THE FLOCCULATION OF CHARGED PARTICLES IN AQUEOUS SOLUTIONS BY CATIONIC POLYELECTROLYTES

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by

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ABSTRACT

The flocculation of a dilute suspension of silica particles (size range 1-3 μm) has been studied using six cationic polyelectrolytes. The flocculation process is monitored by an optical method which measures the fluctuations of light intensity transmitted through the flowing suspension. An increase in light intensity fluctuations indicates aggregation of particles. The reduction in particle concentrations due to aggregation can be confirmed by Coulter counting.

The charge neutralization effect of the adsorbed polymer is the main mechanism for flocculation. The amount of positive charge adsorbed at optimum dosage is about the same for all of the polymers used. The reversal of particles charge is also found to occur at a dosage very close to the optimum flocculation dosage. However, the charge density and the molecular mass of the polymer can affect the rate of flocculation. The polymer adsorption rate can be slow compared to the particle collision rate in a dilute suspension, especially when the polymer is of low charge density and low molecular mass. A high molecular mass polymer of 30% charge density is found to be the most effective flocculant.

The range of effective flocculation dosages is less critical in the presence of added electrolyte but the highest flocculation rate always occurs in the absence of salt. As the particles are neutralized by both the added electrolyte and the adsorbed polymer, a lower polymer dosage is able to bring about effective flocculation in salt solution. The charge screening effect of the added electrolyte allows higher polymer dosages to give effective flocculation before particles become restabilized due to excess polymer. The need to displace adsorbed ions is thought to be responsible for the lowering of the optimum flocculation rate. The larger the size of counter-ions to the particles the greater is the effect on the lowering of the ability of polymer to cause flocculation. The size, degree of hydration and adsorbability of ions are interdependent. The stability of the dispersion is found to be dependent on the ionic strength, the type of electrolytes and the characteristics of the polymers.

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CHAPTER ONE

INTRODUCTION

1.1. General Background

Flocculation of particles is an essential stage in many solid/liquid separation processes. Some particles, particularly those in the colloidal size range (1-1000 nm), are not easily separated by processes such as sedimentation, filtration or flotation. Flocculation of such particles prior to using these processes is necessary to improve the separation process. It plays an important role in many separations including the removal of particles in the treatment of potable water and the recovery of metals in mineral processing. The former is an application where the solid phase is to be removed, whereas in the latter the solid phase is to be recovered. In both cases, the flocculation of particles plays a key role in the separation process.

Particles in aqueous systems are often charged and the electrical repulsion between them is responsible for their resistance to aggregation. The particles are said to be destabilized when the repulsion forces between them are eliminated or reduced to an extent that these particles 'stick' together on collision to form an aggregate. The rate of flocculation is a function of collision rate and collision efficiency. The structure and the physical properties of the flocs formed have an important consequence; they determine how successful the follow-up separation process will be. Despite the considerable research which has been made on the relationship between experimental conditions of the flocculation process and the properties of the flocs formed, much remains to be elucidated.

Previous work on the nature of the surface of suspended particles, the forces involved in the stability of particles and the destabilization of particles in aqueous solutions by organic polymeric flocculants are reviewed in Chapter Two. The collision mechanisms and flocculation kinetics, and the physical properties of the resultant flocs are described. While the treatment of fresh waters to remove suspended particulate matter is well documented, relatively little research has been done on the treatment of sea water. Sea water flocculation is an important process in the treatment of injection water (section 1.2.3.) for secondary oil recovery process and as a pretreatment process for sea water desalination by reverse osmosis. The present work investigates polymeric flocculation of suspended silica particles in high salt solutions.

1.2. Water Treatment For Oil Recovery Processes

Oil is generally found in porous sedimentary rock which is capped with a layer of impermeable rock, forming the oil reservoir. Oil and gas are forced to the surface by natural reservoir pressure when the drilling of the reservoir begins. The pressure difference between the production well and the oil reservoir influences the rate of oil production. The reservoir pressure will reduce as the oil is being produced and the production rate will start to decline. In off-shore secondary oil recovery, sea water is injected into the reservoir to maintain formation pressure and production rate. The permeability of the reservoir is liable to impairment if the injection water is not properly treated to removed suspended particulate matter. The required quality of the injection water is dictated by the pore size of the rock formation. Typically, 650-2600 m^3/h of water is required for injection and 95-98% removal of particles greater than 2 μm is required for a medium permeability formation (Abdel-Ghani *et al*, 1988). As porosity and permeability vary throughout the rock formation and new reservoirs coming into use are more impermeable, the requirements for injection water with respect to particulate contaminants have become more stringent.

1.2.1. Composition of Sea Water

Sea water is a concentrated and complex solution. It consists of a large variety of inorganic ions, in which Na^+ and Cl^- predominate. Table 1.1 lists the concentrations of major constituents of a typical North Sea water sample. Sea water also contains dissolved substances derived from the degradation of natural products of marine and terrestrial origin. There are also suspended particulate matter such oxides, carbonates, weathered aluminosilicates, living and dead micro-organisms. The sources of these dissolved and suspended materials come from rivers, groundwaters, atmospheric precipitation and to a small extent from marine erosion and submarine volcanicity. Hahn and Stumm (1970) obtained an average value for the turbidity of continental runoff of the order of 0.9 g/l based on an estimated values of the suspended load carried by major rivers and of the total runoff made by Turekian in 1968. The residual solid content in deep ocean water is considerably reduced to about 0.05 - 0.1 mg/l (Jacobs and Ewings 1969) through sedimentation of suspended particulate matter.

Table 1.1. A typical composition of North Sea Water (Major Ions) (McKechnie, 1986)

Major ions	Concentration mg/l
Na^+	11000
Ca^{2+}	400
Mg^{2+}	1250
SO_4^{2-}	2500
ClO_4^-	140
Cl^-	19800

The principle of constant ratio between the salts in ocean water was laid down by Forchhammer in 1864 and firmly established by Dittmar in 1884 (Lyman and Fleming 1940). The work has shown that certain constituents bear a virtually constant ratio to the total salt and these are referred to as major constituents of sea water. The chemical composition of sea water is fairly constant, despite any seasonal variations and the individual characteristics of different oceans around the world. In a recent study (Adin and Klein-Banary 1986), eleven Mediterranean sea water samples were characterised. The results were as follows: salinity (30.06 - 38.88 o/oo), pH (7.9 - 8.2), total suspended solids (7.6 - 35.4 mg/l), turbidity (1.0 - 17.5 NTU), number of algae (63 - 2650 cells/ml) and total particle counts for 4 - 300 μm range (1072 - 5292 particles/ml). The above data illustrate that the composition of sea water does not vary very much.

There are a number of chemical and physical processes operating to maintain the consistency of sea water. Concentrations of dissolved materials are maintained by either inorganic processes, such as precipitation or reaction with solid phases, or biological processes e.g. incorporation into skeletal material. Sedimentation and horizontal transport of suspended particulate matter determine the distribution and composition of the suspended phase and sediments (Gibbs, 1977). The pH in sea water is controlled through the whole set of ionic equilibria involving all of the major ions in sea water (Wangersky, 1972); the same mechanism controls the ratios of major ions.

1.2.2. Particulate Matter in Sea Water

The main components of particulate matter from the coastal North Sea were identified to be micro-organisms, detritus of dead and living organisms, quartz and clay minerals by microscopic and X-ray examination (Hunter, 1980). Suspended particulate is mostly negatively charged due to an adsorbed layer of metallic oxide and/or organic surface active materials which dominates the surface properties. Neihof and Loeb (1972) studied the surface charge of particulate matter in sea water. They proposed several interaction mechanisms including Coulombic attraction, adsorption by van der Waals forces, hydrogen bonding, selective anion adsorption or certain desorption and some complicated interaction with electropositive solutes. Gibbs (1977) reported the thickness of oxide coatings on clay particles ranging from 210 molecular layers on the 0.1 μm size fraction to 4,000 molecular layers on the 3.5 μm size fraction. Neihof and Loeb (1974) have shown that both types of positively charged and negatively charged particles interacted rapidly with dissolved organic materials to some extent and that the adsorption was irreversible. Their results indicated that the adsorbed materials were macromolecular substances having multiple binding sites. The strong retention of the adsorbed materials has enabled Hunter (1980) to study the dependence of electrophoretic mobility on pH and on metal ion concentration. Carboxylic acid (-COOH) and phenolic (-OH) groups were found to be the major ionizable functional groups in the organic film exposed to the solution. Phenolic and carboxylic acid groups are major oxygen-containing ionizable groups that occur in terrestrial humic substances. Results also showed a preferential orientation of phenolic groups toward the surfaces containing hydroxyl groups (e.g. oxide) through hydrogen bonding.

1.2.3. Removal of Particles from Sea Water

The removal of suspended particulate matter can be achieved by conventional filtration or direct filtration. Conventional filtration consists of a series of processes: coagulation-flocculation, sedimentation (in which the majority of the solids are removed) and filtration as the final polishing stage. In direct filtration, the process of sedimentation is eliminated and all of the solids are removed by the filters. Raw water of low suspended solid load is suitable for direct filtration (Bratby, 1986), where the conventional filtration can be inefficient. The poor kinetics of coagulation-flocculation limits the formation of settleable flocs. While the objective in conventional water treatment is to produce large settleable flocs, small "pin point" sized flocs are desired in direct filtration. The elimination of the sedimentation process has an economic advantage and in the case of in-line direct filtration the flocculation process is also eliminated.

The elimination of the flocculation process is a subject for debate. It has been shown that a minimum flocculation time is required to produce finished water qualities equivalent to those obtained by conventional treatment (Treweek, 1979) and that the filter run times can be increased when a flocculation period is allowed (Edzwald, 1986). However, Bratby (1986) has shown that the filtrate turbidity was increased with an increase in flocculation time. The reason for the above conflicting observations lies in the characteristics of the raw water. The effect of particle size on filtration efficiency has been modelled by Yao and co-workers (1971). In deep-bed filters, very small particles ($< 1 \mu m$) are transported to the surface of the filter grains mainly by diffusion and larger particles ($> 1\,\mu m$) by interception and sedimentation. Hence, particles of sizes around $1\,\mu m$ have a minimum filtration efficiency. This partly explains why the aggregation of submicron particles can lead to a lower filtration efficiency. However, aggregation of larger particles is expected to improve filtration efficiency.

The range of particles to be removed from sea water is large. The concentration of particles in sea water is low, in the region of a few mg/l. The sizes of the particles are small, mostly less than 10 micron. Despite the high ionic strength of sea water, the use of flocculants is required to destabilize the suspended particulate matter and to improve the removal efficiency. Most suspended matter in sea water is negatively charged for a number of reasons. However, adsorption of minor constituents (both high and low molecular weight materials) on marine particulates in sea water is the most likely cause (Neihof and Loeb 1972). The addition of a flocculant should reduce or even eliminate the electrical repulsion between approaching particles or between depositing particles and filter grains, and thus allowing contact to be made.

Prior to 1950, metal coagulants such as alum or ferric salts were used alone. Since the introduction of synthetic organic polyelectrolytes into the water treatment processes in the late 1950s, polyelectrolytes have been used extensively as coagulation aids or to replace metal coagulants completely. Culp (1977) reported that nonionic and anionic polyelectrolytes are usually better filter aids than cationic polyelectrolytes. Cationic polyelectrolytes are sometimes used to replace inorganic coagulants completely. Morrow and Raush (1974) have shown that proper mixing of polyelectrolyte is required as the destabilization of particulate matter is affected by the mixing energy. Rapid mixing at a velocity gradient of 300-650 sec^{-1} for 3-6 minutes is necessary before filtration (Yeh and Ghosh, 1981).

The trend of using polyelectrolytes as prime coagulants or as coagulation aids is increasing. The use of polyelectrolytes in flocculation may increase floc strength allowing larger and tougher flocs to form. The increased floc strength can withstand the increase in shearing forces on flocs as filtration proceeds and to enhance deposition of flocs on filter grains. The sludge volume is also reduced and the sludge produced by polyelectrolyte treatment is denser than inorganic sludge and has better sludge compaction and settling characteristics.

The selection of the appropriate polyelectrolyte for a particular application is not easy as there are a large variety of polyelectrolytes available. The correct choice of polyelectrolyte is important to get the best result. The effectiveness of polyelectrolyte is influenced by its chemical and physical nature as well as the environment in which it is used. The important polyelectrolyte characteristics are the monomer type, charge density, and molecular weight. Important raw water variables include colloid composition and concentration, water composition and its physical characteristics (Kasper and Reichenberger, 1983). In the treatment of sea water, the high ionic strength can severely affect the conformation of the polyelectrolytes. In solution of very low ionic strength, the polyelectrolyte molecules are more likely to adopt the extended conformations due to electrostatic repulsions between like charges along the molecules (Singley, 1972). In a high ionic strength solution such as sea water, the like charges are neutralized by the presence of indifferent electrolytes and the polyelectrolytes are more likely to be randomly coiled because of the reduced electrostatic repulsion.

It has been thirty years since the introduction of the use of synthetic polyelectrolytes in water treatment processes, during this period very few definite relationships between polymer type and water types have been identified (Kasper and Reichenberger, 1983). Today, initial polyelectrolytes selection is mainly through trial and error. A fundamental understanding of the influences of solution composition and of the characteristics of polyelectrolytes on the effectiveness of polyelectrolytes as flocculants is needed.

1.3 Purpose of the Present Work

The suitability of polyelectrolytes to use as flocculants is influenced by the environment in which they are used. The effects of ionic strength on the effectiveness of polyelectrolytes is important in the use of polyelectrolytes in the treatment of high ionic strength water, such as sea water. The present work studies the aggregation of a suspension of silica particles using cationic polyelectrolytes. The effect of ionic strength is examined in sodium chloride solutions of concentrations up to 5×10^{-1} mol dm^{-3}. The influence of different types of ions are compared and the effect of the presence of two electrolytes is investigated.

An optical technique described in Section 2.5.4. is used to monitor the aggregation of dispersed particles. The optimum dosage range at each ionic strength for each polymer tested are estimated and the results are compared and evaluated. The nature of the polymer is an important factor. The kinetic aspects of the flocculation process are investigated to gain a better understanding of polymer flocculation.

CHAPTER TWO

LITERATURE REVIEW

2.1 Colloidal Interactions

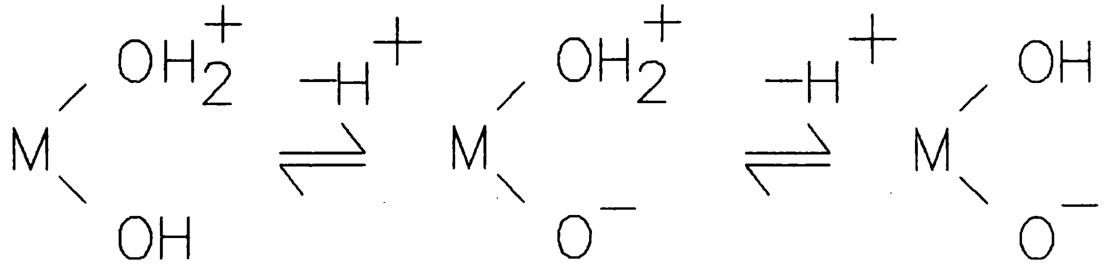
Most substances acquire a surface electric charge when dispersed in aqueous solutions and there are several charging mechanisms. The distribution of charges and potentials around the particles has been treated in the theory of electric double layer. The DLVO theory deals with the interactions of colloidal particles in terms of double layer interaction energies (section 2.1.3.) and gives a quantitative description of the stability of particles in terms of the energy changes which takes place when particles approach one another (section 2.1.4).

2.1.1. Origin of surface charge

There are at least five possible mechanisms by which particles can acquire a surface charge. In most cases, two or more of these mechanisms can operate simultaneously.

(a) Ionisation of surface groups

Certain materials acquire their charge through the ionisation of chemical groups at their surface. The surfaces of many oxides become hydroxylated in water. The hydroxyl groups at the surface may be ionised to give either positive or negative sites depending on the pH of the solution.



For a given oxide, there will be a characteristic pH value at which all positive and all negative charges on the surface are exactly balanced and the surface has no net charge. This is the point of zero charge (p.z.c.) whose value depends on the acid-base properties of the oxide. To some extent, the p.z.c. depends on the previous treatment of the oxide: the chemical and thermal histories; the purity, the crystalline or amorphous form and the ageing of the sample. Parks (1965, 1967) has given an extensive survey of experimental p.z.c. values for many oxides and hydroxides. Some typical p.z.c. values are given below.

oxide	SiO_2	TiO_2	Fe_2O_3	Al_2O_3	MgO
p.z.c.	2	6	8.5	9	12

(b) Ion dissolution

Sparingly soluble ionic crystals dispersed in water exist in equilibrium with a concentration of product ions, the concentration being determined from the solubility. Quite often these crystalline solids can acquire a surface charge by an unequal dissolution of the oppositely charged ions. Ionic solids such as silver halides and calcium carbonate are charged due to ion dissolution.

(c) Isomorphous substitution

The cations inside the crystal structure of some clay minerals can be replaced by cations of similar size but lower charge without structural change, the resultant particles in water are negatively charged because of the substitution of Al^{3+} by Mg^{2+}.

(d) Specific adsorption

Particles can acquire surface charge via the preferential adsorption of certain ions from solution. Surfaces which are already charged (for instance by surface ionisation) have a preferential tendency to adsorb counter-ions, in particularly, those with a high charge number. Surfaces are more often negatively charged than positively charged due to the preferential adsorption of anions. The more hydrated cations have the greater tendency to reside in the bulk aqueous medium and the less hydrated and more polarising anions have the greater tendency to be specifically adsorbed. Large organic molecules are adsorbed via hydrogen or hydrophobic bonding. In natural waters, many particles are negatively charged because of the adsorption of organic anions.

(e) Adsorption of dipolar molecules

Molecules having a permanent dipole may adsorb at interfaces with a preferential orientation. The presence of a layer of orientated dipolar molecules at the surface may alter the nature of the surface.

The nature of the electric double layer is described in the following section.

2.1.2. The electric double layer

The surface charge of suspended particles is balanced by an excess of neutralizing counter ions over co-ions distributed in a diffuse manner in aqueous solution. The electric double layer is made up of the charged surface which may include adsorbed ions and a diffuse layer of counter-ions and co-ions distributed under the influence of electrical forces and random thermal motion, as shown in Figure 2.1.. The simplest quantitative treatment of the double layer was developed independently by Gouy (1910) and Chapman (1913) and is based on the followings assumptions:

(i) An infinite, uniformly charged surface.
(ii) The ions in solutions are point charges distributed according to Boltzmann distribution.
(iii) Dielectric constant of the solvent is uniform.

ψ_o is the surface electric potential and ψ is the electric potential at a distance x from the surface in the electrolyte solution. The net volume charge density, ρ , at points where the potential is ψ can be derived from the Boltzmann distribution relating ρ to ψ by Poisson's equation for a flat double layer, giving the following expression:

$$\frac{d^2\psi}{dx^2}=\frac{2zen_o}{\epsilon}\sinh\frac{ze\psi}{kT} \qquad (2.1)$$

where z - valency of the ion
e - elementary charge
n_o - the bulk concentration of each ionic species
k - Boltzmann constant
T - absolute temperature
ϵ - permittivity of the material

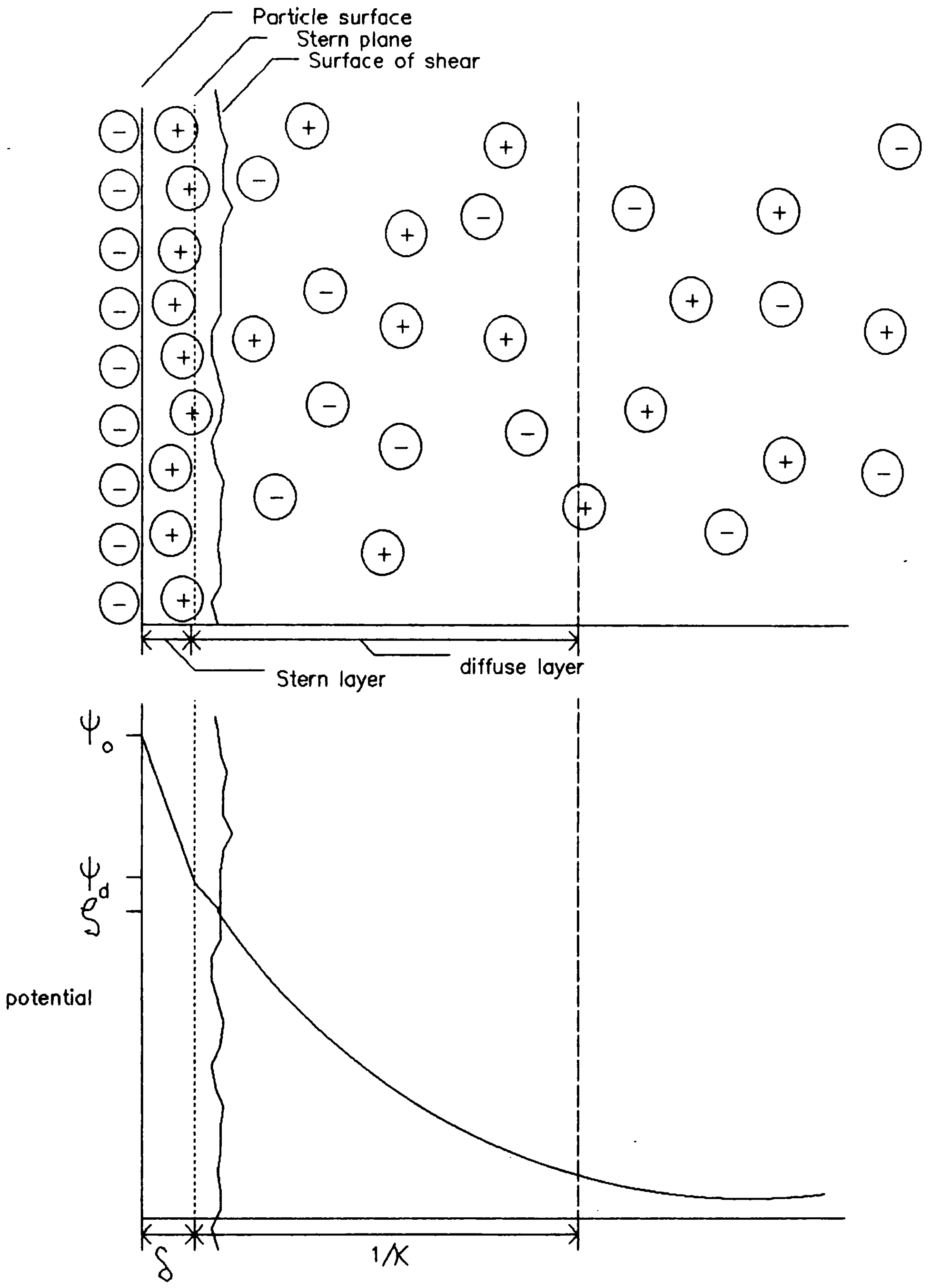


Figure 2.1. The structure of the electric double layer and the potential changes

Taking the following boundary conditions into account:

$\psi = \psi_0$ when $x = 0$

$\psi = 0$ when $d\psi/dx = 0$ i.e. $x = \infty$,

the solution of equation (2.1) can be written as:

$$\psi = \frac{2kT}{ze}\ln\left(\frac{1+\gamma\exp[-\kappa x]}{1-\gamma\exp[-\kappa x]}\right) \tag{2.2}$$

where

$$\gamma = \frac{\exp[ze\psi_0/2kT]-1}{\exp[ze\psi_0/2kT]+1} \tag{2.3}$$

and

$$\kappa = \left(\frac{2e^2 n_0 z^2}{\epsilon kT}\right)^{1/2} = \left(\frac{2e^2 N_A c z^2}{\epsilon kT}\right)^{1/2} \tag{2.4}$$

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

The Debye-Hückel approximation can be applied if $ze\psi_0/2kT \ll 1$. Then,

$$\exp\left[\frac{ze\psi_0}{2kT}\right] \approx 1 + \frac{ze\psi_0}{2kT} \tag{2.5}$$

this would simplify equation (2.2) to

$$\psi = \psi_0 \exp[-\kappa x] \tag{2.6}$$

This means that the potential decreases exponentially with distance from the charged surface at low potential.

