponential factor at low potentials) as the 'thickness' of the diffuse double layer. In aqueous solutions of 10^{-1} or 10^{-3} molar monovalent salt this thickness is about 10 or 100 Å respectively.

Eqn. (1.1) cannot be solved analytically for any other geometry for every value of ψ although for perfectly spherical symmetry computer solutions have been published[16]. But if the restraint of low potential is added and the Debye-Hückel approximation used an analytical solution is

possible[17] for a spherical geometry.

$$\psi = \psi_o \frac{a}{r} e^{-K(a-r)} \qquad (1.9)$$

where $\psi = \psi(r)$ is the potential at a distance r from the particle centre and a is the particle radius. The surface charge density is given by

$$\sigma_o = \varepsilon \frac{\psi_o}{a} (1 + Ka) \qquad (1.10)$$

and the charge Q on the sphere by

$$Q = 4\pi\varepsilon a \psi_o (1 + Ka) \qquad (1.11)$$

The general expression [13,18] for the repulsive energy V_R which results from the overlapping of the diffuse parts of the double layers around two identical particles is complex. However, for the case of the two semi-infinite plates a solution is possible,

$$V_R = 64\, nkT\, \gamma^2 e^{-Kd} \qquad (1.12)$$

where d is the distance between the two plates (d << particle radius a), and for spherical particles at small potentials

$$V_R = 2\pi\varepsilon a \psi_o^2 \ln (1 + e^{-KH}) \qquad (1.13)$$

where H is the shortest distance between the two spheres (H = R-2a if R is the distance between the centres of the

particles). A useful approximation that is also valid for somewhat higher potentials is

$$V_R = \frac{64\pi nkTa}{K^2}\gamma^2 e^{-KH} \qquad (1.14)$$

For spherical particles at high potential no analytical formula is available.

The case of low Ka is particularly important for non-aqueous media at very low salt concentration. For low potentials

$$V_R = \frac{4\pi\varepsilon a^2}{R}\psi_o^2 e^{-KH} \qquad (1.15)$$

In the limiting case where K is very small this becomes

$$V_R = \frac{4\pi\varepsilon a^2}{R}\psi_o^2 \qquad (1.16)$$

1.3 Attractive Particle Interactions

The fact that attractive forces exist between colloidal particles was established at the beginning of this century, notably by Von Smoluchowski's work on the kinetics of flocculation. In 1932 Kallmann and Willstätler recognised them as London-Van der Waals forces[19]. Although the attractive potential energy between two atoms is low and decays with the inverse 6th power of the distance, the total interaction energy between two macroscopic collection

of atoms (i.e. between two colloidal particles) is large enough to compete with double layer repulsion, at least under certain conditions, as was shown in calculations by De Boer[20] and Hamaker[21].

The procedure of computation adopted by Hamaker and De Boer was based on two principles:

(a) The London forces are additive.

(b) If individual contributions between atoms in one colloidal particle and atoms in the other are added, the summation can be replaced by an integration provided that the distance between the particle surfaces is large compared with intermolecular distances.

The first of these premises is perhaps open to dispute[22] but does however offer an effective means of making a rapid assessment of the total attraction.

As in the case of double layer repulsion, the shape of the equation finally obtained depends on the radius of curvature of the particle surface.

For the simplest case, two flat plates of substance 1 in a vacuum:

$$V_A = \frac{-A_{11}}{12\pi d^2} \qquad (1.17)$$

where A_{11} (units of energy[ergs]) is the so-called Hamaker-Van der Waals constant for substance 1. It is defined by

$$A_{11} = \pi^2 q_1^2 \beta_{11} \qquad (1.18)$$

where q_1 is the density (in cm^{-3}) of atoms in the colloidal particle and β_{11} is the constant (in $erg.cm^6$) in the London equation[23]

$$V_{11} = \frac{\beta_{11}}{r^6} \qquad (1.19)$$

Formulating the attractive energy between two equal atoms 1 at distance r. As β increases with the polarizability of atoms, that is, with their size, and A_{11} is also proportional to the square of the density, it can be seen that the attraction becomes larger, the denser the colloidal particles are. V_A is obtained in $erg.\ cm^{-2}$. Note that due to the summation V_A decays much more slowly with distance than does V_{11}.

For two flat surfaces of substance 1 in medium 2 the attraction becomes somewhat more complicated because when now two particles 1 are brought close together from infinite distance, an equivalent amount of medium should be transported the other way round. As a result the attraction now depends not only on A_{11} but also on A_{12} (describing the particle-medium attraction) and A_{22} (describing the medium-medium attraction). To a good

approximation

$$V_A = \frac{-A_{1(2)}}{12\pi d^2} \qquad (1.20)$$

where $A_{1(2)}$ is a "mixed" Hamaker constant, describing the attraction between two particles 1 in a medium 2. $A_{1(2)}$ is defined as

$$A_{1(2)} = A_{11} + A_{22} - 2A_{12} \doteq (\sqrt{A_{11}} - \sqrt{A_{22}})^2 \qquad (1.21)$$

Equation (1.21) shows that $A_{1(2)}$ is always positive and that $A_{1(2)} = A_{2(1)}$ or: the Van der Waals energy is always attractive and if the system is inverted (e.g. oil and water emulsion) the attractive forces will be the same.

For two spherical particles 1 in medium 2:

$$V_A = -\frac{A_{1(2)}}{6}\left[\frac{2}{S^2-4} + \frac{2}{S^2} + \frac{\ln S^2-4}{S^2}\right] \qquad (1.22)$$

V_A is now the total attractive energy (in ergs) and S is the reduced distance between the particles $S = \frac{R}{a}$.

The energy decays rather rapidly. For large separations, V_A decreases with the 6th power of R, as in the London's law [eqn.(1.19)]. For short distances

$$V_A = \frac{-A_{1(2)}}{12}\,\frac{a}{H} \qquad (1.23)$$

Hence for short separations, V_A decreases slowly with distance.

Attraction energies calculated from these equations are likely to be overestimated, especially at large distances ($H > 100\text{Å}$), owing to a neglect of the finite time required for the propagation of electromagnetic radiation between the particles, the result of which is a weakening of V_A, known as the retardation effect. Casimir and Polder have shown that due to retardation the inverse 6th Power law [eqn. 1.19] with increasing distance gradually changes into an inverse 7th power law [24,25]. If the Casimir and Polder correction is applied to the case of flat plates[26] the result can be represented in the form of a correction factor of which ultimately (that is at large distances) changes the inverse 2nd power of eqn.(1.17) into an inverse 3rd power. For water the correction is small for distances below $d = 100\text{Å}$, becoming relatively more important for larger separations. It amounts to 60% around $d = 1000\text{Å}$. However, not withstanding the difficulties involved in computing the Van der Waals attractive energy between colloid particles, most useful theoretical conclusions can still be drawn.

The total energy of interaction is obtained by summation of the attraction and repulsion energies, as illustrated in Figure (1.1). The general character of the resulting potential energy-distance curve can be deduced from the properties of the two forces. The repulsion energy [eq (1.12)] is an exponential of the distance between the particles with a range of the order

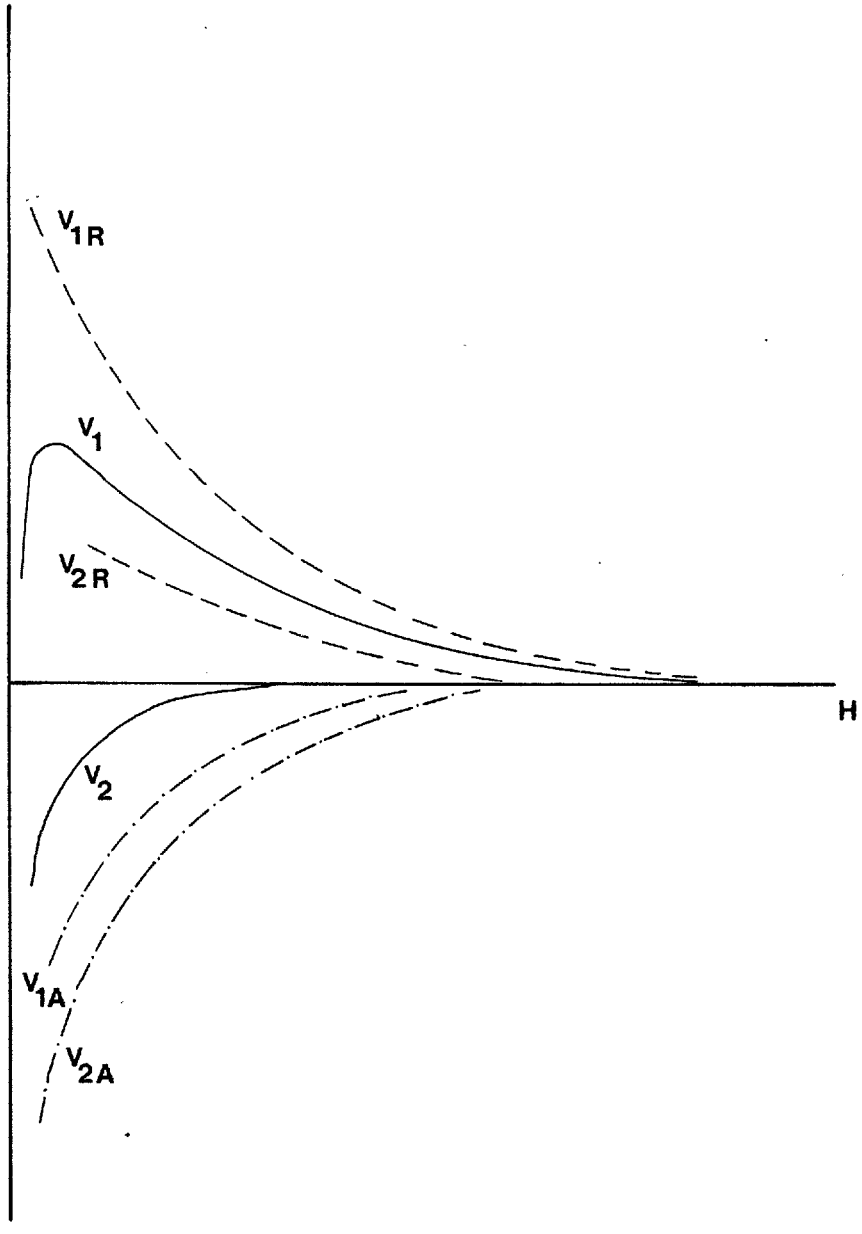


FIG.1.1

of the thickness of the electric double layer, and the attraction energy [Eqn.(1.20)] decreases as an inverse power of the distance between the particles, (considering the case for the two infinite, parallel plates). Consequently, Van der Waals attraction predominates at small and at large interparticle distances. At intermediate distances double layer repulsion may predominate, depending on the actual values of the two forces. Figure (1.1) shows the two general types of potential energy curve which are possible. the total potential energy curve V_1 shows a repulsive energy maximum, whereas in curve V_2 the double layer repulsion does not predominate over Van der Waals attraction at any interparticle distance.

If the potential energy maximum is large compared with the thermal energy (kT) of the particles, the system should be stable; otherwise, the system should flocculate.

1.4 Measurement of the Particle Charge

To determine the magnitude of the electrostatic repulsive energy barrier between two approaching particles a value of the surface potential ψ_o must be obtained.

This may be possible using electrokinetic phenomena: if an electric field is applied tangentially along a charged surface a force is exerted on both parts of the electric double layer. The charged surface (plus attached material) tends to move in the appropriate direction, whilst the ions in the mobile part of the double layer show a net migration in the opposite direction carrying solvent along with them.

These phenomena are defined as:-

Electrophoresis

The movement of a charged surface plus attached material relative to stationary liquid by an applied field.

Electro-osmosis

The movement of liquid relative to a stationary charged surface (e.g. a glass surface) by an applied electric field.

Thus the movement of a colloidal particle in an applied electrical field can give some information about its electrical double layer.

Firstly a closer examination of the double layer must be made. The treatment of the diffuse double layer outlined before is based on an assumption of point charges in the electrolyte medium. The finite size of the ions will, however limit the inner boundary of the diffuse part of the doubly layer, since the centre of an ion can only approach the surface to within its hydrated radius without becoming specifically adsorbed. Stern proposed a model in which the double layer is divided into two parts separated by a plane (the Stern plane) located at about a hydrated ion radius from the surface, and also considered the possibility of specific ion adsorption.

Specifically adsorbed ions are those which are attached (albeit temporarily) to the surface by electrostatic and/or Van der Waals forces strongly enough to overcome thermal

agitation. They may be hydrated at least in the direction of the surface. The centres of any specifically adsorbed ions are located in the Stern layer, i.e. between the surface and the Stern plane. Ions with centres located beyond the Stern plane form the diffuse part of the double layer, for which the Gouy-Chapman treatment outlined previously, with ψ_o replaced by ψ_δ considered to be applicable.

The potential changes from ψ_o (the surface potential) to ψ_δ (the Stern potential) in the Stern layer, then decays from ψ_δ to zero in the diffuse double layer.

When specific adsorption takes place, counter-ion adsorption generally predominates over co-ion adsorption, and a typical double layer situation would be that depicted in Figure (1.2). It is possible, especially with polyvalent or surface active counter-ions, for reversal of charge to take place within the Stern layer, i.e. for ψ_o and ψ_δ to have opposite signs (Fig.1.3). Adsorption of surface active co-ions could create a situation in which ψ_δ has the same sign as ψ_o and is greater in magnitude (Fig.1.4).

The Stern potential can be estimated from electrokinetic measurements. Electrokinetic behaviour depends on the potential at the surface of shear between the charged surface and the electrolyte solution. The potential is called the electrokinetic or ζ (zeta) potential. The exact location of the shear plane (which in reality, is a region of rapidly changing viscosity) is another unknown

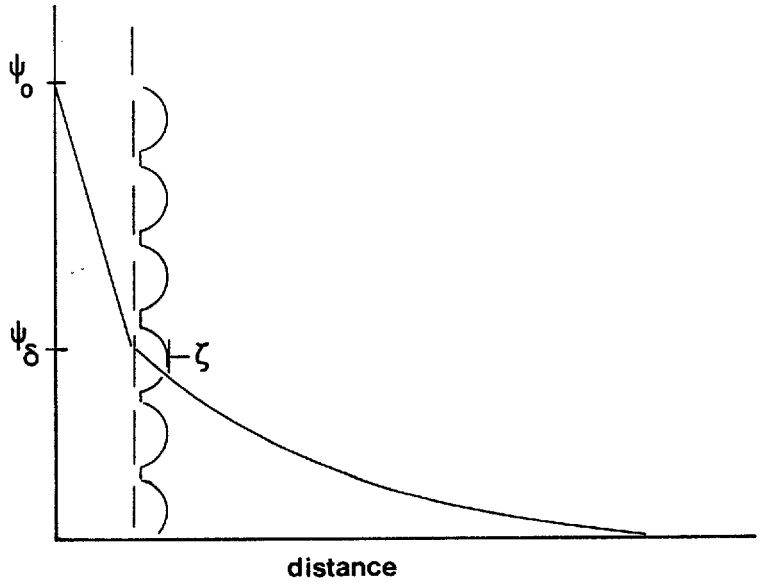


FIG.1.2

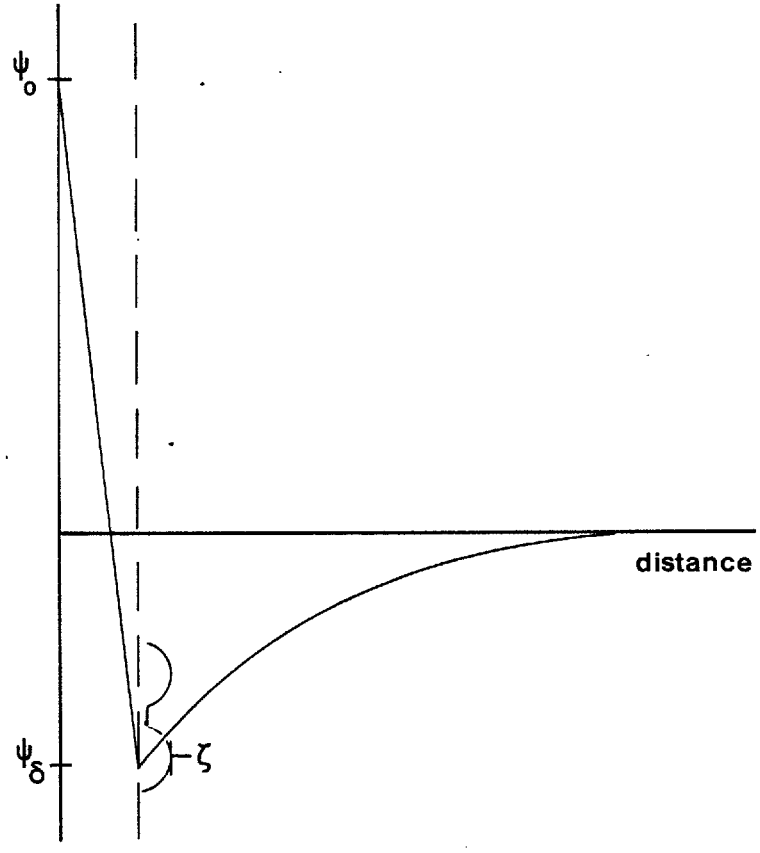


FIG.1.3

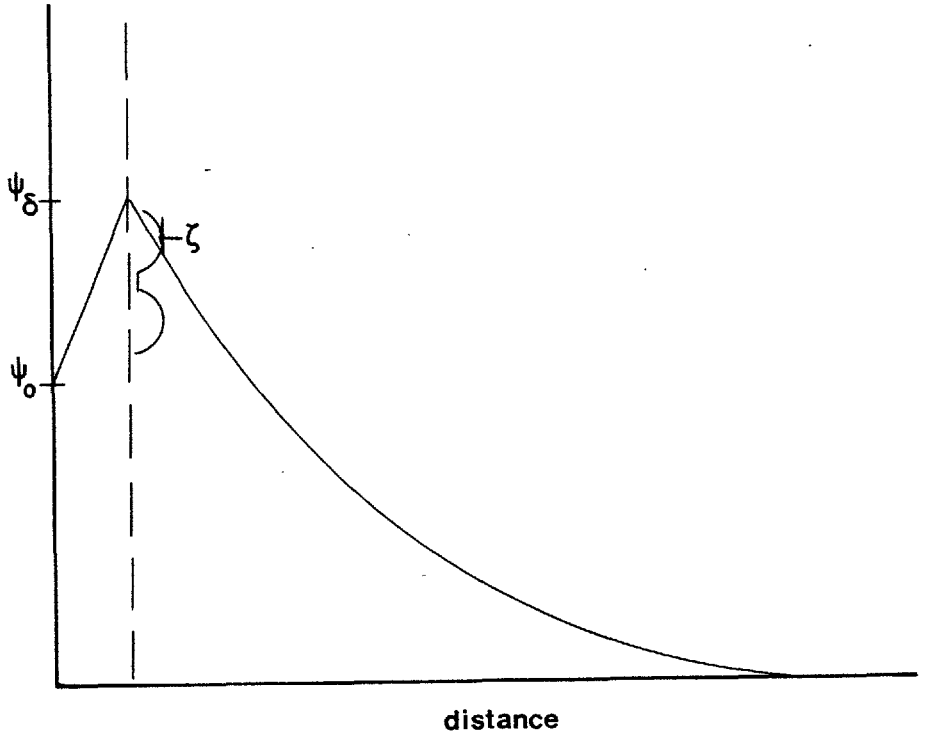


FIG.1.4

feature of the electric double layer. In addition to ions in the Stern layer, a certain amount of solvent will probably be bound to the charged surface and form a part of the electrokinetic unit. It is, therefore, reasonable to suppose that the shear plane is usually located at a small distance further out from the surface than the Stern plane and that ζ is, in general marginally smaller in magnitude than ψ_δ (see Fig. 1.2, 1.3, 1.4). In tests of double layer theory it is customary to assume identity of ψ_δ and ζ, and the bulk of experimental evidence suggests that errors introduced through this assumption are generally small, especially at lyophobic surfaces. Any difference between ψ_δ and ζ will clearly be most pronounced at high potentials, and at high electrolyte concentration (compression of the diffuse part of the double layer will cause more of a potential drop from ψ to zero to take place within the shear plane). The adsorption of non-ionic surfactant would result in the surface of shear being located at a relatively large distance from the Stern plane and a zeta potential significantly lower that ψ_δ. The value of the zeta potential can with reservations be used as a value of ψ_o to estimate V_R.

A number of electrophoresis techniques have been developed for studying the migration of colloidal material in an electric field.

If the material under investigation is in the form of a reasonably stable suspension, or emulsion containing

microscopically visible particles or droplets, then electrophoretic behaviour can be observed and measured directly.

The electrophoresis cell usually consists of a horizontal glass tube, of either rectangular or circular cross-section, with an electrode at each end and sometimes with inlet and outlet taps for cleaning and filling. Platinum black electrodes are adequate for salt concentrations below about 0.001 mol l^{-1} to 0.01 mol l^{-1}, otherwise appropriate reversible electrodes, such as $Cu/CuSO_4$ or Ag/AgCl must be used to avoid gas evolution.

Electrophoretic measurements by the microscopic method (dark field illumination) are complicated by the simultaneous occurrence of electro-osmosis. The internal glass surfaces of the cell are generally charged, causing an electro-osmotic flow of liquid near to the tube walls; the mobile ions of the glass surface double layer carry the solvent molecules along. Since the cell is closed, a compensating return flow of liquid with maximum velocity at the centre of the tube occurs. This results in a parabolic distribution of liquid speeds with depth, and the true electrophoretic velocity is only observed at locations in the tube where the electro-osmotic flow and return flow of the liquid cancel. For a cylindrical cell the 'stationary level' is located at 0.146 of the internal diameter from the cell wall. For a flat cell the 'stationary levels' are located at fractions of about 0.2

and 0.8 of the total depth, the exact locations depending on the width/depth ratio.

An alternative technique is to study the movement of a formed boundary between a sol and a pure dispersion medium under an applied field. The boundary is created in the Tiseluis cell[27] by having the sol and the pure medium in different compartments which have ground glass plates at their ends and can slide over each other, when this is done a boundary is created. Alternatively the boundary can be created by having the colloid and the solution connected by a tap,[28] when this is opened a boundary is created. Both these cells are basically of U-tube form, with an electrode at the top of the two limbs. The sol and the pure liquid must have the same electrolyte concentration to avoid disturbance of the boundary by osmotic flow. The cell must be thermostated, and the electrical current kept to a minimum if convection currents due to the heating effects are not to disturb the boundary. The density difference at the boundary is usually sufficient to prevent disturbance due to electro-osmotic flow at the cell walls:

Electrokinetic theory involves both the theory of the electric double layer and that of liquid flow.

For curved surfaces the shape of the double layer can be described in terms of the dimensionless quantity 'Ka' which is the ratio of radius of curvature to double

layer thickness. When Ka is small, a charged particle may be treated as a point charge, when large, the double layer is effectively flat and may be treated as such.

The Hückel equation considers tha case when Ka is small enough for a spherical particle to be treated as a point charge in an unperturbed electric field, but, allows the particle to be large enough for Stokes' law to apply. Equating the electrical force on the particle with the frictional resistance of the medium

$$Q_E E = 6\pi\eta a v_E$$

$$\text{or} \qquad U_E = \frac{v_E}{E} = \frac{Q_E}{6\pi\eta a} \qquad (1.24)$$

where Q_E is the net charge on the particle (i.e. the electrokinetic unit), E the electric field strength, η the viscosity of the medium, a the radius of the particle v_E the electrophoretic velocity and U_E the electrophoretic mobility.

The zeta potential is the resultant potential at the surface of shear due to the charges $+Q_E$ of the electrokinetic unit and $-Q_E$ of the mobile part of the double layer. i.e.

$$\zeta = \frac{Q_E}{4\pi\varepsilon a} - \frac{Q_E}{4\pi\varepsilon\left(a + \frac{1}{K}\right)} = \frac{Q_E}{4\pi\varepsilon a(1+Ka)} \qquad (1.25)$$

where ε is the permittivity of the electrolyte medium. If Ka is neglected compared with unity then

$$U_E = \frac{\zeta\varepsilon}{1.5\eta} \tag{1.26}$$

The Hückel equation is not likely to be applicable to particle electrophoresis in aqueous media since Ka will not be small compared to unity. The equation, however, does have possible applicability to electrophoresis in non-aqueous media of low conductivity.

Large values of Ka are considered in the Smoluchowski equation. Taking the motion of liquid in the diffuse part of the double layer relative to that of a non-conducting flat surface when an electric field E is applied parallel to the surface. Each layer of liquid will rapidly attain a uniform velocity relative and parallel to the surface, with electrical and viscous forces balanced. Equating the electrical and viscous forces on a liquid layer of unit area, thickness dx, distance x from the surface and having a bulk charge density ρ

$$E\rho dx = \left(\eta\frac{dv}{dx}\right)_{x+dx} - \left(\eta\frac{dv}{dx}\right)_x \tag{1.27}$$

$$= \frac{d}{dx}\left(\eta\frac{dv}{dx}\right)dx \tag{1.28}$$

Inserting the Poisson equation

$$\left[\ \rho = \frac{-d}{dx}\left(\varepsilon\frac{d\psi}{dx}\right)\ \right] \tag{1.29}$$

$$- E \frac{d}{dx} \left(\varepsilon \frac{d\psi}{dx} \right) = \frac{d}{dx} \left(\eta \frac{dv}{dx} \right) \qquad (1.30)$$

Integrating

$$-E \varepsilon \frac{d\psi}{dx} = \eta \frac{dv}{dx} \qquad (1.31)$$

The integration, constant is zero, since when $x = \infty$, $d\psi/dx = 0$ and $dv/dx = 0$. Integrating again (assuming that ε and η are constant throughout the mobile part of the double layer)

$$-E \varepsilon \psi = \eta v + \text{constant} \qquad (1.32)$$

For electrophoresis, the boundary conditions are $\psi = 0$, $v = 0$ at $x = \infty$ and thus the integration constant is zero. Also $\psi = \zeta$ $v = - v$ at the surface of shear, where v_E is the electrophoretic velocity, i.e. the velocity of the surface relative to stationary liquid. Therefore,

$$E \varepsilon \zeta = \eta v_E$$

$$\text{or} \qquad U_E = \frac{v_E}{E} = \frac{\zeta \varepsilon}{\eta} \qquad (1.33)$$

Henry[29] derived a general electrophoretic equation for conducting and non-conducting spheres which takes the form

$$U_E = \frac{\zeta \varepsilon}{1.5 \eta} \left[1 + \lambda F (Ka) \right] \qquad (1.34)$$

where F (Ka) varies between zero for small values of Ka and 1.0 for large values of Ka, and $\lambda = (k_o - k_1)/(2k_o + k_1)$, where k_o is the conductivity of the bulk electrolyte solution and k_1 is the conductivity of the particles. For small Ka the effect of particle conductance is negligible. For large Ka the Henry equation predicts that λ should approach -1 and the electrophoretic mobility approach zero as the particle conductivity increases; however, in most practical cases, 'conducting' particles are rapidly polarised by the applied electric field and behave as non-conductors.

For non-conducting particles ($\lambda = \frac{1}{2}$) the Henry equation can be written in the form

$$U_E = \frac{\zeta \varepsilon}{1.5\eta} f(Ka) \qquad (1.35)$$

where f(Ka) varies between 1.0 for small Ka (Hückel equation) and 1.5 for large Ka (Smoluchowski equation). Zeta potentials calculated from the Hückel equation and from the Smoluchowski equation in their appropriate regions agree closely with values given by the Henry equation.

1.5 Kinetics of Flocculation

The rate at which a sol flocculates depends on the frequency with which the particles encounter one another and the probability that their thermal energy is sufficient to overcome the repulsive potential energy barrier to

flocculation when these encounters take place.

The rate at which particles aggregate is given by

$$\frac{-dn}{dt} = k_2 n^2 \qquad (1.36)$$

where n is the number of particles per unit volume of sol at time t, and k_2 is a second order rate constant.

Integrating, and putting $n = n_o$ at $t = o$, gives

$$\frac{1}{n} = k_2 t + \frac{1}{n_o} \qquad (1.37)$$

During the course of flocculation k_2 usually decreases and sometimes an equilibrium state is reached with the sol only partially flocculated. This maybe a consequence of the height of the repulsion energy barrier increasing with increasing particle size.

The potential energy barrier to flocculation can be reduced to zero by the addition of excess electrolyte, thus creating a situation in which every encounter between the particles leads to permanent contact. The theory of rapid (diffusion controlled) flocculation was developed by Smoluchowski[18]. For a monodispersed sol containing spherical particles

$$n = \frac{n_o}{(1 + 8\pi \, Dan_o t)} \qquad (1.38)$$

where a is the effective radius of the particles and D is the diffusion coefficient. Substituting $D = kT/6\pi\eta a$

and combining equations (1.37) and (1.38) gives

$$k_2^\circ = \frac{4kT}{3\eta} \qquad (1.39)$$

where k_2° is the rate constant for diffusion controlled flocculation.