By equating the surface charge with the net space charge in the diffuse part of the double layer and applying the Poisson-Boltzmann distribution, an expression can be derived to relate the charge density σ_0 at the surface and the potential ψ_0.

$$\sigma_0 = (8n_0\epsilon kT)^{1/2}\sinh\frac{ze\psi_0}{2kT} \tag{2.7}$$

which at low potential reduces to

$$\sigma_0 = \epsilon\kappa\psi_0 \tag{2.8}$$

This surface potential ψ_0 depends on the surface density σ_0 and through κ on the ionic composition of the medium. Equation (2.8) shows that at low potentials, a diffuse double layer can be regarded as a condenser with a distance $1/\kappa$ between the plates. $1/\kappa$ is often referred to as the "thickness" of the diffuse double layer.

For an aqueous solution of a symmetrical electrolyte at 25 °C, equation (2.4) becomes

$$\kappa = 0.329 \times 10^{10} \left(\frac{cz^2}{mol\,dm^{-3}} \right)^{1/2} m^{-1} \tag{2.9}$$

For a 1-1 electrolyte the double layer thickness, $1/\kappa$, is about 10 nm at 10^{-3} mol dm^{-3} and $1/\kappa$ reduces to about 1 nm at 10^{-1} mol dm^{-3}. For unsymmetrical electrolytes the double layer thickness can be calculated by taking z to be the counter-ion charge number. The range of electrical interaction is dependent on the square root of the salt concentration. Typically, $1/\kappa$ is about 900 nm in near-distilled water and it can be as low as 0.4 nm in sea water (Gregory 1977).

In the Gouy-Chapman theory, the ions are treated as point charges. Stern (1924) proposed a model to take into account the finite size of the ions. In the Stern model the double layer is divided by a plane, known as the Stern plane, located at about a hydrated ion radius from the surface. Grahame (1947) modified the Stern model to account for specifically adsorbed ions. Specifically adsorbed ions are likely to be dehydrated, at least in the direction of the surface, so as to attach themselves to the surface specifically. The centres of any specifically adsorbed ions are located in the inner Helmholtz plane (I.H.p). In the Stern layer the closest approach of any non-specifically adsorbed ions are located in the outer Helmholtz plane (O.H.p.). Ions located outside the Stern layer, in the diffuse layer, are distributed according to Gouy-Chapman theory. Figure 2.1. illustrates the structure of the electric double layer, showing that the potential changes from ψ_o (surface potential) to ψ_d (Stern potential) in the Stern Layer and decays from ψ_d to zero in the diffuse double layer.

The Stern potential cannot be measured directly but it can be estimated from electrokinetic or ζ (zeta) potential, as determined from electrokinetic measurements. The ζ potential is the potential at the surface of shear between the charged surface and the electrolyte solution. The surface of shear is an imaginary surface enclosing a sheath around the particle inside which all material forms the kinetic units, so that a certain amount of surrounding liquid and its contained electrolyte ions accompany the particle as it moves. The exact location of the shear plane is not certain. It is usual to suppose the shear plane is at a small distance further away from the surface than the Stern plane. Nevertheless, the ψ_d is usually identified with ζ . The errors introduced through this assumption are usually small (Shaw, 1980), especially at low potential and in the absence of the adsorption of non-ionic surfactant. Lyklema (1977) has demonstrated that ψ_d and ζ coincide for the model AgI colloid in aqueous solution. However, the compression of the diffuse layer at higher electrolyte concentration will cause a steeper potential drop from the Stern plan to the shear plane.

2.1.3 Type of Interactions

Dispersed colloidal particles are in constant Brownian motion. When these particles approach one another, they experience interaction of various kinds; the magnitude of which depends on their distance apart. The resultant energies determine whether or not the colliding particles will form permanent aggregates. The electrical repulsion and van der Waals' attraction are the most studied interactions, which form the basis of the DLVO theory of stability of lyophobic sols (see Section 2.1.4.). There are also short range structure forces, steric interaction due to adsorbed polymer, hydrophobic and hydrodynamic interaction.

(a) Electrical double layer repulsion

The overlapping of the diffuse part of the double layer of approaching surfaces give rise to the electrostatic interaction energy. The interaction, V_R, between two flat interfaces can be calculated from an expression derived from the Gouy-Chapman theory (Verwey and Overbeek, 1948). The V_R between two spherical particles has no exact analytical expression and has to be treated by various approximations and numerical solutions (Verwey and Overbeek, 1948; Honig and Mul, 1971).

Depending on whether or not ionic adsorption equilibrium is maintained during the interaction, either constant surface potential or constant surface charge can be assumed. When electrochemical equilibrium is maintained, interaction is expected to take place at constant potential. On the other hand, as Overbeek (1971) has pointed out, the rate of double layer overlap in a typical Brownian encounter of two particles is too fast for adsorption equilibrium to be maintained. Therefore, the charge rather than the potential will be the constant parameter.

Recently, Dukhin and Lyklema (1990) presented a novel approach to the stability of lyophobic colloids by considering the dynamics of interaction taking the disequilibration of interacting double layers into account. Desorption-adsorption disequilibrium of charge-determining ions is considered as the origin of a relaxation-determined retardation. During the approach of a second particle, the double layer composition is adjusted through a variety of mechanisms. Processes such as charge transfer through the particle, transfer along the surface or through the diffuse part of the double layer can be responsible for the relaxation of the transient excess charge. Dynamics effects become important when the adjustment of double layer has relaxation times that are neither infinitely short nor infinitely long in comparison with the time scale of interaction. The diffuse part of the double layer has a much shorter relaxation time than the surface charges. These authors consider the difference between interaction at constant surface charge and constant surface potential is essentially two extreme cases of no surface charge relaxation at all representing frozen equilibrium and full relaxation representing complete equilibrium respectively. The intermediate situation of relaxation at time scales not very different from the time scale of interaction represents incomplete equilibration which relates to a retarded desorption of charge-determining ion. A number of points emerges from their model:

(i) Under conditions where the relaxation retardation dominates, the stability becomes independent of particle size.

(ii) In addition to the hydrodynamic retardation (see section 2.1.3.c.), there is the possibility of relaxation retardation which may explain the observed rate constants often being slower than the predicted Smoluchowski rate constants.

(iii) The coupling of adsorption-desorption phenomena with relatively fast diffusion processes creates a link with electrokinetic phenomena and double-layer relaxation.

Whether constant potential or constant charge is appropriate will depend on the individual system. While the dynamic aspects of electric double layer interaction are not fully understood, calculations are often made on the basis of "constant potential" or "constant charge" assumptions. Considering that the double layer interaction depends on the potential at the Stern plane rather than the surface potential, and that the Stern layer equilibrium may be reached faster than that at the particle surface, neither assumption may be appropriate.

An expression for the energy of interaction has been derived based on the Linear Superposition Approximation (LSA) which is a compromise between the constant charge and constant potential conditions. For different spheres:

$$V_E = \frac{64a_1a_2}{a_1+a_2}\pi\epsilon(kT/ze)^2\gamma_1\gamma_2\exp(-\kappa x) \qquad (2.10)$$

where V_E is the electrical energy of interaction, a_1 and a_2 are radii of the particles, ϵ is the permittivity of the medium, z is the valency of the ions and e is the elementary charge. The terms γ_1 and γ_2 are dimensionless functions of the surface potential (see equation 2.3).

For identical particles, Equation (2.10) becomes

$$V_E = 32\pi\epsilon a_1(\kappa T/ze)^2\gamma_1^2\exp(-\kappa x) \qquad (2.11)$$

(b) Van der Waals attraction

Individual atoms or molecules attract one another because of the van der Waals attractive forces arising from dipole-dipole interaction (Keesom), dipole-induced dipole (Debye) and interaction due to fluctuations in the electron density distribution (London). As colloidal particles are essentially assemblies of molecules, the van der Waals interaction energy between two particles is the sum of all attraction between all interparticle molecule pairs. It is further assumed that only the London attraction is considered, since colloidal particles are not likely to have a net dipole moment nor a net polarization.

Hamaker (1937) has derived an expression for the London dispersion interaction energy, V_A. For equal spheres, if $x \ll a$ this equation can be simplified to

$$V_A = -\frac{Aa}{12x} \tag{2.12}$$

where A is the Hamaker constant. To evaluate the Hamaker constant, there are the London-Hamaker microscopic approach and the Lifshiftz macroscopic approach. The Hamaker approach is based on the interaction between pairs of atoms centre around a single oscillation frequency. In the Lifshiftz approach the spontaneous electromagnetic fluctuations in two approaching particles becomes correlated. The values of the Hamaker constant range from 0.3×10^{-20} J to 10×10^{-20} J in aqueous dispersions.

Equation (2.12) indicates that the attraction become stronger on close approach and infinite on contact. However, Born repulsion and other short-range interactions become important at close approach, and keep the attraction finite. For interaction through a liquid rather than a vacuum, the van der Waals interaction energy is considerably lower. Equation (2.12) still applies but a modified Hamaker constant has to be used. Consider the interaction between two particles, 1 and 2, in a dispersion medium, 3. The Hamaker constants A_{13} and A_{23} correspond to interaction between the dispersion medium with particle 1 and particle 2 respectively. The effective Hamaker constant is given by:

$$A_{123} = A_{12} + A_{33} - A_{13} - A_{23} \tag{2.13}$$

where A_{12} is due to particle-particle interaction and A_{33} are due to dispersion medium-dispersion medium interaction.

If the attraction between unlike phases is taken as the geometric mean of the attractions of each phase to itself, then equation (2.12) becomes

$$A_{132} = (A_{11}{}^{1/2} - A_{33}{}^{1/2})(A_{22}{}^{1/2} - A_{33}{}^{1/2}) \tag{2.14}$$

When the two particles are of the same material, equation (2.13) can be reduced to

$$A_{131} = (A_{11}{}^{1/2} - A_{33}{}^{1/2})^2 \qquad (2.15)$$

The physical meaning for Equations (2.14) and (2.15) is that the van der Waals interaction is always attractive for like material but a repulsive van der Waals interaction between the particles is possible if A_{33} has a value intermediate between those of A_{11} and A_{22}. There is little evidence of repulsive van der Waals interaction. However, it is important in wetting phenomena (Hough and White 1980) and in phase separation from polymer solution (van Oss *et al* 1979).

The finite time of propagation causes a reduced correlation between oscillations in the interacting bodies, resulting in a smaller interaction. Hence, van der Waals forces are subject to a retardation effect because of their electromagnetic origin. It is often assumed that the retardation becomes significant when the distance of separation between interacting bodies becomes larger than the characteristic wavelength of the electromagnetic interaction. The characteristic wavelength of the van der Waals interaction, λ , has a value of around 100 nm for most materials. However, retardation can be considerable at a much closer separation for spherical particles. The interaction is reduced by a factor of about 2 for spheres of radius 1 μm separated by a distance of 10 nm ($\lambda/10$). Retardation is implicitly induced in the Lifshitz treatment but for the Hamaker approach a modification is required.

Czarnecki and Dabros (1980) studied the effect of surface roughness on van der Waals interaction. Their result has shown that when the roughness layer is thick in comparison with the separation distance, the unretarded interaction are substantially reduced. However, the effect of roughness is less prominent if retardation is taken into account.

(c) Solvation effects

The structure of a liquid adjacent to a solid surface is different from that of the bulk. This structuring effect of solvent molecules is usually of short range, of the order of a few molecular diameters. In aqueous systems, the hydration of surface ionic groups of particles has important consequence in the interaction of approaching particles, since an increase in repulsion is expected. At close approach, the water of hydration must be removed from the approaching surfaces. Ions in aqueous solution are similarly hydrated. Pashley and Israelachvili (1984) studied the hydration effect by measuring the forces between mica sheets in various electrolyte solutions. At low ionic strength, the repulsion follows the expected exponential form for double layer interaction. A short-range repulsion due to adsorbed hydrated ions can be observed at higher ionic strength, about 10^{-3} M. The repulsion forces increase with the degree of hydration and are roughly exponential over the range 1.5 to 4 nm. At high electrolyte concentration, anomalous stability of latex particles has been observed (Healy *et al* 1978) which can be explained in terms of hydration forces.

(d) Steric interaction

The effect of adsorbed polymer on the particles is complex; the presence of adsorbed polymer may modify the van der Waals forces, and also the electrostatic forces in charged particles. The surface-charge density and the distribution of counter-ions between the Stern layer and the diffuse layer may well be changed. While small amounts of adsorbed polymer can promote flocculation (see Section 2.1.3.(e) sensitisation), the stability is often enhanced with higher amounts of adsorbed polymers. Collision of particles coated with an adsorbed layer of polymer causes the adsorbed layers to come into contact and gives rise to steric interaction between the layers. The layers may compress or interpenetrate during an encounter. In most cases, interpenetration of the layers is more likely initially and compression may become appreciable on closer approach.

The interpenetration of the adsorbed layers leads to a local increase in the concentration of polymer segments. Enthalpic and entropic changes will be involved. Depending on the balance between polymer-polymer and polymer solvent interactions, the result may be repulsion or attraction by an osmotic mechanism. The number of possible chain conformation is reduced as the adsorbed polymer is compressed, the reduced entropy may lead to an increased free energy. Similarly, if interpenetration takes place to a significant extent, a decrease in entropy and an increase in free energy will lead to an elastic repulsion. Depending on the magnitude of the respective enthalpic and entropic changes, the system may be sterically stabilized or weakly flocculated. This type of flocculation is reversible and the particles do not come into true contact.

The stability of particles with adsorbed layers is affected by:

(i) the thickness of the adsorbed layer
(ii) the solvation of the adsorbed polymer
(iii) the size of the particles
(iv) the effective Hamaker constant of the coated particles

The adsorbed layer can be considered as a steric barrier of sufficient thickness to prevent particles approaching each other close enough for van der Waals attraction to become significant. Consequently, a thicker adsorbed layer is required for larger particles as the van der Waals attraction is larger for larger particle at a given separation distance. When the polymers have a higher affinity for water than for their own kind, the mixing of polymer chains is not favoured thermodynamically. A repulsion between the surfaces will result. If the solvency of the water for the polymer chains is reduced, the mixing of the chains could become thermodynamically favourable which results in an attraction between the surfaces. The solvency of the water can be changed by an addition of electrolytes or by changing the temperature. When particles are covered by a thick layer of polymers, the Hamaker constant of the adsorbed polymers may be more significant than that of the bare particles in determining the magnitude of van der Waals forces.

(e) Sensitisation

The stability of a colloidal dispersion can be reduced by the addition of a small quantity of polymer which would act as stabilizing agent if used in larger quantity. Two models have been postulated to explain the flocculation of colloidal dispersion on addition of a small quantity of polymer. In the polymer bridging model, as shown in Figure 2.2., segments of polymer molecules become attached to particles at many points (Ruehrwein and Ward, 1952). In the electrostatic patch model (Kasper, 1971; Gregory, 1973), the polyelectrolytes adsorb on oppositely charged particles in such a way that there are areas of either excess positive or excess negative charges on the surface. Attraction of particles occurs when positive "patch" of one particle come into contact with the negative "patch" of another particle, as shown in Figure 2.3..

(f) Hydrophobic interaction

A hydrophobic surface has little affinity for water. As a result, water avoids contact with such surfaces. In aqueous solutions, hydrophobic surfaces tend to associate with one another so as to minimize contact with water. The hydrophobic attraction can be larger than the van der Waals forces and extends to a relatively larger distance. Interaction between hydrophobic surfaces has been demonstrated by Israelachvili and Pashley (1984). These authors have found that the attraction between hydrophobic surfaces in water is much stronger than the conventional van der Waals dispersion force in the range 0-8 nm. Since the attractive force decays exponentially with distance rather than as a power law, it cannot be attributed to a "modified" van der Waals interaction. Attraction between hydrophobic surfaces can be up to about 80 nm (Claesson and Christenson, 1988). The origin of hydrophobic interaction remains controversial. Some researchers believe that there is a "hydrophobic bond" associated with it (Nemethy and Scheraga, 1962; Tanford, 1980). Others recognise the hydrophobic effect as an entropic effect (Marcelja et *al*, 1977; Pratt and Chandler, 1977; Rao et *al*, 1979 and Mihaly et *al*, 1981a, 1981b,). The entropic effect arises from the configurational rearrangement of water molecules around hydrophobic species and that the hydrophobic interaction involves a further structural rearrangement of water as two hydrophobic particles comes together. An increased free energy results from the reduced entropy of the restricted structuring of water molecules in between hydrophobic material. A lower free energy state is achieved through the migration of water molecules from the gap to the bulk water where there are unrestricted hydrogen-bonding opportunities. Dispersions of hydrophilic mineral are usually stable in aqueous solution and cannot be floated. However, in mineral

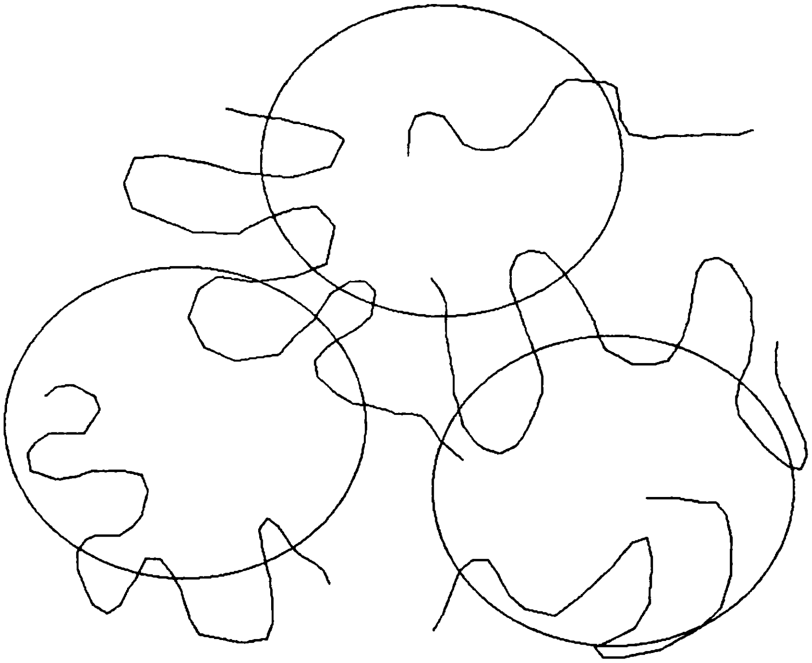


Figure 2.2. Schematic illustration of bridging flocculation

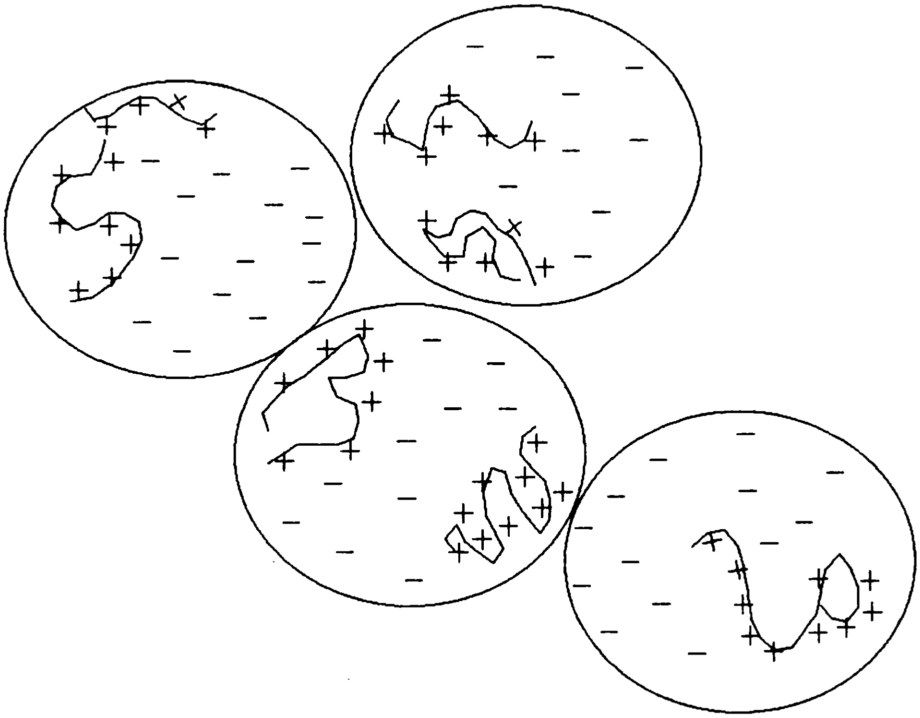


Figure 2.3. "Electrostatic patch" model for the interaction of negatively charged particles with adsorbed cationic polyelectrolyte

processing such a dispersion can be successfully aggregated and floated after treatment with suitable flotation reagents. The collector used in flotation is usually amphiphilic in nature. It is generally believed that the hydrophilic part of the molecules adsorb onto the mineral particles with the hydrophobic part projecting toward the aqueous phase. The precise nature of hydrophobic attraction in the aggregation of particles has not been fully established.