For a hydrosol at room temperature, the time $t_{\frac{1}{2}}$ in which the number of particles is halved by diffusion controlled flocculation is calculated from the above equations to be of the order of $10^{11}/n_o$ seconds, if n_o is expressed in the unit, particles cm^{-3}. If the effect of Van der Waals attraction on the collision rate is taken into account, $t_{\frac{1}{2}}$ is predicted to be lower by a factor of about 1.5 to 2.0. In a typical hydrosol, the number of particles per cm^3 maybe about 10^{10} to 10^{11}, and so $t_{\frac{1}{2}}$ is of the order of a few seconds.

Smoluchowski's theory of rapid flocculation has been found to hold reasonably well for a number of sols when there is sufficient electrolyte present to remove the repulsive potential energy barrier[18].

When there is a repulsive energy barrier, only a fraction 1/W of the encounters between particles lead to permanent contact. W is known as the stability ratio, i.e.

$$W = \frac{k_2^\circ}{k_2}$$

1.6 Experimental Systems Studied in Colloid Flocculation

To relate these theories to the ability of polymers to reduce the stability of colloids a number of different situations must be considered.

The explanation seems simple in the case of polyelectrolytes with the opposite charge to that of the colloid; a lowering of surface potential through interaction with the polyelectrolyte will occur. An example would be the flocculation of dilute polystyrene latexes, negatively charged because of carboxyl groups, by means of polyamines of relatively low molecular weight; Gregory found that rapid flocculation approximately coincided with charge neutralisation[30]. Low molecular weight polyethylenimine (10^3 - 3 x 10^4) has been shown to reduce the charge on negatively charged silica to zero, where flocculation was the most effective and at higher dosage to reversed the charge[31]. On the other hand, it has long been known that flocculation is not restricted to systems where the colloid and polymer are of opposite sign, examples of flocculation by non-ionic polymers have been reported (e.g. polyvinyl alcohol flocculates silver iodide sols [Lankveld and Lyklema [32]]) and the literature contains many examples of interaction of anionic polymers with negatively charged dispersed colloids. As early as 1912 Lange found that a gold sol maybe sensitised by a protein bearing the same sign of charge. More recently, Kragh and Langston[33] made a thorough study of the flocculation of silica by gelatine (i.e. where the gelatine was positive,

the silica being negative), nevertheless marked flocculation could be observed for an appreciable range above the iso-electric point (where both were negative). Furthermore, in this system, flocculation had nothing to do with zeta potentials, because even with positively charged gelatine the amount required to produce good flocculation had little influence on the potential of the silica, which remained at around -35mV. There was no question, therefore of discharge of the electrical double layer.

It might be suggested thst flocculation of a negative colloid by a negatively charged protein could be connected with the amphoteric nature of the latter, which even somewhat above its isoelectric point carries a few cationic groups. Similarly, the flocculation of clays (net negative) by anionic polyacrylamides has sometimes been ascribed to interaction of carboxylate groups with "positive sites", such as those said to be formed on the edges of platelets of clay minerals by aluminium species released from the lattice. On the same lines, La Mer and his co-workers suggested that flocculation of certain mineral slimes by potato starch was associated with interaction of a few phosphate groups in the starch with polyvalent cations in the pulp. However, although such strictly local ionic interactions may well contribute to the attachment of the polymer, there is no doubt that other mechanisms beside electrostatic attraction may participate or even predominate. A clear example was provided by Griot[34] who

found that a commercial "pure polyacrylamide" would flocculate fresh suspensions of the thermal silica, "Aerosil", it is known, however (and was checked by titration) that such polyacrylamides contain 1 to 2% of carboxyl groups and are therefore not perfectly non-ionic. Griot also converted these groups into amides by chemical reaction and then established that the carboxyl-free polymer retained its flocculating power unchanged. Griot concluded that its affinity for silica depended on hydrogen bonding. Also according to Overbeek[35], with exclusively negative hydrophilic colloids like starch, flocculation can be produced with a negative sol like AgI.

It has been shown then that flocculation can occur without reducing the surface potential to zero, thus the aggregated particles are no closer than their double layers will allow. This means that the polymer chains must be long enough to span that distance, to tie the particles together. When considering this it is necessary to recognise that modern polyacrylamide-type flocculants have molecular weights in the region 1 to 5 million, or a degree of polymerisation of 14,000 to 70,000 monomer units. If fully stretched out, these molecules would be several μm in length, and even in their statistically coiled form would extend to about 0.1 μm. Such dimensions are of the same magnitude as the double layer thickness. This is more evident in the cases where flocculation only occurs above a minimum electrolyte concentration i.e. at

at less than a certain double layer thickness. This model of polymer chains bridging between particles has been supported by the fact that an increase in molecular weight improves the rate of flocculation.

A study of these parameters has been carried out by Ash[36]. A series of polyethyleneoxide homopolymers (m.w. 6.10^3 - 10^7), and poly(ethylene oxide)/poly(propylene oxide) random and block copolymers were added to a polystyrene latex (particle dia. 0.4 μm) at a barium chloride concentration ranging 3 to 40 mM, and the stability ratio, W, measured. In general the stability ratio of the latex passes through a minimum with increasing polymer concentration, the value of this minimum decreasing with increasing electrolyte concentration. The optimum polymer concentration for flocculation moves to lower values with increasing molecular weight, and at the same time the "trough" becomes narrower.

The dimensions of a polymer coil in solution are dependent on the chemical nature of the monomer units. In the case of a polyelectrolyte the repulsive force between adjoining ionised groups extends the coil to dimensions greater than that of a random coil. Obviously any increase in the end-to-end distance of the polymer molecule will improve its performance as a flocculant. An example of this is the work of Michaels[37] which looks at the flocculation of negatively charged clay with partially hydrolysed polyacrylamide. As the fraction of hydrolysed groups on the

polymer increases the extent of flocculation goes through a maximum at 25% to 30% of the monomer units hydrolysed. This brings to light two opposite effects, the number of free acid groups, lengthening the "bridging" distance of the chain and reducing intramolecular hydrogen bonding. But increasing the repulsion between the polymer and the particle lowering the chances of a polymer adsorbing.

Sommerauer et al[38] have investigated the role played by various cations (in particular Ca^{2+} and Cu^{2+}) in the flocculation of negative silver bromide sols by anionic polyelectrolytes and view bridging as the dominant mechanism. They concluded that the mechanism by which polymer adsorption occurs involves formation of a complex in the vicinity of the interface between the counter-ions and the functional groups (carboxylate and sulphate) of the polyelectrolyte, the concentrations of both species being considerably enhanced near the interface. The adsorption of counter-ions is, of course, much more rapid than adsorption of the polyelectrolyte. The fact that divalent ions are so much more effective than monovalent ions (even in 10^{-2}M KNO_3 the degree of flocculation produced is much less than in 5.10^{-5}M $Ca(NO_3)_2$), argues in favour of this mechanism. Complex formation with potassium ions does occur to a limited extent, but the fact that complexes formed with divalent ions lead to local sites of positive charge on the polyelectrolyte must obviously facilitate adsorption onto a negative surface.

Similarly, for cationic polyelectrolytes to adsorb on positively charged mercury surfaces, Miller and Grahame[39] showed that the presence of anions (particularly those that specifically adsorb on mercury) is necessary.

Kuz'kin and Nebera[40] have pointed out that the presence of electrolyte may simply act to screen the Coulombic repulsion between the particle surface and the polyelectrolyte, rather as in the interaction between two charged colloidal particles, without specific effects occurring. This point of view has received support from Slater et al[41]. They showed that it was possible to "activate" the adsorption of 30% hydrolysed polyacrylamide onto freshly dispersed quartz particles in water by the presence of copper (II) ions, and hence induce flocculation. This occurred over a narrow range of pH and copper (II) ion concentration (at high Cu^{2+} concentrations and high pH, $Cu(OH)_2$ is precipitated). However, aged quartz could not be activated by copper(II) ions even though copper(II) ions are still adsorbed at the particle surface. The authors conclude that the primary mechani of adsorption in this case must be hydrogen bonding between the silicon hydroxide groups and the polyelectrolyte, and that copper (II) ions only play a charge screening role. It would seem that bridging is the dominant mechanism in flocculation by polyelectrolytes of the same sign as the particles, and the general features are broadly similar to those occurring in flocculation by neutral polymers.

It has been found that the diameter of adsorbed polymer molecules is commonly of the same order of magnitude as that in solution. Some degree of flattening is to be expected with a polyelectrolyte adsorbing onto a surface of opposite charge. Unfortunately, no reliable method has yet been devised for measuring the dimensions of adsorbed polyelectrolytes or obtaining the number of monomeric units actually attached to the particle surface.

In the absence of experimental data, useful indications have been obtained from theoretical calculations carried out (on very different bases) by Silberberg[42] and by Clayfield and Lamb[43]. Although a polymer molecule may be very strongly adsorbed as a whole, the attachment can be by a large number of weak "bonds", segments can rearrange without net desorption and a relatively long period will be needed to attain a quasi-equilibrium configuration.

The fact that adsorption of flocculant is effectively irreversible under conditions of good flocculation does not mean that the polymer cannot be displaced. By change of conditions, such as pH or addition of a high concentration of a surface competitor (e.g. sodium tripolyphosphate), it is generally possible to displace a flocculant that would be completely immune to washing with water. Obviously, the polymer molecule does not suddenly "jump off"; it is gradually eased off by displacement of segments in random order (not necessarily by zip fastner action from the ends). Conversely of course, it the same reagents are

applied before the polymer is added it will neither be adsorbed nor cause flocculation.

Factors tending to make the solution phase a "better solvent" for the polymer will tend to desorb it. Conversely, addition of salts etc., will tend to salt it out and thus increase adsorption. But increased adsorption does not necessarily improve flocculation, if at the same time, the extension of the polymer is reduced. The conditions for extended molecules together with adequate strength of adsorption are therefore fairly restrictive.

It is generally accepted that an optimum polymer dosage exists for the best flocculation, beyond this the colloid may not be destabilised. This ability of nonionic polymers to stabilise colloids improves with molecular weight as shown by Ash's results[36]. This effect is referred to as steric stabilisation; the particle is completely coated by a layer of polymer essentially preventing the approach of the particle cores to a separation where the mutual Van der Waals attraction would be sufficient for aggregation to occur. Any overlap of these layers would be resisted by the osmotic interaction of flexible chain molecules. As the two hard cores come together the polymer layers must overlap or be compressed resulting in a loss of configurational entropy and an unfavourable change in free energy. The success of this mechanism to stabilise will depend on the polymer segment density around the particles or how well the surface is covered with polymer. The range

of the effect will depend on the molecular weight and the solubility of the polymer in the medium, dictating if the coils are collapsed or extended. The polymer must also be strongly adsorbed onto the surface to prevent displacement.

Attempts have been made by La Mer, Smellie and Healey[44,45] to determine the optimum polymer concentrations using simple quantitative theories, which although simiplify the complex system, aids understanding. It has been found experimentally that the behaviour of polymer-solid adsorption systems can frequently be approximated a simple adsorption isotherm of the Langmuir type as shown in equation (1.40),

$$\frac{\theta}{(1-\theta)} = bP \qquad (1.40)$$

Where θ is the fraction of adsorption sites on the surface of the solid particles covered by adsorbed polymer, P is the equilibrium concentration of polymer in solution, and b is an adsorption constant depending on the properties of the polymer and of the particle. P is related to the initial concentration of polymer, P_o, by the expression given in equation (1.41).

$$P = P_o - kw\theta \qquad (1.41)$$

Where k is a constant depending upon the specific surface area of the solid and the number of adsorption sites per

unit area, and w is the solids content of the suspension. Combination of equations (1.40) and (1.41) gives equation (1.42),

$$\theta = \frac{b(P_o - kw\theta)}{1 + b(P_o - kw\theta)} \qquad (1.42)$$

showing the increase of θ with increasing polymer content, P_o, and with decreasing concentration of suspended solids, w.

The principal theories of flocculation as stated, assume that polymer molecules attached to solid particles still have free active centres that can be adsorbed on the remaining free surface of other particles. This process results in "bridging" between solid particles and in the consequent formation of large flocs having a three-dimensional network structure. The bridging mechanism involves a bimolecular process, the rate of which is dependent upon the concentration both of particles carrying flocculant, $n_o\theta$ (where n_o is the number of solid particles unit volume), and of particles with free surface able to adsorb flocculant, $n_o(1-\theta)$. The rate of floc formation can thus be given by equation (1.43),

$$\frac{-dn_o}{dt} = k_1 n_o^2 \theta(1-\theta) \qquad (1.43)$$

where k_1 is a constant. The flocs break-down at a rate which is directly proportional to the volume of a floc and inversely proportional to the surface area and to a bridging factor,

$\theta(1-\theta)$. The rate of floc break-down is given by equation (1.44),

$$\frac{dn_o}{dt} = \frac{k_2 R}{\theta(1-\theta)} \qquad (1.44)$$

where R is the radius of the floc and k_2 is a constant. From equation (1.43) and (1.44) the radius of flocs at equilibrium, R_e, can be obtained (eqn. 1.45).

$$R_e = \frac{k_1}{k_2} n_o^2 \theta^2 (1-\theta)^2 \qquad (1.45)$$

Equation (1.45) indicates that the best conditions for flocculation are when $\theta = 0.5$, or when half the adsorption sites are taken up. Kane, La Mer and Linford[46] found that the optimum filtration rate occurs when $\theta = 0.5$.

In practice, the overall rate of flocculation is also dependent upon such factors as the rate of addition of flocculant to the suspension and the agitation. Both adsorption and bridging equilibria are affected by the duration and intensity of agitation[47].

In a theoretical model of polymer adsorption onto suspended particles, the form of the adsorbed polymer chain must be taken into consideration. Bridges can conceivably be formed by physical entanglement or hydrogen bonding between extended segments of chains. However, this mechanism is not likely to be an important one, since flocculation occurs at low surface coverages of the

suspended particles, where polymer-polymer interactions will be at a minimum[47].

As indicated many factors control the stability of colloidal particles to aggregation. To gain the most from any study of polymeric flocculants as many as possible of these factors should be controlled. To meet this requirement model systems must be devised, since practical ones are not usually well defined.

Firstly an important parameter is particle size, it affects both the repulsive and attractive forces between particles. Also any experimental method to follow flocculation is only suitable over certain ranges of particle sizes. The particles met in practical flocculation systems (e.g. clays) have normally a distribution of sizes so it is difficult to define the effect of particle size. The experimental method may not be able to detect the small particles on the tail of the distribution but as the system flocculates these small particles will aggregate and be detected, resulting in an increase in the particle number instead of a decrease. It is best then to view a system with a very narrow size distribution, preferably monodispersed.

The particle concentration in simple terms sets the rate of particle-particle collisions and from this the kinetics of flocculation. If it is assumed that the diffusion rate of polymer to the particle surface is greater than the collision rate of particles then after a polymer has attached itself to a particle surface and it has the

ability to do this at a number of points along its length, it will collapse down onto the surface irreversibly, reducing its bridging range. Thus if another particle does not come into its presence, due to particle collisions, early enough it may not form an effective bridge. The variation of particle concentration may show if this is the case. This would be of particular interest for a polyelectrolyte system which has the opposite charge from that of the particle, since any change in particle concentration should not effect flocculation if only charge neutralisation occurs.

The molecular weight of a polymer (or the dimensions of the polymer coils) has an influence on the flocculation and possibly restabilisation of a colloid. To determine the importance of this factor the molecular weight of the flocculant must be known (and if possible be monodispersed) and varied to show any dependence.

1.7 Experimental Techniques used in Flocculation Studies

To investigate the stability or changes in stability of a colloid some technique must be used to assess the degree of aggregation of the dispersed particles. In practice, some are specific to a particular technology, but others are more general[48]. The methods used for estimating both flocculation and coagulation depend on being able to monitor some suitable property, either of the total system (e.g. light scattering, rheology, or electrical conductivity), or of the aggregates themselves

(e.g. sedimentation rate, filtration rate or floc volume), or of the supernatant liquid above the aggregates (e.g. again some optical property). It is usual to compare measurements after some arbitrarily chosen time. Fewer kinetic studies have been reported [49-53] that is, where measurements are made continuously as a function of aggregation time. However to carry out such kinetic experiments requires a low particle concentration if the flocculation time is to be measurable, and it is likely that the performance of polymer flocculants are dependent on the particle concentration.

During flocculation the number of particles decrease and the particle size increases so any technique that measured either of these would be absolute.

The optical properties of the dispersions can give some information on the extent of flocculation. The procedure most widely used is simply to compare the turbidity (often at some arbitrary wavelength) of a set flocculating systems after some chosen time. One of the problems is that the turbidity may not increase uniformly with the degree of flocculation, and this non-linearity can make comparison difficult. Also, partial sedimentation of flocs out of the light beam may occur. For these reasons some authors deliberately first centrifuge their dispersions to remove large flocs, and then measure the residual turbidity of the supernatant. This procedure is sufficient to determine the degree of flocculation semi-quantitatively,

but may lead to spurious results if precautions are not taken. The fact is that, but for a few cases an absolute particle size cannot be determined from turbidity measurements of dispersions. The relationship of light scattered to particle size is a complex one depending on the wavelength of light and the refractive index difference between the medium and the particle. The analysis is only simple for small particles which can be considered as Rayleigh scatterers[54] (i.e. particle size $< \lambda/20$ [$\backsim$ 30nm]). Oster[55] has taken the case of Rayleigh scatterers and using Smoluchowski's theory of particle aggregation kinetics, obtained an expression linking the rate of change of turbidity with time to the kinetic rate constant for flocculation. In practice the straight line relationship between turbidity and time predicted by his equation is not found and the rate constant values which should determine the gradient of the plot are obtained from the limiting initial slope of the turbidity-time plots.

Particles of dimensions equivalent to the wavelength of light cannot be considered as single scatterers but as multiple scatterers. The interference of the many scattered rays from one particle results in a complicated relationship between size and scattered light intensity, accommodated in both Rayleigh Gans theory (for particles of small refractive index difference from the medium) and the general Mie theory. The intensity does increase with size for large changes but has a sinusoidal 'ripple' which can result in small increases in size resulting in

a decrease in scattered intensity. Also one value of intensity could represent a series of sizes. However, at lower scattering angles the scattered intensity increases proportionally with size to greater values of diameter before oscillations begin. Measuring the intensity at very low angles (c.a. 1°)[56] is very useful since in this region the change in intensity with particle size, or time with a kinetics experiment, is practically linear, up to very large sizes of particles (micron size).

The size of colloidal particles can be determined by electronmicroscopy. This can be a time consuming operation as care must be taken to measure a large enough sample of particles to give a representative result. The difficulty with the method is that the colloid sample must be evaporated on the specimen grid. During this drying process aggregation or de-aggregation can occur. Nevertheless, electron-microscopy has found increasing use recently in studying floc structure[57].

Indirect particle counting instruments tend to be much faster. For example, Coulter counters[58] can count at around 10^4 particles per second. This is done by detecting the change in electrical resistance across a small orifice as the dispersion particles are sucked through it, the passage of each particle is thus counted. The lower limit of detectable size, 0.8 μm, is set by the sensitivity of the instrument. The counting must be carried out in the presence of electrolyte, to increase the

electrical conductivity, which can affect the state of the dispersion. Also the colloid may have to be extensively diluted, counting is normally carried out at 10^6 - 10^7 particles per ml. Another factor is the possible disruption of aggregates on passing through the counter orifice. This would not be the case with the strong flocs resulting from the action of polymeric flocculants but could be a problem for weak aggregates.

Various forms of gravitational (particle size > 2μm) and centrifugal (particle size < 2 μm) sedimentometers have been described[48]. The major criterion here is that Stoke's law should apply, if any size relationship is to be obtained from the settling rate. A flocculating system will normally subside rather than sediment, as such, leaving a clear boundary line above the flocs. Since subsidence is primarily a matter of compaction, that is, of compression of a loose, three demensional network, Stoke's law cannot really be applied. However, the movement of this boundary as dispersions settle has been used as an empirical measurement of flocculation kinetics. La Mer and Healy[59] have suggested relationships between the boundary height and time, involving two constants. A number of attemptshave been made to relate settling rates either to the flow of supernatant fluid through the settling bed[60,61], or to the detailed floc structure[62].

The rate of flow of the supernatant in filtration of colloid suspensions has been used as a measure of

flocculation. The rate of flow of this through a bed of flocculated solid is known to depend on a number of filter-bed characteristics, such as porosity of the filter cake, thickness of the cake, and size of the solid particles. An equation[64] has been developed to show the effect of polymer concentration on filtration rates and predicts an optimum polymer dosage for a maximum filtration rate.

Stable dispersions tend to sediment into close-packed cakes of small volume whereas coagulating or flocculating systems settle with large sediment volumes. Measurements of sediment volume after some fixed time may therefore be used to compare degrees of aggregation, although under normal gravitational conditions, equilibrium may not be established within a reasonable time limit. Results are often expressed in terms of the ratio of the final sediment height to the initial height. Wolff[65], on the other hand, has suggested the use of "half-value" times, that is, the time at which the sediment height reaches half its final value, the latter being determined by extrapolation where necessary.

Settlement rate, sediment volume and filtration rates are probably of more practical than theoretical value, since they cannot be easily related to the polymer flocculant.

The current development of ultramicroscope counters, particularly those using laser light[66], could well prove useful in following flocculation processes. Particularly

as they can be applied over a much wider range of particle sizes. They also work in the range of most interest, micron and sub-micron, which is outside the range of any other sizing method, toolarge for bulk light scattering and too small for the Coulter counter. This type of instrument works in principle by injecting the colloid, at a constant known rate, into a stream of water which carries the particles, one after the other, by the benefit of the cell design, through a laser beam. As each particle passes a flash of scattered light results which is focused by a microscope onto a photomultiplier tube. Thus for each particle injected an electric pulse is generated which is counted. This type of instrument is not commercially available. To follow any flocculation experiment the laser ultramicroscope method would seem the most satisfactory, giving a fast accurate count of the number of particles present in the colloidal suspension.

CHAPTER 2

PARTICLE COUNTING

2.1 Introduction

The automatic particle counter used in this work is based on the instruments designed by McFadyen and Smith[66]. The counter utilises the principle of the flow ultramicroscope in which the particles in a flowing suspension are seen as they pass through a region of side illumination in the field of view of the microscope. As they pass through, the flashes of scattered light are counted, either manually or by photo electric detection.

Instruments of this type come in two forms; some instruments count only a portion of the illuminated particles by viewing only a small area of the flowing suspension and assume this to be representative of the whole sample, whereas other instruments count all the particles in the sample. The second was the type used in the present work with obvious advantages. Counting all the particles is achieved by restricting the dispersion to be counted to a narrow stream which is passed through a laser beam. The flow rate of particles is adjusted so that in general each particle passes through the illuminated counting zone separately from other particles. The narrow particle stream is achieved by allowing the particles to emerge at a controlled rate from the needle of a microsyringe into a stream of flowing water. Hydrodynamic focusing is employed to narrow the particle stream still further.

The instruments designed by Smith et al[66] detected the scattered light at 90° and 45°[67] the device used in this work collects the scattered light at 30° (to the incident beam). Certain benefits are obtained by moving to low scattering angles, as briefly mentioned earlier. Firstly, more light is scattered at lower angles for a given particle, and secondly, the interference effects with larger particles are not so pronounced, resulting in the roughly linear relationship between particle size and light intensity to greater sizes of particles. However, moving to lower scattering angles does create design problems for the instrument.

2.2 Design of Instrument

The instrument consists of a cell where the particles are passed through the laser beam, a microscope to focus down onto the particle stream, a photomultiplier to detect the light flashes and an electronic system to count the generated pulses.

Cell

Fig. (2.1) shows a sectional view of the cell and indicates the relative positions of the particle flow, the light beam and the ultramicroscope objective. The basic configuration used was devised by earlier workers using visual observation for counting[68]. Since with this arrangement the particle travels along the axis of observation and the image does not shift on the retina of the eye, the light energy is more concentrated and small particles more

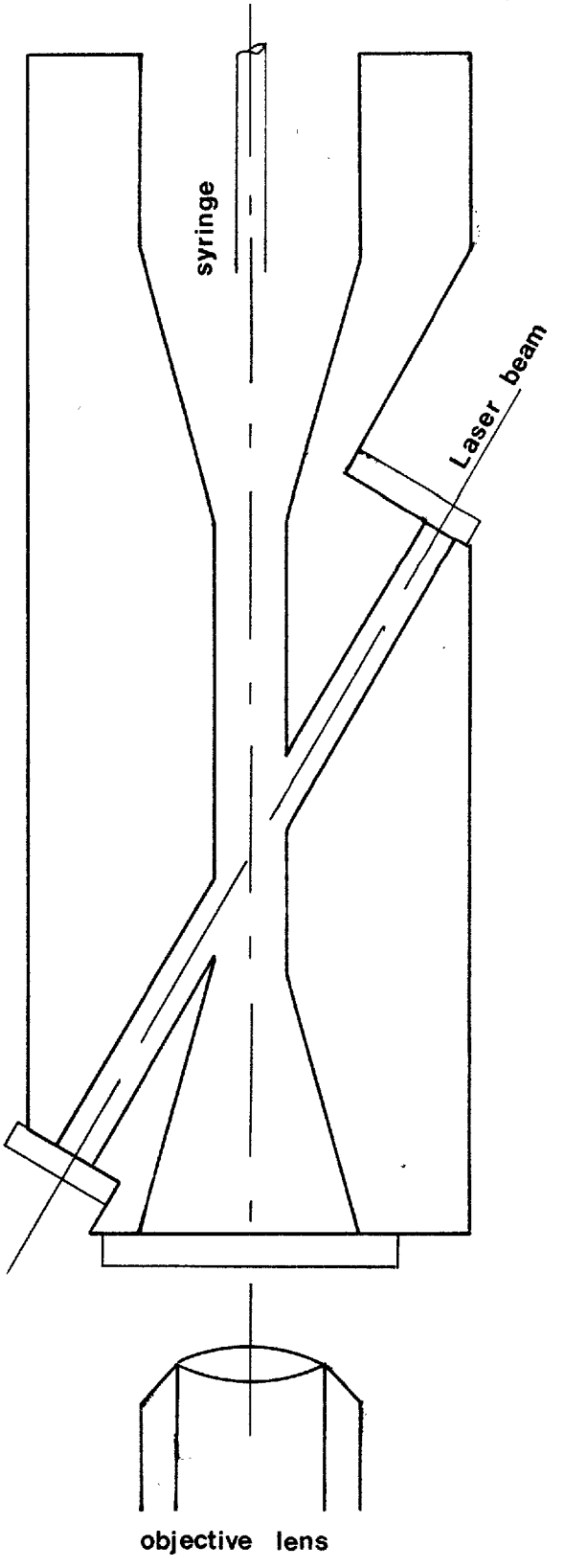


FIG. 2.1

easily visible. Although counting was not carried out by eye the alignment of the instrument was carried out by eye and this configuration was employed.

The design of the cell creates the narrow stream of particles which is required if all of them are to be counted. The syringe injects the particles at a constant rate into the core of the laminar flowing water, and, as the cross-section of the cell is gradually reduced and the velocity of liquid increases, the particles are spaced out along the axis. Also, since the particles are injected approximately into the axis of flow and there is no turbulence as the liquid moves along the axis, with the reducing diameter, the particles are focused inward and thus come through in a very small region of the cross-section. The position of the syringe needle relative to the central axis can be altered using the three adjusting screws.

The syringe used is a 10 µl 'Pressure-Lok' syringe (Precision Sampling Corp.019102). The needle is actually the barrel of this syringe with the plunger moving right along its length, and at the limit of its travel just protrudes from the end, removing any chance of blockage. The syringe is loaded by pulling the plunger right back, opening the side loading channel, through which the dispersion is passed to fill the needle. This facility allows the syringe to be filled without removing it from the cell.

The body of the cell and the cell holder were made of brass. The cell holder has an internal diameter of 6 mm, into one end is screwed the syringe and into the other the cell. The three water inlets are placed towards the syringe end of the holder, symetrically positioned perpendicular to the cell axis.

The cell as its widest point is 6 mm reducing down to 2 mm (at a 15° taper) for the illuminated section, and out again to 6 mm at the window end. The laser beam passes through a 1 mm channel, set at 30° to the cell axis. The windows at each end are set at 90° to the beam to stop refraction. The water flows out of the cell through a tube at the bottom, below the window and a vent at the top of the cell allows any air bubbles to escape. Also the level of water in the vent tube sets the pressure in the cell, so that no great pressure is applied to the seals of the syringe.

The cell holder is mounted on an optical bench. Its height and its position along the length of the bench can be finely adjusted. The design of the mounting block for the holder allow it to swivel across the plane of the bench top with the aid of two adjusting screws. The cell and holder can also be tilted in the two vertical planes parellel and perpendicular to the optical bench top. Using these adjustments the laser beam can be aligned and the particle stream centralised in the beam.

Internal reflections of the incident beam can result in large background intensities and must be minimised by careful adjustment of the alignment. They are normally caused when the angle between the beam and the cell centre line is not the desired one and the beam strikes the edge of the exit hole instead of cleanly passing through it. The problem is more critical at lower scattering angles when the internal reflections are more likely to be in a forward direction, shining into the microscope objectve. Any alteration of the cell design to alleviate the problem may upset the liquid flow and the hydrodynamic focussing. Thus when the entrance and exit holes for the beam were widened and moved back to create a shoulder to protect the microscope from any relected light, the particles did not come through in the small region as required due to turbulence in the cell.

The general problem of effectively 'stopping' the laser beam is more difficult at lower scattering angles, since the microscope is looking along a line close to the incident beam and stray light may pass into the objective lens. The technique used in this cell is to allow the laser beam to pass out of the cell and be stopped outside. To design a cell to allow this to happen as the scattering angle is reduced, the point where the beam intercepts, the particle stream must be moved back relative to the front of the cell. This would lengthen the required working distance of the microscope, which is difficult at high

magnifications. Shortening the distance between the window and the illuminated zone is possible but this moves the water exit point nearer this critical zone and could disturb the liquid flow. Also to accommodate the exit channel for the beam the taper of the front of the cell must be reduced and this limits the range of scattering angles viewed. In practice it was found that all these problems could be overcome when viewing scattering at 30° but are expected to become a problem at lower angles.

The microscope used to view the particles could be moved in both a vertical and horizontal direction for alignment. A x 20 objective lens (long working distance (12 mm)) and a x 10 eyepiece were fitted to the microscope. To carry out the initial alignment a x 10 objective was often used. Once the apparatus has been aligned the photomultiplier tube is placed behind the eyepiece so that counting can be carried out. When counting small particles against a background of larger dirt particles in the water supply the field of view can be restricted by placing a small aperture about 4 mm diameter in front of the eyepiece. This reduced the count due to background particles, the number of these being proportional to the area viewed, without markedly reducing the signal from the small particles.

The light source was a 6 mW Helium-Neon laser (Scientifica and Cook Ltd.). The power of the laser determines the intensity of the scattered light off the particles and thus the lower limit of size countable. The

work carried out involved fairly large particles (0.5 μm and greater) and the light source was adequate.

The laser was focussed down into the cell with a long focal length convex lens (10 cm), positioned so that the particles passed through the beam well within the focal distance and in the small region where the particles passed through the beam, the beam appeared to be virtually parallel. Thus the variation with intensity across this zone can be taken as small.

Water Supply and Sol Injection

The water flowing through the cell was provided by an overhead tank, using gravity feed. The water must be dust-free if the particles to be counted are to be seen. The most successful method found to attain this was to fit a Millipore filter 'in line' between the reservoir and the cell.

The flow of water through the cell determines the residence time of a particle in the beam and also dictates the chance of two particles being in the beam at the same instance. The upper limit of the flow should be the point where turbulent flow sets in, upsetting the stability of the particle stream. However, the actual upper limit of water flow is set by the resistance offered by the Millipore filter. At this flowrate no turbulence was apparent in the cell. The filter was changed frequently to maintain a good flowrate. As stated the water flowrate determines the residence time of the particle in the beam and thus the

time period of the scattered light flash. The water flow thus sets the pulse width of the resultant electrical signal and when the pulse width reached an unacceptable value the filter was changed.

Attempts to pre-filter the water and use directly from a reservoir were unsuccessful due to contamination occurring during storage.

The colloid suspension was injected from the syringe at a constant rate by a 'pusher' driven by a constant speed synchronous motor. The motor turned, through a reduction gear, a brass tube internally threaded. As the tube turned the threaded rod inside the tube moved outward and its rotational motion was resisted by a pin located in a groove along its length. The threaded rod moving out at a constant rate was used to push the syringe plunger. The pusher unit was designed so that the pushing rod could quickly be moved back without reversing the direction of rotation of the motor. The unit moved the syringe forward at a rate of 1.37×10^{-3} mm s^{-1} which is equivalent to a volume injection rate of 2.28×10^{-7} ml s^{-1}. The injection rate and the particle concentration of the suspension determines the counting rate and must be altered to get an appropriate figure. Altering the particle concentration would seem the simplest alternative but if the suspension is unstable it maybe advisable to use a high injection rate so that particles are injected before they sediment in the syringe.

Electronics

The photomultiplier used was an EMI type 9524B which has a higher than usual sensitivity to red light. The photomultiplier was powered by a Hewlitt Packar high tension supply which gave a D.C. supply up to 3000V. The unit was set up with the cathode of the photomultiplier at a negative H.T. of 700V and the anode at earth potential.

The output of the photomultiplier was connected to an oscilloscope (Tektronic Ltd Type 547). The oscilloscope was set to trigger its display on the input signal. but only if this was above a set minimum voltage and rising in a positive gradient. Everytime the oscilloscope triggers a standard pulse was sent off to drive a counter-timer unit (Advance Electronics Timer counter TC3).

The time base of the oscilloscope was set to give a display time in excess of the pulse width, during this time after the oscilloscope has triggered it cannot trigger again and one particle can only be registered. The display time was set at 5 ms. This is necessary to avoid multiple counting of one particle since occasionally the pulses do not have a regular profile and have more than one peak. This can be due to irregular shaped particles, clusters of particles, or a second particle entering the beam directly after the first one.

However, during the time the oscilloscope is displaying a particle passing through the beam will not be counted, thus a correction for this dead time must be made. If n

counts per second are recorded, during each second the machine was not counting for $n\tau$ seconds, where τ is the dead time (5 ms). Thus n counts were recorded for a time interval of $1-n\tau$ seconds and the correct count rate is

$$n_{cor} = \frac{n}{1-n\tau} \qquad \text{counts sec}^{-1}$$

Obviously the higher the count rate the longer the device is switched off, and the greater the correction, reducing the precision of the result. The maximum count rate used was 50 c/s, a correction factor of 33% of the raw count. The counting was carried out over intervals of 10 seconds and normally the average of at least ten intervals was taken as the result.

The magnitude of the voltage pulses obtained from the photomultiplier at a given H.T. setting is governed by the amount of light scattered by the individual particles. This in turn depends on particle size and material so that for each type and size range of particle it is necessary to select a suitable trigger voltage level.

The oscilloscope only triggers on pulses greater than the set level, thus if all the pulses are to be counted this level must be set below the lowest pulse height. This value can be obtained by noting the change in count rate with trigger level. Firtsly if the sample is monodisperse and all the peaks are of one height, as the level is increased the count will be constant until the trigger level is greater

than the pulse height and the count rate will fall off quickly to zero, as shown in Figure (2.2). However, if the sample has a distribution of sizes the count rate should be constant up to a certain trigger level, equivalent to the intensity of the smallest particle, and then fall off slowly above that value, depending on the distribution (Fig.2.3). To count all the particles the trigger level must be set at a value equivalent to the 'plateau' region in the trigger level-count rate plot. At very low trigger level settings the background signal due to small dirt particles in the water or A.C. noise may be counted.

The other approach used in this work was to analyse the pulses from the photomultiplier using a multichannel pulse height analyser (Nuclear Enterprised Ltd,model 6900) which builds up a distribution of the number of pulses against voltage of a pulse by detecting the height of each pulse and adding one count to appropriate voltage channel. The advantage of this is firstly that a search for a suitable trigger level is not necessary since it is simple to discriminate between the peak in the distribution due to the particles of interest and the one due to the background signal. Also it maybe possible in some cases to see a change in the distribution of particle size with flocculation.

The pulses from the photomultiplier could not be directly fed into the multichannel analyser because the analyser could only deal with pulses with a much faster rise time than those from the photomultiplier. To overcome

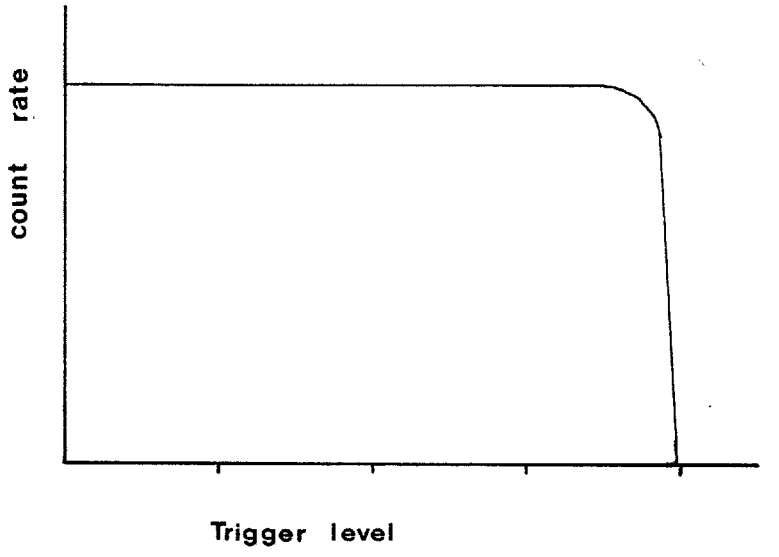


FIG.2.2

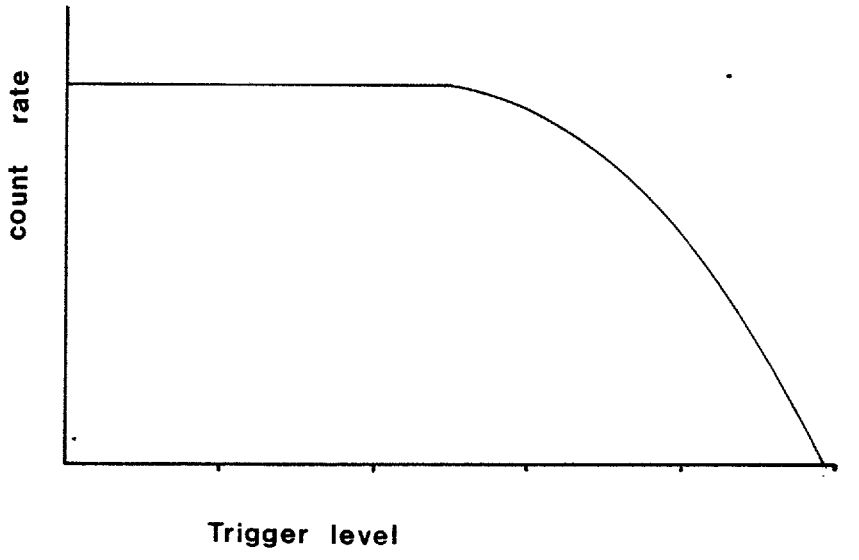


FIG. 2.3

this a pulse height detector was constructed which took the signal from the photomultiplier and detected the maximum height of the rising signal and then sent a standard pulse with the same amplitude but with a much faster rise time to the analyser. After this it 'switched off' for a preset dead time to allow the particle to leave the beam before looking for the next pulse.

2.3 Light Scattering Theory

The relationship between particle size and the scattered light intensity can be evaluated using the general theory of scattering by a sphere[69].

Considering figure (2.4), with the scattering particle at the origin of the x,y,z axes, the incident ray is travelling along the z axis, polarised in the ox direction. The scattered ray is in the yz plane. The scattering direction is taken from the origin through the point defined by the polar co-ordinates r, θ, ϕ, where ϕ is the angle between the direction of the polarisation of the incident ray and the plane of the scattered ray, θ is the angle of observation and r is the distance from the origin to the point of observation. Then the scattered light intensity observed for unit incident intensity is defined, as,

$$I = \frac{\lambda^2}{4\pi r^2} (i_1 \sin^2\phi + i_2 \cos^2\phi) \qquad (2.1)$$

where λ is the wavelength of light in the medium, and i_1

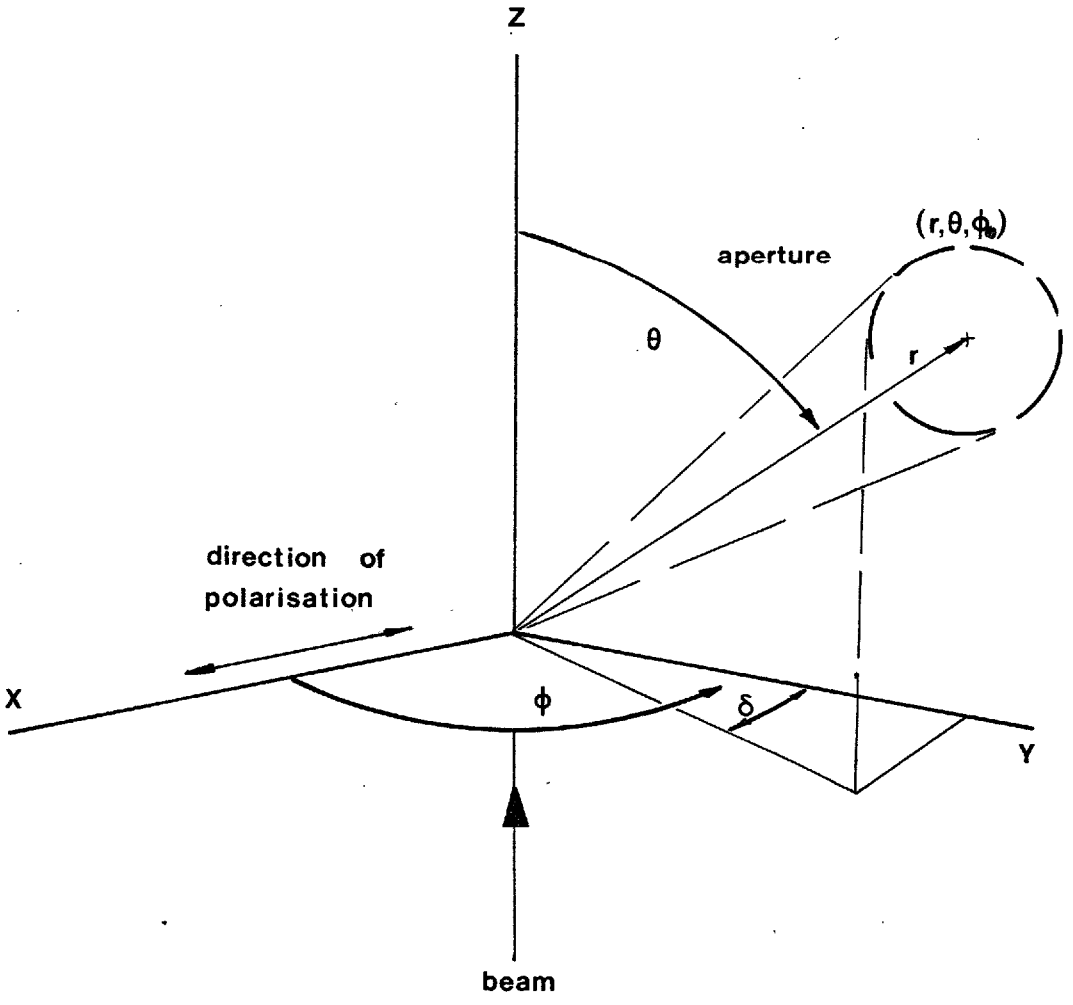


FIG. 2.4

and i_2 are the intensity functions, which are functions of the observation angle θ, the refractive indices of the particle and the medium, and x, where

$$x = \frac{2\pi a}{\lambda} \quad , \quad (\quad a \text{ is the radius of the particle}).$$

In the case in question the light collected by the photomultiplier is over a range of θ and ϕ. Thus the scattered intensity must be summed over an area. This is done by integrating equation (2.1) above, over all values of θ and ϕ allowed by the geometry of the device, then

$$\frac{\text{Power}}{\text{Unit Incident Intensity}} = \int_{\phi_1}^{\phi_2}\int_{\theta_1}^{\theta_2} Ir^2 \sin\theta \, d\phi d\theta$$

$$= \frac{\lambda^2}{4\pi^2} \int_{\phi_1}^{\phi_2}\int_{\theta_1}^{\theta_2} (i_1 \sin^2\phi + i_2 \cos^2\phi)\sin\theta \, d\phi d\theta \qquad (2.2)$$

But θ and ϕ are not independent variables if they are limited by a circular aperture. The limits of ϕ are a function of θ i.e. ϕ varies between $\frac{\pi}{2} - \delta$ and $\frac{\pi}{2} + \delta$ where $\delta = f(\theta)$.

It must be determined how δ varies with θ around the aperature edge. Tan $\delta = \frac{x}{y}$, where x and y are co-ordinates of points on the edge. Thus x and y must be found as a function of θ. The value of x can be found by carrying out a rotation of the axes of $\pi/3$ round ox to give the new axes oz', oy', shown in figure (2.5). The edge of the circular aperature can be described by the equation,

$$x^2 + y_1^2 + z_1^2 = r^2 \tag{2.3}$$

and $$q = \theta + \pi/3 \tag{2.4}$$

where q is the angle of observation in the new co-ordinates. While,

$$y_1 = r \cos \alpha \tag{2.5}$$

and α is defined by, $\frac{\pi}{6} - \alpha \leqslant \theta \leqslant \frac{\pi}{6} + \alpha$

Then $$x^2 + z_1^2 + r^2\cos^2 \alpha = r^2 \tag{2.6}$$

thus $$x^2 + z_1^2 = r^2 (1 - \cos^2\alpha) \tag{2.7}$$

$$= r^2\sin^2\alpha \tag{2.8}$$

and since $$z_1 = r \cos q, \tag{2.9}$$

$$x = r (\sin^2\alpha - \cos^2(\theta + \pi/3))^{\frac{1}{2}} \tag{2.10}$$

Returning to the original axes to find y, then

$$z = r \cos \theta \tag{2.11}$$

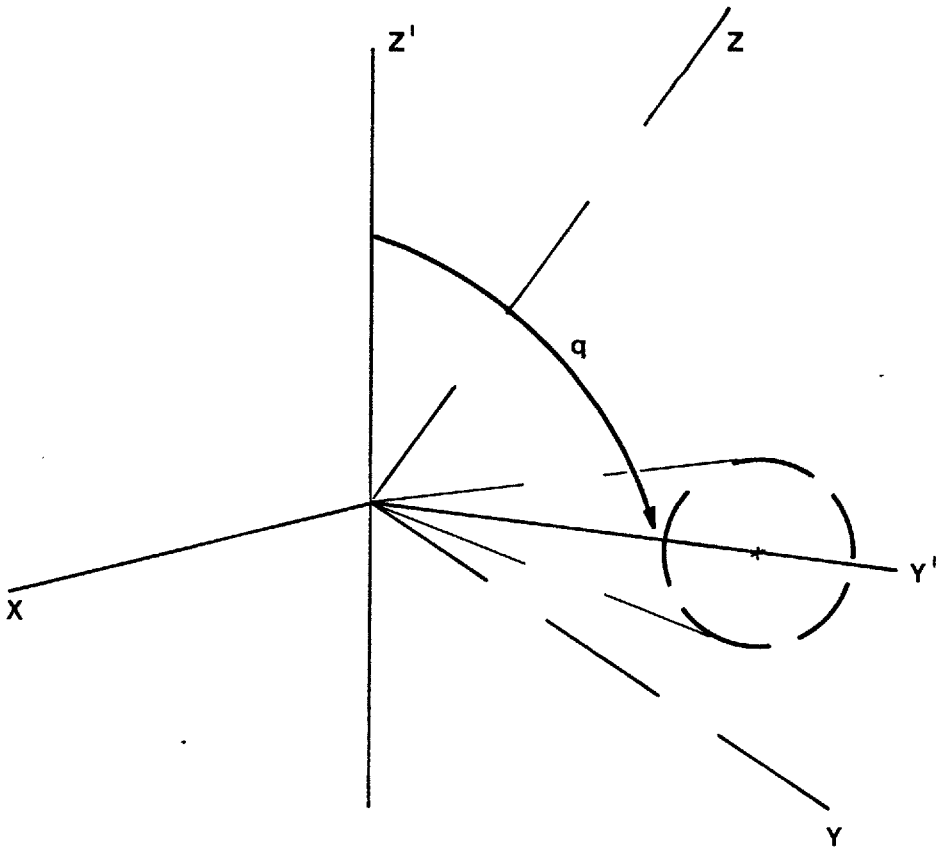


FIG. 2.5

and $$x^2 + y^2 + z^2 = r^2 \qquad (2.12)$$

Substituting equations (2.10)and (2.11) into the above,

$$y = r(\sin^2\theta - \sin^2\alpha + \cos^2(\theta + \pi/3) \quad) \qquad (2.13)$$

It then follows if $\tan\delta = \frac{x}{y}$

$$\delta = \tan^{-1}\left[\frac{\sin^2\alpha - \cos^2(\theta + \pi/3)}{\sin^2\theta + \cos^2(\theta + \pi/3) - \sin^2\alpha}\right]^{\frac{1}{2}} \qquad (2.14)$$

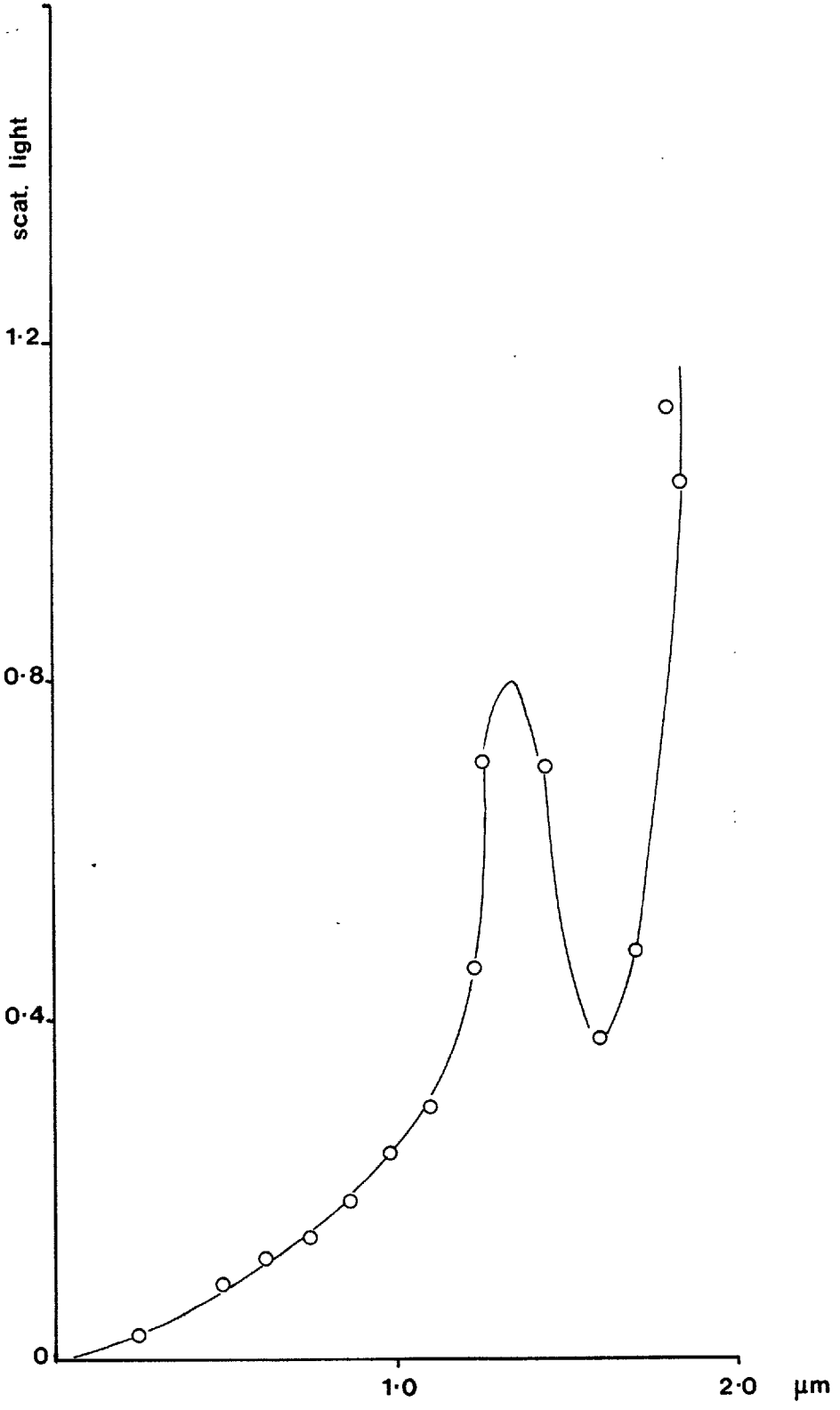
Thus integrating eqn (2.2) between the limits $\pi/2 - \delta$ and $\pi/2 + \delta$ gives

$$\frac{\text{Power}}{\text{unit incident intensity}} = \frac{\lambda^2}{4\pi^2}\int_{\frac{\pi}{6}-\alpha}^{\frac{\pi}{6}+\alpha} i_1\sin\theta(\delta+\tfrac{1}{2}\sin^2\delta)\,d\theta + i_2\sin\theta(\delta-\tfrac{1}{2}\sin^2\delta)\,d\theta \qquad (2.15)$$

The integral was evaluated for the range of θ, using a value for α of 9° set by the cell used. The functions i_1 and i_2 were calculated by computer[70] for a range of θ and X with the refractive indices of polystyrene and water.

Figure (2.6) shows a plot of the total light collected per unit incident intensity for a range of diameters

FIG.2.6



of polystyrene spheres in water. It can be seen that the amount of scattered light collected rises until a diameter of about 1.4 μm, then falls until a value of 1.6 μm then rises again. This means that above a diameter of 1.2 μm more than one size of particle can have the same intensity. This also indicates for polystyrene particles up to 1.2 μm any distribution of particle size will be directly related to the distribution of scattered light intensities. Moving to lower scattering angles will increase the diameter where the first maxima occurs and also the value of intensity for any diameter.

However, if the spheres are aggregated, in the form of doublets, triplets or larger flocs the scattered light will not be that multiple of the value for the singlet particle. This is shown in the figure (2.7);

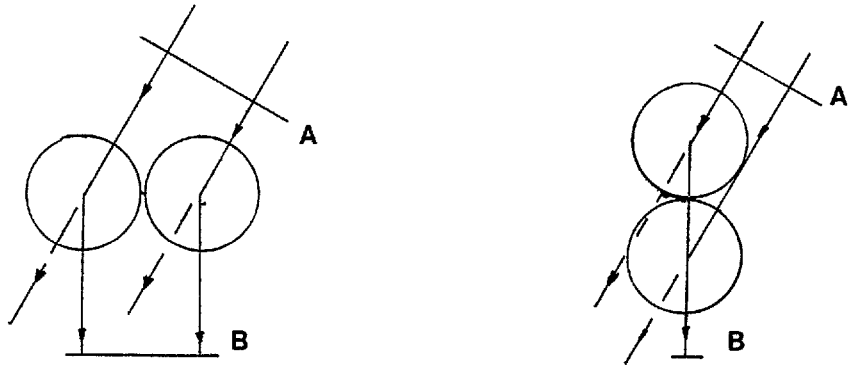


Fig. 2.7

The path between lines A and B taken by the incident rays and then the scattered rays are not all of equal length. The outcome of this is that the two rays at line B are out of phase and will lead to interference between the rays. If the difference in path length is an integral number of wavelengths the interference will be constructive, for a non-integral number it will be destructive. The difference in path length will depend on the size of the particles, their orientation to the incident beam and the scattering angle θ. Also the scattered rays off one particle which strike another will be rescattered by it, leading to multiple scattering.

A general theory of scattering by an arbitrary configuration of arbitrary scatters has been developed by Twersky[71] but it leads to a very intricate system of equations. Thus it is difficult to predict the scattering intensities of large particle aggregates or interpret the pulse height distribution obtained, especially since one form of aggregate can give a series of values depending on its orientation as it passes through the beam. In general it can be said that as the particles flocculate into doublets, triplets, and so on, the pulse height distribution will broaden, with some flocs scattering more than a single particle and some less.

For small particles (and angles) where interference is less important it would however be possible to obtain a complete size distribution for a flocculating system giving the number of dimers, trimers, etc. present.

2.4 Results for the Particle Counter with Simple Systems

Figure (2.8) shows the pulse height distribution for the multichannel analyser of the 0.53 μm polystyrene latex (prepared as discussed in chapter 3). If the theoretical light scattering calculation is considered a virtual straight line relationship exists between the energy of scattered light and the diameter of the particles in the 0.5 μ range, and assuming the electronic response of the equipment is linear the pulse height distribution found can be taken as the size distribution of the particles. It must also be assumed that the peak of the distribution of pulse height's corresponds to the mean size of the latex as the voltages recorded for the pulses cannot be absolutely converted to particle diameters. To estimate the width of the 0.53 μ size distribution the weight-average diameter ($\bar{D_w}$) was compared to the number-average diameter ($\bar{D_n}$), where

$$\bar{D_w} = \sum_i \frac{w_i D_i}{\sum_i w_i}$$

and w_i is the weight of particles of diameter D_i.

While $$\bar{D_n} = \sum_i \frac{n_i D_i}{\sum_i n_i}$$

and n_i is the number of particles of diameter D_i.