(g) Hydrodynamic interaction

When particles approach each other, the disperse medium must drain from the region of contact. As the separation between the approaching particles decreases, it becomes increasingly difficult for the medium to drain. The effect is to retard the approach of particles. This hydrodynamic or viscous interaction is of longer range than the colloidal forces. At closer approach, the hydrodynamic resistance is partly overcome by the van der Waals attraction but the particle collision rate can be greatly reduced.

2.1.4. Stability of Colloidal Particles

Deryagin and Laudau (1941) and Verwey and Overbeek (1948) have independently developed a quantitative theory to relate the stability of lyophobic sols in terms of the energy changes between particles at infinite separation and at a separation x. The classical DLVO approach to colloid stability is based only on van der Waals and electrical interactions. These contributions are assumed additive and combine to give the total interaction.

$$V_{Total} = V_A + V_E \qquad (2.16)$$

where V_{Total} is the total energy of interaction, the summation of the energy of attraction, V_A and the energy of repulsion, V_E. Both the V_A and V_E are distance dependent. V_E decreases approximately exponentially (equation 2.11) whereas V_A decreases according to an inverse power law (equation 2.12) with the distance between the particles. Since the decrease with distance of V_A is less marked than with V_E, van der Waals attraction will predominate at small and large interparticle distances. The attractive and repulsive potential energies for the interaction of colloidal particles are depicted in Figure 2.4..

The total potential energy curve in Figure 2.5. shows a number of features: an energy barrier, a primary and a secondary minimum e The magnitude of these determine the stability of the colloid. Aggregation occurs at larger separation distance in the secondary minimum, at which the particles do not come into close contact. For small particles, the secondary minimum is never deep enough for aggregation to occur. For large particles (radii greater than $1\mu m$) and in solutions of moderately high ionic strength, aggregation into the secondary minimum may occur to give a weak, reversible aggregation. This phenomenon has been studied by Hogg and Yang (1976). At small separation distance, two colliding particles need to have sufficient energy to overcome the energy barrier to come close enough into the primary minimum in order to form a stable aggregate. Generally, a barrier height of a few kT units is sufficient to maintain colloidal stability.

The DLVO theory predicts the effect of an inert electrolyte on colloidal stability reasonably well, at least in a semiquantitative manner. The strong dependence of the critical coagulation concentration on the counter-ion valence is also predicted by the empirical Schulze-Hardy rule (Schulze, 1882, 1883; Hardy, 1900). However, there are other types of interaction which have to be considered. The total potential energy can be described by summing these contributions.

$$\begin{aligned} V_{Total} = {} & V_{att}(van\ der\ Waals) + V_{rep}(short\ range) \\ & + V_{rep}(electrostatic) + V_{rep}(steric) \\ & + V_{rep}(solvation) + V_{rep}(other\ effects) \qquad (2.17) \end{aligned}$$

It can be seen from Equation (2.17) that the interaction of two particles approaching each other is very complex. In practice, it is not necessary to consider all these contributions simultaneously, nor is

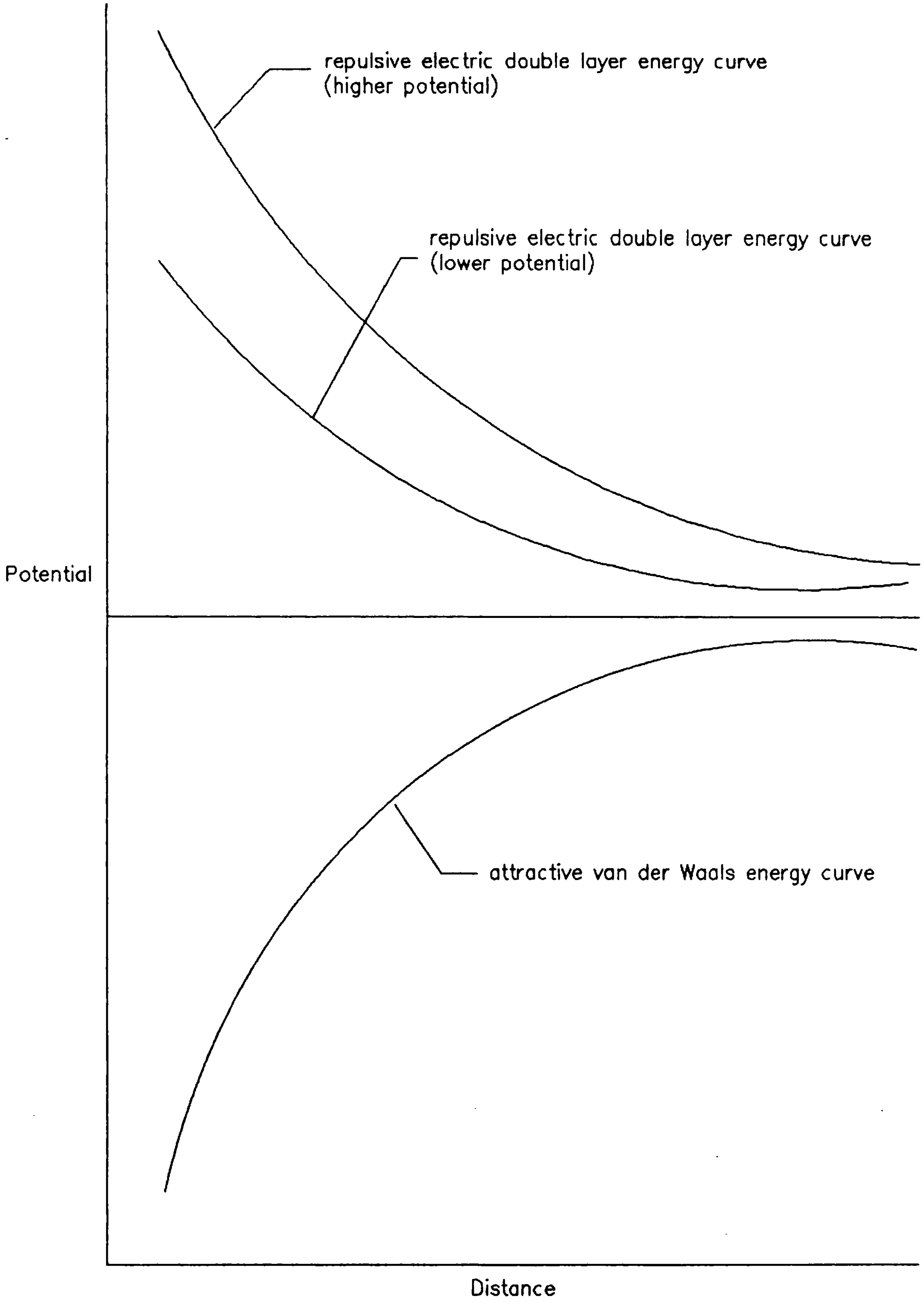


Figure 2.4. Potential energy diagram for colloidal particles

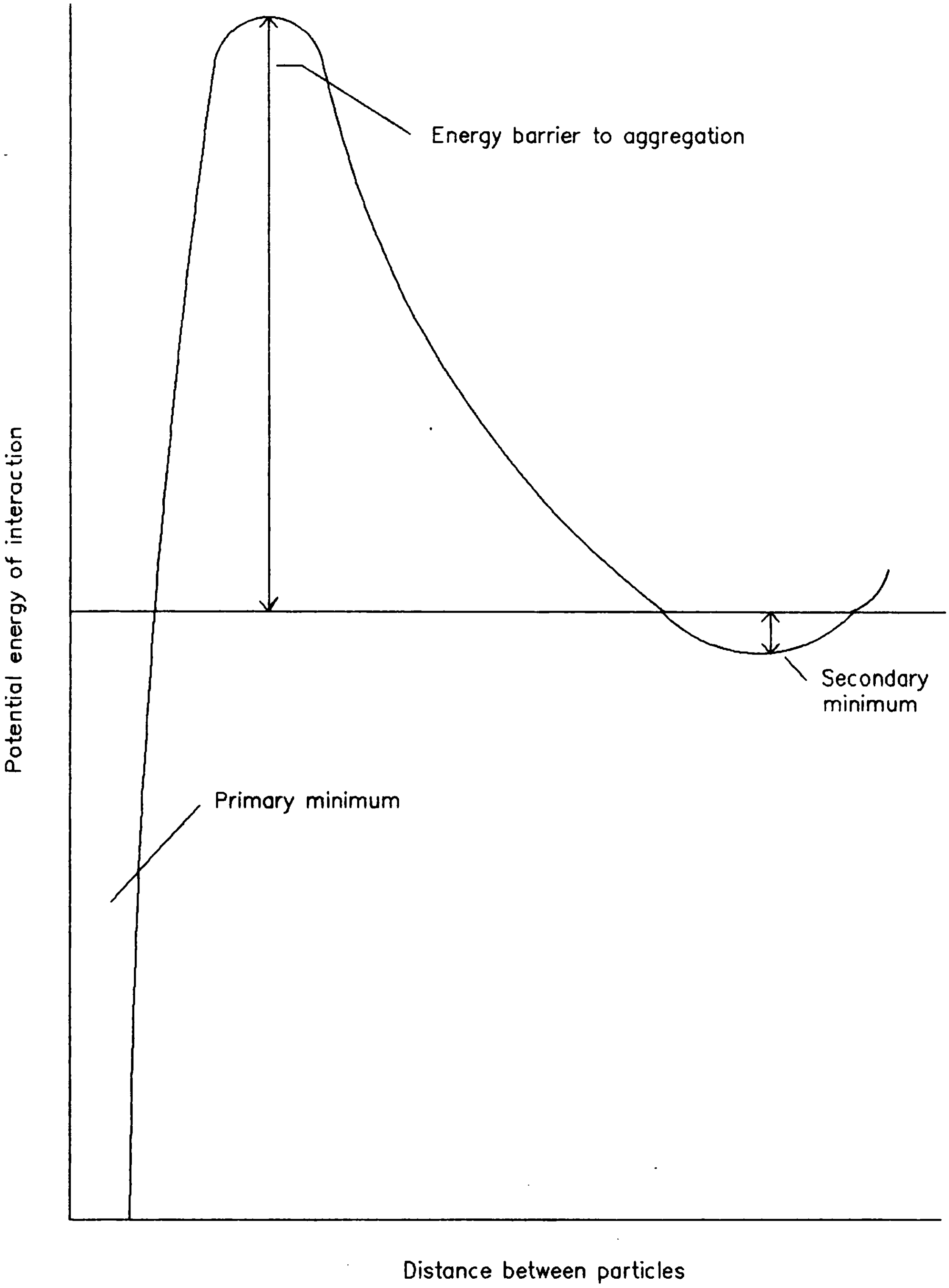


Figure 2.5. Total interaction energy curve, obtained by the summation of an attraction curve and a repulsive curve

it possible in most cases. Therefore, in general only the van der Waals forces and the long range repulsion forces either from electrostatic or from steric contributions are considered.

2.2. Aggregation Kinetics

The rate at which a suspension aggregates depends on the rate of collision of the particles and the collision efficiency factor. Under practical conditions, the important particle transport mechanisms are Brownian Motion (perikinetic flocculation), fluid motion (orthokinetic flocculation) and differential settling. Collision mechanisms and factors affecting collision efficiency are considered in the following sections.

2.2.1. Perikinetic flocculation

Perikinetic flocculation occurs as a result of random Brownian motion of the particles and the collision rate can be calculated from diffusion theory. The first quantitative treatment of flocculation kinetics was put forward by Smoluchowski (1916). Consider a suspension containing spherical particles of radii a_1 and a_2, and number concentration N_1 and N_2, the collision frequency J_{12} (per unit volume and unit time) is given by:

$$J_{(12)} = (2kT/3\eta)N_1N_2(a_1+a_2)^2/a_1a_2 \tag{2.18}$$

where k is Boltzmann's constant, T the absolute temperature, η the viscosity of the fluid.

The rate constant K_{peri} for perikinetic flocculation can be written as:

$$K_{peri} = \frac{2kT}{3\eta}\frac{(a_1+a_2)^2}{a_1a_2} \tag{2.19}$$

By making a number of simplifying assumptions, such as spherical particles initially of uniform size, the following expression for the change in total number concentration of particles, N_T, with time, t, has been derived:

$$\begin{aligned}\frac{-dN_T}{dt} &= (4\alpha kT/3\eta)N_T^2 \\ &= K_F N_T^2 \end{aligned} \tag{2.20}$$

where α is the fraction of successful collisions, and K_F is known as the flocculation rate constant. α is the collision efficiency factor which depends on the colloidal stability of the particle; it allows for the possibility that not all collisions may be successful in producing aggregates.

Equation (2.20) shows that the flocculation process is second order with respect to particle concentration and that the flocculation rate constant K_F is independent of particle size, as the size terms cancel from Equation (2.19) when $a_1 = a_2$. The term $(a_1 + a_2)^2/a_1a_2 = 4$ when $a_1 = a_2$. The value of the size term is about 5 for particles of sizes differing by a factor of 3, so that the assumption of a constant size term is still reasonable. As flocculation proceeds, the opposing effects of decreasing diffusion coefficient and increasing collision radius with larger particle size on collision rate cancel out for similar sized particles. However, the rate for larger differences in size becomes appreciably faster than for equal particles. Furthermore, particle size can affect α . Therefore, the Smoluchowski approach to perikinetic flocculation is only applicable at the early stages of flocculation.

In dilute electrolyte solutions, repulsion between charged particles can be significant and consequently the collision efficiency can be very low. The experimental flocculation rate for a fully destabilised suspension is often slightly less than the predicted Smoluchowski rate. The effect of hydrodynamic interaction can account for the discrepancy and this aspect will be considered in Section 2.2.4..

2.2.2. Orthokinetic flocculation

It is known that gentle agitation of a destabilized dispersion often leads to a large increase in flocculation rate and forming much larger flocs than would be formed by diffusion alone. The particle transport mechanism is due to the relative motion of particles, the so-called orthokinetic flocculation. Laminar shear and isotropic turbulence are two types of fluid motion considered in the derivation of rate equations for orthokinetic flocculation. In the Smoluchowski treatment of orthokinetic flocculation in a uniform laminar shear field (1917), it is assumed that particles follow fluid streamlines and the collision frequency depends on the size of the particles and on the velocity gradient or shear rate, G. The collision frequency is

$$J_{(12)} = \frac{4}{3} G (a_1 + a_2)^3 N_1 N_2 \tag{2.21}$$

where J_{12} represents the number of collisions in unit volume and unit time among particles of radii a_1 and a_2, and number concentration N_1 and N_2.

The rate constant K_{ortho} for orthokinetic flocculation can be written as:

$$K_{ortho} = \frac{4}{3} G (a_1 + a_2)^3 \tag{2.22}$$

The rate of decrease of the total particle concentration, N_T, for a monodispersed suspension is

$$-\frac{dN_T}{dt} = \frac{16}{3} \alpha N_T^2 G a^3 \tag{2.23}$$

The term α indicates the fraction of successful collisions. The dependence of the rate on the third power of particle size accounts for the higher flocculation rate commonly observed for orthokinetic flocculation of larger particles.

All practical flocculation processes take place under turbulent conditions. The Smoluchowski treatment of uniform laminar shear is no longer applicable. An approach to treat flocculation in turbulent flow was due to Camp and Stein (1943). They derived an average shear rate, $\overline{G}$, from the rate of turbulent energy dissipation to the fluid in the flocculation vessel.

$$\overline{G} = (P/\mu V)^{1/2} \tag{2.24}$$

where P is the net power input to a volume V of fluid.

This Camp-Stein approach is an over-simplification, since the turbulent flow is much too complicated to be treated by simple averaging of the power input. However, the result is very close to that from a more rigorous treatment by Saffman and Turner (1956) for particle collisions in isotropic turbulence.

2.2.3. Differential settling

Differential settling refers to the collision process in which collisions of particles arise from particles of different size or density settling at different rates. A settling particle overtakes and collides with a particle of lower sedimentation velocity. Assuming the Stokes law applies, the collision frequency for spherical particles of equal density is

$$J_{12} = (2\pi g/9\mu)(\rho_s - \rho)N_1 N_2(a_1 + a_2)^3(a_1 - a_2) \qquad (2.25)$$

where g is the acceleration due to gravity, and ρ_s and ρ are the densities of the particles and fluid respectively. This collision mechanism depends on different particles having different sedimentation velocities. It is enhanced by a higher particle density and by a wide range of particles.

2.2.4. Hydrodynamic effects

It has previously been mentioned that the collision efficiency factor can be less than one even when the particles are fully destabilised because of hydrodynamic interaction. It is generally believed that the displacement of the fluid from the narrowing gap between the two approaching particles at close approach is the origin of hydrodynamic forces which tend to prevent particles coming into close contact. However, attractive forces such as van der Waals forces can overcome the viscous resistance and allow particles to come together to form aggregates. In the case of oppositely-charged interacting particles, there may be long-range attractive forces bringing the particles together. The effect of hydrodynamic forces can retard the approach of particles many particle diameters apart.

Hydrodynamic effects in perikinetic flocculation cause a reduction in diffusion coefficient of the approaching particles. In orthokinetic flocculation, hydrodynamic effects are more prominent and can greatly reduce the flocculation rate. It causes particles in shear flow to deviate from rectilinear paths and the presence of a particle can influence the trajectories of neighbouring particles. The collision efficiency is reduced as the particle size and the shear rate are increased. Hydrodynamic effects become much more important for particles of different sizes (Adler, 1981). However, it is possible that hydrodynamic forces are much less significant when the interacting particles are porous as in loosely bound aggregates of colloidal particles (Wolynes and McCammon, 1977). When interparticle repulsion is significant, flocculation in shear flow is very difficult to analyse. Colloidal and hydrodynamic forces combine in a complex manner. It is possible that a suspension could be stable over a certain range of shear rates, but flocculate at higher and lower values (Hirtzel and Rajagopalan, 1985).

2.3. Flocculation by Polymers

The nature of organic polymeric flocculants and polymeric flocculation are described in this section.

2.3.1. Organic polymeric flocculants

Chemical additives are often used to improve the separation of particles by processes such as sedimentation, filtration and flotation. The use of synthetic organic polymer flocculants in the water treatment field began in the late 1950's. There are a few characteristics of polyelectrolytes that make them more suitable for a certain specific water treatment application. The most important characteristics are the nature of the monomer units that make up the polyelectrolyte, the type of charged group, the varying charge density, the molecular weight and the structure (linear or branched) of the polyelectrolyte. A wide range of properties can result from synthesis of polyelectrolytes and this makes the selection of polyelectrolytes a very difficult task. Knowledge of the polyelectrolytes/particulates interactions is of great importance to the selection. However, it is not always possible to predict the optimum type for specific application. The efficacy of polyelectrolytes in any system is evaluated through laboratory screening and in-plant testing.

Polyelectrolytes can be nonionic, anionic or cationic in character depending upon the monomer unit of the polyelectrolyte. Most commercial products are based on homopolymerization or copolymerization of acrylamide monomers. Acrylamide is often homopolymerized to form polyacrylamide, a nonionic polymer (Mangravite, 1983). Acrylamide is copolymerized with acrylic acid or sodium acrylate to make anionic polymers (Yen, 1976). Alternatively, anionic polymers can be made via the homopolymerization of acrylamide and hydrolysis of some of the acrylamide groups to sodium acrylate (Yen, 1976). Cationic polymers are commonly made by copolymerization of acrylamide with a suitable cationic monomer, such as dimethylaminoethyl acrylate or methacrylate (Gregory, 1986). Charge density depends on the number of ionisable groups and the degree of ionisation. The number of ionisable groups is determined during polymer synthesis e.g., the degree of hydrolysis of polyacrylamide or the proportion of cationic monomer incorporated. The degree of ionisation depends on the nature of the ionic groups and the solution conditions. The cationic charge of the unquaternized or partially quaternized polyamines is pH dependent. Quaternary polyamines are very slightly affected by pH, remaining positively charged over a broad pH range.

2.3.2. Flocculation mechanisms

Ruehrwein and Ward (1952) proposed that it is possible for a polymer chain to adsorb onto more than one particle, especially when the molecular dimensions of the polymer are comparable with the size of colloidal particles. The particles are said to be "bridged" by adsorbed polymer and this flocculation mechanism is termed bridging flocculation. In order to bring about bridging flocculation, adsorbed polymers must extend far enough from the particle surface to attach to other particles and there must be sufficient unoccupied surface available for adsorption of segments from these extended polymer chains (see Figure 2.2).

In Michaels' study (1954) on the flocculation of clay suspensions by polyacrylamide, the flocculation was found to improve as the molecular weight of the polymer increased and that a certain degree of hydrolysis (or anionic character) gives better flocculation. The better flocculation is attained when the extent of anionic substitution is increased up to a point at which maximum chain extension is achieved without marked electrostatic interference with polymer adsorption.

Bridging mechanism is dominant for the flocculation process when nonionic flocculants or when polyelectrolytes of the same charge as the particles are used. Hydrophobic bonding, hydrogen bonding and dipole-crystal field effects have been suggested to bring about the specific interaction for the binding of polymer segments onto particles surface. In the case of polyelectrolytes of the same charge as the particles, a further possibility arises in which the presence of some critical concentration of electrolyte (often a divalent metal salt) is required for adsorption (Sommerauer et *al*, 1968). In such cases, no adsorption occurs in the absence of added salt. There is also evidence (O'Gorman and Kitchener, 1974) to show that the adsorption of anionic polyelectrolytes is not simply an ionic strength effect, but that ions such as Ca^{2+} promote adsorption by binding anionic group of the polymer chains to the charged sites on the particle surface. In the flocculation of particles by oppositely charged polyelectrolytes, the bridging mechanism plays a dominant role if the molecular weight of the polyelectrolytes is high, the charge density is low and the particle concentration is high.

An alternative mechanism, known as the electrostatic patch effect, was proposed by Kasper (1971) and Gregory (1973). It may not be physically possible for the particle charge to be neutralised individually by the adsorption of oppositely charged polymers. Even when the particle is electrically neutral as a whole entity, there are areas bearing the original particle charge and regions of excess opposite charge due to adsorbed polyelectrolyte. Strong electrostatic attraction can result when positive and negative areas of different particles come into contact (see Figure 2.3). This mode of flocculation can be significant when particles having low density of immobile surface charges interact with high charge density polymers.

Polymeric flocculation can be considered to comprise the following processes (Akers, 1972):

(a) Transport of polymer molecules to the suspended particles.

(b) Adsorption of polymer molecules on the particles.

(c) Re-arrangement of the adsorbed polymer molecules to an equilibrium configuration.

(d) Collisions of particles to form stable aggregates either by bridging or by electrostatic patch effects.

(e) Break-up of aggregates

These processes occur simultaneously and that they may influence one another. Consequently, the analysis of the overall process is rather difficult. The kinetic aspects of flocculation by polymer, involving the transport and adsorption of polymer molecules, and particle collisions, are described in Section 2.3.3. Very little is known regarding the re-arrangement of the adsorbed polymer molecules and the influence it has on the subsequent steps. This aspect will be discussed in detail in Section 2.3.3.d.. In the present section the features of polymer adsorption and particle flocculation are outlined.

The adsorption of polymer molecules and the flocculation of particles have been considered by Gregory (1982) as collision processes. The rate equation of perikinetic (diffusion controlled) and orthokinetic (shear induced) collisions are used to estimate the rates of polymer adsorption and particle flocculation. The calculated results show that with an increase in polymer size, the rate of polymer adsorption would decrease if perikinetic collision is dominant and the rate would increase if orthokinetic collision is dominant. The rate of polymer adsorption will nearly always be greater than the flocculation rate when the rate of collision is diffusion controlled. In sheared suspensions, the relative rates of polymer adsorption and particle collision are shear dependent. The flocculation process depends to a certain extent on the relative rates of polymer adsorption and particle collision.

Flocculation of a suspension does not begin immediately following an addition of polymer. For both the bridging mechanism and the electrostatic patch effect, colliding particles need to acquire enough adsorbed polymer to be sufficiently destabilized for flocculation to occur. When the bridging mechanism dominates, there must be enough polymer bridges between interacting particles so that the aggregates formed are of sufficient strength. In situations where the electrostatic patch effect dominates, electrostatic repulsion between particles must be reduced sufficiently to allow oppositely charged areas of colliding particles to attract one another. Subsequently, particles are likely to undergo several collisions with other particles before acquiring enough adsorbed polymer molecules to allow stable aggregates to form, despite the number of polymer molecules is certainly many times more than that of particles in any systems. The time lag between the addition of polymer and the onset of flocculation can be more pronounced in dilute suspensions.

2.3.3. Kinetic aspects of polymer adsorption and flocculation

The adsorption of polymer molecules on particles is an essential step in both bridging and electrostatic patch mechanisms. As mentioned previously, colliding particles need to acquire enough adsorbed polymer for flocculation to occur. The relative rates of polymer adsorption and particle collision are compared, using both diffusion-controlled (perikinetic) and sheared-induced (orthokinetic) transport mechanisms to model the collision process.

(a) Polymer adsorption rate

The polymer adsorption rate can be modelled by the rate of arrival of polymer molecules at particle surfaces, especially when the surface coverage is low. The adsorption of polymer on dispersed particles is essentially a transport-limited process, although the rate of adsorption is likely to be reduced as particle surfaces become more fully covered by adsorbed polymer and leave fewer adsorption sites. The assumption of a transport-limited rate is acceptable because optimum flocculation usually occurs at considerably less than complete surface coverage.

The rate of polymer adsorption, modelled as collision process among particles and polymers, can be described by Equation (2.26) as follows:

$$J_{ads} = K_{ads} N_{particle} N_{polymer} \qquad (2.26)$$

where J_{abs} is the number of particle-polymer encounters occurring in unit volume per unit time and K_{ads} is a rate constant, when there are initially $N_{particle}$ particles and $N_{polymer}$ polymer molecules per unit volume.

Under practical conditions, the number concentration of polymer molecules presents in the system will be more than that of particles. A substantial fraction of the added polymer has to be adsorbed to destabilize the particles sufficiently, in order to bring about flocculation. The reasons have been described in Section 2.3.2.. The time t_{ads} required to adsorb a fraction f of the added polymer can be derived from Equation (2.26) (Gregory, 1982):

$$t_{ads} = -\ln(1-f)/K_{ads}N_{particle} \tag{2.27}$$

In the derivation of Equation (2.27), the particle number concentration is assumed to remain constant and that the rate constant is independent of surface coverage. However, the available surface area will decrease as adsorption occurs, leading to a decrease in K_{ads} and in the number of particles $N_{particle}$ as flocculation occurs. As a result of a decrease in K_{ads} and in $N_{particle}$ during the course of flocculation, the actual adsorption time will be greater than t_{ads} as calculated from Equation (2.27). Nevertheless, the calculated t_{ads} can serve as a useful estimate of the minimum time needed for the adsorption of a predetermined amount of polymer. A significant feature of Equation (2.27) is the inverse dependence of the adsorption time on the number concentration of particles. It can be deduced from Equation (2.27) that a longer adsorption time for a certain degree of adsorption is more likely to be observed in dilute suspensions as the rate of polymer adsorption are an inverse function of particles concentration. The term "rate of adsorption" is of little meaning without specifying the particle concentration. For a given polymer concentration, t_{ads} is shorter at a higher particle concentration but the surface coverage of the particles will be lower.

(b) Flocculation rate

Equation (2.26) can be used to describe the rate of flocculation by substituting $N_{polymer}$ with $N_{particle}$. Hence,

$$J_{Floc} = K_{Floc}(N_{particle})^2 \tag{2.28}$$

The flocculation rate is modelled as collision process among particles. The flocculation rate is a function of the collision frequency and a collision efficiency factor, α , which is the fraction of collisions leading to permanent aggregates. A collision efficiency of unity is not generally observed for a number of reasons, including hydrodynamic interaction, electric double layer repulsion and steric stabilization.

In polymer flocculation, the collision efficiency is frequently assumed to be proportional to the term $\theta(1-\theta)$, where θ is the fraction of the particle surface covered by polymer (Healy and La Mer, 1964). Successful collisions occur when coated and uncoated areas of colliding particles come into contact. It follows that the maximum rate of successful collision will occur when $\theta = 0.5$. A higher than the expected flocculation rate is possible. Hogg (1984) has considered the case where colliding particles are able to rotate to give a more favourable interaction.

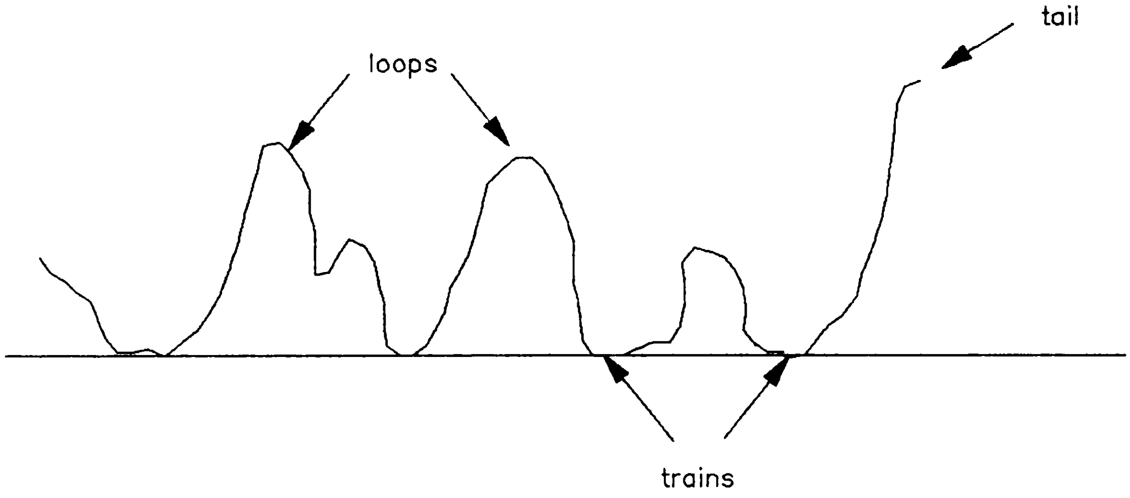


Figure 2.6. A schematic diagram showing the comformation of an adsorbed polymer molecule in trains, loops and tails

It is known that polymers adsorb in loops and trains with the tails of the polymer extending considerably further from the surface (Cosgrove, 1987), as depicted in Figure 2.6.. The relative number of segments in the three physically distinct parts: tails, loops and trains depends on the adsorption parameters of the system. The capture of particles by adsorbed polymers which extend some way from the particle surface would give an increase collision radius, leading to a more rapid flocculation. Even in cases where the polymer adsorbs onto oppositely charged particles with a rather flat conformation, an enhanced flocculation rate has been observed due to the "electrostatic patch" effect (Gregory, 1976). The meaning of "surface coverage" cannot be defined easily when the conformation of adsorbed polymer is taken into account. It is, therefore, difficult to apply unambiguously the concept of "surface coverage" to polymer flocculation kinetics.

(c) Comparison of rates

Aggregation kinetics have been described in Section 2.2.. The collision rate constants for perikinetic flocculation and orthokinetic flocculation can be written as Equations (2.19) and (2.22) respectively:

$$perikinetic: \quad K_{peri} = \frac{2kT}{3\eta}\frac{(a_1+a_2)^2}{a_1 a_2}$$

$$orthokinetic: \quad K_{ortho} = \frac{4}{3}G(a_1+a_2)^3$$

The variation of the rate constants with particle size for both collision mechanisms are shown in Figure 2.7. To compare the different rate constants as function of particle size, the diameter of one particle is taken as $1\,\mu m$ and the diameter of the second particle varies from 0.01 to 10 μm. Shear rates of 50 s^{-1} and 20 s^{-1}, and the viscosity of water at 25 °C have been assumed in the calculation. The value of $2kT/3\eta$ in water at 25 °C is typically $7 \times 10^{-18}\ m^{-3}s^{-1}$ and this value is used in the calculation.

The calculated collision rate constants as shown in Figure 2.7. illustrate that perikinetic collision are predominant for particles of sizes $0.1\,\mu m$ or less. For large particles, say, of sizes above $1\,\mu m$, orthokinetic collision becomes important. Although the choice of values for particle sizes and shear rates would change the calculated collision rate constants, the general trend is expected to be the same. Perikinetic collision is a more significant transport mechanism for small particles, especially if the shear rate is low.

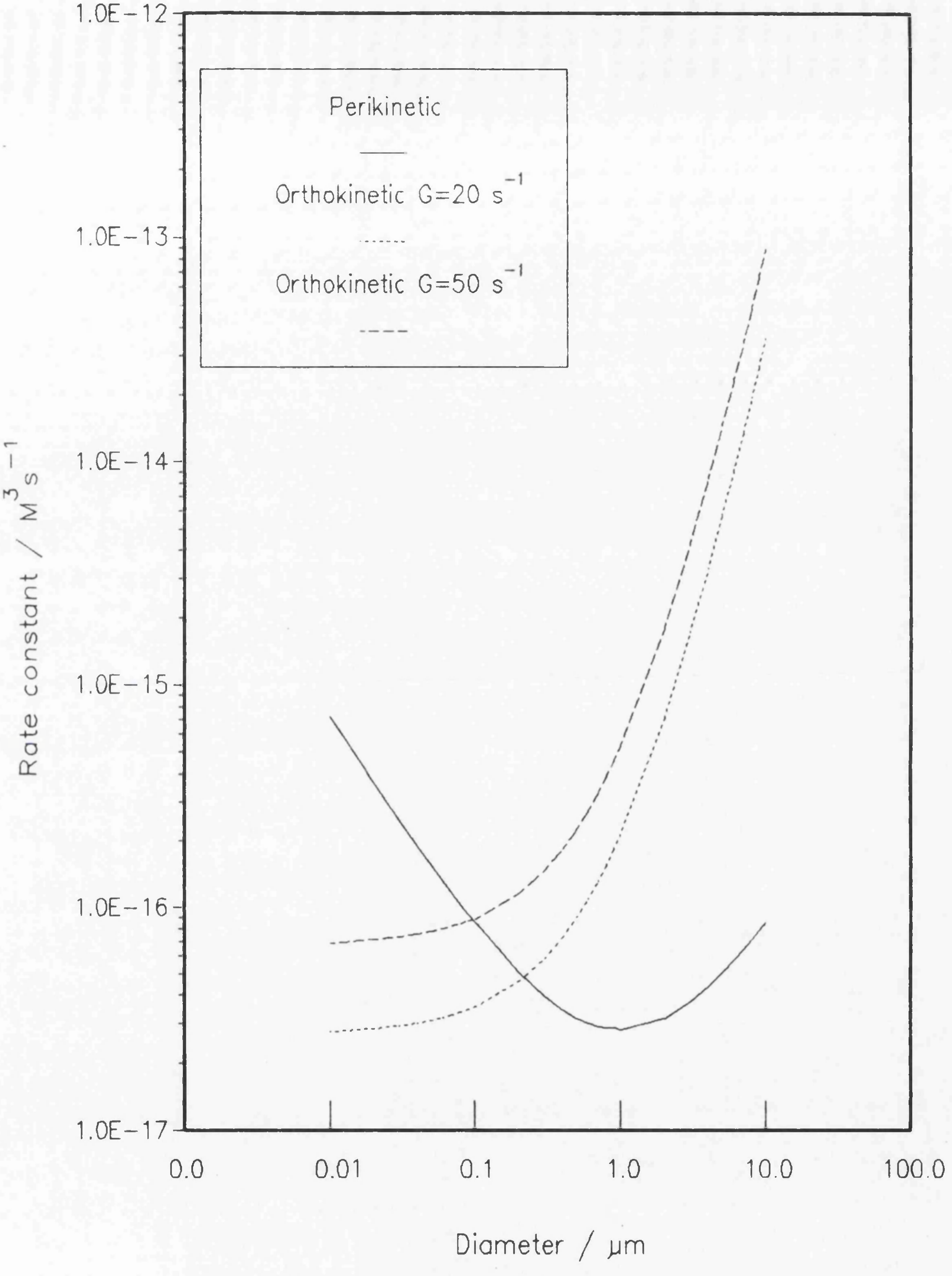


Figure 2.7. Comparision of collision rate constants for different transport mechanisms. The diameter of one particle is fixed at 1 µm.

By assuming the following: particle number concentration of 10^8 cm^{-3}, shear rate of 50 s^{-1}, particle radius (a_1) of 1 μm , polymer radius (a_2) of 100 nm and that 95% of the added polymer needs to adsorb ($f = 0.95$), an estimate of polymer adsorption time can be calculated using Equation (2.27) and the appropriate rate constants for perikinetic and orthokinetic transport mechanisms. The adsorption time calculated using the above assumptions are:

Perikinetic: t_{abs} = 353 s
Orthokinetic: t_{abs} = 337 s

Flocculation does not begin until the particles are destabilised by having an appropriate amount of adsorbed polymer. The above estimates show that polymer adsorption is not an instantaneous process. The time required for a certain fraction of added polymer to adsorb can be considerable, depending on a number of factors. In a study made by Wigsten and Stratton (1984) on the flocculation of latex by cationic polymer, the relative slow adsorption of polymer was observed. These authors suggested that if the polymer radius was less than 80% of the particle radius, polymer adsorption may be the rate limiting step in orthokinetic flocculation. To illustrate that polymer adsorption step can be rate limiting, the adsorption time needs to be compared with the characteristic flocculation time, t_{floc}, which is the time in which the total number of particles is reduced to half of the initial value as a result of aggregate formation. The characteristic flocculation time t_{floc}, can be derived from Equation (2.28) by integration giving Equation (2.29):

$$t_{floc} = \frac{2}{K_{floc} N_{particle}} \tag{2.29}$$

Assuming that $N_{particle}$ is the initial number concentration of particle and that all particles are monodispersed having radius a_1. The corresponding collision rate constants for perikinetic and orthokinetic flocculation are given in Equations (2.19) and (2.22). Hence, the characteristic flocculation times are:

$$Perikinetic: \qquad t_{floc} = \frac{3\mu}{4N_o kT} \tag{2.30}$$

$$\text{Orthokinetic:} \quad t_{floc} = \frac{3}{16GN_0a_1^3} \qquad (2.31)$$

The flocculation times can be calculated for the conditions assumed above ($N_0 = 10^8$ cm^{-3}, $a_1 = 1\ \mu m$, $G = 50$ s^{-1}). These are then compared with the corresponding adsorption times calculated earlier ($f = 0.95$, $a_2 = 100$ nm):

Perikinetic: $t_{ads} = 353$ s; $t_{floc} = 714$ s.
Orthokinetic: $t_{ads} = 336$ s; $t_{floc} = 38$ s.

The above results show that when shear is applied both t_{ads} and t_{floc} are shorter than by diffusion alone. However, the adsorption step may be rate limiting in orthokinetic flocculation as indicated by the t_{ads} being longer than t_{floc}. It is likely that particles would undergo several collisions with other particles before acquiring enough polymer to form stable aggregates. On the other hand, under perikinetic conditions the adsorption step is unlikely to be rate limiting as t_{ads} is shorter than t_{floc}.

These t_{ads} and t_{floc} are calculated using a set of arbitrary values and could be very different for other values of shear rate, particle concentration, polymer concentration, and the dimensions of the polymer and the particle. Nevertheless, the practical implication is highlighted. At shear rates above, say, 50 s^{-1}, which correspond to gentle agitation, both adsorption and flocculation are mainly orthokinetic in character. The adsorption time may be longer than the characteristic flocculation time. The characteristic of the polymer would have a dominant role to play. The charge density of the polymer may determine how much adsorbed polymer is needed to form stable aggregates, and this in turn can affect the value of t_{ads}.

(d) Re-conformation of adsorbed polymer

The adsorption of polymer is often regarded as an irreversible process since the chance of desorption of all adsorbed segments of a polymer molecule to occur simultaneously is remote. However, there is experimental evidence to show that the adsorption of polymer segments is reversible. The displacement of poly(vinylpyrrolidone) from silica by a number of low molecular weight organic compounds such as dimethyl sulphoxide, pyridine and N-methylpyrrolidine has been demonstrated by Cohen Stuart *el al* (1984). The displacement of labelled nonionic and hydrolyzed polyacrylamide from kaolinite by sodium metaphosphate, tripolyphosphate and unlabelled polyacrylamide has been studied by Dodson and Somasundaran (1984). Phosphates were used in their work because it is known that phosphates have a strong affinity for clay minerals. These authors have shown that the extent of polymer desorption depends strongly on the initial amount of polymer adsorbed. No desorption occurs at low polymer coverage, where polymer molecules are probably adsorbed with a rather "flat" conformation. The extent of desorption also depended on the charge characteristics of the adsorbed polymers and the displacers. They concluded that adsorption of phosphates on kaolinite increases the electrostatic repulsion between the kaolinite and the negatively-charged polymers. Hence, the more anionic tripolyphosphate is a stronger displacer than the metaphosphate in the desorption of hydrolysed polyacrylamide whereas the two phosphates are indifferent in the desorption of the nonionic polyacrylamide. Addition of unlabelled polyacrylamide was found to displace previously adsorbed labelled polyacrylamide. Under dynamic condition, segments of polymers are absorbing and desorbing continuously. It is possible that as soon as some segments of a polymer molecule are detached from the particle, segments of another polymer molecule would occupy the vacated sites. Progressively, desorption of the entire molecule is possible. Furusawa *el al* (1982) have shown that smaller polymer molecules can be displaced by larger ones, where the polymers under investigation differ only in their molecular weight. Furthermore, the extent of displacement is more pronounced the larger the difference in their molecular weight. It can be said that polymer adsorption is a dynamic, reversible process where the adsorption and desorption of the polymer molecules take place continuously.

Grant *et al* (1975) have shown that adsorbed polymers may take several hours to attain an eventual equilibrium conformation. The results they obtained are not relevant to practical flocculation processes as the flocculation of particles often takes place before adsorption equilibrium is reached. Information on the re-arrangement of adsorbed polymer molecules is scarce. The re-comformation of adsorbed polymer can have significant effect on the flocculation of particles.