It was found that $\frac{\bar{D_w}}{\bar{D_n}} = 1.18$

FIG.2.8

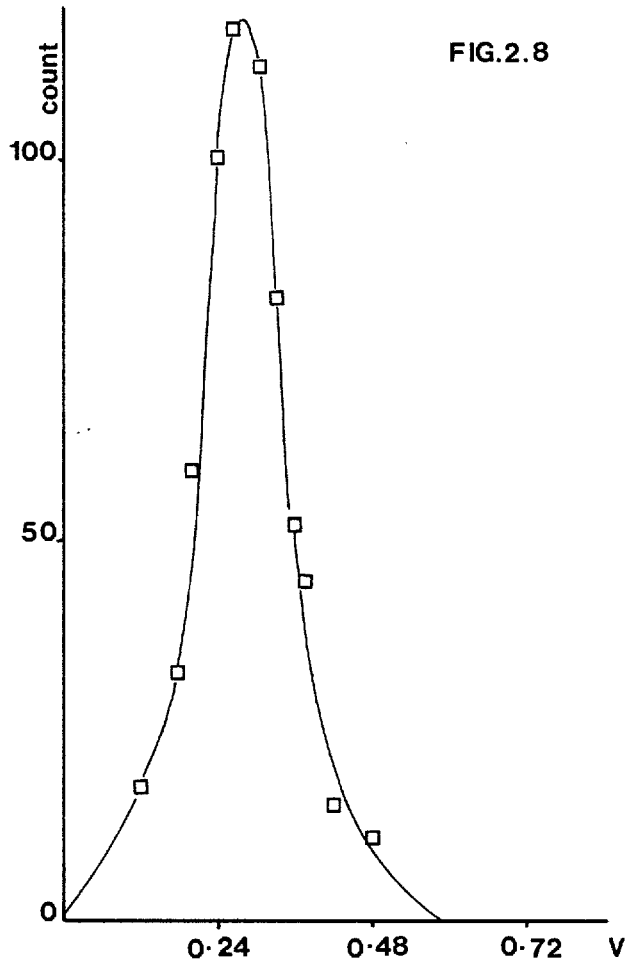
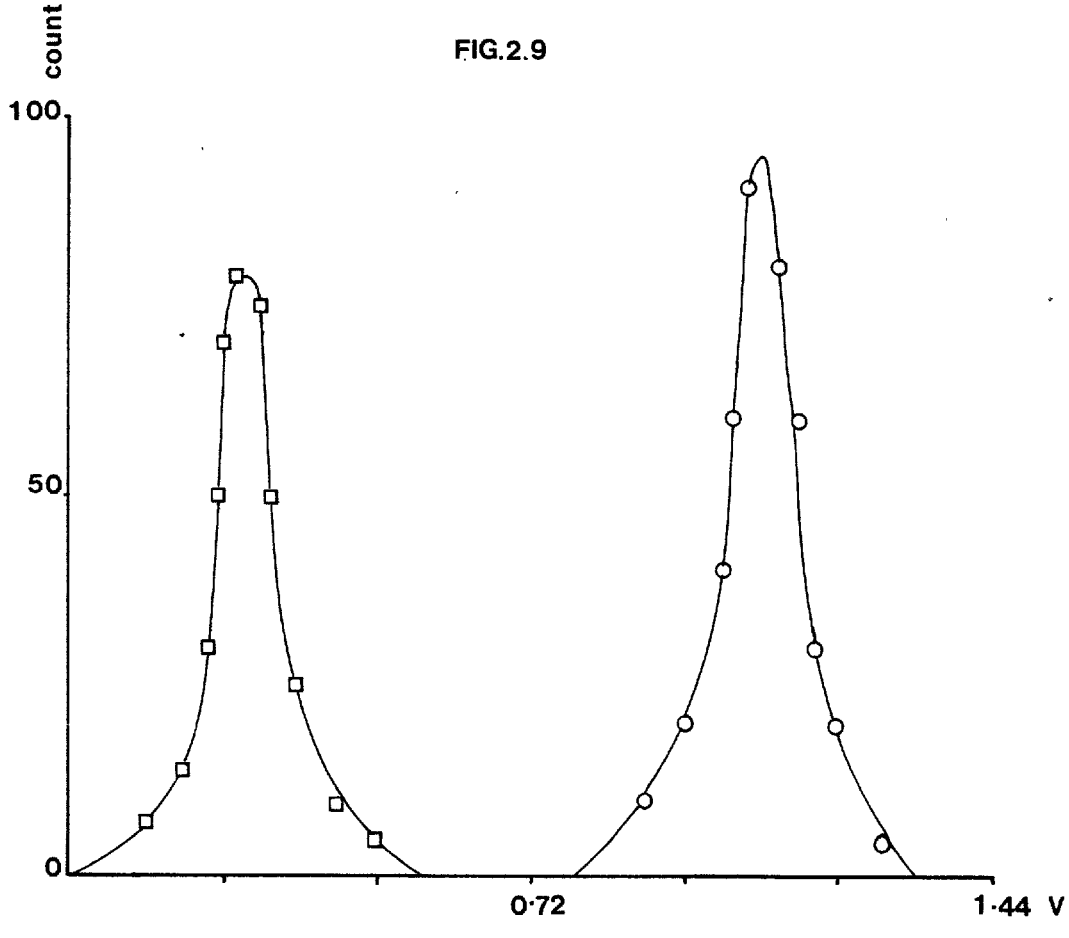


FIG.2.9



This can be compared to the electronmicroscopy study of this latex in Chapter 3 where a size distribution was measured and a value of $\frac{\bar{D}_w}{\bar{D}_n} = 1.13$ was found.

The pulse height distribution of a mixture of 0.53 μ and 1.86 μ mean diameter latexes was measured with the particle counter and is shown in Fig.(2.9). This shows two distinct peaks in the distribution for the two very different sizes of particle, indicating how different sizes of particles can be discriminated.

To check the absolute accuracy of the particle counter a sample of 1.86 μ polystyrene latex was counted and it was found that there were 8.6×10^6 particle/ml present. The sample was then counted with a Coulter particle counter and a result of 8.5×10^6 particle/ml was measured. It can be seen that the two methods agree reasonably closely on the number of particles present.

The mean particle diameter of two different polystyrene latexes dispersions of known weight concentration was calculated from the particle count rate measured by the counter. The two latexes where found to have mean diameters of 0.52 μ and 0.82 μ by this method. The mean diameters were then found by measuring the diameter of a large number of particles from a series of electronmicrographs of the two latexes by the method mentioned in chapter 3. The mean diameters calculated in this way were 0.54 μ and 0.84 μ. This comparison with a different method verifies the accuracy of the particle counter constructed.

CHAPTER 3

NON-AQUEOUS MODEL SYSTEMS

3.1 The Requirements of a Model System

To understand the flocculation process, and the importance of each parameter involved in the process, a model system must be devised. The model system would ideally have a well defined colloid particle, flocculating polymer, and mechanism of flocculation.

In most experiments carried out in the past reasonably well characterised polymers have been used, with known molecular weight and chemical composition[72]. This work has led to some understanding of the effects of these two factors. However, in many of these experiments the colloid used has been poorly defined, in many cases clays have been used. With such systems, because of a wide particle size distribution and varying particle geometry, the dependence on particle parameters cannot be easily seen.

Polymer latex particles have been used as a model colloid. These have the advantage that they can be made monodisperse in size, have a perfect spherical geometry, and well characterised surface groups. They can also be obtained in a range of sizes. Such a colloid system can reveal the effects of particle size and can also make the estimation of attractive and repulsive forces simpler.

Polystyrene is the most popular latex used. The particles are stabilised by a surface charge created during

the polymerization by the ionic initiator fragments and also by adsorbed surfactant if used.

The interactions that can occur between such a particle and the flocculating polymer can be electrostatic, as in the work of Gregory[30] with polyelectrolytes, or simple physical adsorption as in the work of Ash[36]. The latter shows the adsorption of polyethylene oxide onto polystyrene and the subsequent flocculation and restabilisation, which happens only in the presence of reasonably high electrolyte concentrations (M /80).

To devise a model system which will give information on the bridging of polymer coils between particles it is worthwhile looking at how a polymer attached to a colloidal particle can be arranged. The chain segments can lie along the surface of the particle forming a 'train' for all of its length, or part of its length and have some of the segments hanging off in the liquid. These segments can be part of a free chain end in space, or part of a 'bridge' between two particles, with segments further along the chain attached to another particle. Alternatively the segments further along could be attached to the same particle forming a 'loop'.

A free chain end hanging off a surface, at low polymer dosage, will eventually either form a bridge or a loop. The probability of bridge formation is dependent on the distribution of chain segments in space (the polymer coil configuration and dimensions) and the concentration of

attachment sites in space, set by the particle concentration and the number of attachment points per particle. If the surface of the particle is taken to be flat, a reasonable approximation if the radius of the particle is large in comparison to the dimensions of the polymer coil, and a polymer chain is attached at point B on the surface (Fig.3.1).

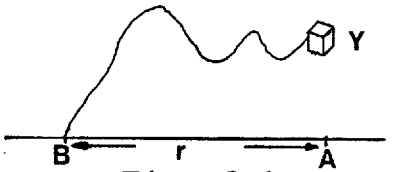


Fig. 3.1

Then along the length of this coil is a group Y, n segments along, each of length l, which can associate with surface site A. From chain statistics the concentration of Y around A can be found,

$$[Y]_{\text{around A}} = \left(\frac{\beta}{\pi^{\frac{1}{2}}}\right)^3 e^{-\beta^2 r^2} \qquad (3.1)$$

where $$\beta = \left(\frac{3}{2cn\,l^2}\right)^{\frac{1}{2}} \qquad (3.2)$$

c is a correction factor for non-ideal coils. If they are m sites like B per unit area then within the area $r \longrightarrow r + dr$ the total number of sites is $2\pi mrdr$. Thus the total concentration of Y groups around A is,

$$[Y]_{\text{around A}} = \left(\frac{\beta}{\pi^{\frac{1}{2}}}\right)^3 2\pi m \int_0^\infty re^{-\beta^2 r^2} dr$$

$$= \frac{m\beta}{\pi^{\frac{1}{2}}} \qquad (3.3)$$

But, there are also Y' groups belonging to chains to other particles which can associate with A. The concentration of these groups is dependent on the number of particles per unit volume and the number of chains attached. The probability of bridging to looping is therefore equal to the relative concentration of Y' to Y.

Thus the probability of bridging =

$$\frac{[\text{particles}] \times (\text{chains per particle})}{m\ \beta/\pi^{\frac{1}{2}}} \qquad (3.4)$$

Thus considering equations (3.2) and (3.4) one can see that as the chain length between surface associating groups increase the probability of bridging increases, i.e. we get improved flocculation as the molecular weight increases.

In a model system to check out such postulations the chain length between attachment points must be known and variable. The best approach would be to have a polymer that only attached at its ends. Also it must be available in a range of molecular weights and its solution properties well characterised. However to get strong single point attachment, to stop rearrangement, would be impossible with any interaction less than a chemical bond. If a chemical link was used between the polymer and the particle the reaction must be fast enough to occur during a particle-particle collision.

The system chosen to fit this scheme was based on polystyrene latex. This was modified by substituting a

known number of reactive amine groups onto the particle. A well established reaction is the chloromethylation of polystyrene and subsequent reaction with a primary amine to form the secondary amine.

A flocculant was prepared based on isocyanate ended polyethyleneoxide polymers. These will react with the amine groups at very low concentrations to high conversions. This system has been used with two linear polymers to investigate polymer networks[73]. Thus a polystyrene latex, crosslinked by divinylbenzene, can be dispersed in an organic solvent, chloromethylated to a controllable level of substitution, and aminated. Isocyanate ended PEG polymers can be made with a range of molecular weights and possibly used to flocculate the polystyrene particles dispersed in an organic solvent. The solution properties of PEG are well known and the chain statistics can be predicted. With such a system the possibility exists to compare the actual bridging efficiency with that predicted, and discover the effect on flocculation efficiency of molecular weight, flocculant concentration and particle concentration.

3.2 The Mechanism of Emulsion Polymerization

In an emulsion polymerization system the monomer is suspended in the water phase and has only limited solubility in that phase. The monomer is normally suspended with the aid of an emulsifying agent, usually a fatty acid salt. The concentration of the surfactant is well above its critical micelle concentration and the

micelles are swollen with monomer. The monomer then is in three forms; a small amount is dissolved to saturation in the water phase, some is in the swollen micelles and the remainder is in monomer droplets, which, if agitation stops, coalesce into a bulk organic phase.

The initiator is completely water soluble and the free radicals are generated in the aqueous phase. The free radical diffuses from the aqueous phase into the micelles to initiate polymerization. The kinetics of this have been laid out by Smith and Ewart[74] in their micellar theory of particle formation, which states:-

1) Polymerization takes place in the micelles not in the monomer droplets, as the micelles have a greater surface area per unit mass for the diffusing radicals.

2) Polymerization in the aqueous phase is very slow due to the low monomer concentration. Normally the oligomeric radical is adsorbed in a micelle. If a reasonable molecular weight is reached the growing polymer precipitates to form a particle.

3) Termination in the aqueous phase is unlikely due to the low radical concentration and all the radicals enter the swollen micelles to form polymer particles.

4) The radical in a particle continues to grow and the particle absorbs more monomer, to keep the particle growing and also to keep the polymer swollen. The water phase is saturated with monomer, so that the monomer flux into the particles originates from the monomer droplet and perhaps from other micelles. Thus the monomer droplets act as an inert reservoir of monomer.

5) It can be calculated from the known termination rate constants that two radicals in a polymer particle will mutually terminate within a few thousandths of a second. This implies that after a radical has entered a micelle it will grow until a second radical enters which terminates the growing chain. Polymerisation will then stop until another radical enters to initiate another chain.

6) Each particle absorbs radicals at a rate proportional to its surface area, thus the smaller particles grow proportionally faster than the larger ones.

7) It is assumed that micellar soap is consumed by two mechanisms: either it is absorbed onto growing polymeric particles, or it becomes "non-micellar" when a micelle absorbs a radical to become a particle. When the micelles disappear because all the soap is absorbed onto the particles, particle nucleation stops.

At the beginning of the polymerization the size distribution of particles is broad due to varying times of nucleation, with some particles nucleating earlier than others. Also, radicals will enter the particles later or earlier than the average time resulting in a Poisson distribution of propagation times and dead times. However as a particle experiences more of these propagation-dead time cycles it should reach an average growth rate for its size.

As the small particles grow faster than the larger ones the size distribution narrows as the polymerization continues after nucleation has stopped. Eventually as most of the monomer is consumed the concentration of monomer in the particles will drop. Termination is known to be diffusion controlled, so that the termination rate constant must decrease with increasing conversion due to the Trommsdorff gell effect. It would follow that the Smith-Ewart assumption of instantaneous termination becomes less likely resulting in an accumulation of radicals in the particles and to a broadening of size distribution.

Experimental support of the Smith-Ewart theories have been provided and are widely accepted[75].

If the latexes made by this method are used as well characterised model colloids the emulsifier that is adsorbed on the particle surface must be extracted. Removal of soap from these conventional latexes by dialysis or by ion exchange is a challenging task[76,77]. This has generated interest in preparing latexes without the presence of an emulsifier, and it has been reported that stable polystyrene latexes can be prepared in this way. The stability of the resulting latex is ascribed to the presence, on the surface of the latex particles, of ionizable carboxyl and sulphonate or sulphate groups resulting from the initiation reaction.

The development of emulsifier free polystyrene latexes may be traced to Matsumoto and Ochi[78] who obtained a narrow particle-size distribution using only monomer and persulphate initiator in water. The role of temperature, monomer concentration, initiator concentration and agitation on the particle size and uniformity was investigated. The strong acid group stabilisation was reported to correspond to two acid groups per molecule on the surface of the particle.

The investigation of these latexes has been pursued by Rotera[79], Furusawa[80], Ottewill[81] and others. The range and number of polymerization variables affecting latex properties have been extended, and now include electrolyte concentration and pH in addition to those already mentioned.

The limitations of the methods available for synthesis of emulsifier-free latex have been, the low final solids concentrations, slow conversion rates, and often low attainable conversions. To overcome this slow conversion rate Hamola, Inoue and Robertson[82] have devised a system where methanol is added to the reaction mixture. This increases the solubility of the monomer in the aqueous phase and thus increases the availability of monomer at the polymerization sites. Methanol also has the advantage of being a non-solvent for polystyrene and can easily be removed after polymerization by stripping or dialysis. At 30% methanol levels their results show a substantial increase in conversion rate and final conversion. The particles produced varied in size from 0.5 to 2.0 μ depending on the methanol, styrene, initiator and electrolyte levels used. The size distributions being very narrow with standard deviations from 7% to 2% of the diameter with increasing size.

They suggest the formation of particles occurs firstly by solution polymerization of styrene, initiated by the thermal decomposition of the potassium persulphate, to form active oligomers which are soluble in the methanol-water phase. The oligomers, which are visualised as having surfactant properties, grow until they terminate by recombination while still soluble, or with growth of the styrene chains they aggregate and precipitate or micellize into particles or nuclei. The particles grow by further aggregation[81,83] and by continued polymerization. Eventually they reach a size

where they swell with monomer taken up from solution, and the site of the polymerization shifts from the solution to the particles. Initiation still occurs in the water-methanol phase and is propagated in the particle by active oligomer particles which diffuse to, and into the particle. A sufficient monomer concentration is also maintained in the particle by diffusion.

This method of soap-free polymerization of styrene in the presence of methanol was used to produce the latexes used in this work. The only modification was the addition of divinyl benzene to some preparations, to produce cross-linked particles which would swell rather than dissolve in organic solvents. Shashoua and Beaman[84] found that for a mole ratio of 0.003 and above of divinyl benzene to styrene, the latex particles were completely crosslinked.

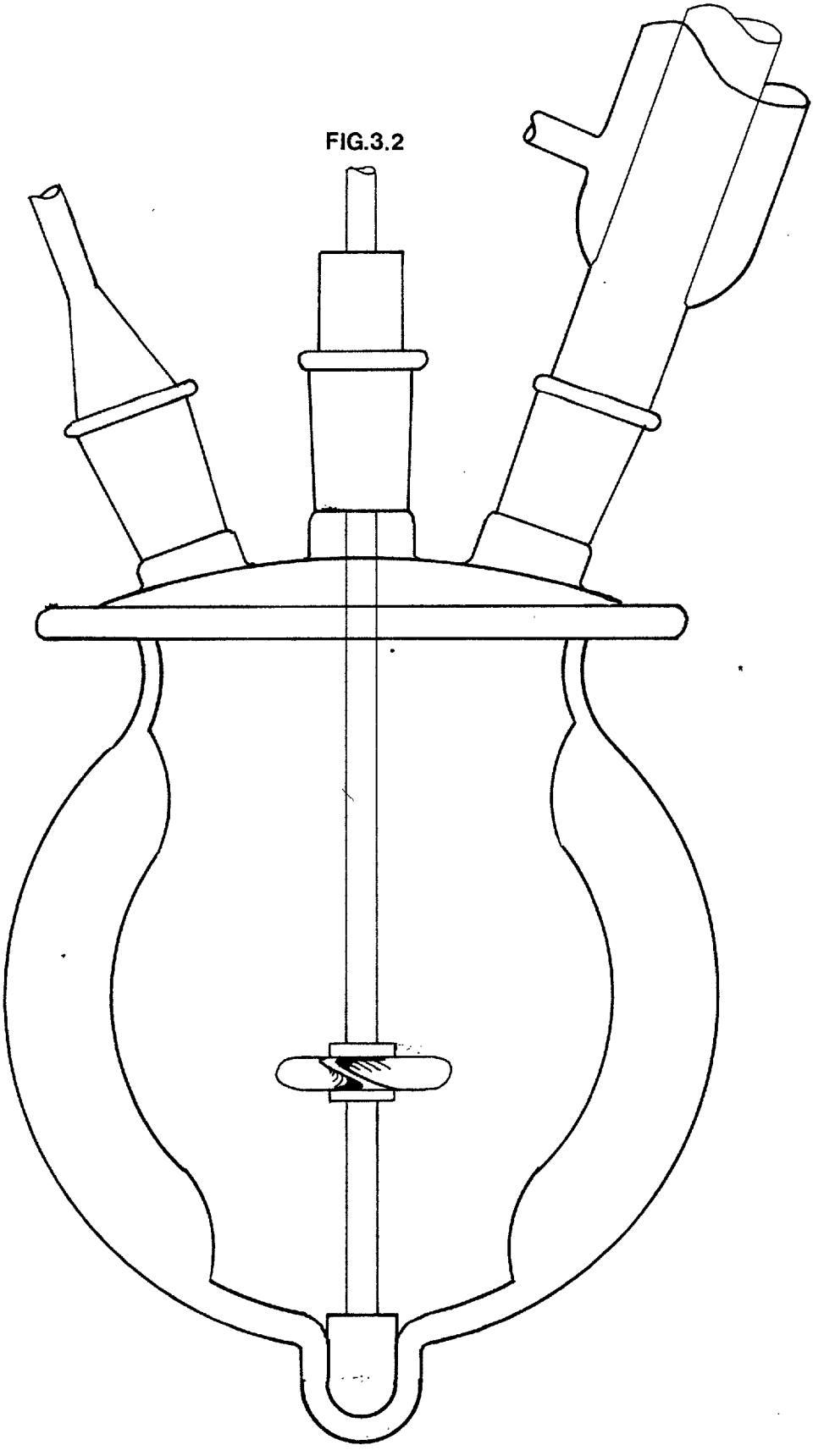
EXPERIMENTAL

3.3 Emulsion Polymerization

The polymerizations were conducted in a baffled round bottom flask (Fig. 3.2) with a stainless steel marine propellor whose shaft ran on a Teflon bearings in the bottom and at the top of the flask. This allowed the mixture to be stirred at a substantial speed (300 rpm), the baffles aiding mixing. The flask was fitted with a nitrogen inlet and a condenser.

Into the flask were placed styrene (redistilled 50 ml) distilled water (300 ml), methanol (150 ml) and divinyl benzene (0.4 ml). These were then mixed with the stirrer to form a

FIG.3.2



greyish emulsion and the flask purged with nitrogen. The flask was then placed in a water bath at 75°C and the initiator potassium persulphate (0.625 g) added.

Within 30 minutes the greyish emulsion changed to a very stable milky white one. The reaction was carried out over ten hours. After this time the latex was cooled, filtered through glass wool to remove any coagulated material and then dialysed (Visking tubing) against distilled water for five days to remove the methanol and initiator.

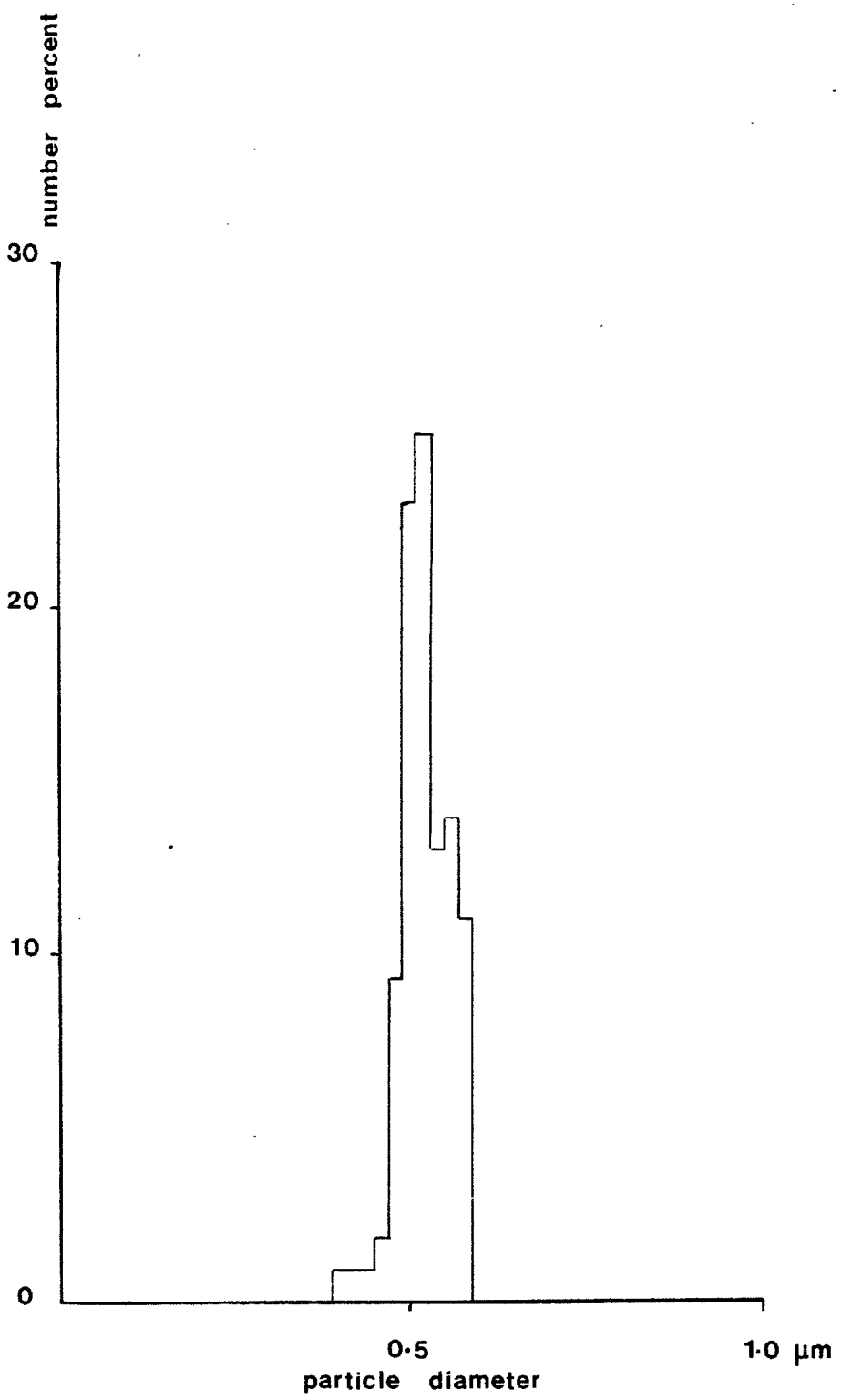
The particle size was determined by electronmicroscopy. A sample of the latex was diluted to a few ppm and a drop placed on a 'Formvar' coated sample grid and dried. The size of at least a hundred particles was determined to obtain the average size.

Other preparations were done by varying the monomer and initiator concentration to produce different size particles the results are summarised in Table 3.1.

per cent monomer in reaction mixture	Styrene:DVB molar ratio	per cent Potassium persulphate in reaction mixture	Mean dia of particles µm
10	1:0.06	0.125	0.53
10	1:0	0.125	0.54
30	1:0	0.125	0.84
10	1:0	0.05	0.21

TABLE 3.1

FIG.3.3



A typical size distribution shown Fig. 3.3, e.g. 0.53 μm mean diameter has a standard deviation of 7% and the ratio of the weight average diameter to number average diameter, $\frac{\bar{D}w}{\bar{D}n}$, equals 1.13. The electronmicrographs of the other latexes showed similar narrow size distributions.

3.4 The Chloromethylation and Amination of Polystyrene Latex Particles

Before any further reactions may be carried out the polystyrene must be recovered from the aqueous suspension and dispersed in an organic solvent (carbon tetrachloride). Drying polystyrene by evaporation or freeze drying and then dispersing the dry powder in CCl_4 with the aid of a whirling blender (Sunbeam Ltd) resulted in an unstable dispersion which settled out, probably due to irreversable aggregation during drying. Successful phase changing was achieved by removing the bulk of the water by centrifugation and then mixing the still very wet slurry of polystyrene with CCl_4. This was followed by azeotropic distillation to remove the rest of the water to produce a stable suspension.

The dispersion (300 ml containing 9 g of polystyrene) was then chilled to ice water temperature and chlorodimethyl-ether (8 ml) added, followed by stannic chloride catalyst (1 ml). After a period of time chosen to produce the desired substitution a dioxan, water mixture (10:1) was added (50 ml) to stop the reaction. Concentrated hydrochloric acid (25 ml) was then added to extract the stannic chloride into the aqueous phase. The mixture was separated and the organic

phase is then run into methanol to precipitate the polystyrene. This was filtered off, washed and while still moist dispersed in benzene using a high shear mixer. The methanol still present was removed by distillation.

The degree of substitution of chloromethyl groups was dependent on the amount of chlorodimethylether and stannic chloride added as well as the reaction time, as shown in Table 3.2.

The chloromethylated polystyrene was then reacted with an excess of n-butylamine (25 ml) at room temperature for three days. The dispersion was then precipitated into methanol and the polystryene dispersed again in benzene.

To determine the degree of substitution a number of methods were used.

(a) The reaction of the substituted amines with 1, -fluoro -2, 4-Dinitrobenzene gives a product that absorbs U.V. at 376 nm. The extinction coefficient was determined by reaction of an aliphatic secondary amine (diethylamine) of known concentration and measuring the U.V. absorption. Thus gave an extinction coefficient in benzene of $1.75 \times 10^7 cm^2/mol$.

To carry out the analysis 1 g of the aminated polystyrene dispersed in 20 ml of benzene was reacted overnight with 0.2 ml, 1, -fluoro -2, 4-dinitrobenzene

in the presence of 0.5 ml triethylamine. The product was precipitated into methanol and then reprecipitated from benzene.

This method is limited to high degrees of substitution as the polymer is in the form of a cross-linked particle and scatters light in the spectrometer, which becomes significant at high polymer concentrations required to detect lower substitutions and generally lowers the sensitivity.

(b) The Infra Red spectra of the chloromethylated polystyrene, measured by preparing a thin film on a sodium chloride plate by evaporation shows the $-CH_2Cl$ absorption at 1260 cm^{-1}. The extinction coefficient for this is known[73] (8.4×10^4 $cm^2 mol^{-1}$) and likewise is the value for the standard 1600 cm^{-1} peak for polystyrene ($E = 1.98 \times 10^4 cm^2/mol$). By comparison of the two absorptions for a sample the degree of substitution can be determined. With this method it must be assumed that all the chloromethyl groups are converted to the secondary amine.

(c) For very low levels of substitution the amine groups of the aminated polystyrene were reacted with carbon-14 labelled benzoyl chloride. Aminated polystyrene (3g) was dispersed in benzene (25 ml) to which was added the labelled benzoyl chloride (0.5 ml) and N,N, di-isopropyl ethylamine (1 ml). This was left for two days at room temperature, after which it was precipitated into methanol

TABLE 3.2

Weight of Polystyrene Particles	Vol of CCl_4	Vol of Chloro-dimethyl ether	Vol of Stannic Chloride	Reaction time (min)	Degree of Substitution	Method of Analysis
10 g	150ml	40ml	0.8ml	25	1:300	U.V.
14	150	40	1.0	60	1:32	U.V.
12.5	100	13	2.0	60	1:8.7	I.R.
12.5	100	13	1.0	60	1:13.8	I.R.
10.0	100	4	1.0	30	1:50	I.R.
12.0	100	4	0.5	30	1:129	I.R.
9.0	300	8	1.0	30	1:1600	C^{14}
9.0	300	8	1.0	30	1:1090	C^{14}

and reprecipitated from benzene. A sample was then dried under vacuum, and the rest reprecipitated and then dried. Samples of known weight (0.5 g) of the second and third precipitated labelled polymer were dissolved in 10 ml of a scintillation 'cocktail', which consisted of 0.3% diphenyloxayole (PPO), 0.03% 1, 4-bis (5-phenyloxayol-2-yl)-benzene (POPO) and 5% napthalene in benzene. Likewise was a sample of polystyrene with a known amount of the labelled benzoyl chloride used and a sample of unreacted aminated polystyrene.

By comparison of the counts obtained from these samples in a liquid Scintillation Counter the extent of substitution of the aminated polystyrene particles can be determined. The close agreement of the activity for the second and third precipitated samples indicated that all the unreacted benzoyl chloride had been removed.

3.5 Preparation of Isocyanate ended Polyethylene Oxide

Two different molecular weights of polyethylene oxide (6,000 and 300,000) were used for the preparation of isocyanate ended polymers. The polymers were first dried. The 6000 molecular weight polymer was dried by bubbling nitrogen through the molten polymer, under reduced pressure at 110°C for six hours. The polymer was then dissolved in dry benzene and freeze dried to azeotrope off the last traces of water.

The 300,000 molecular weight polymer was dried under high vacuum at room temperature for three days. Samples of dry polymer (20 g) were dissolved in dry benzene (300 ml) and reacted overnight with an excess of hexamethylene-diisocyanate (20 ml). They were then precipitated into petroleum spirit (60-80°C B.pt.) which had been dried over calcium hydride, and filtered. The polymers were dried under high vacuum. The precipitation and filtration steps were carried out in a dry box under a nitrogen atmosphere.

To determine if all the chain end groups had been converted to isocyanate the infra-red spectra of the 6000 m.w. polymer in a solution of dry dioxan was obtained. The extinction coefficient for the 1720 cm^{-1} carbonyl absorption of the urethane link was known[73] and used to determine the number of end groups (E = 51000). The spectra for a 5% w/v solution of polymer gave 2.0-2.1 x 10^{-5} mol/ml of urethane links, while a 5% w/v for 6000 m.w. is equivalent to 1.67 x 10^{-5} mol/ml of end groups.

To determine the extent of reaction for the 300,000 m.w. polymer I.R. spectroscopy is not sensitive enough and a carbon-14 method was used. The isocyanate ended polymer (10 g) was dissolved in dry benzene (250 ml) and reacted with 1 ml of C-14 labelled methanol. After two days this was precipitated into ether, filtered off and dried under high vacuum for 7 hours. The polymer was then reprecipitated twice from dichloromethane and dried each time. Samples of the three reprecipitations were dissolved in the scintillation

cocktail mentioned earlier (section b) and the count compared with the labelled methanol used. The results of the counting gave the following equivalent molecular weights (two CH_3O- groups per chain) for the three successive reprecipitations:- 125000, 139000 and 130000. It can be assumed that a constant activity had been obtained and all free labelled methanol had been removed.

To determine the original number of hydroxyl groups per gram of the 300000 m.w. polymer or its number average molecular weight, the unreacted polymer (3g) was dissolved in dry dichloromethane (100 ml) and reacted with carbon-14 labelled benzoyl chloride (0.5 ml) in the presence of N,N, di-isopropylethylamine (0.8 ml). This was left for two days at room temperature and precipitated into ether. It was then reprecipitated from dichloromethane three times. The scintillation count was carried out for the samples from the four reprecipitations and compared with the original benzoyl chloride used to determine the number of polymer ends with attached benzoyl groups. The counts for the four reprecipitations did not reach a constant value as can be seen from Table 3.3, showing the equivalent molecular weights for the four precipitates.

Precipitation	Molecular weight
1	43,000
2	167,000
3	256,000
4	271,000

TABLE 3.3

This was probably due to hydrolysis of the ester link and loss of the benzoyl groups from the polymer ends reducing the count after each precipitation. Thus no guide to the molecular weight can be taken from this experiment.

3.6 Determination of the Maximum Number of Chains that can be attached to the Polystyrene Particles

To determine the maximum number of high molecular weight PEG molecules with isocyanate end groups that can be attached to the partially aminated polystyrene particles (0.53 μm unswollen diameter, 1 in 1090 substitution of amine groups), the particles were reacted in dry benzene with a great excess of the PEG polymer and left for a few hours. After this the free isocyanate groups were reacted overnight with carbon-14 labelled methanol and the particles precipitated into methanol, filtered, washed with methanol and reprecipitated from benzene.

The number of labelled CH_3O-groups associated with the polystyrene particles through the attached PEG chains were estimated by scintillation counting of the two precipitates and the original methanol used. This was found to have a constant value of 2.0×10^{-6} moles per gram of polystyrene or 9.12×10^{4} polymer chains per particle. Each chain has then 960 Å^2 of surface area relative to the unswollen diameter of the particle. It is worthwhile noting that each particle initially had 4.27×10^{5} reactive amine sites.

3.7 Flocculation Reaction

Varying amounts of the isocyanate ended polyethylene oxide polymer were added to the aminated polystyrene particle dispersion in benzene to try to bring about gross flocculation. The particle dispersion (10 ml) was placed in a dry test tube with a glass stopper. A particle concentration of 0.05 g/ml was used, that is 7.6×10^{11} particles/ml of 0.53 μm diameter spheres with 1 in 1090 substitution. The PEG polymer was added by pipette from a stock solution. Both the 6000 and 300,000 molecular weight polymers were tried, over a range of dosage equivalent of 10^2 to 10^4 chains per particle.

No indication of flocculation was evident in terms of settling of the dispersions at any polymer dosage tried. It was suspected that the particles were not free of electrical charge and that this charge was interfering in the flocculation process. Attempts were therefore made to measure the charge on the particles.

3.8 Measurement of Particle Charge

To estimate the electrostatic repulsive forces between the polystyrene particles dispersed in an organic solvent an attempt was made to determine the surface potential. Although the dissociation of ionic species is very small in a medium with a low dielectric constant the electrolyte concentration is also very low resulting in very little screening of the charge. The overall effect is that the low surface potential decays very slowly with distance and the repulsive forces exist over greater distances.

The expression for the repulsive potential energy, V_R for small κ has been derived in Chapter 1 (equ. 1.16) Also since the ion concentration is so low the potential at the particle surface and the shear plane for electrokinetic measurements will be the same, so $\psi_o = \zeta$ the zeta potential. This gives the equation:-

$$V_R = \frac{4\pi \varepsilon a^2 \zeta^2}{R} \qquad (3.5)$$

To estimate V_R electrokinetic measurements must be carried out to determine the zeta potential. In the case of organic liquids κa is small so the Huckel equation (1.26) can be used to relate the electrophoretic mobility to the zeta potential.

Electrokinetic measurements are simple to carry out in an aqueous system but with a non-aqueous one the difficulty is to obtain a homogeneous electric field, a field which is constant throughout the electrophoresis cell. If the electric field is not constant polarisation effects will occur: particles having a higher dielectric constant than the continuous phase will always move to the place of highest field energy. The velocity of this displacement is proportional to $\frac{\alpha}{2} \frac{dE}{dx}^2$ in which α is dependent on the difference between the two dielectric constants and x is a distance. The fact that this velocity is proportional to the second power of the electric field E, whereas the electrophoretic velocity is proportional to the first power of E means that at lower field strengths electrophoresis wins. If a homogeneous field exists $\frac{dE}{dx} = 0$.

The electric field strength is the voltage applied across the two electrodes of the cell divided by the path length taken by the charge carrier. In the case of a non-aqueous system both the zeta potential and the dielectric constant are less than that for an aqueous one, this means for the same resultant velocity a much greater field must be applied. If the distance between points on one electrode and ones on the other are not the same this will result in a variation in E across the cell perpendicular to the direction of the field. This is not important in the case of aqueous systems where the applied voltage is much smaller.

Another factor is that the conductivity of organic liquids is very low and not much greater in magnitude to that of glass. The outcome of this is that some of the electric current finds its way through the glass walls of the cell, causing a non-homogeneous field to be set up.

To overcome these effects various cells have been designed. Germant[85] worked with a system where the particles and the liquid have very similar dielectric constants (polystyrene and hydrocarbon mixtures). He also devised a cell that had a separation between the electrodes which was much less that the distances between the electrodes and the cell walls. The result was that the resistance between the electrodes through the liquid is less than through the glass walls.

Van der Minne and Hermanie[86] used a thin wall cappilary tube as a cell, where the cross-sectional area of the liquid

was greater than that of the glass. They also found if the tube was placed in an evacuated chamber they got a better result which they put down to surface conductivity on the outside of the glass, if the chamber was filled with alcohol no electrophoresis was observed as all the field was leaking away. Coating the outside of the tube with silicone oil and oven-baking is known to eliminate surface conductivity and was also done, improving the result.

Using quartz rather than glass has the advantage that it has a much lower conductivity. In fact quartz cells designed for aqueous dispersions can be used for organic dispersions where the liquid's conductivity is not very low, e.g. acetone, nitrobenzene and methanol.

The electrophoretic mobility of the aminated polystyrene particles dispersed in butanone (1.4×10^{-4} g/ml) was measured in a flat quartz cell (Fig.3.4) mounted on a Rank microelectrophoresis apparatus. The cell was thermostated at 25°C in a bath of iso-octane. The movement of the particles was viewed through the ultramicroscope of the apparatus and the velocity determined by measuring the time for a particle to cross a grid square of the graticule in the eye piece. The velocity of ten particles were taken with the field applied in one direction and ten with it applied in the opposite direction. A field of 10.34 v/cm was applied during the measurements. The velocity was determined at various depths in the cell to determine the velocity profile (shown in Fig.3.5) since both electrophoresis and electro-osmostic effects occur. A pure electrophoretic mobility of

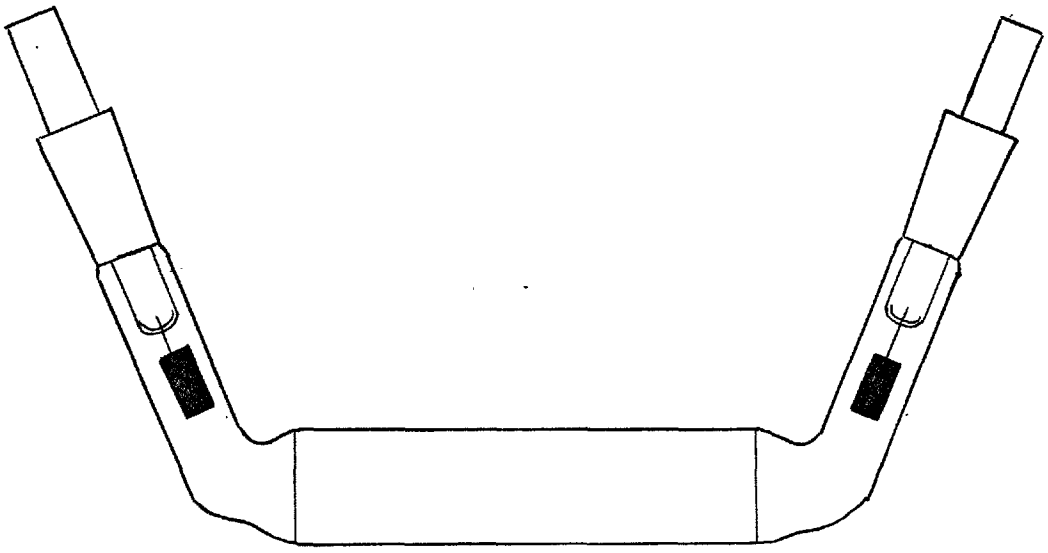


FIG.3.4

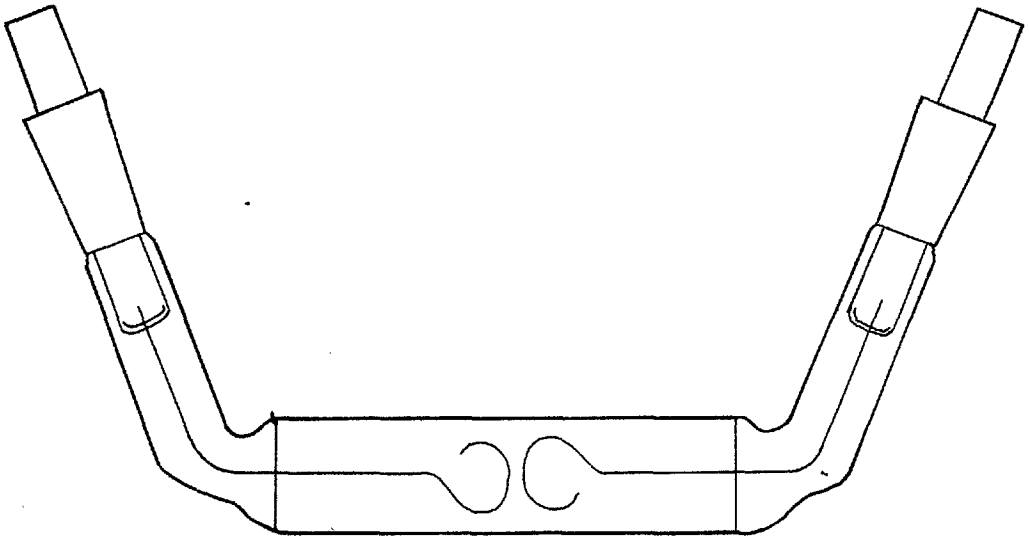


FIG.3.6

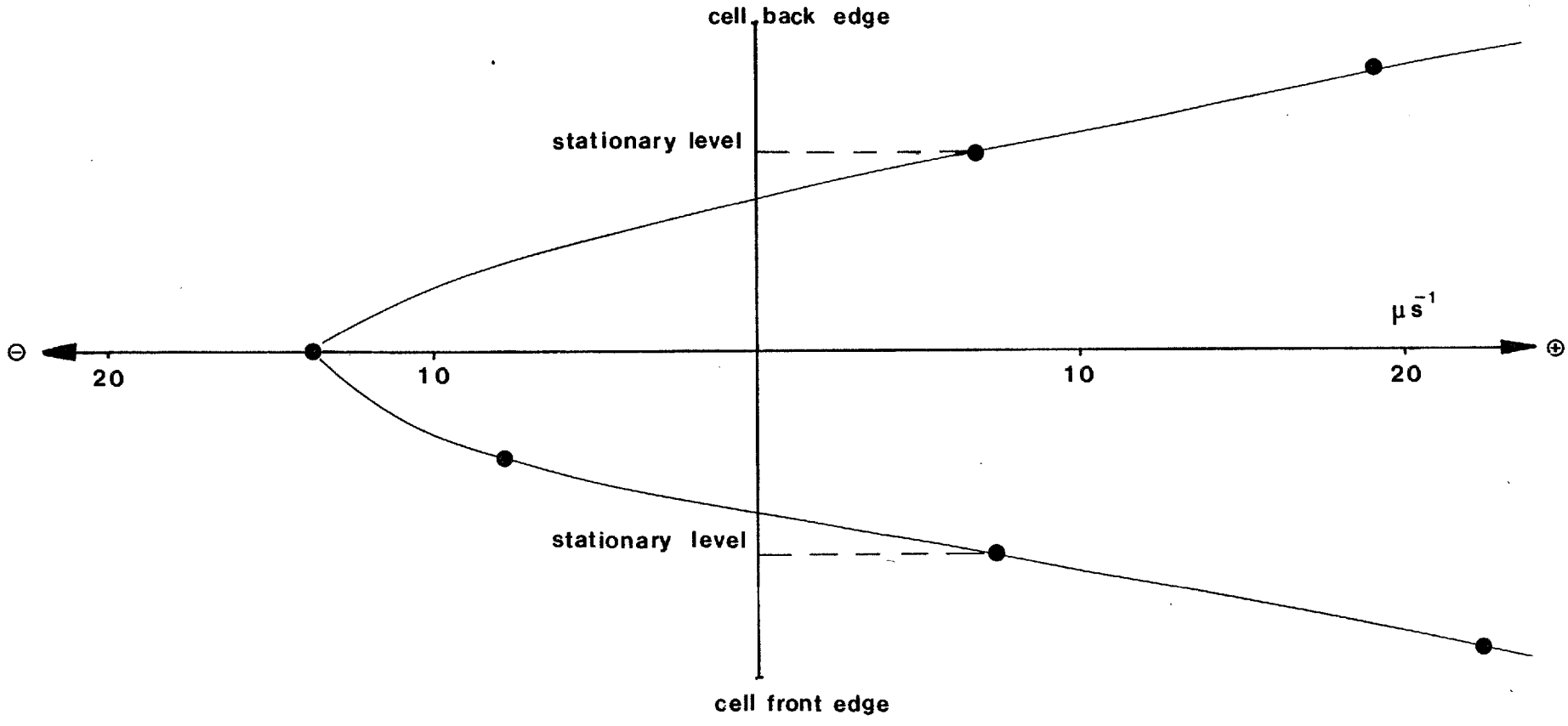

cell back edge
stationary level
μs⁻¹
⊖
⊕
20
10
10
20
stationary level
cell front edge

FIG.3.5

0.68 $\mu s^{-1}/v\ cm^{-1}$ was measured, equivalent to a zeta potential of 57 mV. Applying equation (3.5) for two particles whose surfaces are 1000 Å apart, V_R = 100 kT.

The experiment was repeated with the aminated polystyrene dispersed in benzene but polarisation effects were evident with particles rising to the top of the cell, as well as moving towards the correct electrode. Nitrobenzene was added to give a dispersion in a 5% nitrobenzene in benzene mixture. This improves the conductivity of the liquid phase without greatly changing the dielectric constant (ε_r = 3.2, for benzene ε_r = 2.3). A field of 288 V/cm was applied and no polarisation effects were seen. The mobility measured was 2.78 x 10^{-2} $\mu s^{-1}/V\ cm^{-1}$ giving ζ = 13.4 mV and at a 1000Å separation V_R = kT.

The electrodes of the quartz cell were changed to the form used by Gemant (Fig.3.6), the electrode separation was only 2.72 mm compared to 7.63 cm previously. The electrophoretic mobility of the aminated polystyrene dispersed in the 5% nitrobenzene in benzene was measured again, a potential of 30 V was applied. A mobility of 0.170 $\mu s^{-1}/V\ cm^{-1}$ was obtained, giving a zeta potential of 82 mV and a predicted value of V_R = 34 kT at a 1000 Å particle-particle separation.

A cell of the type devised by van der Minne and Hermanie was constructed (Fig. 3.7). The 2 mm internal diameter capillary tube used was made of glass and had a 4 mm outside diameter. Two flat surfaces were ground on the

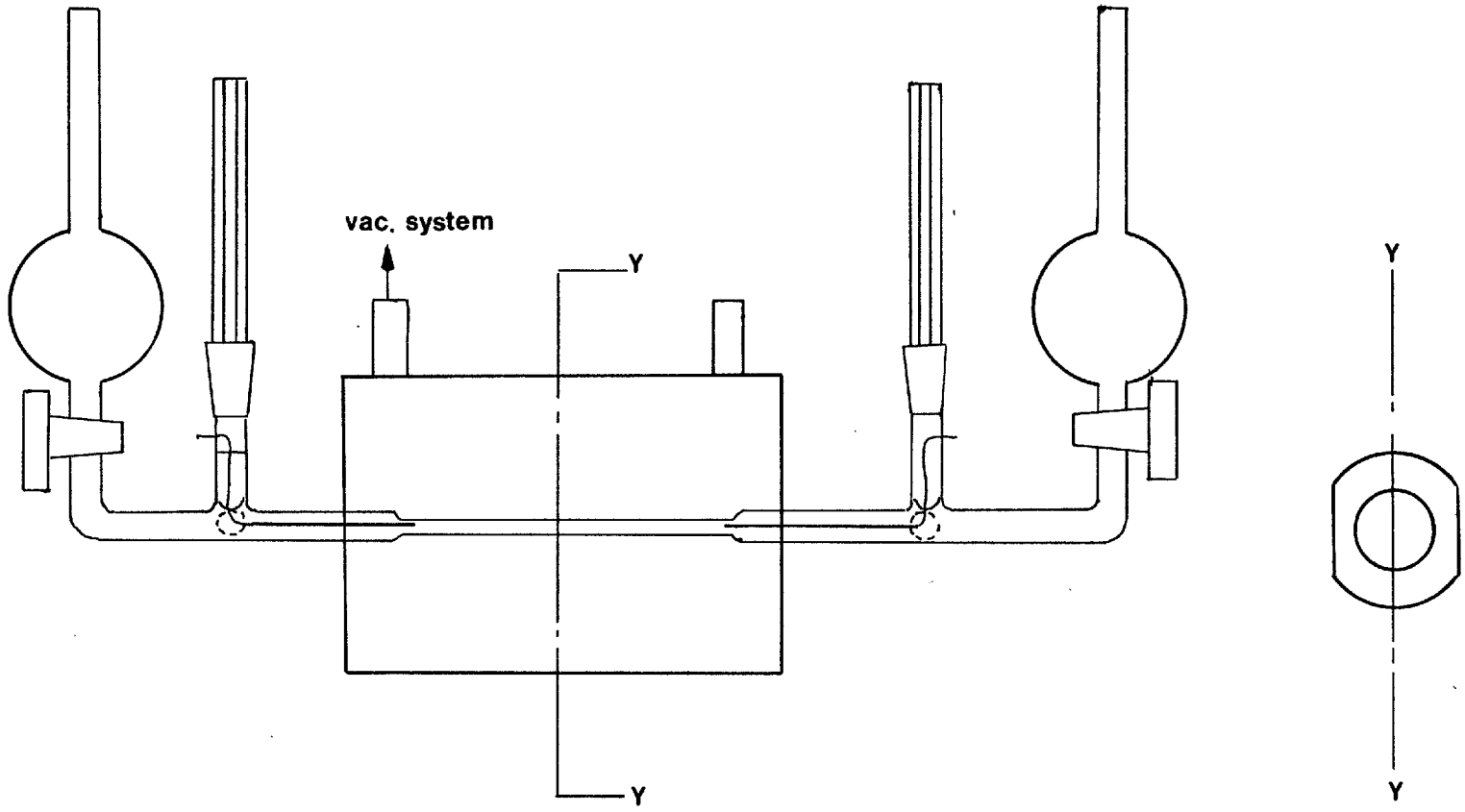


FIG.3.7

tube to reduce the lens effect and make it possible to see the back of the tube to determine all of the velocity profile. The outside of the tube was treated with silicone oil at 390°C for 30 minutes. The cell was mounted on the Rank microelectrophoresis apparatus and measurements made on the aminated polystyrene in the nitrobenzene-benzene mixture. A voltage of 420 V was applied (E = 110 V/cm), but polarisation effects were observed with the direction of movements of particles independent of the direction of the field.

It is obvious that some charge exists on the particles though it is difficult to measure its magnitude.

3.9 Discussion

(a) Preparation

Emulsion polymerization was successful in producing particles well characterized in shape and size. A narrow size distribution was always obtained. At low conversions a wider distribution could be obtained, but it was never observed in practice. When the latexes are sized by electronmicroscopy then they are seen as close packed ordered arrays as well as single independent particles. These groups of particles normally are only one particle high but can involve up to tens of particles in the flat plane. The packing of the particles is thought to occur during the drying of the sample but it is difficult to tell from the electronmicrographs if any aggregates of particles exist in the aqueous dispersed state. It has been assumed that coagulated particles in the aqueous phase would appear in the electronmicrographs as "clumps" of particles, built up in three dimensions rather than two dimensional arrays. It could be imagined that as the latex is dried on the sample grid the particles move to stay in the wet phase rather than be left dry and as they do they come closer together, held apart by their electrical charge. As the water evaporates the dissociated ions causing the surface charge will move towards the particle surface reducing the charge, allowing the particles to approach and finally contact.

It can be seen that the weight-average diameter to number-average diameter ratio for the particles obtained

by electromicroscopy and the particle counter (Chapter 2) are reasonably close (1.13, 1.18). The close agreement on the width of the size distribution would imply that very few aggregates occur in the aqueous dispersion, as the value from the particle counter is for the aqueous dispersion and the value from the electromicroscopy was obtained assuming no aggregates existed.

Transferring the polystyrene particles from an aqueous to a non-aqueous dispersion without any coagulation was not a simple procedure. In the two different liquid phases different forces keep the particles apart, in the aqueous one electrostatic forces exist, and in the non-aqueous one it was thought principally osmotic forces were at work since the crosslinked particles are swollen in the organic solvent. However if the latex is allowed to dry out the particles are irreversibly aggregated, since no surface charge will exist when the counterions are not solvated and Van der Waals attractive forces will be large. Also the polymer chains at the surface of the touching particles may entangle in each other. The procedure used of centrifuging off the bulk of the water and azeotropically distilling off the rest, after adding benzene does not allow the particles to dry out and a repulsive force always exists between the particles. Thus a stable dispersion was obtained.

The chloromethylation reaction was varied in terms of reactant concentrations and reaction times to get different levels of substitution. In very general terms it would seem

that the reaction time has a marked effect on the level of substitution, it was noticed in one case that increasing the time from 25 to 60 minutes increased the level of substitution by a factor of ten. This could be explained with respect to some sort of inhibition period which would reduce the actual time the reaction is occurring over. In this case the comparitive reaction times between the two cases could be different by a much larger factor.

The polystyrene particles which had been chloromethylated to high levels of substitution tended not to be so readily redispersed after they had been aminated. The reason for this effect may be that the whole of the particles are covered in amine groups, since it is unlikely that these groups are uniformly substituted through the whole volume of the particle. If the surface of a particle was completely covered with amine groups it would change the solubility characteristics of it. If the fully aminated polymer did not swell in the solvent the particles would precipitate. For this reason samples with lower levels of substitution were prepared. When these particles reacted with an excess of isocyanate ended polymer about a fifth of the amine groups substituted were found to have reacted with the polymer. This would imply that at least a fifth of the groups which were substituted were on the surface.

The experimental techniques devised to determine the level of substitution had varying degrees of success. The Ultra Violet spectroscopy method was very limited because

of scattering of light from the particles in the sample. Even with the reference cell filled with standard polystyrene which should scatter the same amount the method was not successful for detecting low levels of substitution. The Infra-Red spectroscopy method was a straight forward one and only limited by the extinction coefficients of the groups.

The carbon-14 technique of analysis at low substitution gave good results. A constant activity was reached after successive precipitations of the polystyrene. This would imply that neither any unreacted benzoyl chloride was left in the microgel nor were any of the amide links being hydrolysed. The polystyrene was not found to 'quench' the activity greatly, only a difference of about 5% was found in the activity of the standard benzoyl chloride with and without polystyrene present. However this effect may cancel out when comparing counts all made in the presence of the polymer particles.

The preparation of the isocyanate chain ended polyethylene oxide molecules would seem to be effective from the analysis of the polymers produced. The interesting fact is that for both the 6000 and the 300,000 molecular weight polymers the analysis of the reaction product indicate more chain ends than the original polymer molecular weight would imply. In the case of the 300,000 molecular weight polymer the difference is about a factor of two. The figures of 6000 and 300,000 (quoted by supplier) are possibly weight average molecular weights while the end group analyses gives a number average molecular weight.

The weight average molecular weight can easily be twice that of the number average value. To check this the hydroxyl end groups of the 300,000 m.w. polymer were counted by reaction with C^{14} labelled benzoyl chloride but successive reprecipitations did not lead to a constant activity which suggests the benzyol groups were being hydroylsed and coming off the chain ends.

Reacting the aminated particles with the excess of isocyanate ended polymer showed that it is possible to get the reaction between the two species to occur. Using an excess made it possible to detect the chains attached to the particle by labelling their free ends, obviously there was little chance of both ends of a chain being attached to one particle or even another particle. The surface area per attached chain was estimated at 960 $\text{A}^{\circ 2}$ although this was relative to the unswollen diameter. The swollen diameter from the work of Shashoua and Beaman[75] could be about double the unswollen diameter.

(b) Particle Charge

The results of the electrophoresis experiments indicate why no flocculation could be obtained in this system. Although the techniques used are not numerically accurate and it is difficult to be definite that no effects other than electrophoresis are occurring it is certain that the particles are charged. In the experiment measuring the electrophoresis in butanone true electrophoresis was seen and the estimate of the zeta potential (57 mV) is good. A zeta potential

of this magnitude even in water would create a substantial barrier to flocculation and in butanone with its lower dielectric constant,low electrolyte concentration (and thus little charge screening) there is no chance of the particles approaching within the 1000 Å of each others surface required for bridging (a 1000 Å is a reasonable approximation to the end-to-end distance of a 300,000 m.w. P.E.O. molecule). When the polystyrene is dispersed in benzene which has a lower dielectric constant than butanone the dissociation of the surface ionic groups will be less and the surface charge will be less, but due to the lower dielectric constant the charge will be more effective.