In polymeric flocculation by the bridging mechanism, it is crucial that the adsorbed polymers must extend far enough from the surface into the solution to exceed the range of electrostatic repulsive forces and become attached to other particles (see Figure 2.8). Pelssers *et al* (1990) proposed a model for bridging flocculation kinetics taking the re-conformation of polymers into account. These authors considered the average number, n_{act}, of active polymer molecules (polymer molecules which can extend beyond the closest distance of separation between interacting particles) per particle to be a prime factor for successful bridging flocculation. Flocculation occurs when n_{act} exceeds some threshold value n_{crit}. No flocculation takes place when n_{act} is smaller than n_{crit}. After the addition of polymer, the value of n_{act} increases due to the adsorption of polymer. When n_{act} reaches n_{crit}, the particles are said to be "activated" and flocculation can lead to stable aggregates. The concept of n_{crit} is in good agreement with some earlier work on polymeric flocculation (Gregory and Nelson, 1984; Gregory, 1988; Gregory and Lee, 1990), where an appreciable lag time is often observed between the addition of polymer and the onset of flocculation. This lag time is not observed in salt destabilised systems and it is more pronounced in dilute suspension with low polymer dosage. The rate of polymer adsorption is generally slower with a lower polymer dosage.

The adsorption of free polymer always increases n_{act}, whereas the re-conformation of the adsorbed molecules may not always decrease n_{act}. The adsorption of certain segments of a polymer enables the remaining part of the molecule to re-arrange itself onto the particle as long as there are vacant sites exist. As a result of that, most adsorbed polymer molecules would have a tendency to relax toward a rather flat conformation, unless the surface is almost saturated with polymer. Some flattening by re-conformation does not necessarily mean the length of the loops and tails would become insufficient to bridge over

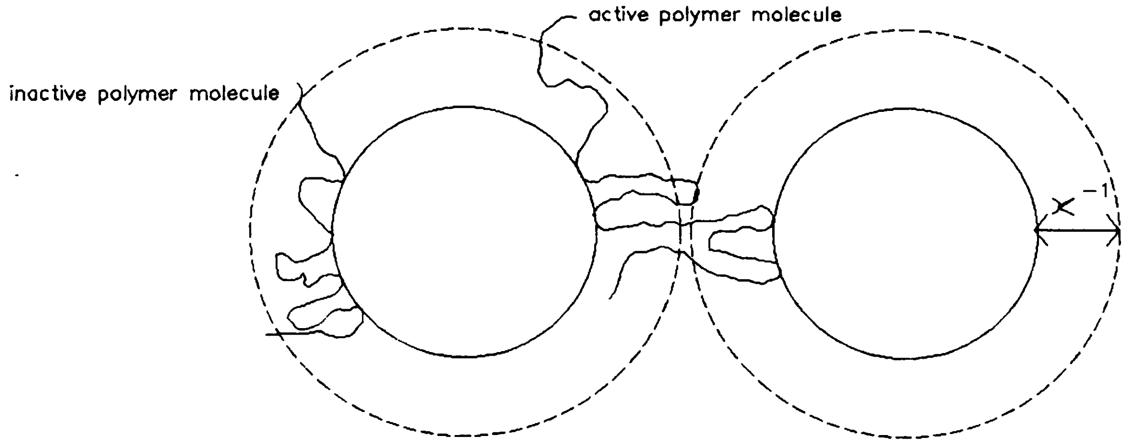


Figure 2.8. A schematic diagram showing a particle with an extended ("active") polymer molecule and a flatttened ("inactive") polymer molecule

the range of effective electrical repulsion between the particles. The length of these loops or tails can be expected to be smaller than the original ones, the number of n_{act} may not be affected as long as they span across the distance of electrostatic repulsive forces. Formation of more loops due to re-conformation of polymers may give rise to more or stronger "bridges" between attaching particles, depending on the initial polymer coverage. Polymer bridges are formed when these extended polymer segments make contacts with vacant adsorption sites on other particles. The bridging may be too weak to withstand the shearing forces imposed by the shear conditions, if too few bridging contacts are made (Black *el al* 1965). Conversely, the bridging will be hindered if too many adsorption sites are occupied by adsorbed segments.

According to Pelssers *et al* (1990), polymers may lose their ability to "bridge" colliding particles if the thickness of the adsorbed layer becomes shorter than the range of electrostatic repulsive forces, due to the flattening of adsorbed polymer molecules with time. They then suggested that flocculation is possible when the rate of polymer adsorption outweighs the rate of re-conformation. The significance of polymer re-conformation on the flocculation of a suspension depends not only on the properties of the polymer (molecular mass, charge density, flexibility of the polymer) but also on the ionic strength of the solution and the particle concentration of the suspension. These authors have found that n_{crit} decreased strongly with increasing molecular mass. Depending on the conformation of the adsorbed polymer molecules, not all of them can give rise to loops and tails which are sufficiently large to extend beyond the range of electrostatic repulsive forces. Possible explanations for the decreased n_{crit} with increasing molecular mass of polymer are that more loops of adequate length can be formed from larger polymer molecules and that more or stronger bridges between aggregating particles can be formed. The value of n_{crit} is lowered in the presence of salt. The number of loops or tails extending beyond the distance of the repulsive forces becoming higher as the range of electrostatic repulsive forces is reduced. As a result, the average number of polymer molecules per particle needed for flocculation is lowered. It should also be pointed out that the number of polymer contacts between aggregating particles may be the decisive factor for successful bridging flocculation rather the number of "active" polymer molecules per particle. In dilute suspension and for low polymer dosage, the effect of the flattening of polymer molecules on the flocculation of the suspension can be significant. The rate of polymer adsorption is proportional to the polymer application rate and to the particle concentration of the suspension. The flattening of the adsorbed molecules can be hindered by the presence of other adsorbed molecules. It is well known that the adsorbed layer thickness of a polymer increases with surface coverage (Luckham and Klein, 1990). As more polymer is adsorbed onto a surface, the adsorbed polymer begins to stretch further away from the surface. This effect is more prominent with the adsorption of non-ionic polymer. It is possible that the attractive forces among polymer molecules are stronger than those between polymers and particles. The driving force of this may be the strong hydrophobic interaction among polymer molecules or the lower Gibbs free energy state of the system arising from an increase in entropy as the adsorbed polymer molecules become more extended into the solution.

In the flocculation of charged particles by oppositely-charged polymer via the "electrostatic patch" mechanism, the conformation of the adsorbed polymer changes from a three-dimensional coil to a nearly "two-dimensional" flattened coil on the particle surface. There is no information on the time taken for polymers to re-arrange onto the particles. The rate of polymer re-conformation will depend on the particle-polymer interaction. If the particle-polymer interaction is strong, such as those with a high charge density polymer, the rate of polymer re-conformation can be very fast. It can be assumed that following the adsorption of some segments of a polymer, the remaining part of the molecule would adsorb rapidly onto the particle. It is expected that the flattening of the adsorbed polymer is more rapid with polymer of high charge density. In dilute suspension or in cases where the concentration of polymer is low, the rate of particle-polymer collision can be slow. The re-arrangement of adsorbed polymers can be regarded as a form of polymer adsorption, and hence an effective means to increase polymer coverage. In situations where re-conformation is fast in comparison with polymer adsorption, polymer re-conformation could be a dominant mechanism to increase polymer coverage rather than the adsorption of further polymer molecules. The significant of this mode of polymer adsorption on the flocculation of particles will be discussed in Sections 4.13. and 4.14..

2.3.4. Effects of the characteristics of polymers on flocculation

The selection of a suitable polymer for a particular application can be time consuming because these are a great variety of polymers commercially available. Methods for the evaluation of polymer performance in coagulation, sedimentation, filtration and sludge conditioning have been investigated by Dentel *et al* (1988). The use of polymers in water treatment processes has been reviewed by many workers, (Kasper and Reichenberger, 1983; Novak, 1983; Bratby, 1980; Edzwald, 1986 and Mangravite *et al* 1986). The flocculation of suspended particles by polymers is a complex process involving an initial period of polymer adsorption followed by particle aggregation.

The flocculation mechanism depends on the characteristics of the system. Edzwald and Lawler (1983) have pointed out that polymer effectiveness depends on the polymers, the particles and the solution chemistry. Characteristics of polymers are types of charge, charge density, polymer composition and molecular mass. The concentration, surface chemistry and surface area of the particles are also important. Water qualities which may affect the effectiveness of polymers are pH, temperature, and the presence of dissolved materials. The characteristics of some important parameters in flocculation are summarised in Table 2.1..

Black *et al* (1966) have found that in systems of particles and polymers of opposite sign, the mechanism of action of polyelectrolytes is a combination of polymer bridging and charge neutralization. Mangravite *et al* (1986) have shown that particle concentration plays an important role in the flocculation mechanism of dispersed kaolin clay with high molecular weight polymer. These authors found that the charge density of high molecular weight polymers has a direct inverse effect on the polymer dosage when the clay phase ratio is below 10^{-3}. At 10^{-2} phase ratio, the effect of cationic charge density is much reduced. All the polymers investigated had high molecular weight typically associated with bridging mechanism. However, their work has shown that the polymer dosages were more sensitive to molecular weight than to charge density at high particle concentration. These authors suggested that the decreasing effect of cationic charge density and the increasing effect of molecular weight may be due to the lower amount of humic acid to each clay particle in the high solid content suspension but the authors did not offer an explanation for the effect of the presence of humic acid. It is possible that the effects were due to the different mechanisms of flocculation at different particle concentrations.

It has been shown by Linquist and Stratton (1976) that at the concentration of polyethyleneimine (PEI) required to initiate flocculation of a colloidal silica system, complete adsorption of PEI occurred regardless of molecular weight, pH or ionic strength whereas adsorption increased with an increase in molecular weight at higher

Table 2.1. Summary of characteristics of flocculation parameters (modified after Edzwald and Lawler, 1983)

Parameter	Charge Neutralisation	Bridging
Polymer		
Molecular Mass	little effect Very high molecular mass can give bridging effect	high molecular mass more effective
Charge Density	more effective with high charge density because of greater neutralization effect	more effective with high charge density because of expansion of polymer chains
Optimum Dose	near zero charge dose proportional to the total surface charge of particles	usually not zero charge dose proportional to particle concentration
Overdose	restabilization due to charge reversal	restabilization due to no vacant bridging sites available
Colloidal Particles		
Concentration	Poor flocculation kinetics at low concentration	Poor flocculation kinetics at low concentration
Solution		
pH	Affect charge density of colloids Affect charge density of non-quaternary polymers	Affect charge density of colloids Affect charge density of non-quaternary polymers
Ionic Strength	Higher ionic strength can aid destabilization	Higher ionic strength can aid destabilization can reduce polymer molecule extension thus reducing bridging ability

polymer concentrations. These results showed that the conformation of adsorbed PEI molecules can be affected by the polymer dosage. The conformation of the adsorbed PEI molecules at high polymer dose can be influenced by the characteristics of the polymer which subsequently effect the amount adsorbed.

Graham (1981) studied the flocculation of amorphous silica microspheres with cationic polyelectrolytes and compared the number of charges added at each polymer optimal dose. His work has shown that the optimal dose is strongly influenced by the distribution and the strength of the charges on the polymer, and the nature of the polymer structure. He proposed that overall particle charge neutralization is not necessarily effected because polymer-polymer interactions on the adsorbent surface and restricted polymer backbone flexibility will tend to reduce the number of attached polymer-chain segments.

Treweek and Morgan (1977) found that cationic polyelectrolytes, such as polyethyleneimine, were effective in the flocculation of suspension of E. Coli.. Polyethyleneimine with a wide range of molecular weights (600 to 60000) were strongly adsorbed to the bacterial cells but efficient flocculation was achieved only with high molecular weight samples (above 35000). The mechanism of flocculation with high molecular weight polymer was then identified as that described by the electrostatic patch model. The small size of lower molecular weight polyethyleneimine was hypothesized to be unable to give rise to patches of excess cationic charges. As a result, poorer flocculation obtained. The mechanism of flocculation with low molecular species was attributed to the reduction of double layer repulsion, similar to the effect of inert inorganic electrolyte. Robinson (1974) showed that the use of cationic and nonionic polymers in clarifying highly turbid waters of maximum turbidity approximately 5000 JTU gave results comparable to those using aluminimum sulphate, whereas anionic types did not produce the required degree of clarification. Morrow and Raush (1974) were able to treat both low and high turbid waters successfully with polydiallyldimethylammonium chloride in place of metal coagulants. They pointed out that the reported unsatisfactory performance of polyelectrolytes when used alone may be a result of the velocity gradients used during the rapid mixing stage was too low.

2.4. Characteristics of Aggregates

The success of a water treatment process depends to a certain extent on the properties of the aggregates produced. Harding (1972) found that flocculation is primarily dependent on particle size distributions in the suspension. O'Melia (1978) has shown the dependence of flocculation on particle size and size distribution, and that flocculation is more rapid in heterogeneous suspension. Several investigators have referred to the size distribution (Reed and Mery, 1986; Black and Vilaret, 1969; Hudson, 1973), floc volume concentration (Camp, 1968), floc density (Lagvanker and Gemmell, 1968), and strength of aggregates (Koglin, 1985) as important characteristics of aggregates.

Various types of aggregate structures may be formed, depending on the nature of the system and the forces involved. It can be said that "compact" aggregation structures are mainly formed by the addition of single particles to growing clusters and the more "open" structures are formed from cluster-cluster aggregation. The nature and magnitude of the interparticle forces involved and the manner in which the particle in an aggregate are arranged determine the mechanical properties of the aggregate structure. Most aggregates are broken by shear stresses in excess of some critical value. The distance of separation between particles in aggregates produced as a result of the lowering of the electrostatic repulsive forces by the addition of electrolyte depends on the magnitude of the resultant attractive forces as well as the hydration repulsion. The redispersion of some flocculated colloids by washing away the electrolyte seems to suggest that aggregation occurs in a "hydration minimum", rather than in a true primary minimum (Frens and Overbeek, 1972; Healy *et al*, 1978). The size of an aggregate under given conditions may be taken as a measure of aggregate strength in many empirical determinations of aggregate strength. However, aggregates can be expected to be stronger if they are more compact (more particle-particle contacts) even though the size of the aggregate containing a given mass of particles will be smaller. The interpretation of such measurements is not straightforward. Aggregates of a wide range of sizes have to be assumed to have the same porosity to validate such measurement but porosity generally increases with size.

Polymeric flocculation usually produces stronger aggregates than those resulting from electrolyte coagulation and so the aggregates are likely to be larger under given shear conditions. Particles are held together by the adsorbed polymers rather than the weaker van der Waals forces. Obviously the magnitude of the binding forces in polymeric flocculation must depend on the number of attachment points and the strength by which each point is attached. Stronger aggregates are produced through polymer bridging rather than by electrostatic patches. Polymer bridging produces stronger aggregates but they are not easily re-formed when broken at high shear rates, this may due to the re-arrangment or scission of adsorbed polymer molecules. On the other hand, aggregates broken by shear can re-form when the shear is reduced in cases where polymers act predominantly by electrostatic patches.

An increase in the energy dissipation to the system increases the disruptive forces the aggregate experience, in addition to enhancing the flocculation rate. The limiting aggregate size depends on the applied shear rate and on the strength of the aggregates. Subsequently, the more intense the agitation, the smaller is the limiting aggregate size. Effective shear rate varies at different locations in the system, (Glasgow and Kim, 1986). Therefore, the limiting aggregate size will depend on the maximum shear rate, whereas the flocculation rate will be more closely linked with the average value.

Cutter (1966) proposed that a stirred tank could be partitioned into three zones:

(i) maximum turbulence intensity near the mixer blades
(ii) an impeller zone
(iii) a bulk zone

The bulk zone occupies 90% of the total volume and the energy dissipation in this zone is 0.25 times the average power dissipation. The zone of maximum turbulence intensity occupies 0.5% of the volume and dissipates energy at 50 times the average power dissipation. The partitioning of the tank into the three flow regimes is shown in Figure 2.9..

Very complex behaviour is found in the break-up of aggregates under turbulent conditions. The nature of the break-up process depends on the size of the aggregates relative to the turbulence microscale. For aggregates of greater size, deformation and rupture may occur as a result of fluctuating dynamic pressure. For smaller aggregates, viscous shear forces predominate and may cause either an erosion of primary particles from the aggregates surface or fragmentation of the aggregates. It is possible that collisions between aggregates may also lead to aggregate break-up. The relevance of the turbulent scale to the probability of break-up has been considered by Parker and co-workers (1972). The "strength" parameters that occur in their model will depend on the mechanisms of particles binding in the aggregates and the internal morphology of the aggregates.

The density of an aggregate can be defined as the mass of particles and the water included in the aggregate divided by the "envelope" volume. However, it is the "effective" density of an aggregate which determines the sedimentation rate (Tambo and Watanaba, 1979) and flotation rate. The effective density, $\rho_{effective}$, is the density of the aggregate, $\rho_{aggregate}$, minus the density of water, ρ_{water}.

$$\rho_{effective} = \rho_{aggregate} - \rho_{water} \qquad (2.32)$$

The formation of compact aggregates is important to ensure the success of a sedimentation process. Large aggregates give a more rapid sedimentation rate but the increase in size may be accompanied by a reduction in density which may affect the sedimentation rate. The reduction in density for compact aggregates is usually not enough to outweigh the size effect. Compact aggregates are more easily dewatered, the drag is less as there is less solid surface in contact with water.

In deep bed filtration, the effect of particle aggregation on the capture of particles can be considered in terms of the changes in particle size and effective density of aggregates on the capture efficiency for different transport mechanisms. The capture of particles through inertia or gravity forces is higher for the larger and for the more compact (higher density) aggregates. Aggregation of particles has a tendency to lower the density of the resultant aggregates, a compromise has to be made. Unfortunately, there are no practical guide-lines on what can be regarded as the optimum for a suspension containing a range of particle sizes. The requirements for the two transport mechanisms considered may not necessarily be the same. The diffusion of particles is usually observed when they are very small (of colloidal size range). Therefore, the aggregation of particles will have little effect on this capture mechanism. The interception of particles can be considered as the final effect before contact on filter gain is made in all cases. It is obvious that larger particles are more easily intercepted. Needless to say, the surface chemistry of the aggregates would also be an important factor in the deposition of aggregates.

As filtration progresses, the deposits are accumulating in the filter pores. The pore sizes become smaller due to the accumulating deposit and the flow velocity is increased accordingly. The increased flow velocity leads to an increased liquid shear stress at the deposit surface, some of the deposited particles may become detached and re-suspended into the flow. Deposit with a higher shear strength will be less liable to detachment. Rupture of part of the deposits at a plane of weakness causes a particle, or more usually an aggregate of particles, to detach and be entrained in the flow. An alternative detachment mechanism occurs when a considerable amount of deposit has accumulated in the filter pores, say, after 20 to 30 hours of operation (Ives, 1980). The detachment is caused by suspension particles colliding with an unstable deposit and causing an "avalanche"

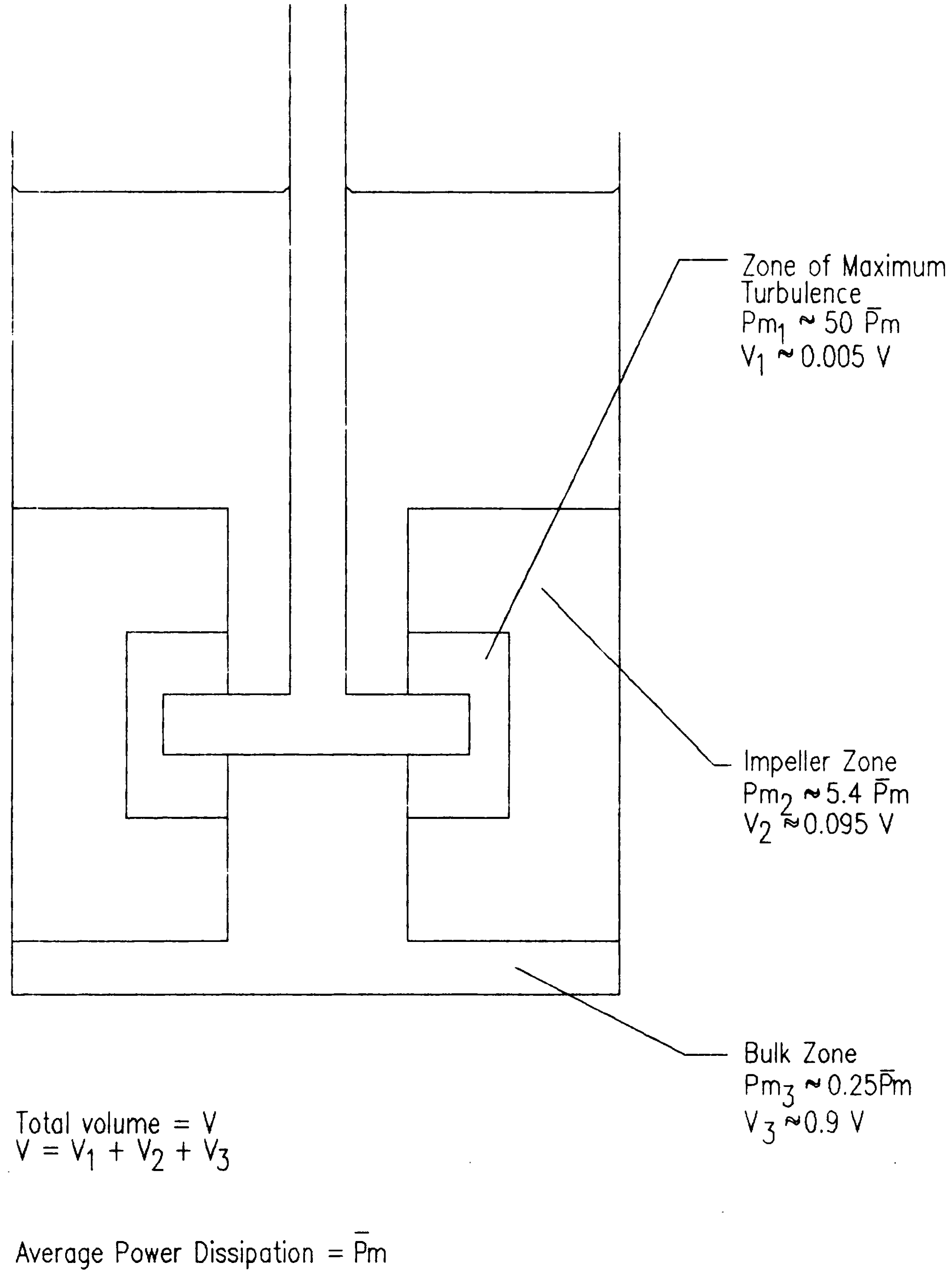


Figure 2.9. Partitioned energy dissipation in stirred tank

with many aggregates breaking away into the flowing liquid. The more compact aggregates are preferred in deep bed filtration as they are more tolerant to the higher shear stress. The open structure aggregates may lead to the blocking of filter pores and a reduced filtration rate. They are more liable to restructuring under pressure and therefore increase the chance of filter-break through due to the rupture of aggregates.