The electrokinetic measurements in benzene were upset by the low conductivity of the liquid. This was partly overcome by adding nitrobenzene. This might explain why the mobility when the electrodes were far apart was less than when they were close together in the second type of cell, since when they are far apart the resistance to electrical current through the quartz cell is comparable with that through the liquid and this loss of current reduces the electric field acting on the particles. But in both experiments no polarisation effects were seen and the electric field appeared to be homogeneous in this respect. The apparatus designed by Van der Minne and Hermanie which was also tried was not acceptable with very obvious polarisation effects. This possibly is due to the fact that the capillary was made of glass which is relatively quite conductive and the liquids being used in this work were

lower in conductivity than the ones used by the above workers in this type of cell. The cell would probably have been better with a quartz capillary but such a capillary with a concave surface, required to view the lower depths of the cell, was not available.

It must be accepted that a large electrostatic force exist between these polystyrene latex particles dispersed in organic liquids of low dielectric constant. The actual magnitude has not been absolutely measured but the indications show that the forces are in the range which easily prevent particles moving under Brownian motion approaching within polymer bridging distance of each other.

To reduce the charge by the addition of an oppositely charged species is not as simple as in the aqueous case. Firstly few electrolytes will dissolve to an appreciable concentration, only surfactant type molecules with a long oil soluble chain can do this. The quaternary tried, benzyl dimethyl n-hexadecyl ammonium chloride did coagulate the particles by reducing the charge on them but only over a very narrow concentration range, above which it probably reverses the sign of the charge. The quaternary unfortunately upsets electrophoresis measurements, when present polarisation effects are seen. This may be due to the great affinity this species has for glass surfaces which it firmly adsorbs onto and in this case could increase the surface conductivity upsetting the electric field. The result was that no reliable control could be achieved over the surface charge.

(c) Flocculation

The theoretical model devised predicts most of the important factors effecting polymer bridging. It displays the increasing bridging efficiency with increased molecular weight or chain length, an accepted fact. In also shows the importance of particle concentration, implying an increase in bridging with an increase in this concentration. This has been shown in the other systems considered in this work. However it is a very simplified model and does not consider the factors which resulted in the failure of the model system investigated. It assumes the concentration of reactive chain ends associated with other particles around a free reactive site on a particle surface is the average concentration for the system for these free chain ends. The fact that repulsive forces exist between particles exclude reactive chain ends linked to other particles from the volume around the reactive particles sites to some degree. If the repulsive potential is small at separation distances equivalent to the end-to-end length of the polymer coils then the assumptions of the model are acceptable. In the experiment used to review the model theory this was not the case with large repulsive forces reducing the concentration of bridging chains to virtually zero.

To achieve the objectives with the model system devised a reasonably sized and characterisable double layer is needed. Such a double layer would keep the particles separate and stable but be small compared with the dimensions of the polymer chain and thus not appreciably interfere with

the bridging mechanism. This would require the use of a liquid phase of high dielectric constant which did not interfere with the chemistry of the system.

It may thus still be possible to achieve in general outline a system which conforms to our objectives but many difficulties might arise. For example most high dielectric constant liquids would be difficult to purify to the extent needed for the chemistry of the system developed to be 100% effective.

This was not persued further in this work, instead we switched our attention to aqueous systems which meet some but not all of the specifications required of an ideal model flocculation process.

CHAPTER 4

4.1 AQUEOUS SYSTEMS

Flocculation processes in aqueous systems have two general types of mechanism. Firstly in the case of non-ionic polymers which rely on physical adsorption onto to the particle surface and can link particles together at low dosage, while at high dosage stabilise the particles due to steric effects. Secondly is the case of polyelectrolytes which form an electrostatic interaction with the particle surface (assuming they have opposite charge). This association will result in some reduction in the surface charge and may lead to coagulation by this process. Also at low dosage chains could bridge between particles to form flocs. At high polyelectrolyte concentrations the particle surface charge can be reversed and all the available association sites for the polyelectrolyte are blocked to bridging chains.

It would be worthwhile to investigate examples of these two catogaries of systems which are in a well defined form. Such a system of the polyelectrolyte type is the flocculation of polystyrene latexes with a cationic polyelectrolyte, normally a polyquaternary. As stated earlier these latex particles are well characterised in terms of size and shape, and their electrostatic charge is easily obtained by electrophoresis measurements. The polyelectrolyte must be available in a range of molecular weights and in this work a quaternary was used made from polydimethylaminoethylmethacrylate which can be polymerized to different degrees. Also the charge density or number of charged groups on the polymer chain must be known.

In such a flocculation system the effects of features like molecular weight of the polymer, the size of the latex particles and the concentration of the latex particles on the aggregation of particles are of interest. The influence of these parameter may give more insight into the flocculation process.

Particle concentration is of importance because it determines the frequency of particle-particle collisions and hence the time that an attached chain on a particle has to arrange itself before it comes in contact with another particle. The longer this arrangement time obviously the flatter the configuration the chain will adopt as it collapses down onto the oppositely charged surface and the less likely it is to form a bridge. A variation of particle concentration and the resultant change in particle stability at the same relative polymer dosages could show if bridging was the cause of flocculation. If no bridging occurs and the polymer was collapsed onto the particle surface, reducing the charge, and thus causing flocculation, no change would be seen with variation of particle concentration. This was the result obtained by Gregory[87] when flocculating polystyrene latexes with low molecular weight polyimine. He observed no change in stability with particle concentration and interpreted this as charge neutralisation not bridging.

A model non-ionic system is more difficult to arrange since the colloids that form these type of interactions are not of regular shape or size, the commonly used ones are

Kaolin and precipitated calcium carbonate. These also have a density which is not close to that of water like polystyrene and they therefore tend to settle.

Kaolin may be flocculated by polyacrylamide which can be prepared in a range of molecular weights. This sytem has been investigated by a number of workers but some investigation is worthwhile to compare results with those from the polyelectrolyte system.

The flocculation process can be followed as a reduction in the particle number using the particle counter discussed earlier. This will allow a more detailed and accurate study of the process, especially in the regions where little actual flocculation is taking place but where dimers and trimers are being formed.

4.2 Electrophoresis of Polystyrene Latexes

The electrophoretic mobility of the 0.54μ latex was determined so the size of the electric double layer and the repulsive energy could be estimated. Also the mobility was measured after an amount of the polyelectrolyte had been added which was greater than that to flocculate the colloid but resulted in a stable latex (5.51×10^{-3}g of 388,000 m.w. per gram of Polystyrene) to determine the charge on the particles at this point. The mobilities were measured on a moving boundard apparatus. A diagram of the cell, which was based upon a design of Kerker, Bowman and Matijevic[88], is given in Figure 4.1.

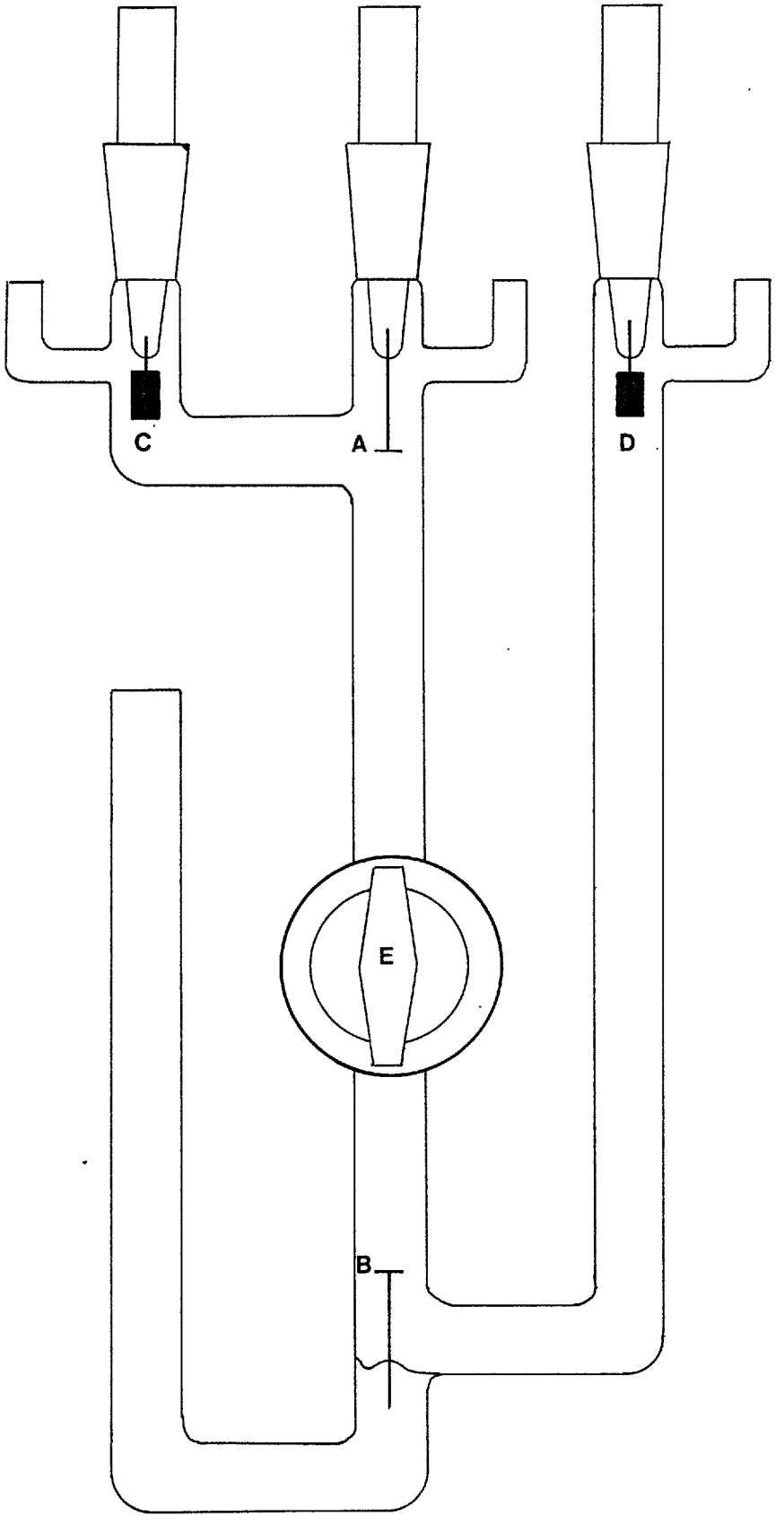


FIG.4.1

The stopcock E, which was made of Teflon, was drilled to give a hole of the same diameter as that of the uniform bore tube AB. The mean internal diameter over the length AB, was 7 mm. The electrodes for the application of potential (C and D) were made from platinum foil which was rolled into a cylinder. The electrodes for the measurement of potential were made from platinum discs (A and B). The distance between the electrodes was 17.509 cm. The latex dispersion (9.41×10^{-4} gm l^{-1}) was introduced via the limb D until the stopcock E was completely filled and then the stopcock was closed. After removel of excess dispersion from above the stopcock, the supernatant liquid was introduced, then after temperature equilibration the boundary was formed by slowly opening the stopcock. The potential was applied across C and D and the migration of the boundary measured using a cathetometer over a period of time, Fig. 4.2 shows the plot of height against time for the two latex samples to be linear. The supernatant fluid was as near as possible in electrolyte concentration (5.16×10^{-4}M NaCl) to the interparticular fluid of the latex dispersion. The density of the polystyrene latex dispersion was sufficiently close to that of the supernatant electrolyte that great care was required to form a stable boundary. To facilitate the rapid formation of a sharp boundary 0.5% sucrose was added to the dispersion. Ottewill and Shaw[89] have shown that 0.5% sucrose has a negligible effect on the mobility of polystyrene latexes.

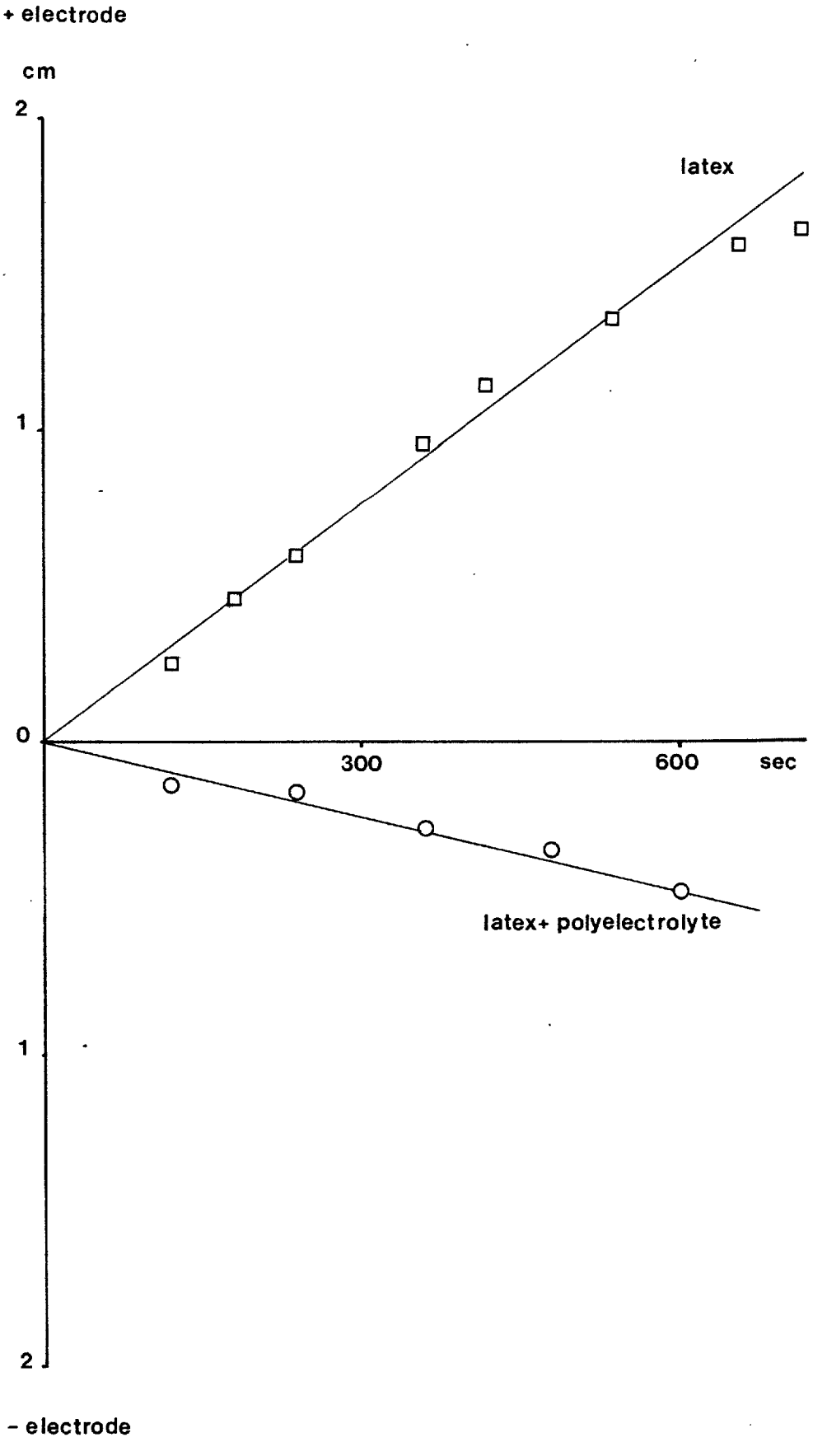

+ electrode
cm
2
1
0
1
2
latex
300
600
sec
latex+ polyelectrolyte
- electrode

FIG.4.2

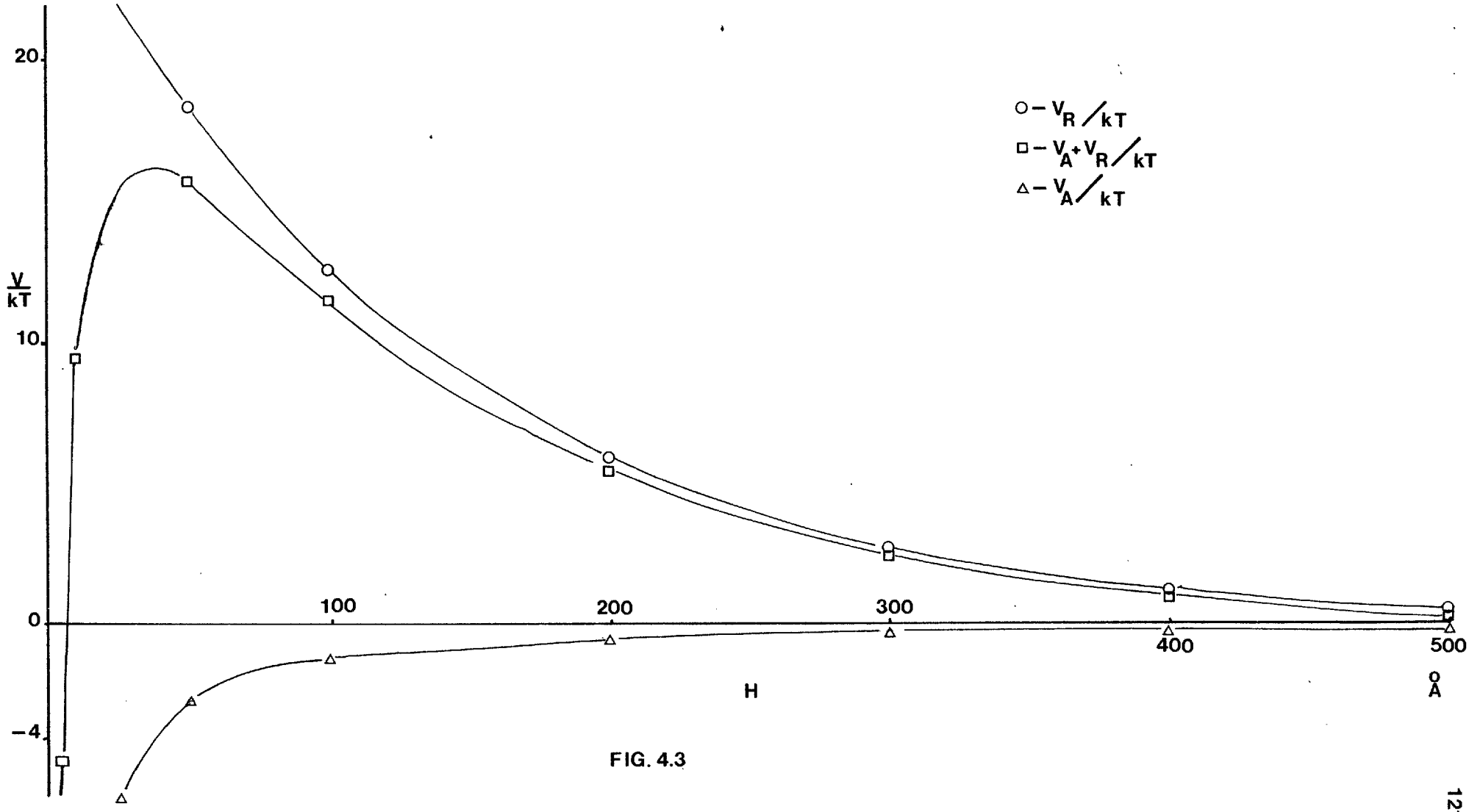


FIG. 4.3

The potential across AB was measured on a digital voltmeter and the potential across CD adjusted to give a reasonably boundary velocity. A potential across AB of 107 V was used for the initial latex and a mobility of $-4.09\ \mu s^{-1}/V\ cm^{-1}$ was measured. While a potential for the latex with the polyelectrolyte of 174 V in the reverse direction, was used and a mobility of $1.02\ \mu s^{-1}/V\ cm^{-1}$ was measured.

Using equation (1.33) and the mobility of the latex, the zeta potential can be calculated (ζ = 52.7 mV). Applying equation (1.14) the value of V_R/kT was calculated for a range of particle-particle distances, H and the results plotted in Figure (4.3).

The attractive potential energy V_A was also calculated using equation (1.22) and the Hamaker constant $A_{1(2)}$ (3×10^{-21} J) determined by Ottewill and Shaw[90].

4.3 Polymerization of Dimethylamino Ethylmethacrylate

The polymer was prepared by polymerizing the monomer in solution using Azobisisobutyronitrile as an initiator. The reaction conditions were varied in the three preparations carried out to give three different molecular weights.

The three reactions were carried out by dissolving the monomer in a solvent and adding the initiator, the quantities used are shown in Table (4.1). The reaction mixtures were then heated to 80°C overnight in a water-bath with reflux when required, under a nitrogen atmosphere. The reaction mixtures were precipitated into petroleum spirit (60-80) and the recovered polymers dried under vacuum.

TABLE 4.1

Weight of Monomer (grams)	Volume Solvent (ml)	Weight of Initiator (grams)
12	108 acetone	0.2
50	150 butanone	0.1
60	40 butanone	0.022

4.4 Characterisation of Poly(dimethylamino ethylmethacrylate)

Molecular weight and chain dimensional information may be obtained indirectly from measurements of the flow of a polymer solution through a capillary tube. The presence of a small amount of polymer in a large volume of solvent has a considerable effect on its viscosity.

Assuming Poiseuille flow[91] in the capillary tube, the coefficient of viscosity η may be related to the flow time of the solution t by the equation

$$\eta = A^1 \rho t \qquad (4.1)$$

where A^1 is a constant and ρ is the density of the liquid ($g\ cm^{-3}$). When dealing with polymer solutions, it is convenient to define the parameters

(i) the reduced viscosity η_r by $\eta_r = \eta/\eta_o$

(ii) the specific viscosity η_{sp} by $\eta_{sp} = \eta_r - 1$

$$= \frac{\eta - \eta_o}{\eta_o}$$

where η_o is the coefficient of viscosity of the solvent.

In polymer systems $\frac{\eta_{sp}}{c}$ is found to be a function of the polymer concentration c and to approach a finite limit as the concentration tends to zero. The limiting value of viscosity is known as intrinsic viscosity $|\eta|$ defined as

$$|\eta| = \lim_{C = 0} \left(\frac{\eta_{sp}}{C}\right)$$

which is a characteristic of a given solute/solvent system.

The determination of the concentration behaviour for dilute solutions is therefore based on an expansion in concentration, and several similar empirical expansions have been proposed, each with its own appropriate definition of intrinsic viscosity. Theoretically, all the expansions should reduce to a common value of viscosity at zero concentration.

Two of the empirical equations will be used for extrapolation:

(i) The Huggins relationship[92]

$$\frac{\eta_{sp}}{C} = |\eta|_H + K_H |\eta|_H^2 C$$

where K_H is the Huggins constant.

(ii) The Kraemer relationship[93]

$$\frac{\ln \eta_r}{C} = |\eta|_K + K_K |\eta|_K^2 C$$

where K_K is the Kraemer constant. The appropriate definitions of intrinsic viscosity are

$$|\eta|_H = \lim_{C = 0} \frac{\eta_{sp}}{C}$$

$$|\eta|_K = \lim_{C = 0} \frac{\ln \eta_r}{C}$$

Using equation (4.1) the parameters η_{sp} and η_r may be written in terms of the flow times t for the solution and t_o for the solvent. For dilute solutions the density of the solution may be taken as equal to that of the solvent, so that

$$\eta_{sp} = \frac{t - t_o}{t_o} \qquad \eta_r = \frac{t}{t_o}$$

It has been recognised that the intrinsic viscosity is proportional to a power of the molecular weight somewhat less than 1. The relation is expressed in the equation.

$$|\eta| = K M^{\alpha}$$

where K and α are constants determined from a double logarithmic plot of intrinsic viscosity and molecular weight. Both K and α are functions of the solvent as well as of the polymer type.

Intrinsic viscosity measurement leads to the viscosity-average molecular weight, defined by the equation (Schaefgen 1948).

$$\overline{M}_v = \left[\sum_{i=1}^{\infty} W_i M_i^{\alpha} \right]^{1/\alpha} = \left[\frac{\sum_{i=1}^{\infty} N_i M_i^{1+\alpha}}{\sum_{i=1}^{\infty} N_i M_i} \right]^{1/\alpha}$$

Thus $\overline{M}_v$ depends on α as well as on the distribution of molecular species.

The K and α values for Poly(dimethylaminoethyl-methacrylate) were found in the literature[94] ($K = 5.78 \times 10^{-4}$ dl g^{-1}, $\alpha = 0.5$ at 25°C in benzene). The viscometry measurements were carried out in a Ubbelohde viscometer, this has the advantage that the measurement is independent of the amount of solution in the viscometer and successive dilutions can be carried out in the viscometer to obtain measurements at a series of concentrations.

The viscometer was thermostated at 25°C in a constant temperature water bath. A solution of known concentration (0.5 g dl^{-1}) of the polymer was placed in the viscometer and the flow time measured using a stopwatch ($\pm$ 0.1 sec). The measurement was made five times and did not vary more than 0.2 sec in the approximate 100 sec efflux time. The flow time was then measured after successive dilutions. This procedure was carried out for the three polymers prepared. All the solutions and solvents used were filtered through a sinter glass filter to remove any dust before going into the viscometer. The intrinsic viscosity determined (Fig. 4.4) represented molecular weights of 388,000, 1.2×10^6 and 2.37×10^6.

4.5 Quaternisation of Poly(dimethylamino ethylmethacrylate)

The polymers prepared were converted to the quaternary by reaction in solution with a two fold excess (compared to the original amount of monomer) of methyl iodide. The 2.37 million molecular weight polymer was reacted in dioxan (200ml) and the other two molecular weights were reacted in acetone (200 ml).

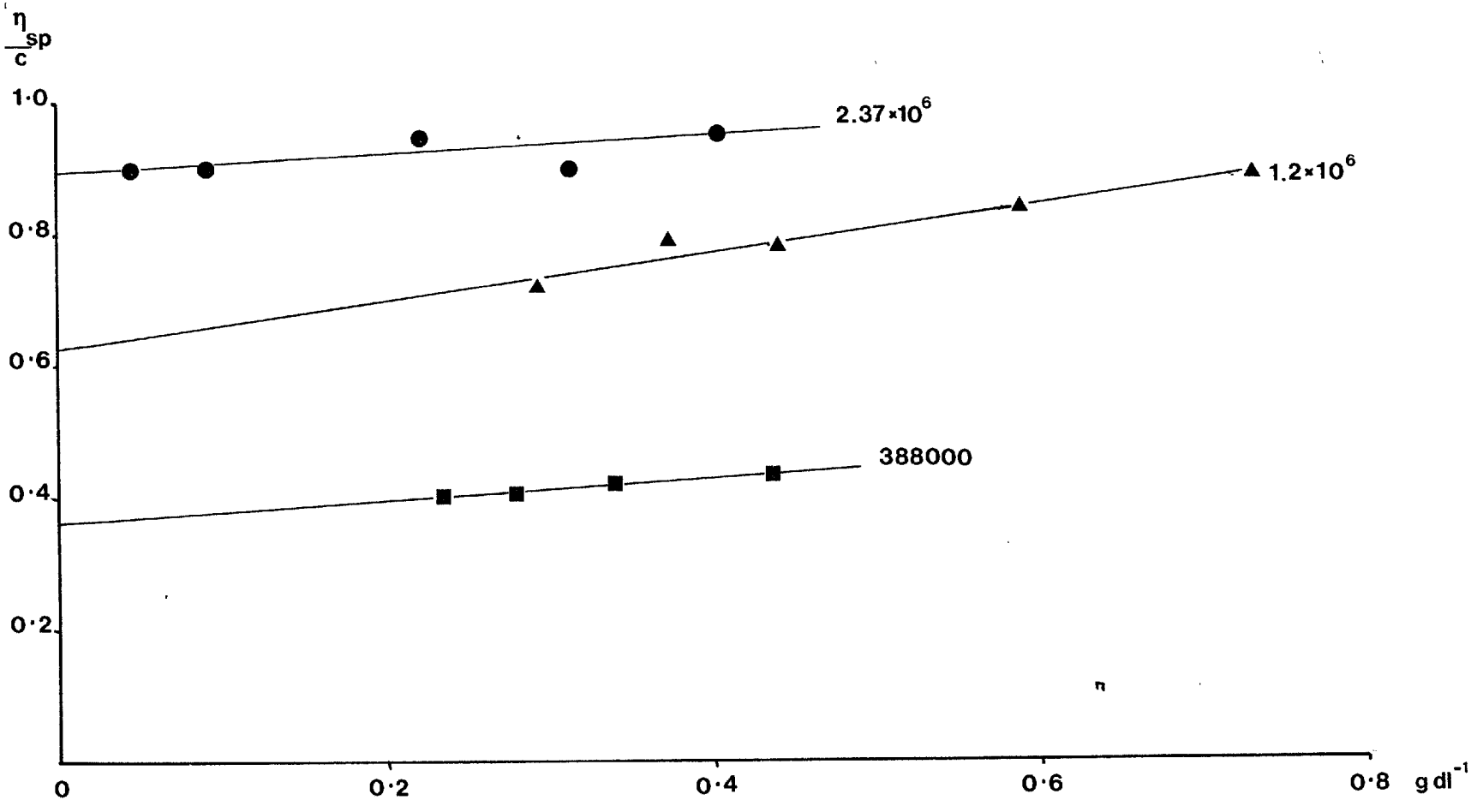

$\frac{\eta_{sp}}{c}$
1·0
0·8
0·6
0·4
0·2
0
0·2
0·4
0·6
0·8
g dl^{-1}
2.37×10^6
1.2×10^6
388000

FIG.4.4

The reaction occurs very quickly after about two minutes the solution turns cloudy and within a few seconds the polymer precipitates. The solvent and excess methyl iodide were removed by evaporation under vacuum until the polymer was a dry powder.