In flotation, the rate of upward motion of moving aggregates or aggregates plus gas bubbles is determined by an equilibrium of forces including gravity, buoyancy and drag resistance. It is obvious that low density flocs are desirable in flotation. Buoyancy is a characteristic parameter of the solids to be removed but it can be modified by the attachment of gas bubbles. Drag forces depend on aggregate size and shape and they are impossible to predict because of the varying motion of particles.

Dissolved Air Flotation (DAF) technology is particularly effective in the removal of low density material such as algae. The DAF process has gained wider acceptance in water treatment in recent years. Edzwald *el al* (1990) have shown that flocculation is needed for good flotation performance. Maximum particle removal was achieved when the particles carry little or no electrical charge.

Mineral particles are rarely floated individually in ore flotation, in particularly, fine-sized particles of less than 10 μm are often aggregated with a suitable organic flocculant before treatment with the appropriate collectors (Fuerstenau and Herrera-Urbina, 1989). The floatability of aggregated particle are better than the individual particles. Possible explanations are: higher collision rates due to an increase in size, better attachment to air bubbles (either the electrostatic repulsive forces are sufficiently reduced and/or the hydrophobicity of the mineral particles is increased due to the presence of the collector chemicals), and the aggregate/air bubble complex is more stable because of the irregular shape of the aggregates.

2.5. Instrumentation and Experimental Methods

The techniques available to study colloidal systems are vast. This section describes only those instrumentation and experimental techniques used in the present study.

2.5.1. Photon-Correlation-Spectroscopy

One of the many techniques used in studying colloidal system is photon-correlation-spectroscopy. It involves the scattering of laser light by a colloidal suspension but the technique is different from conventional light-scattering (Randle, 1980). In conventional light scattering, the intensity of light scattered by a colloidal sample is measured as a function of scattering angle. This angular profile can be used to deduce the particle dimensions. Photon-correlation-spectroscopy is based on the calculation of the diffusion coefficient D of particles by measuring the intensity fluctuations of light scattered by the particles as they undergo Brownian motion The random position of the particles gives rise to a random diffraction or "speckle" pattern of the scattered light. The random configuration of the "speckle" pattern changes due to the Brownian motion of the particles. The time taken for the intensity at one point in the pattern to fluctuate from an intensity maximum to a minimum corresponds to the time required for a particle to move one wavelength. This intensity fluctuation can be measured with a photomultiplier. A digital correlator measures the correlation function of the scattered light and the diffusion coefficient D can be obtained. The hydrodynamic radius a_h is related to the diffusion coefficient D by the Stokes-Einstein equation

$$D = \frac{kT}{6\pi\eta a_h} \tag{2.33}$$

2.5.2. Particle mobility by microelectrophoresis

The stability of particles can be assessed to some degree by measuring their electrophoretic mobilities. Suspensions containing highly charged particles are generally stable. The charge characteristics of particles can be inferred from their electrophoretic mobilities.

The surface charge of suspended particles is compensated by the adsorption of counter-ions in bulk solution. The accumulation of these counter-ions causes a gradual reduction in the potential from its value at the surface, ψ_o , to zero in bulk solution. The charge separation at the interface between two phases can give rise to electrokinetic effects when one of the two phases moves tangentially to the second phase (Hunter, 1981). The four electrokinetic phenomena are electrophoresis, electro-osmosis, streaming potential and sedimentation potential.

The ultramicroscopic technique (particle microelectrophoresis) is the most common method for measuring electrophoretic mobility (particle mobility). The particles move under the influence of an electric field while the liquid remains stationary. The charged particle moves in the appropriate direction, while the ions in the mobile part of the double layer show a net migration in the opposite direction.

The material under investigation is placed in an electrophoresis cell which consists of a glass tube with an electrode at each end. The glass walls are usually negatively charged, causing an electro-osmotic flow of liquid near to the tube walls. As the cell is closed, there will be a compensating return flow of liquid with maximum velocity at the centre of the tube. The true electrophoretic velocity is only observed at locations in the tube where electro-osmotic flow and return flow of the liquid cancel, the so-called stationary levels. The average particle velocity is measured at both stationary levels by averaging at least 20 measurements in each direction.

Particle mobility is calculated from the particle velocity, V, when an electric potential, E, is applied between two electrodes separated by a distance, L. The particle mobility is then

$$\mu = \frac{V}{E/L} \left(units \;\; of \;\; \frac{ms^{-1}}{Vm^{-1}} \right) \qquad (2.34)$$

The conversion of particle mobility to zeta potential requires knowledge of the magnitude of the double-layer thickness relative to the particle radius (κa). The conversion is not always carried out and in many practical cases it is sufficient to correlate particle mobility to stability.

2.5.3. Counting of particle by Coulter Counter

One of the most widely used particle size analysis devices is the Coulter counter which operates by measuring the electrical resistance of an electrolyte across an orifice. A dilute dispersion is made to flow through a small orifice. The passage of a non-conducting particle through the orifice causes a momentary increase in the electric resistance between electrodes placed either side of the orifice. The magnitude of this increase in resistance depends on the size of the particle. Lloyd and co-workers (1970) have shown that the change in orifice resistance, i.e. height of voltage peak, is proportional to particle volume providing that the particle diameter does not exceed 20% of the orifice diameter. Allen (1966) has shown that there is an error of 7.8% for the equivalent spherical diameter of rod shaped particles and 3.6% for spheres when a linear response is assumed up to a 40% diameter ratio. The voltage pulses are amplified and passed to a discriminator circuit. The electronic circuitry of the system is such that all pulses greater than a pre-set level are counted. That is, particles above a certain size are counted every time the resistance rises above the corresponding preselected cut-off value. More sophisticated versions have a multichannel analyser, so that a frequency distribution of particle sizes can be obtained.

2.5.4. Flocculation monitoring by optical methods

Measurements of the light scattered by suspended particles are often made to monitor the flocculation of suspensions. In general, there are two types of light-scattering experiments that may be performed: angular light scattering, where the intensity of the scattered light is measured as a function of the scattering angle, and the turbidity (or optical density) determination, where the intensity of the transmitted beam is measured. A third flocculation monitoring technique, based on fluctuations in the intensity of transmitted light, was developed by Gregory and Nelson (1984). The basis of the technique is described below.

A narrow beam of light passes transversely through a tube, through which the suspension under investigation flows. The amount of light transmitted decrease exponentially with increasing suspended solids content. There are inevitable local fluctuations in particle concentration. As the sample is continually being renewed by the flow of suspension through the tubing, the particle concentration of the illuminated sample at any instant shows random variation about the mean value. This gives rise to the random fluctuations in the transmitted light intensity (see figure 2.10.).

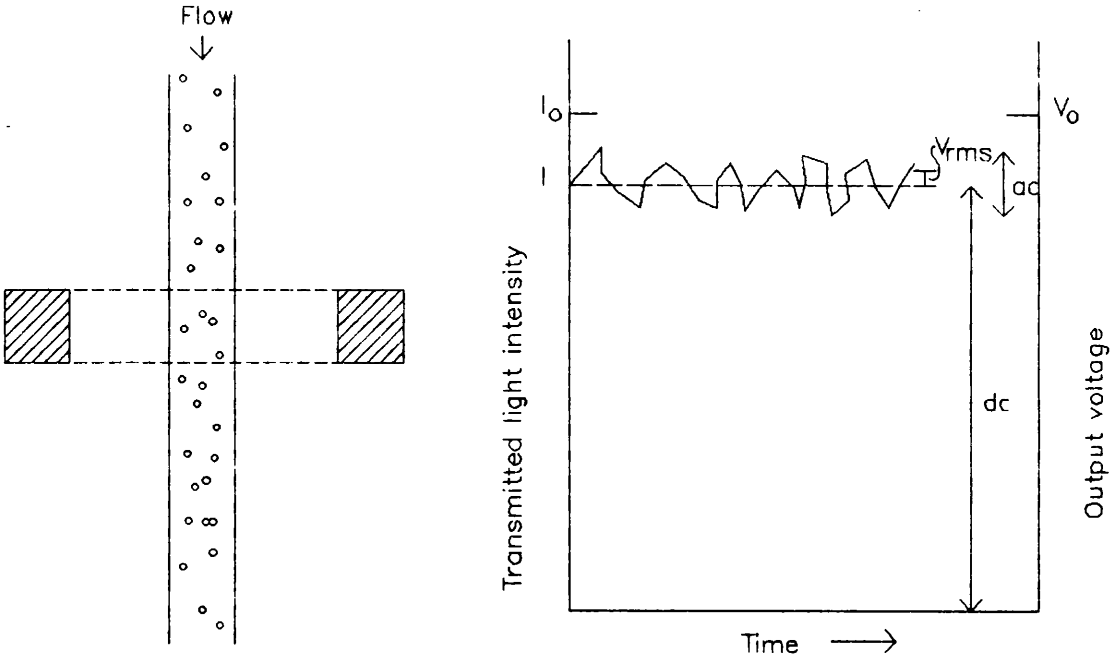
The light intensity is monitored by a sensitive photodiode and the output voltage is proportional to the intensity. The output consists of a large d.c. component which corresponds to the average transmitted light intensity and a small a.c. component due to the random variation in solid concentration. The simplest measure of a fluctuating signal is to derive its root mean square (r.m.s.) value. Gregory (1985) has shown that the r.m.s. value depends on the square root of the particle concentration, the scattering cross-section of the particles and the sample volume.

$$V_{rms} = V_o n^{1/2} \frac{K}{A} \qquad (2.35)$$

where V_{rms} - rms voltage for the flowing suspension
V_o - d.c. voltage corresponding to the incident light intensity
n - average number of particles in sample volume
K - average scattering cross-section of the particles
A - effective illuminated cross-sectional area

Gregory and Nelson (1984) have verified experimentally that for given experimental conditions where the effective area and incident intensity of the light beam are constant, the measured r.m.s. value depend on the square root of the average number of particles (solid content) in the beam. However, the r.m.s. value cannot be taken to

(a) a stable suspension



(b) a flocculated suspension

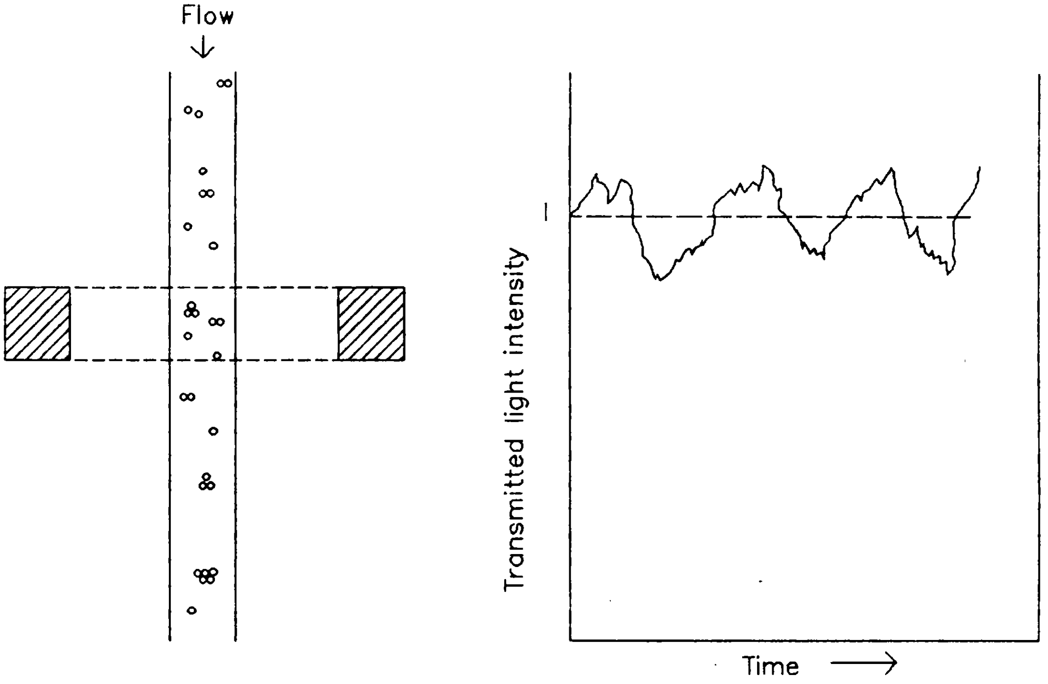


Figure 2.10. Principle of the monitoring technique

The intensity of light transmitted through a flowing dispersion shows random fluctuations about the mean. (a) a stable suspension and (b) a flocculated suspension.

interpret suspended solids concentration. This is because the r.m.s. value is greatly affected by changes in the state of aggregation of particles. The use of the r.m.s. measurements in monitoring flocculation rests on the sensitivity of r.m.s. value to aggregation. During the course of aggregation, the r.m.s. value changes as the results of particle concentration reduction and increasing scattering cross-section. Although these have opposite effects on the r.m.s. values, the net effect is always a substantial increase in fluctuations as reflected in the measured r.m.s. values. The r.m.s. value divided by the d.c. value gives a Ratio value, R, which is found to provide a more sensitive indication of aggregation than the r.m.s. value or the d.c. value. The Ratio (r.m.s./d.c.) value, R, is termed "Turbidity Fluctuation" and is generally used to derive an empirical measure of the state of aggregation since this ratio is not affected by contamination of optical surfaces or drift in electronic components.

CHAPTER THREE

EXPERIMENTAL MATERIALS AND METHODS

3.I. Materials

Analar grade reagents were used. Solutions were prepared with de-ionised water from an Elga "Spectrum" unit. The specific conductivity of the water was maintained below $1\mu S\ cm^{-1}$. The pH of the water was not adjusted to any preset value. The charge density of the types of polymers used in this work is not influenced by the pH of the solution (Dentel, 1991).

3.1.1. Silica suspensions

The silica particles used were Sikron F600, a product of Quarzwerke, GmbH, Cologne, FRG. The original sample was dispersed in deionised water and fractionated by differential sedimentation. Particles mainly in the size range $1-3\ \mu m$ were collected. The size distribution of the silica particles was determined with a Coulter Counter, Model T1, using a $50\ \mu m$ orifice tube.

Two samples of silica suspensions denoted A and B were prepared. The average equivalent diameter of Samples A and Sample B were $2.6\ \mu m$ and $1.9\ \mu m$ respectively. The size distribution of the two samples are presented in Appendix I. The solid content of the samples were determined by taking an known aliquot of each sample and dried to constant weight.

3.1.2. Polystyrene suspensions

Polystyrene latex particles were prepared by emulsifier-free polymerization and were used without purification. The particle size, as determined by Coulter counting, is given in Appendix II. 91% of the particles are in the size range $2\pm0.25\ \mu m$. The original latex suspension was diluted 1000 times to give a standard latex suspension. $200\ \mu l$ of the standard suspension was diluted to 20 ml with 2% NaCl for particle size analysis. The volume of the resulting suspension required for each particle count was set at 0.05 ml. Assuming all particles were spherical, the volume fraction was calculated for particles in each size-range taking the value at the mid-point of each size range as the diameter. The polystyrene content estimated from Coulter counting was found to be 5.7 %v/v.

3.1.3. Polymeric flocculants

Six cationic polymers were used and these were samples kindly donated by Allied Colloids Ltd., Bradford, U.K.. The properties of the polymers used are listed in Table 3.1.. The molecular structures are shown in Figure 3.1.. Four of the cationic polymers used were copolymers of acrylamide and dimethylaminoethyl acrylate (DMAEA). They were Percol 140 (P140), Percol 326 (P326), Percol 292 (P292) and Percol 63 (P63). The dimethylaminoethyl acrylate are fully quaternized and hence these polymers are positively charged over a wide pH range. The molar proportion of DMAEA determines the charge density and is given as "% cationic". The charge density of the polymers listed were given by the manufacturer. Percol 1597 (P1597) was poly(2-hydroxypropyl-N,N-dimethylammonium chloride), an epichlorohydrin-dimethylamine polymer. This group of polymers is sometimes called quaternized polyamines, polyquaternary amines, and epi./DMA polymers, (Mangravite, 1983). The latter refers to the primary raw materials epichlorohydrin and dimethylamine. P1697 was poly(diallyldimethylammonium chloride), usually referred to as Poly(DADMAC). The "% cationic" of P1597 and of P1697 are 100%. P1597 and P1697 were supplied as a 40% aqueous solution. The active concentration was reported in this work.

Stock polymer solutions (0.1% w/w) were prepared as follows: Polymer (100 mg) was accurately weighed into a 250 ml conical flask. Methanol (3 ml) was added to disperse the polymer particles. Sufficient amount of water was added to make up a 0.1% w/w stock solution. The resulting solution was fitted to a mechanical device which agitated the solution slowly for 30 minutes to allow the dispersed polymer particles to dissolve fully. Stock polymer solutions (0.1% w/w) were used within a week. Working polymer solutions (0.01% or 100 mg/l) were prepared daily.

Table 3.1. Properties of polymers used

Polymer	% Cationic	Intrinsic viscosity (cm^3/g)	Molecular mass *	Diameter (nm) **
P140	5	6	2.4×10^6	100
P326	15	2	4.5×10^5	60
P292	15	6.5	2.7×10^6	110
P63	30	7	3.0×10^6	140
P1597	100	_	$3\text{-}4 \times 10^4$	70
P1697	100	_	$3\text{-}4 \times 10^4$	70

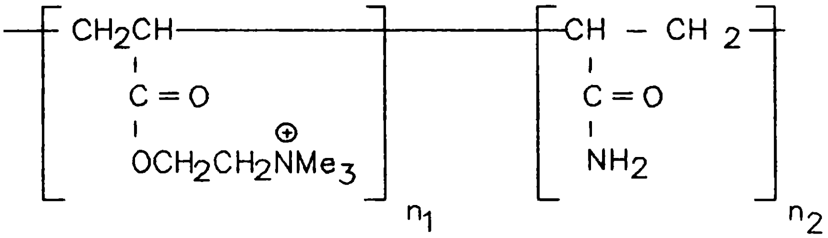
* The molecular mass were calculated from the intrinsic viscosity values (given by the manufacturer), using the Mark-Houwink equation, $[\eta] = KM^{\alpha}$, with constants $K = 3.7 \times 10^{-2}$ cm^3 g^{-1} and $\alpha = 0.66$, as quoted by Gill and Herrington (1987).

** The dimensions of the polymers in 0.5 M NaCl were determined by photon correlation spectroscopy (i.e. calculated from the diffusion coefficients.)

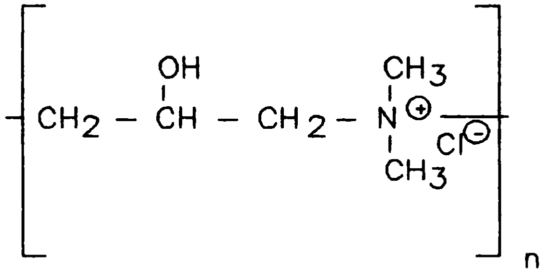
3.2. Methods

The effects of the ionic strength (adjusted by using sodium chloride at different concentrations), the molecular mass and charge density of the polymers on the aggregation of the silica particles were monitored with a Photometric Dispersion Analyser, PDA 2000 (Rank Bros Ltd, Cambridge, U.K.). The influence of different types of ions and the effect of the presence of two electrolytes were also investigated.

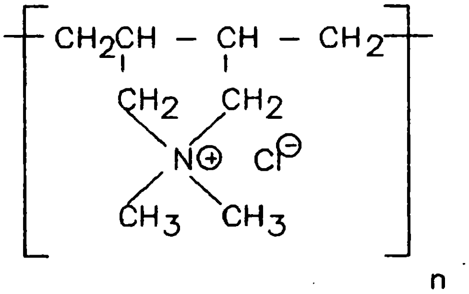
The main constituents of sea water are Na^+ and Cl^- ions. Typically, the concentrations of these ions are of the order of 0.5M. To study the effect of high ionic strength on the use of polyelectrolytes, flocculation was carried out in 0.5M NaCl. To compare the influence of different types of ions, further flocculation tests were carried out in 0.5M $NaNO_3$ and in 0.5M KCl.



Acrylamide/dimethylaminoethyl acrylate copolymer (fully quaternized)



Epichlorohydrin–dimethylamine polymer



Poly(diallyldimethylammonium chloride)

Figure 3.1. Molecular formula of polymers used

Sea water consists of a mixture of ions. The effect of the presence of two electrolytes was studied by carrying out flocculation tests in solutions containing a mixture of 0.01M $CaCl_2$/0.5M NaCl. The results are compared with those in 0.1M $CaCl_2$ and those in 0.5M NaCl. The same method was adopted to study a mixture of 0.05M $MgCl_2$/0.5M NaCl. The concentrations of $CaCl_2$ and $MgCl_2$ solutions chosen were comparable to those of a typical sea water.

The coagulation of a latex suspension was followed with a PDA 2000 and the results are compared with the reduction in particle concentration as monitored with a Coulter Counter. Changes in the state of aggregation have pronounced effects on the r.m.s. value, as described in Section 2.5.4.. Aggregation is always accompanied by an increase in the monitored Ratio value (Turbidity Fluctuation). A suspension of 2 μm latex particles was chosen for the work to avoid experimental errors arising from the limitation of Coulter counting technique. Particles of sizes less than 1 μm diameter cannot be counted accurately because the noise to signal ratio of the device becomes significant in that range. It is common practice to set the threshold at an equivalent spherical diameter of 1 μm. However, any study of the flocculation of a polydispersed suspension by Coulter counting containing particles less than 1 μm is likely to be unreliable. During the course of aggregation, submicron particles aggregate into aggregates of sizes larger than 1 μm and make the analysis of data very difficult.

3.2.1. Flocculation procedures

Flocculation tests were carried out in a 250-ml beaker, with 200 ml of silica suspension at a concentration of 65 mg/l, (Sample A was used). The solid concentration used in the experiments needs to be sufficiently low to reflect the flocculation mechanisms of a dilute suspension and should allow the changes in the values of Turbidity Fluctuation to be monitored easily. The solid concentration chosen satisfies the above requirement and the concentration range is comparable to many natural waters. A variable speed, two-blade paddle stirrer was used for mixing. The suspension was stirred at

200 rpm. The experimental set-up is shown schematically in Fig 3.2.. The sample was withdrawn at a rate of 3 ml/min, through a polyethylene tube of 1 mm internal diameter which passed through the cell of the PDA 2000 and the flow was re-circulated to the flocculation vessel. The Turbidity Fluctuation was monitored continuously on a chart recorder.

The polymer was added by pipetting a predetermined volume of polymer solution of concentration of 100 mg/l into the suspension. Rapid mixing of polymer and particles can be achieved by this method of polymer addition, minimising the possibility of local overdosing. Flocculation tests were carried out for a range of dosages over a range of ionic strengths (adjusted by adding sodium chloride) for each polymer. The results are discussed in Section 4.1..

Flocculation tests were carried out with Sample B at a concentration of 50 mg/l, using four cationic polymers (P140, P326, P292 and P63), to investigate the influence of different types of electrolytes at high salt concentration and the effect of the presence of two electrolytes. The solid concentration chosen for Sample B was lower than that for Sample A because of the smaller average particle size of Sample B. For a given solid concentration, the particle number concentration will be higher for a sample of lower average particle size. The flocculation of silica particles in 0.5M NaCl, 0.5M $NaNO_3$ and 0.5M KCl is discussed in Section 4.3. and the flocculation in solutions containing mixtures of $CaCl_2$/NaCl and of $MgCl_2$/NaCl are discussed in Section 4.4..

3.2.2. Particle electrophoretic mobilities measurements

The effects of adsorbed polymers and ionic strengths on the electrophoretic mobility of the particles was determined with a Mark 2 Particle Electrophoresis Apparatus (Rank Bros Ltd, Cambridge, U.K.), using a flat cell. A predetermined amount of polymer was added to the silica suspension. The mixture was mixed rapidly for 30 seconds. Then, it was allowed to stand for 30 minutes prior to the determination of particle mobility. The particles were observed with dark-field illumination. The direction of the current was alternated between

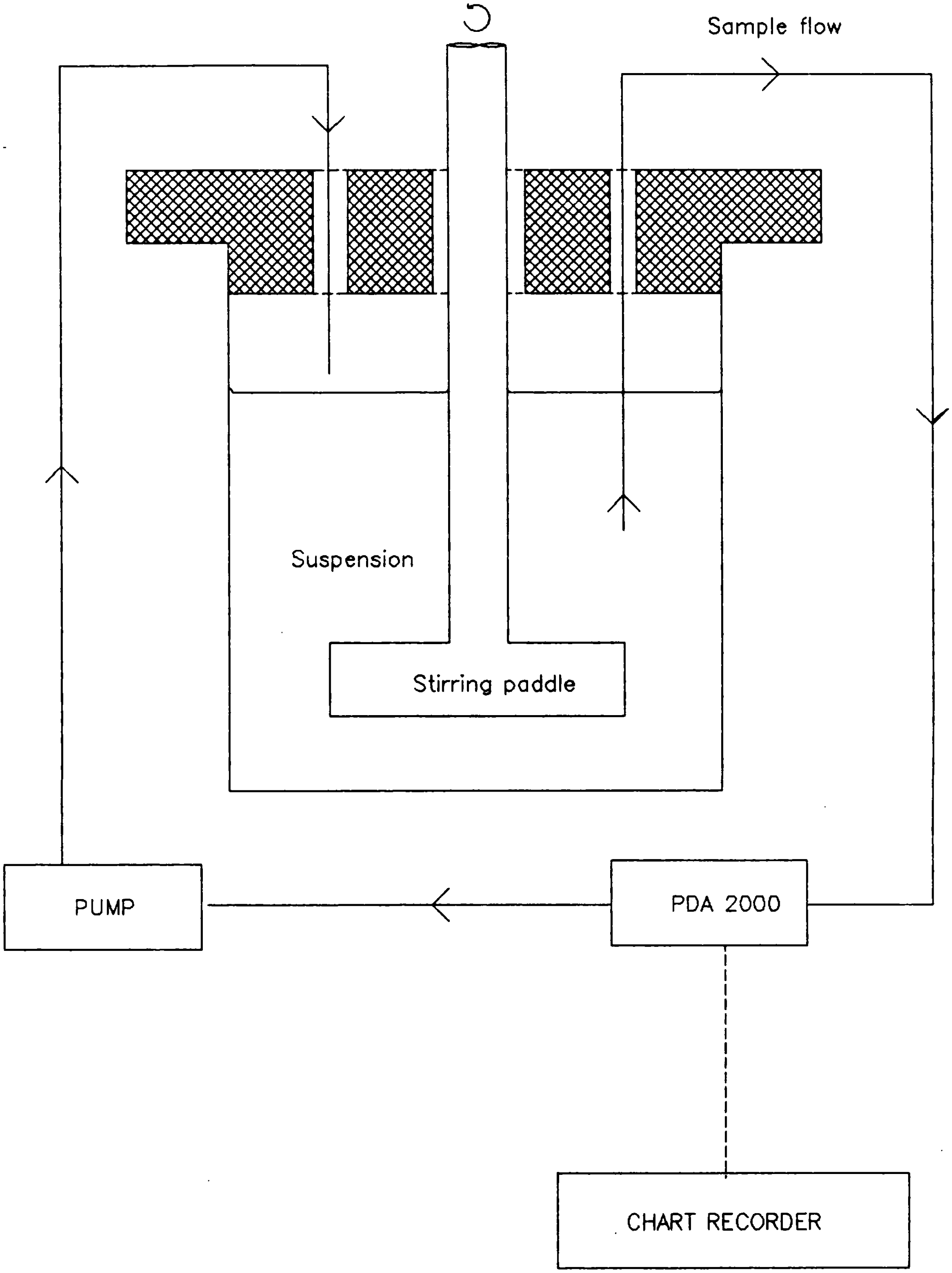


Figure 3.2. Schematic diagram of experimental set-up

each measurement to minimise errors due to electrode polarisation. Timings were made at both stationary levels. An average mobility value, for about 20 particles, were determined. The results are discussed in Section 4.2..

3.2.3. Particle counting

The experimental arrangement was similar to that set up for the flocculation test described in Section 3.2.1. (shown in Figure 3.2.), except that the flow was not re-circulated to the flocculation vessel. The suspension was stirred at 50 rpm, to reduce aggregate break-up due to excess shear stress.

The concentration of the latex suspension was 5.7×10^{-3}% v/v. The suspension was allowed to flow through the monitor via 1 mm i.d. tubing and the ratio signal was monitored on chart recorder. 0.5 ml of the suspension was diluted to 20 ml with 2% NaCl and 0.5 ml of which was sampled by the Coulter Counter for particle size analysis. The flow was stopped to conserve material, by closing a tap connected to the end of the sample tube. 2.0 ml of a 1 M magnesium chloride solution was added to destabilize the suspension (the final electrolyte concentration of the latex suspension was 10 mM Mg^{2+}). The suspension was allowed to flow through the monitor at intervals, during which the values of Turbidity Fluctuation were noted and samples were withdrawn for particle count determinations. The results are discussed in Section 4.5..

CHAPTER FOUR

EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1. Flocculation Tests

Flocculation tests were carried out as described in Section 3.2.1.. The state of aggregation was monitored for about 15 minutes after polymer addition. The value of Ratio (r.m.s./d.c.), Turbidity Fluctuation, can be adjusted by the D.C. Gain and the R.M.S. Gain controls to enhance the sensitivity of the instrument to the state of aggregation of particles. Although the values of Fluctuation Turbidity are measured in an arbitrary unit, it is adequate for the purpose of comparing the degree of flocculation of a given suspension provided that the instrument settings are fixed for that suspension. The instrument controls were arranged to give the Fluctuation Turbidity a value of about 0.5 for an unflocculated suspension in this work. A characteristic curve from such an experiment is shown in Fig. 4.1. which was obtained using Percol 140 at a dosage of 150 $\mu g/l$ in a salt-free solution.

The flocculation curve can be arbitrarily divided into four regions, as shown in Figure 4.1.. The Turbidity Fluctuation changes very little with time in Region A. This reflects the slow adsorption of polymer mentioned in Sections 2.3.2. and 2.3.3.c.. At this stage, most particles have not yet adsorbed enough polymer to become destabilized and particle collisions may not result in aggregate formation. As more polymer is adsorbed, the particles becomes destabilized and thus collisions of particles will form stable aggregates. As a result, the values of the Turbidity Fluctuation begin to show a distinct rise with time which marks the initiation of flocculation (Region B).

The Turbidity Fluctuation increases linearly with time in Region C, which could be interpreted as a constant rate of flocculation of the suspension. At the beginning of this phase, many particles have acquired sufficient amount of polymer needed for the formation of stable aggregates. As discussed in Section 2.3.3.b, the concept of half surface coverage for maximum successful collision rate may no longer

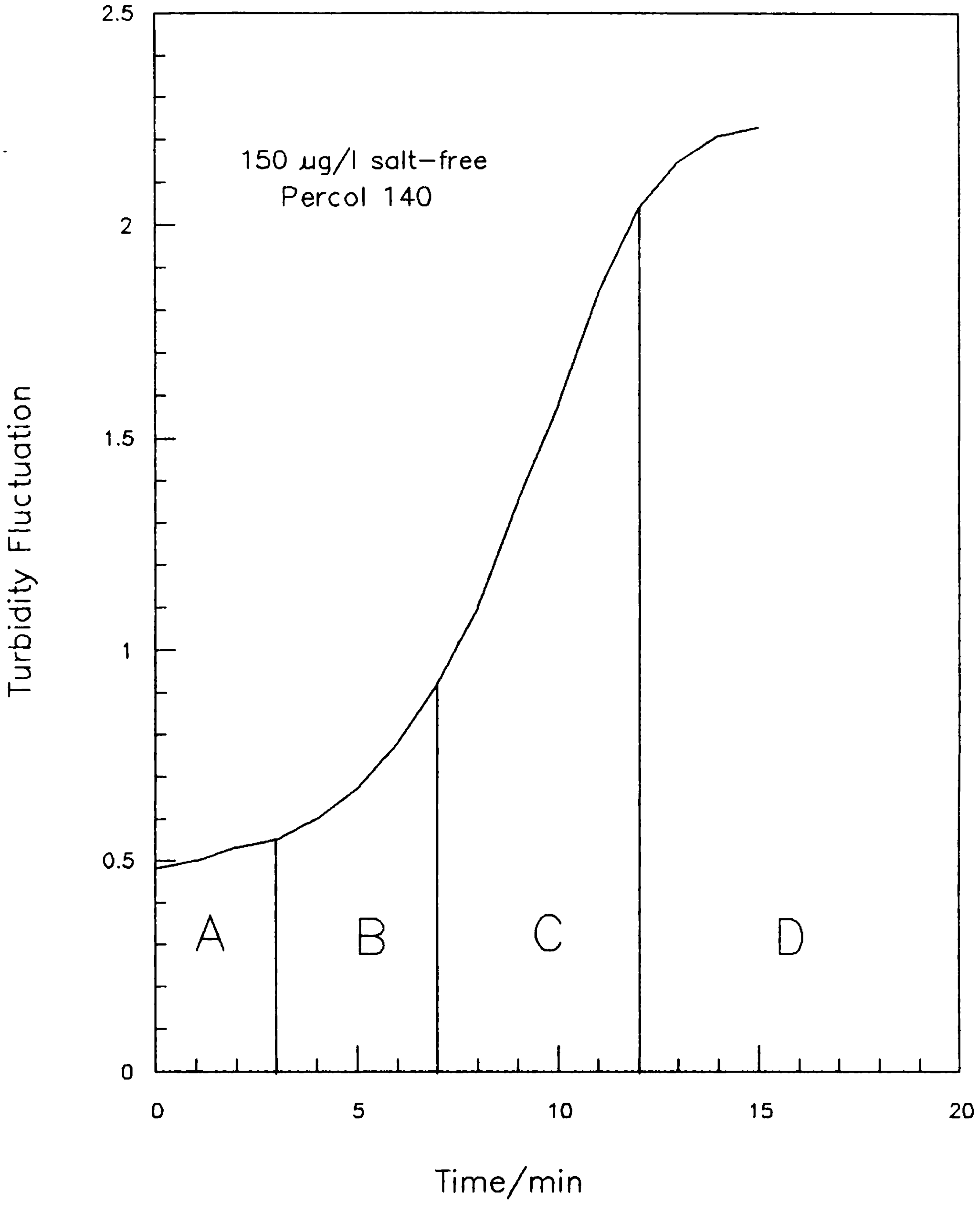


Figure 4.1. A typical flocculation curve

be applicable to polymer flocculation kinetics. Nevertheless, a maximum successful collision rate should occur with a specific amount of adsorbed polymer. The amount of adsorbed polymer required to bring about this maximum rate will depend on the characteristics of the polymer, the particle concentration and the ionic strength of the solution. Further adsorption of polymer may reduce collision efficiency. The interaction of oppositely-charged patches on different particles will be less likely. An excess coverage of polymer may lead to a reversal of surface charge. The number of suitable vacant sites to allow for polymer bridging are also reduced. The size distribution of the suspended particles changes as the flocculation of the suspension proceeds, forming larger aggregated particles. Under the given shear conditions where the dominant transport mechanism is orthokinetic collision, the larger collision radii of aggregated particles can enhance the collision rate of flocculating particles. The net effect of the enhanced particle collision rate and reduced collision efficiency seems to give a steady flocculation rate as indicated (Region C), although there is no theoretical basis for these. The slope of the flocculation curve can be considered as an empirical measure of the flocculation rate, since the Turbidity Fluctuation is an indication of the state of aggregation.

In Region D, there is a leveling-off of the Turbidity Fluctuation. Depending on the amount of polymer added, restabilization of particles is possible when excess polymer is adsorbed. This could lead to a declining flocculation rate. Even when the amount of polymer added is insufficient to restabilize the particles, the aggregates will eventually reach a limiting size as determined by the stirring conditions and by the aggregate strength. This partially explains the maximum observed in the flocculation curve.

4.1.1. Effect of polymer dosage

Figures 4.2.-4.7. show the flocculation curves obtained when different amounts of the six polymers under test were added to salt-free suspensions. The polymer used in Figure 4.2. was Percol 140. At the lowest dosage, 25 $\mu g/l$, the Turbidity Fluctuation