The extent of this reaction was estimated by titrating the iodide present in an aqueous solution of the polymer (0.5% w/v) with silver nitrate solution (0.176 molar). The end point was determined by measuring the conductivity of the solution with a conductivity bridge (Mullard Equipment Ltd., type E7566/3). As the silver nitrate is added the conductivity of the solution falls proportionally until all the iodide is precipitated then rises sharply with excess silver nitrate. The end point was determined by finding the intercept of the two slopes before and after the sharp change (e.g. Fig.4.5).

It was found that both the 388,000 and the 2.37 million molecular weight polymer had 66% of their monomer units quaternised while the 1.2 million had 44% quaternised.

Adsorption indicators like Fluorescein for the titration with silver nitrate are not compatable with the polymer flocculant as they depend on a surface adsorption onto the silver iodide colloidal precipitate to give a colour at the end point. But with the polymer present it adsorbs onto the silver iodide flocculating the colloid and interfering with the adsorption of the indicator.

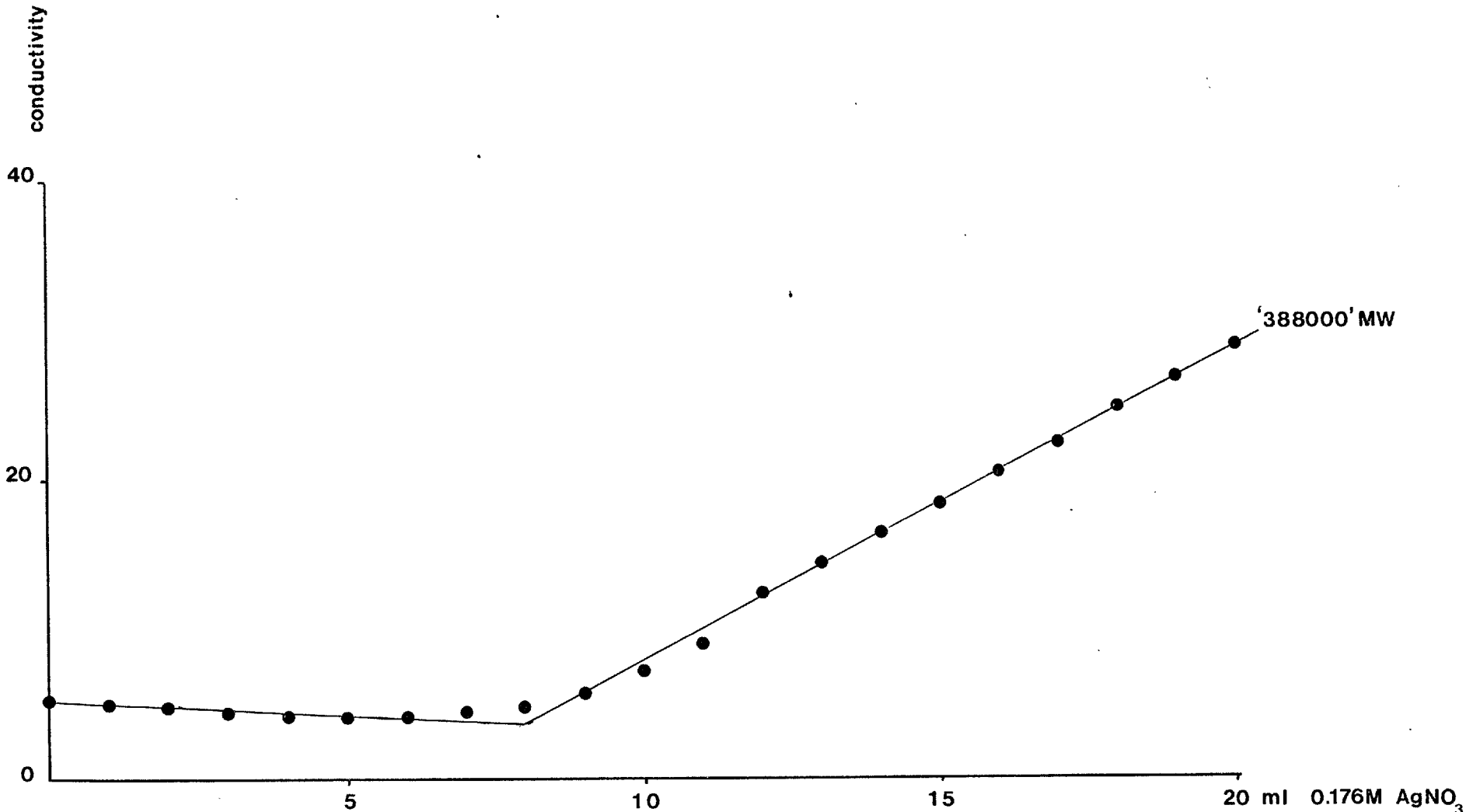


FIG.4.5

Likewise the end point cannot be seen by noting the point where the silver iodide colloid produced coagulates, when the stoichiometric amount of silver nitrate is added as the polymer flocculates the colloid before this occurs at the end point.

4.6 The Flocculation of Polysytrene Latex Particles by Quaternised Poly (dimethylamino ethylmethacrylate)

The flocculation experiments were carried out with two different particle sizes of latex (0.54 μ and 0.84 μ) each at three different particle concentrations. In each case the colloid was flocculated with the three polymeric flocculants prepared.

A 10 ml sample of the colloid in each case was placed in a glass vessel and was vigorously stirred by a magnetic stirrer. The polymer solution was quickly added by burrette or pipette and distilled water added to make a total volume of 12 ml. After a few minutes the stirring was reduced and the sample left gently stirring for 30 minutes to equilibrate. A portion of the sample was then taken and diluted to a concentration suitable for counting in the particle counter. This was carried out for a range of polymer concentrations and the results plotted as the ratio of particle number to the initial particle number against the weight of polymer added per gram of solid colloid.

The following latex concentrations were used:-

Particle Diameter	g ml^{-1}	Particles ml^{-1}
0.54μ	9.41×10^{-4}	1.36×10^{10}
"	1.88×10^{-4}	2.71×10^{9}
"	3.76×10^{-5}	5.42×10^{8}
0.84μ	5.125×10^{-3}	1.56×10^{10}
"	1.025×10^{-3}	3.12×10^{9}
"	2.05×10^{-4}	6.23×10^{8}

The results are shown in Figures 4.6 to 4.11.

4.7 Preparation of Kaolin for Flocculation Studies

The Kaolin (supreme grade, English China Clays) was fractionated to reduce the width of the particle size distribution, primary to remove the very light and very heavy fractions.

A 1% w/v suspension of the kaolin was made up in water, well stirred and then allowed to stand for 15 minutes. The supernatant was then carefully decanted and discarded to remove the small light particles still suspended. Then fresh distilled water was added and the mixture stirred again. The supernatant was decanted again and the process repeated until all the solids settled within 15 minutes.

Ammonium hydroxide (0.88 S.G.) was then added to increase the pH of the suspension from 3 to 9 and sodium phosphate added to a concentration of 10^{-6} g ml^{-1}. The

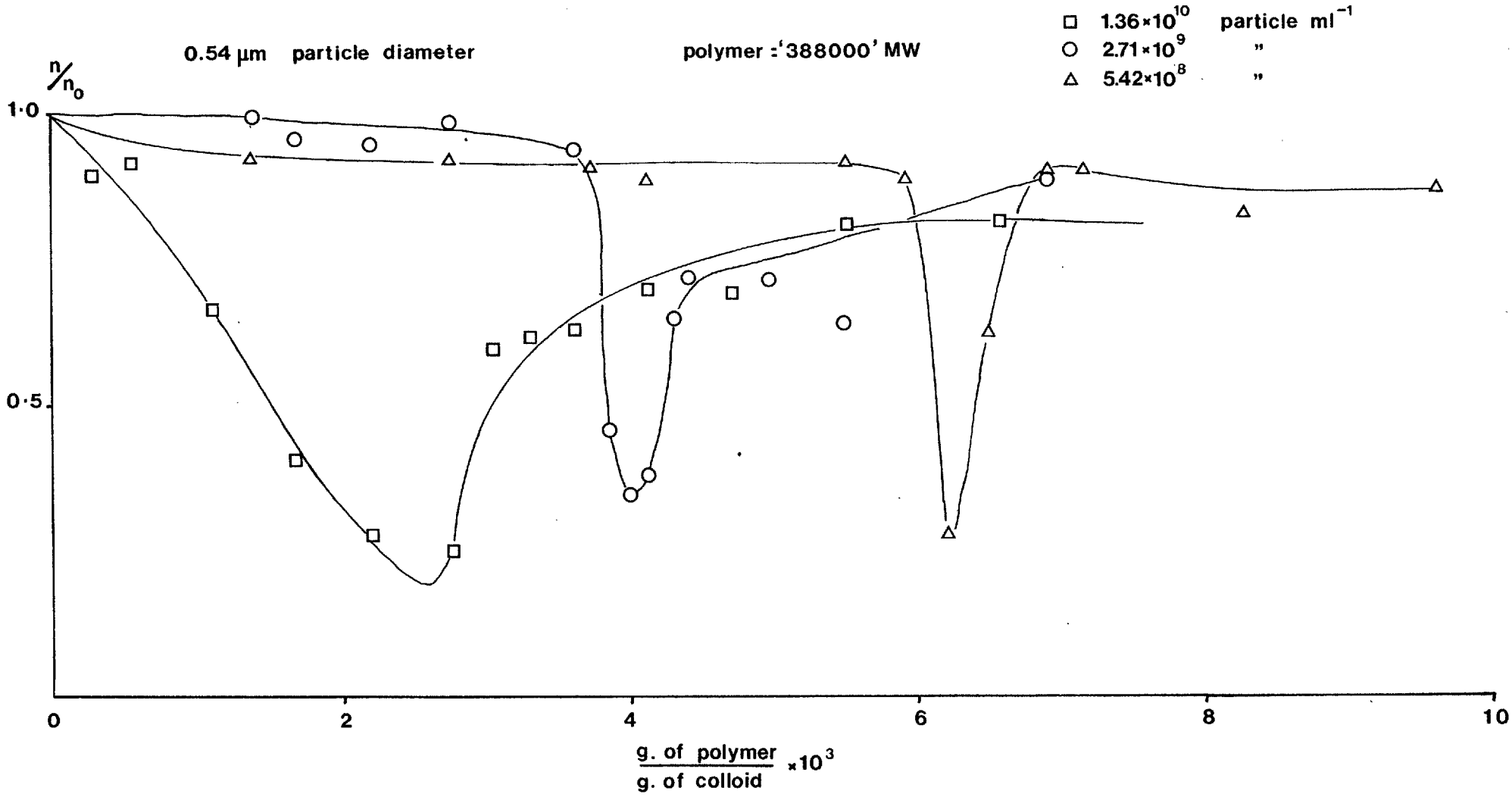
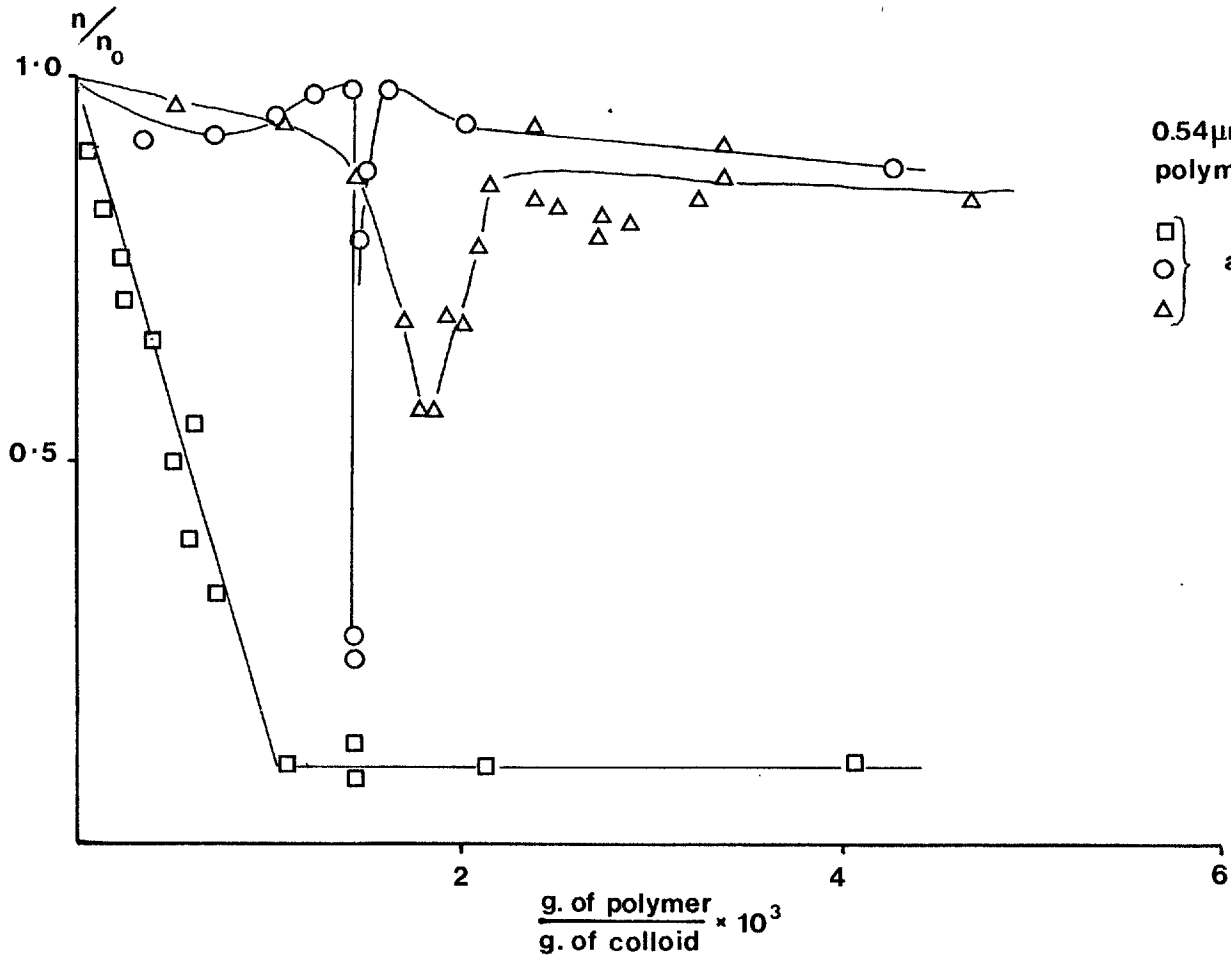

0.54 µm particle diameter
polymer :'388000' MW
□ 1.36×10^10 particle ml^-1
○ 2.71×10^9 "
△ 5.42×10^8 "
n/n_o
1·0
0·5
0
2
4
6
8
10
g. of polymer / g. of colloid ×10^3

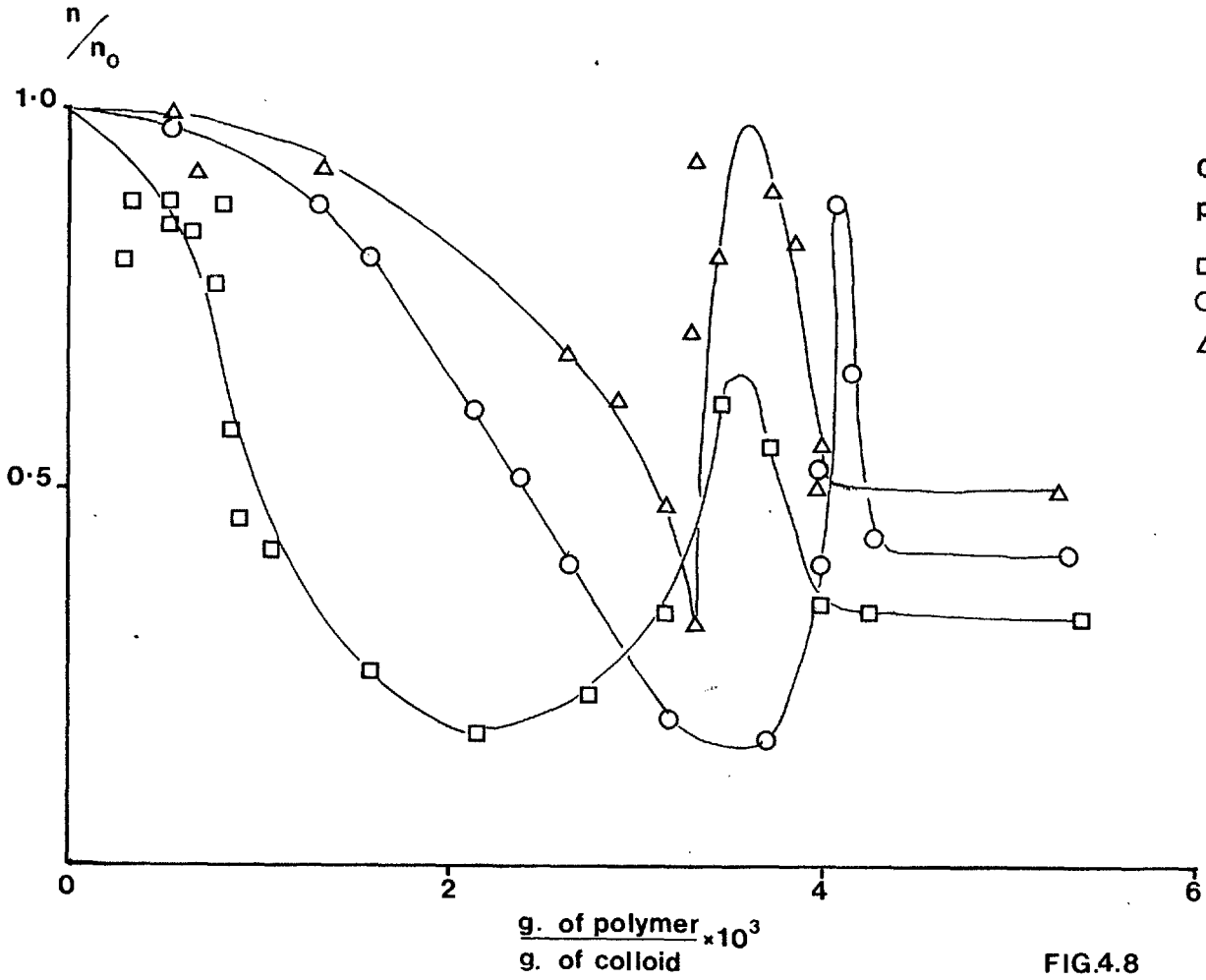
FIG.4.6



0.54μm particle diameter
polymer: '1.2 × 10^6' MW

□ ○ △ as FIG.4.6

FIG.4.7



0.54μm particle diameter
polymer: '2.37×10⁶' MW

□ ○ △ as FIG.4.6

FIG.4.8

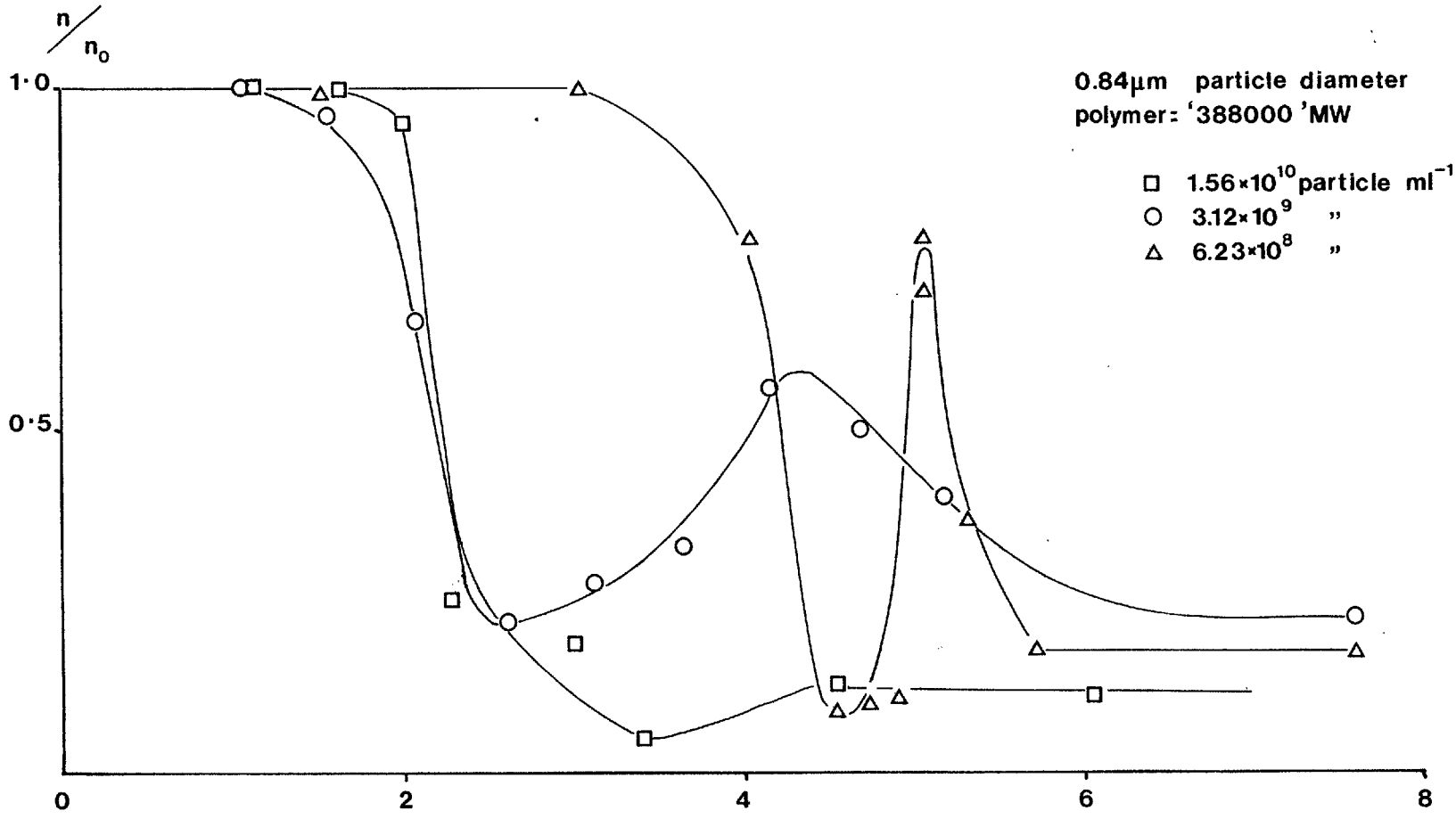

n/n0
1·0
0·5
0
2
4
6
8
0.84μm particle diameter
polymer: '388000 'MW
□ 1.56×10^10 particle ml^-1
○ 3.12×10^9 "
△ 6.23×10^8 "
g. of polymer / g. of colloid ×10^3

FIG.4.9

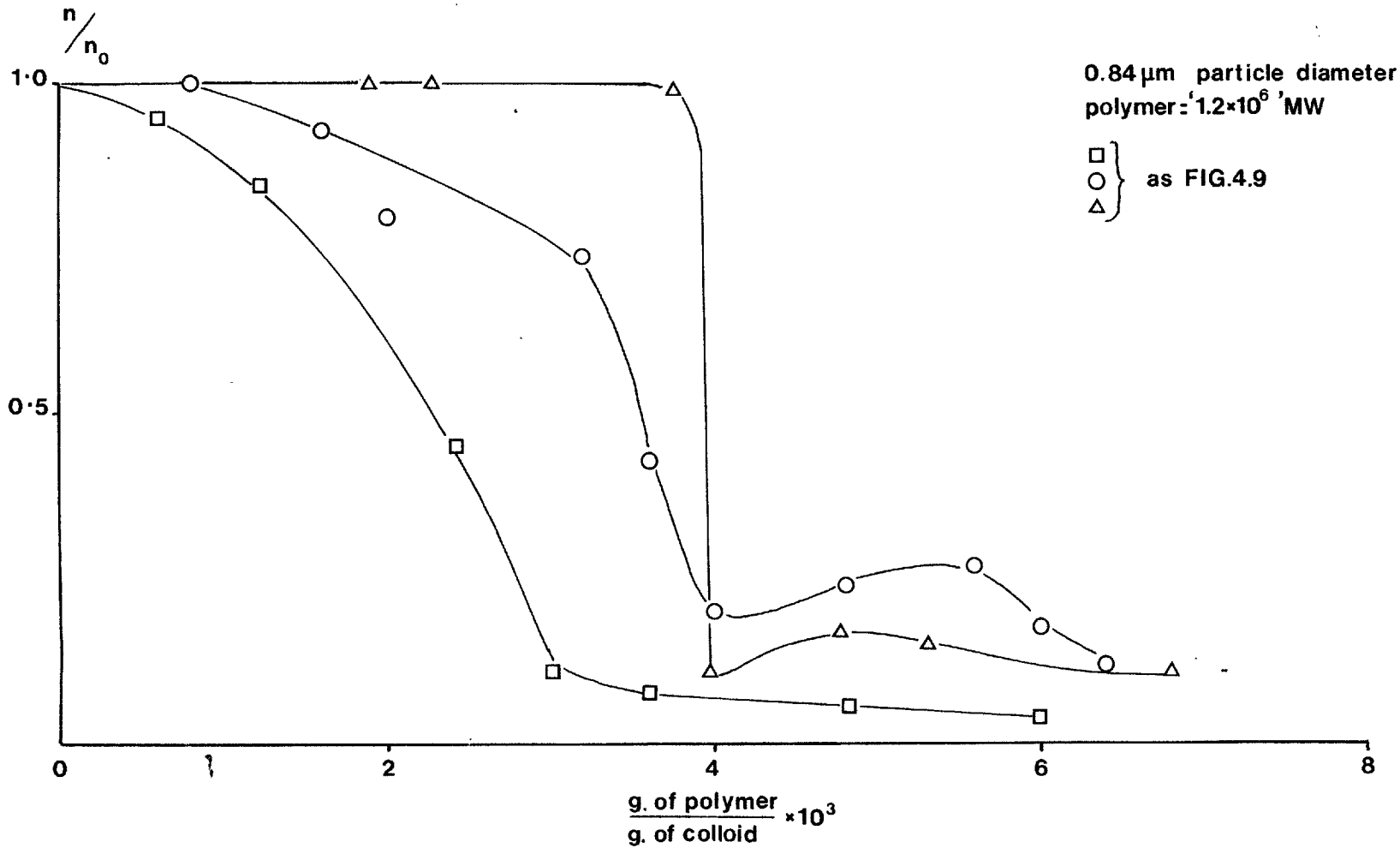

n/n0
1·0
0·5
0
1
2
4
6
8
0.84 µm particle diameter
polymer: 1.2×10^6 MW
as FIG.4.9
g. of polymer / g. of colloid ×10^3

FIG.4.10

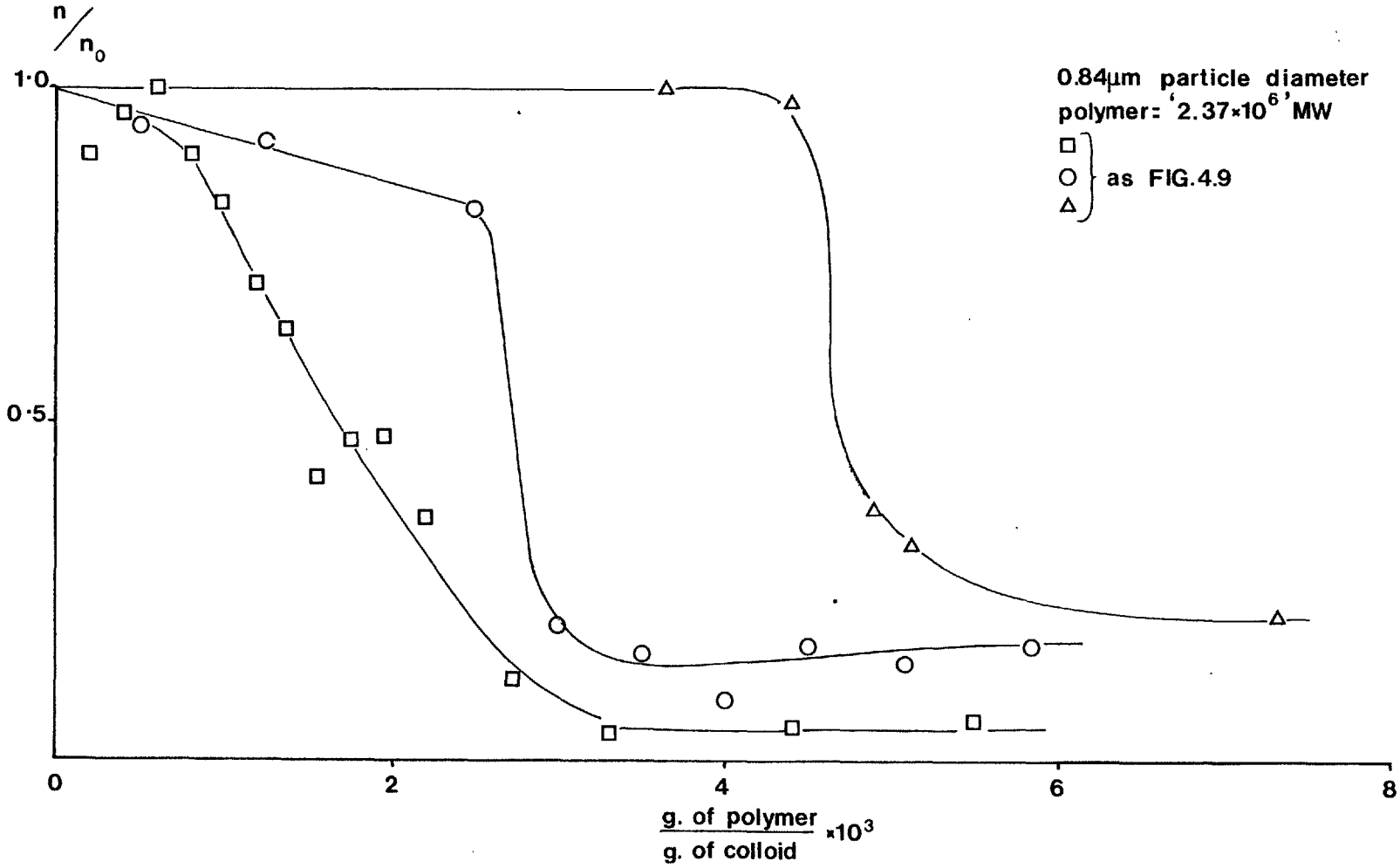

n / n0
1·0
0·5
0
2
4
6
8
g. of polymer / g. of colloid ×10³
0.84μm particle diameter
polymer: '2.37×10⁶' MW
as FIG.4.9

FIG.4.11

phosphate ions adsorb on the few positive sites on the predominantly negatively charged particles and improve stability. The large heavy particles were allowed to settle out of the now more stable suspension and the stable colloid poured off. This was repeated until no more fast settling solid was evident (within 30 minutes).

To determine the concentration of the colloidal suspension a sample of known volume was evaporated to dryness and the dry weight of solids found. The suspension was then diluted to a concentration suitable for the flocculation studies and the pH reset by addition of ammonium hydroxide.

4.8 Polymerisation of Acrylamide

The acrylamide (5g) was polymerised in aqueous solution (100 ml) using potassium persulphate (0.1g) as an initiator. The reaction was carried out at 90°C overnight under a nitrogen atmosphere. The polymer was precipitated into methanol and dried under vacuum.

The molecular weight of the polymer was determined by viscosity measurements at 25°C using the technique mentioned earlier. The values of K and α were found in the literature[95] ($K = 6.31 \times 10^{-5}$ and $\alpha = 0.8$ for $|\eta|$ in dlg^{-1}). A value of $|\eta| = 2.80$ was found (Fig.4.12) which is equivalent to molecular weight of 6.44×10^5.

4.9 Flocculation of Kaolin with Polyacrylamide

The flocculation of kaolin suspension at pH9 were carried out at two concentrations (5.91×10^{-3} g ml^{-1})
(" 10^{-4} ")

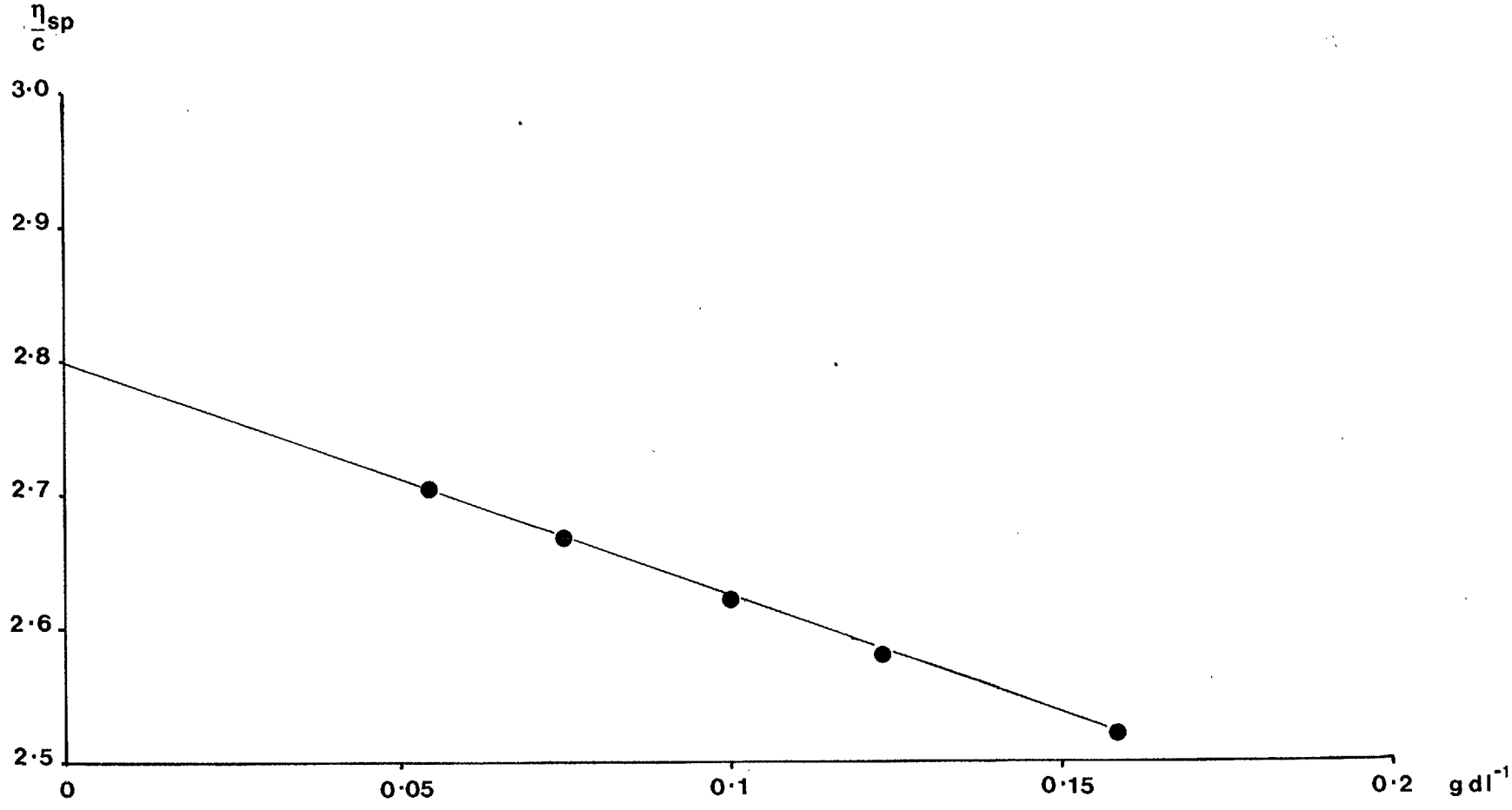
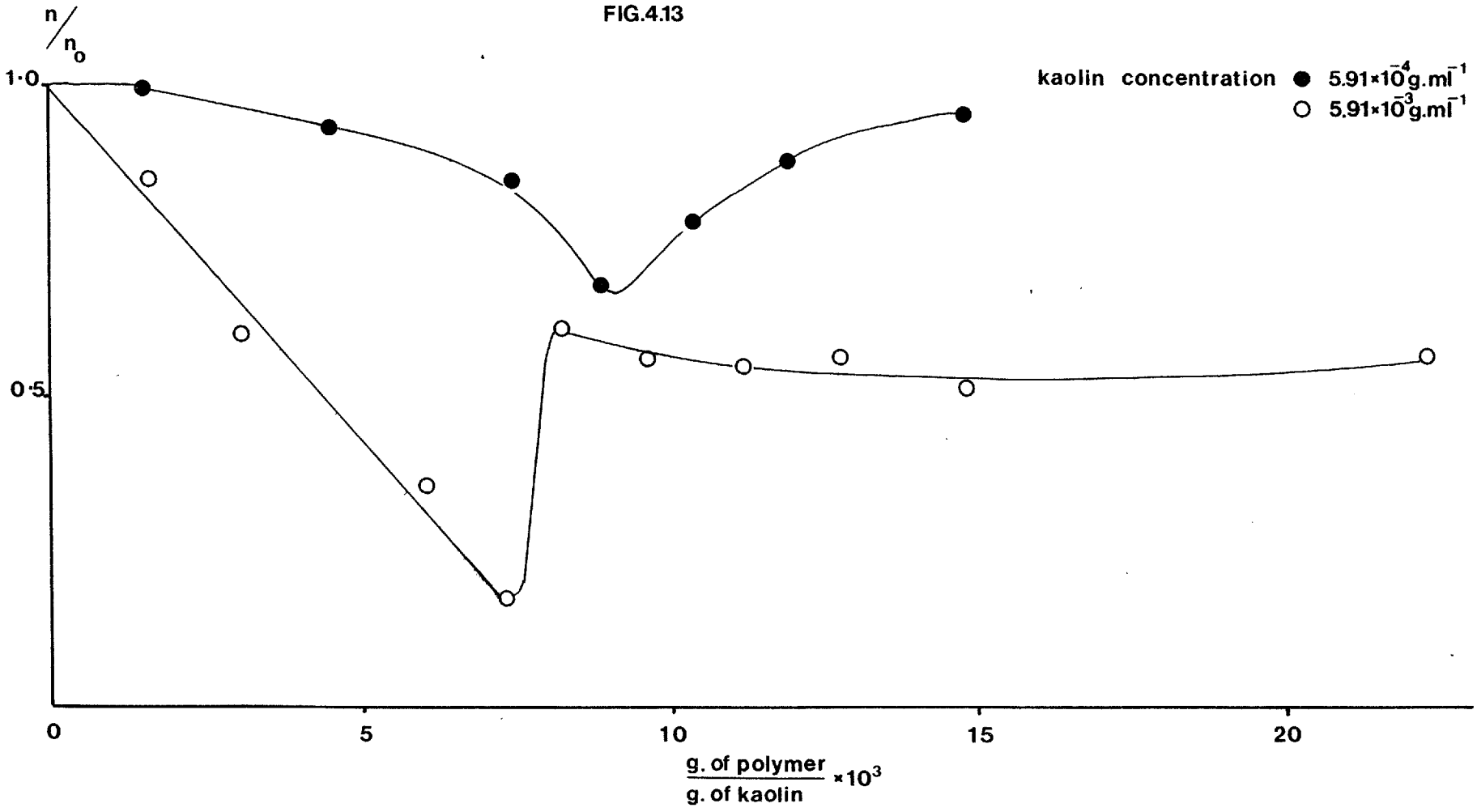


FIG.4.12

FIG.4.13


n/n0
1·0
0·5
0
5
10
15
20
kaolin concentration
5.91×10⁻⁴g.ml⁻¹
5.91×10⁻³g.ml⁻¹
g. of polymer / g. of kaolin ×10³

using the 6.44×10^5 molecular weight polyacrylamide prepared.

The flocculation experiments were carried out in the same manner as the earlier experiments and the results are plotted in Figure (4.13) in the same manner as before.

4.10 Discussion of Aqueous System

The zeta potential of the polystyrene latex measured by electrophoresis indicates that a particle particle separation greater than a 100 Å must be bridged by the polyelectrolyte. This would seem possible since these molecules are firstly of reasonable molecular weight and even considering them as random coils the end to end length would be in the order of a 1000 Å. In fact the charged groups along the chain extend this length by electrostatic interactions resulting in rod-like molecules.

The analysis of the quaternised poly [dimethyl amino ethyl methacrylate] shows that not all the amine groups are converted. This may be due to the different solubility of the initial polymer and the polyelectrolyte produced, which results in the polymer precipitating out as the reaction proceeds, hindering the movement of the methyl iodide to the amine groups on the polymer. The variation in the number of groups quaternised with the three polymers made, is also likely to be a result of this. It seemed that the polymer stayed in solution in acetone longer as the reaction proceeded than it did in dioxan; this did not

relate to the extents of conversion.

The flocculation experiments show a number of trends as molecular weight of the polymer, the particle concentration and particle size vary. The results can be best explained if the graphs of relative particle number to polymer dosage are split into two regions, the first at polymer additions up to the amount causing maximum flocculation and the second at additions greater than that causing maximum flocculation.

In the first region a number of points are worthy of mention; for the smaller particles,

1. As the particle concentration increases the initial slope of the plot increases. This can be explained by the polymer not collapsing down onto the particle surface as much before a particle-particle collision occurs. Thus at higher particle concentrations it is more likely that a bridge will be formed and the polyelectrolyte will be more efficient as a flocculant.

2. An increase in polyelectrolyte molecular weight at the high particle concentration increases the initial slope marginally from the lowest to the intermediate molecular weight, and little from the intermediate to the highest molecular weight. However, at the lower particle concentration the initial slope is markedly greater with the highest molecular weight.

Such an effect is possibly due to the bridging distance of all three polyelectrolytes being greater than the dimensions of the electrical double layer, when the polymer molecules are not extensively collapsed onto the particle surface at high particle concentrations, so they can all span this distance. The other factor is that these plots are in terms of weight of polymer therefore the number of chains for the lower molecular weights is greater, so that even if the probability of an individual longer chain bridging is greater, the lesser number of chains may counteract this advantage. The theoretical model mentioned in chapter 3 predicts the probability of bridging to depend on the square root of the number of monomer units in a chain, but the number of chains present in unit mass is dependent on the inverse of this number of monomer units, the outcome may be a weak dependence on molecular weight.

4. At lower particle concentrations, especially with the lower molecular weights, the colloid flocculates over a narrow range of polymer dosage. This sharp drop in stability is likely to be due to surface charge neutralisation.

It occurs over a narrow range because if the latex is considered to have a high surface potential then the DLVO theory predicts in such a case that the repulsive forces between two particles is independent of reasonable changes in surface potential, a consequence of the exponential decay of the potential. This would seem logical if the polyelectrolyte is lying on the particle surface, a situation

that could occur with the less frequent collisions at lower particle concentrations. The polymers presence would alter the potential close to the particle surface, not out in the diffuse part of the double layer which determines the repulsion. For very low potentials the repulsive interaction becomes very dependent on the surface potential, in fact proportional to ψ_0^2. As the polymer dosage increases and more is adsorbed onto the surface a point may come when the surface potential will have fallen to a value where V_R becomes very dependent on it and the latex becomes very unstable with a small change in the amount of polymer added.

When the flocculation occurs suddenly over a narrow range of polymer addition the value of this dosage is not constant for different particle concentrations but occurs at higher values with lower particle concentrations.

This would imply that even in this case charge neutralisation is not the only mechanism causing aggregation and some particle bridging occurs. It could be that the double layer thickness has to be reduced before the chains on the particle surface can bridge. The distance the chains can bridge is controlled by the frequency of collision or how much of the chain length is associated with the surface. Again the double layer may change suddenly with polymer addition and allow bridging. So if the chain ends are lying close to the surface, at low particle concentrations more polymer is required to reduce the double layer.

All the above trends seen with the small latex particles were also observed with the larger particles.

In the second region of the plots beyond the maximum flocculation dosage a number of features are evident.

In the case of the small latex;

1. addition of the lowest molecular weight polyelectrolyte beyond the maximum flocculation dose results in an increase in stability to aggregation at all particle concentrations. Electrophoresis showed in this case the particles had now a positive charge due to the adsorbed polymer. The repulsive force caused by this charge would rise quickly due to the low surface potential having a great influence over V_R which would then change markedly with adsorbed polymer.

2. The intermediate molecular weight polymer at additions above the flocculation dosage with the two lower particle concentrations, result in a stable latex. This again is probably due to the creation of a positive surface potential. With the higher particle concentration, however, the latex does not restabilise. This is more difficult to explain and will be considered later.

3. Beyond the maximum flocculation dosage for the highest molecular weight polyelectrolyte the latex increases in stability to a maximum and then flocculates extensively at greater polymer dosage.

It would seem that there is something more complicated than just charge reversal occurring in this case. This phenomena will be reviewed later.

4. With the larger particles the higher molecular weight polyelectrolyte does not restabilise the latex at any excessive dosage at any particle concentration. This occurs even after flocculation results at a very sharp minimum polymer concentration, when charge reduction is thought to be the major factor. This would suggest that the polymer can reduce the negative surface charge but cannot generate a sufficient surface potential to stabilise the particles. It is true that it requires a greater surface charge with a larger particle to create the same surface potential.

5. The intermediate molecular weight polyelectrolyte does not restabilise the latex at high particle concentrations but at lower particle concentrations it stabilises them marginally over a limited range of dosage, but the colloid again flocculates at greater additions.

The lowest molecular weight polymer does not flocculate the latex for a limited extra addition, but again at larger dosage the latex flocculates. This happens at all particle concentrations.

In the case of the two lower molecular weight polyelectrolytes the level of the maximum stability to flocculation increases with reduced particle concentration.

The stability of a charged colloid particle is determined by the charge on its surface and the distribution of ions in space around that surface. In the case of a polyelectrolyte attached onto that surface both these factors will be effected. No established theory is known which can predict the consequences of this, although theories have been but forward for the case of a homopolymer adsorbed on charged interfaces[98], which predict an increase in zeta potential in the presence of the polymer due to an excluded volume effect pushing the ions away from the surface. If the polyelectrolyte extends well beyond the double layer it is possible that its effect on this is not important and flocculation occurs by bridging.

It can be visualised that the polyelectrolyte diffuses faster than the particles so the polymer attaches itself by an electrostatic interaction to the particle by one point and then proceeds to collapse onto the particle surface attaching along its length to the charge sites, but as this is occurring another particle will approach which may attach itself to the extended end of the collapsing chain forming a bridge. The time between a chain attaching onto a particle and another particle arriving is determined by the particle concentration. If this time is long for low particle concentrations, the chain will be associated over a greater fraction of its length with the surface, and may not be able to bridge across to the other particle. Certainly of course the chain lying on the particle surface will have reduced the surface charge, thus reducing the

electrostatic forces between particles and allowing closer contact between particles.

This model explains the dependence of the efficiency of flocculation on particle concentration. It shows how at high concentrations a large bridging distance is possible that bridges will be formed. At low particle concentrations it implies short lengths of chain available for bridging with less probability of bridging and at the limit no bridging with eventual flocculation at one particular dosage when all the charge is neutralised. The effect of molecular weight can also be related; with higher molecular weights the molecules will always have a greater bridging range as they associate with the particle surface and so be less effected by changes in the particle concentration. All these concepts fit in with the results in the first region of the graphs.

In the second region of the plots when the colloids are stable to flocculation it could be imagined that the polymer chain segments lie close to the particle surface, at low particle concentrations or low molecular weights. The ionic groups on the polymer would then just be like surface bound ionic groups and generate a surface potential.

If it is considered that there is only a limited number of sites on the particle where the ionic groups on the chains can attach, then beyond the charge neutrality point the 'extra' ionic groups will be on chains hanging off the particle. For the same weight of polymer with a higher

molecular weight these 'extra' groups will be on fewer chains and further off the surface. Thus the same number of ionic groups would be distributed further from the surface in the case of a higher molecular weight and less likely to create a surface potential. As the number of chains attached to a particle increases with dosage more of each chain's length will be hanging off, if there is only a limited number of attachment sites. This effect will be accentuated with higher molecular weights.

The ionic groups away from the particle surface will possibly tend to shield the surface charge from approaching particles, as an ordinary electrolyte would do, allowing the particles to approach close enough to aggregate under van der Waals forces. Thus the shielding effect would be more likely as the dosage of polymer increased with higher molecular weights. Under such conditions the stability maxima is seen with polymer addition in the second region. It could be that a surface potential firstly builds up stabilising the latex but then the shielding layer of chain ends grows and the stability reduces again.

In the case of the larger particles it is more difficult to create a surface potential and one is only really attained with the lowest molecular weight at the lowest particle concentration which allows a longer time for the chains to arrange themselves on the surface.

The layer of polymer chains hanging off the particle surface offer no resistance to approaching particles when

they overlap as their rod-like configuration has a small entropy contribution and changes very little with the reduced volume. The electrostatic interaction between two polyelectrolyte molecules is not significant beyond about 50 Å.[97] Thus the chains can slide past each other as two particles approach each other.

The approach of the two particles would be limited by the length of the chain ends hanging off the particle surface, if the particles came closer than this distance the chains would have to be compressed which would not be favourable. The lengths of these chains could be of the order of 2000-3000 Å and considering that van der Waals forces for the bare particles are only significant up to particle surface separations of 200 Å the effect of adsorbed polymer layers on van der Waals forces must be reviewed.

An analysis of the effect of adsorbed polymer layers on the interparticle attraction energy, V_A has been made by Vold[96]. If the particle coated with solvated polymer is taken to be a larger particle of radius equivalent to the hard core radius plus the polymer layer thickness, the Hamacker constant for it will depend on the constant for the particle and the polymer. The Hamacker constant can be taken to be proportional to the density of a particle and since the polymer layer is likely to be less dense than the original particle, the constant for the coated particle should be less than that for the bare particle. The outcome is that for a constant surface separation the

attraction between two bare particles is greater than for two coated particles. However if a constant particle centre separation is considered the attraction between the coated particles would be greater, having a larger radius.

In the case of the particles coated with the polyelectrolyte and the proposed small repulsive interaction the outer surfaces of the coated particles can overlap, so no matter how small the Hamaker constant for these particles are at such small or effectively negative surface separations van der Waals forces will be large between two particles, even though the cores are far apart.

The other possible explanation is that when the electrostatic repulsion is reduced by the chain ends shielding the surface charge the chain ends from another approaching particle slide past the chains of the particle and find any negative sites which have not been taken up due to steric effects by the chains on the surface, to form bridges. Although this mechanism would seem unlikely since it would take more than one point of association for a chain to form a strong link and to find many such free negative sites together on the surface would seem improbable.

It may be possible for the polyelectrolyte to have some sort of non-ionic interaction with the particle surface since it has a large organic part as well as the ionic one, which could result in bridging when all the negative surface sites are taken up and is more likely to occur when the

chains hanging off the surface are long as they could be in the second region of flocculation.

The intermediate molecular weight had a different degree of quaternisation and the effect of fewer charge groups may be the cause of the slightly different results with this polymer. Its performance seems more dependent on particle concentration especially with the smaller latex. The sharp range of polymer dosage at lower particle concentrations which brought about flocculation was not shown with the other two molecular weights. At the high particle concentration it did not restabilise the latex at all, unlike the other polymers. It would be worthwhile to investigate the effect of varying the fraction of monomer units quaternised on the flocculation, although some work into the chemistry of preparation would have to be done.

The results of all these flocculation experiments are dependent on how the polyelectrolyte is arranged around the particles when they collide with each other. This is determined by the factors mentioned. The interesting practical significance of the results are that an excess of polymer is not likely to stabilise the colloid which can be a problem in less well defined industrial systems.

The flocculation of Kaolin with polyacrylamide give well established results in terms of colloid stability with changing polymer dosage. As this is increased from zero the clay particles flocculate until a maximum degree

of flocculation is obtained, after which the particles gain in stability to flocculation. Varying the concentration of kaolin shows a change in the effectiveness of the flocculant, giving greater efficiency at high particle concentration at all levels of polymer addition. This was seen with the polyelectrolyte and must be a feature of a bridging mechanism since polyacrylamide can only function in this way.

The general concept of the particle concentration determining the way polymers adsorb onto the particle surface can explain the results seen with polyacrylamide. The longer the time a chain is allowed to arrange itself on the surface the flatter the configuration it will take up before contacting another particle, reducing the possibility of it bridging and blocking more adsorption sites to bridging chains from other particles.

Up to the point of maximum flocculation the reduction in particle number is directly proportional to the polymer dosage, especially at the high particle concentration, implying that the number of particle bridges is dependent on the amount of polymer adsorbed.

The sharp rise in stability after the maximum flocculation dose is difficult to explain since theory[44,45] predicts maximum flocculation at half coverage of the particle surface and beyond this a steady fall in flocculation as the particle surface is covered with polymer and steric effects hinder bridging. This sort of performance is seen

at the low kaolin concentration with a more gradual rise towards the initial particle number.

At the higher particle concentration a constant level of aggregation was obtained at high polymer dosage or some extent of bridging is always possible. This could be due to the particle surface not being saturated with polymer fast enough with the high particle collision frequency and bridging occurs before all the available polymer is adsorbed. In fact the model of the system where the polymer is instantly adsorbed uniformly over the particles which then collide and bridge may not be true. Small aggregates of particles may form before all the polymer is adsorbed and the excess polymer beyond that required for optinum flocculation could be unevenly distributed, most of it on the outside of the small aggregates stabilising them and giving this dramatic effect. This would explain the sharp change in particle number after the maximum flocculation polymer dosage and the constant result with increasing dosage after that.

The wide size distribution of the colloid must be considered which would cause such effects with a range of collision frequencies. This could be investigated by preparing kaolin samples with narrow size distributions by fractionation on the basis of sedimentation rates.

CONCLUSION

The object of the work was to study the flocculation of well defined colloidal systems and investigate the influence of some parameters.

The non-aqueous system was an ideal model system which was well defined in terms of the colloid and the flocculating polymer, but it was found that the electrostatic interaction between particles was large and difficult to determine. This prevented polymer bridging between particles and was due to the very low dielectric constant of the solvent, resulting in a large interaction from the very few ionised groups on the particles. The problem could be solved by switching to a solvent with a higher dielectric constant which will not interfere with the chemistry, where a better defined and sized double layer exists.

The flocculation of polystyrene latexes with the polyelectrolytes showed some interesting characteristics. The most effective flocculation occurs at high particle concentrations and to some extent with higher molecular weights. A dependence on these two parameters would indicate that charge neutralisation is not the primary flocculation mechanism since a constant number of ionic groups are not required for flocculation. The molecular weight of the polyelectrolyte and the particle concentration most likely control the arrangement of polymer chain segments around the particles as they collide and in this way determine their stability to flocculation. It could be assumed when

the chains lie close to the surface of the particle they are less likely to bridge, but reduce the surface charge which will alter the repulsive interaction to some extent. Bridging would be a more efficient way of aggregating the particles, requiring only a few chains to hold them together whereas charge neutralisation requires many chains to achieve stochiometry. How the chains are arranged around the particles when they collide is probably determined by the time the chains have after they initially adsorb to collapse onto the oppositely charged surface before a collision occurs, which is determined by the frequency of collision or the particle concentration.

The increase of stability to flocculation at polymer dosage greater than the optinum for flocculation is not always seen and often occurs only over a limited range of addition, with a secondary region of flocculation. This again is a question of how the stability of the particle is altered by the attached polymer. It was shown that the zeta potential is reversed when the latex is stable with large polymer dosage, also it has been suggested that steric stabilisation may not be significant for the rod-like polymer. This implies charge reversal is the method of restabilisation.

In the cases where the latex does not regain stability or only gains it over a limited range of polymer addition, the reverse surface charge must not be large enough to prevent flocculation. The influence of an adsorbed polyelectrolyte on the electrostatic interaction between

particles is not well understood and can only be crudely explained in terms of D.L.V.O. theory, but again is probably dependent on the distribution of charged chain segments about the particle surface. It would follow that this is dependent on the molecular weight of the polyelectrolyte and how long it has to arrange itself on the surface before the collision. The colloid would seem to be less stable at high particle concentrations and molecular weights, when the chain segments are likely to be away from the surface and may shield the surface charge as an electrolyte would do, reducing the electrostatic interaction.

If the particles flocculate there must be some force holding them together. The range this force must act over is dependent on the length of the polymer chains hanging of the surface, which are unwilling to be compressed and this leads to particle-particle centre separations which are greater than the range of the van der Waals interaction of the bare particles. It is known but that polymer layers on particles do alter the van der Waals interaction resulting in larger forces for the same particle-particle centre separation, as the particles can be treated as particles of radius equivalent to the distance out to the edge of the polymer layer, but with a lower Hamacker constant. Finally in this case where there is no force hindering contact or substantial overlap of these polymerlayers the van der Waals interaction may hold the particles together.

A possible secondary bridging mechanism cannot be discounted in this second region of flocculation unless this phenomina is seen with other polyelectrolytes, since such a mechanism would have to depend on a non-ionic interaction specific to this polymer.

Flocculation of kaolin with polyacrylamide gave the accepted general result of flocculation followed by restabilisation due to steric stabilisation as the polymer dosage is increased. Total stability is not re-established at high polymer dosage at the higher kaolin concentration which could be due to not all the polymer being adsorbed before collisions occur, resulting in a non-uniform coverage of the particle surfaces, with excess polymer coating the surface of small flocs of particles. Also there was initially a wide distribution of particle sizes and diffusion rates resulting in a range of collision frequencies, possibly with the smaller particles flocculating before all the polymer is adsorbed.

The flocculation experiments were successfully followed using the laser ultramicroscope particle counter which has been shown with simple systems to give accurate counting results when compared with other methods. As a method it has the advantage of directly counting particles quickly in a size range unsuitable for other types of instruments. A possibility of analysing the pulse heights of the electrical signal generated by the scattered light off the particles can be seen to determine the size distributions of particles and of small aggregates of small particles. This is dictated by the light scattering characteristics of the particles.

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