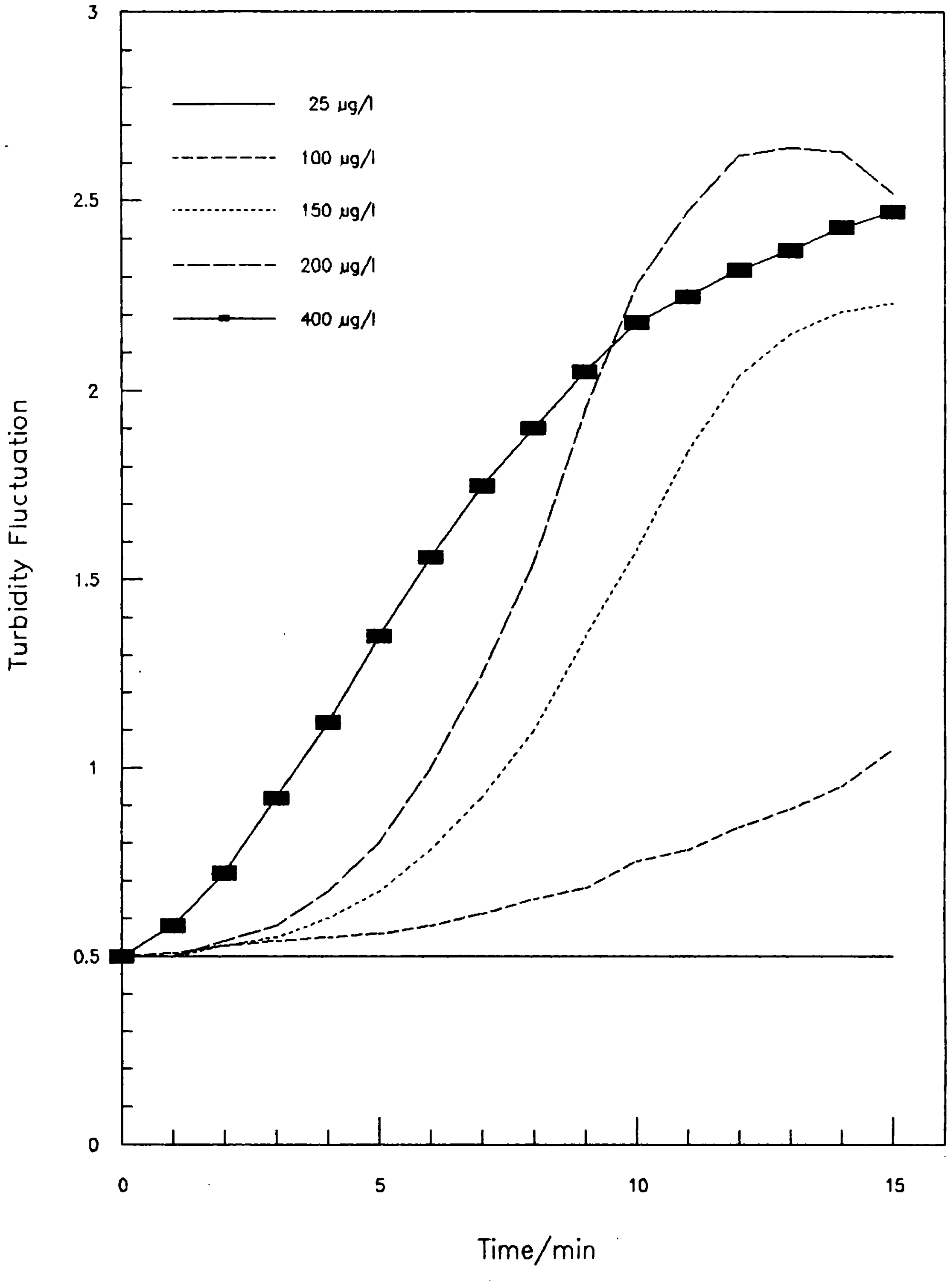


Figure 4.2. The effect of dosage on flocculation
(Percol 140) salt–free

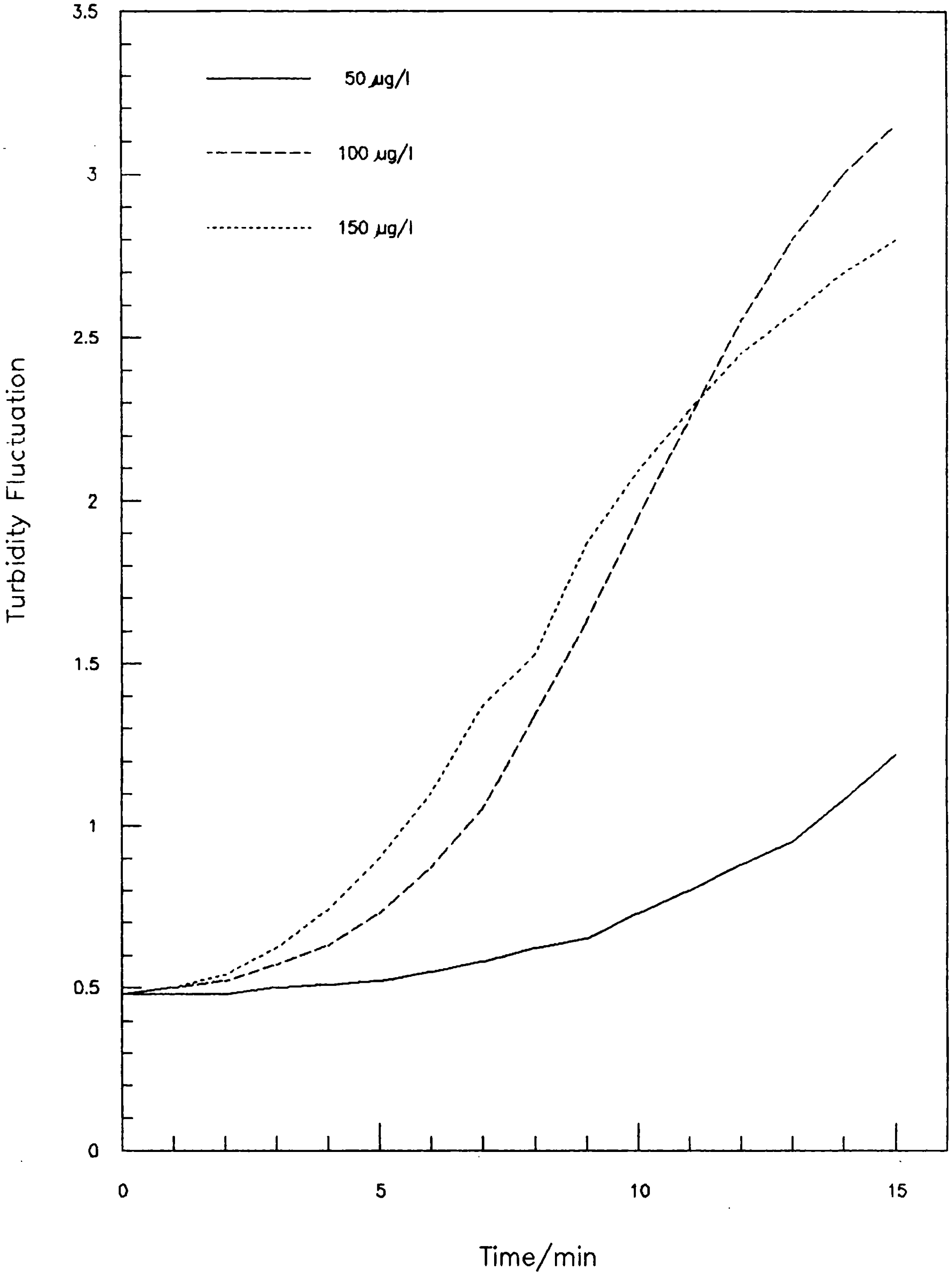


Figure 4.3. The effect of dosage on flocculation
(Percol 326) salt-free

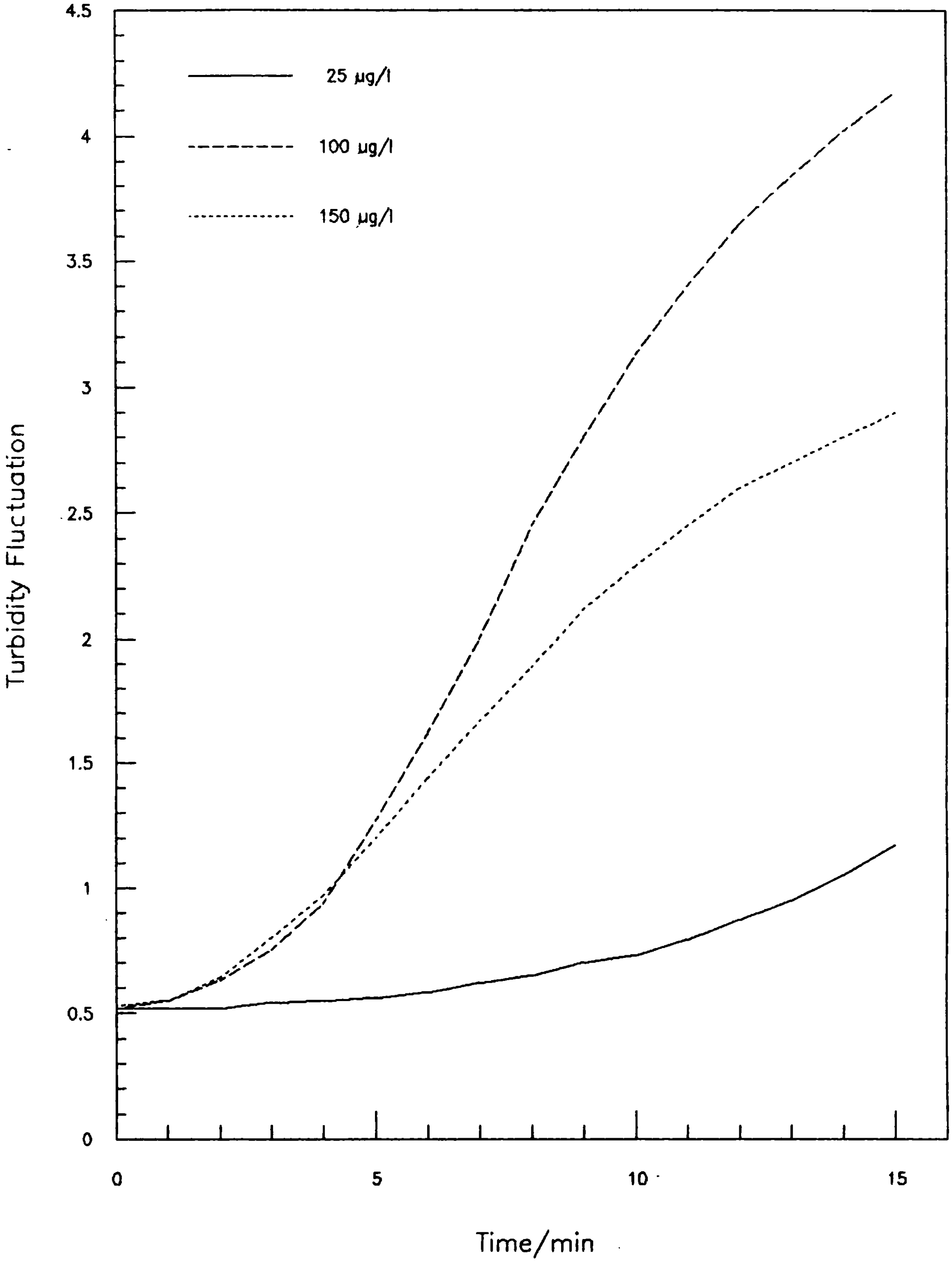


Figure 4.4. The effect of dosage on flocculation (Percol 292) salt–free

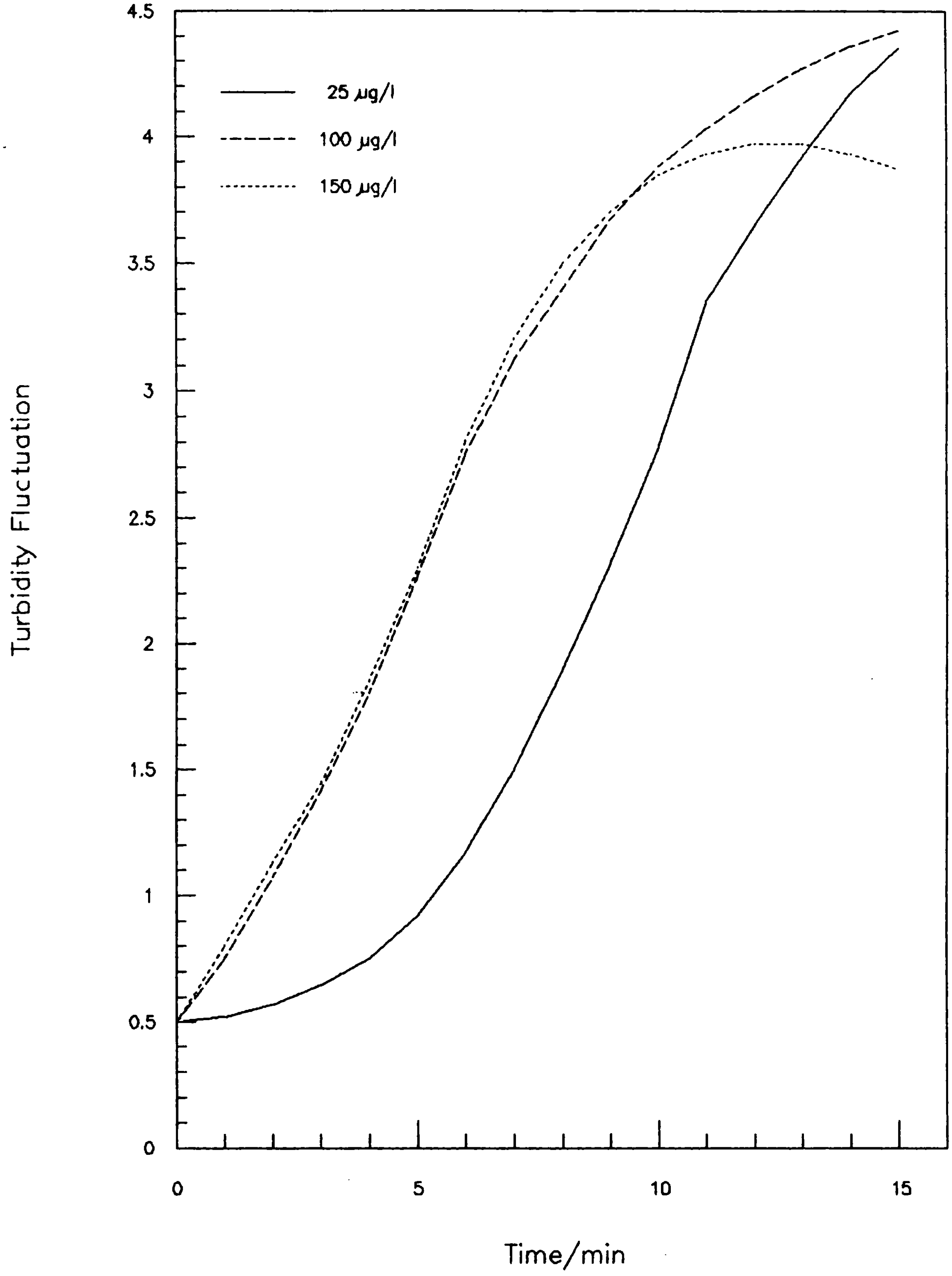


Figure 4.5. The effect of dosage on flocculation (Percol 63) salt–free

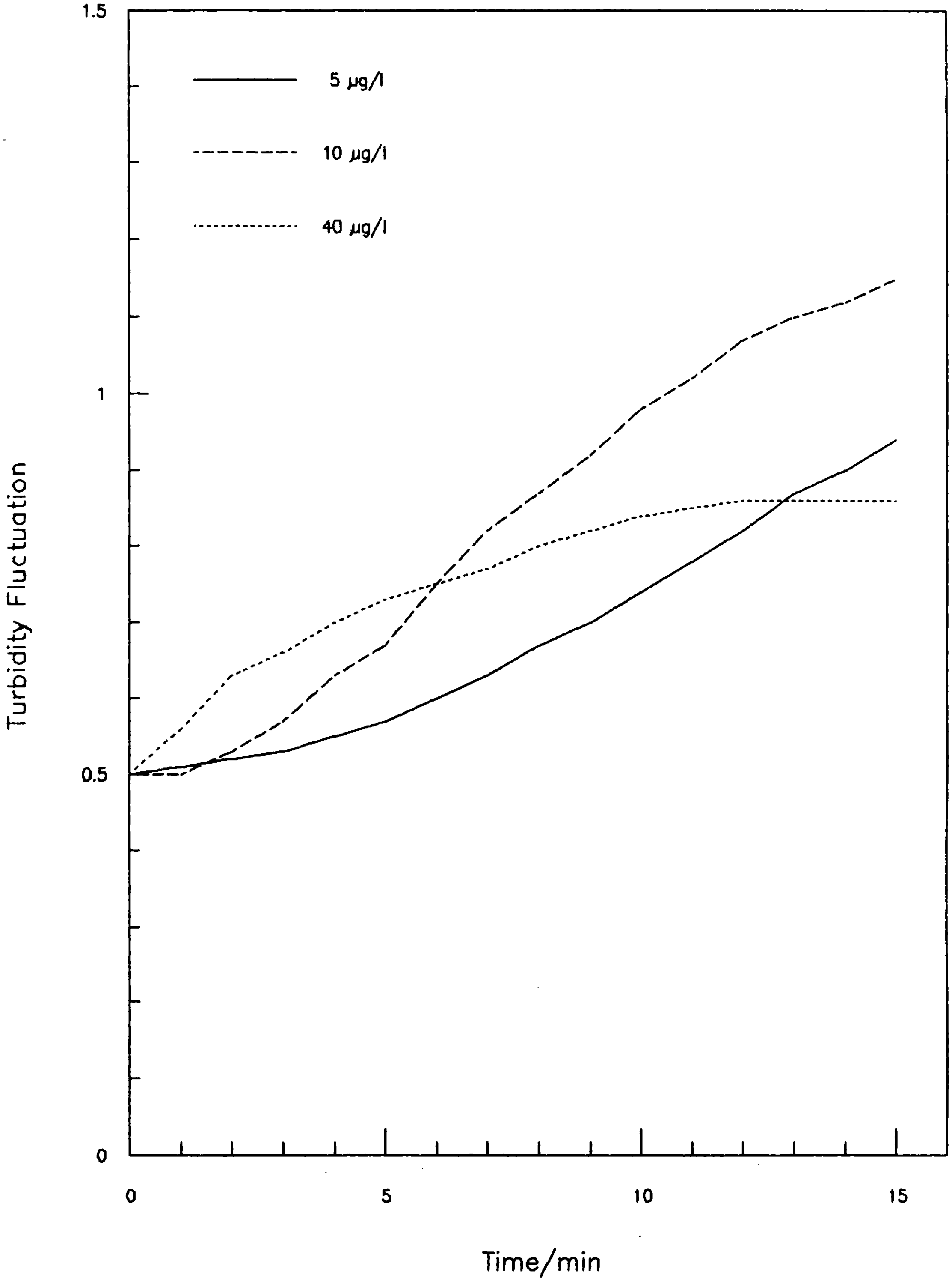


Figure 4.6.The effect of dosage on flocculation
(Percol 1597) salt–free

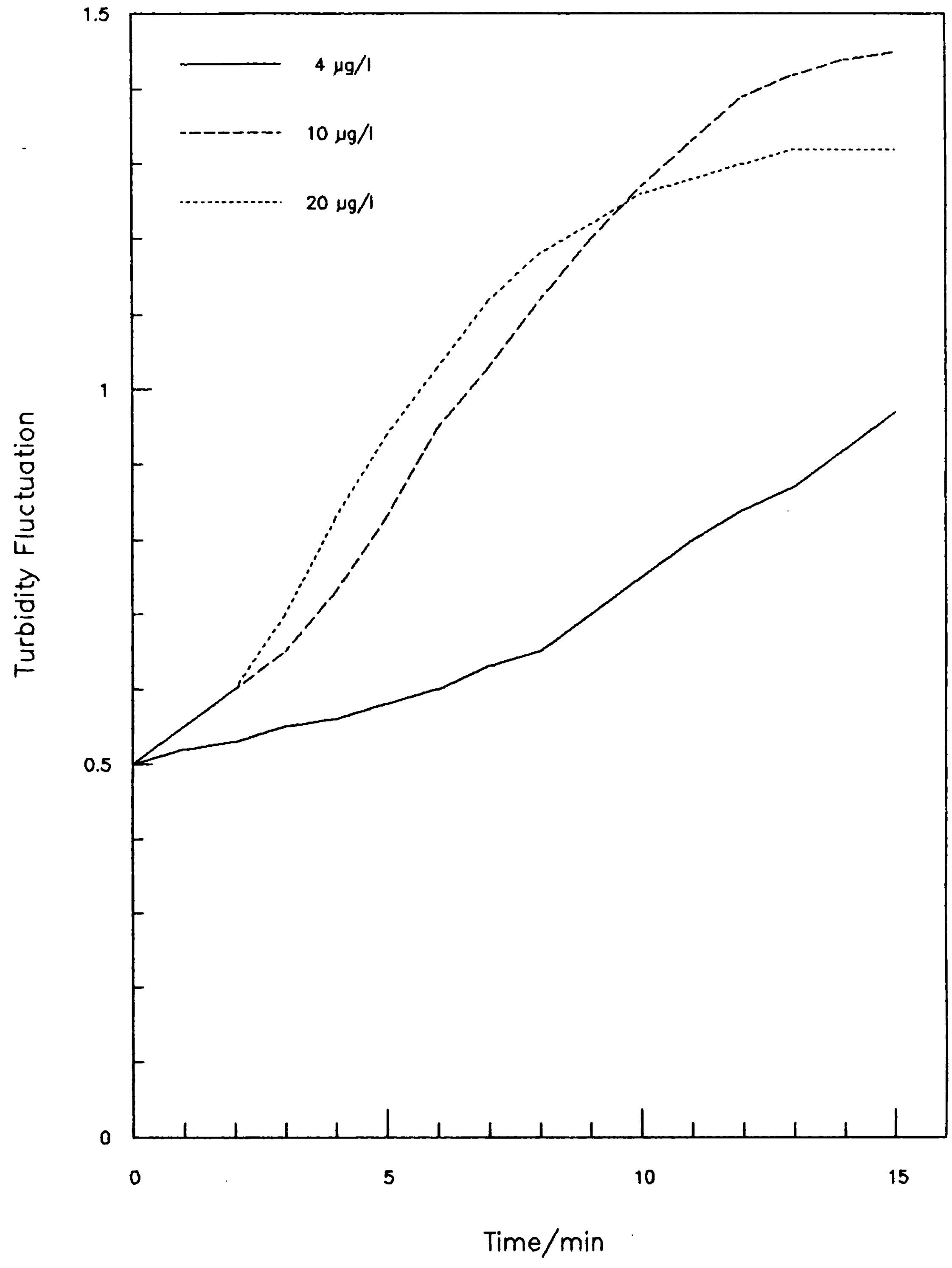


Figure 4.7 The effect of dosage on flocculation
(Percol 1697) salt–free

is essentially unchanged which indicates little or no flocculation in the 15 minutes flocculation time. Two distinct effects are observed with increasing dosages. The initial "lag phase" (Region A) reduces as the dosage increases. The rate of particle-polymer collision is increased with an increase in polymer concentration. The higher the polymer dosage, the shorter the time required for the particles to acquire enough polymers to become destabilized. At a high dosage (400 $\mu g/l$) flocculation begins immediately after addition of polymer, as indicated by the disappearance of Region A. The second effect is the slope of the flocculation curve in Region C. Up to a certain dosage, the slope becomes steeper with an increase in dosage. Thereafter, the slope decreases with an increase in dosage. The steeper slope may be interpreted as a more rapid flocculation. Therefore, the slope in Region C can be used as an empirical measure of the flocculation rate.

The dosage at which the slope is steepest corresponds to the optimum flocculation. The adsorption of polymer dominates the re-conformation of polymer, with increasing polymer concentration. The flattening of adsorbed polymer molecules on particles may be insignificant, especially, when the charge density of the polymer is low. When the "Polymer bridging" mechanism is predominant, the flocculation of the suspension is likely to proceed faster with the adsorbed polymer molecules in a more extended conformation. On the other hand, too much adsorbed polymer may leave too few adsorption sites for polymer of other particles to adsorb. In the case where the "Electrostatic patch" mechanism is predominant, the uneven distribution of charges on particles are more pronounced with a higher polymer concentration. This may result in a stronger attraction among particles, giving a better flocculation. However, an excess amount of adsorbed polymer can lead to repulsion.

The optimum dosage for a given system is very difficult to define unambiguously, the optimum operational dosage may not be the dosage for optimum flocculation. In the case of Percol 140 as shown in Fig 4.2., the optimum dosage appears to be about 200 $\mu g/l$ where the slope is steepest and the maximum value of Turbidity Fluctuation is highest. However, the maximum flocculation rate is not attained until about 5 minutes after dosing. Whereas, at a higher dosage (400 $\mu g/l$) the initial "lag phase" is not observed and the maximum flocculation rate is attained immediately after dosing. When an excess amount of polymer is added, the rate of polymer adsorption is faster. The particles rapidly acquire excess polymer and the collision efficiency is reduced. Up to about 8 minutes after polymer addition, a dosage of 400 $\mu g/l$ gives a greater degree of flocculation than lower dosages. However, the maximum value of Turbidity Fluctuation attained is lower than those attained when using lower dosages such as 150 $\mu g/l$ and 200 $\mu g/l$. Similar trends are found with flocculation tests performed with other polymers, see Figures 4.2.-4.7..

The above observations point out that optimum operational dosage is dependent on the specific requirements of the process. The operational optimum dosage will depend on whether a rapid flocculation is required or a moderate flocculation time, say, 10 minutes, is allowed. A high polymer application rate is necessary in applications where rapid destabilization is required. Even though, a lower polymer dosage would lead to a higher degree of flocculation if a longer flocculation time was allowed. Another consideration needs to take into account is the characteristics of the aggregates formed. The aggregates formed have to be suitable for separation by the subsequent process. So far, there is little published work relating the characteristics of aggregates and flocculation conditions.

4.1.2. Effect of ionic strength

The ionic strength of the solution can affect polymeric flocculation in several ways. The destabilization and restabilization of negatively charged particles by cationic polymers occur primarily by charge neutralization, in particular, when the particle concentration is low. The destabilization is partly caused by charge neutralization due to adsorbed polymer and partly by reduction of electrical repulsion due to the salt effect. A reduction in the effective range of the electric double layer also encourages the bridging of particles by adsorbed polymer molecules. In the presence of a moderate amount of inert electrolyte, less polymer is needed to bring about flocculation and flocculation occurs over a broader range of polymer concentrations. An increase in ionic strength reduces the repulsion between charged segments of the polymer chain (the polymer chain adopts a more compact comformation) as well as reducing the range of inter-particle repulsion. These effects may affect the polymer adsorption and flocculation efficiency, leading to an optimum ionic strength at which the use of polyelectrolytes is most effective. This aspect is discussed in more detail in Section 4.1.5

Figures 4.8.-4.13. show the flocculation curves for the same polymer dose at a range of salt concentrations from deionized water to 500 mM NaCl. In order to highlight the salient features of the effect of ionic strength, flocculation curves at different dosages are presented for different polymers. The combined effects of ionic strength and polymer dosage on flocculation is discussed in Section 4.1.5.. The response of polymer towards the effect of ionic strength of the solution depends on the characteristics of the polymer. The trend observed for the fully quaternised acrylamide/dimethylaminoethyl acrylate copolymers studied at their respective polymer doses are similar, the addition of an electrolyte at the given concentrations increases flocculation. The opposite trend was observed for Percol 1697. Later, it was found that flocculation with Percol 1697 proceeded faster in salt-free suspensions than in the presence of added electrolyte at the given concentrations (see Section 4.1.5. and Figures 4.23.). Percol 1597, a polymer of the same charge density as Percol 1697, shows little response to added salt at the concentrations studied. The reason for this discrepancy has not been established. The chemical nature of the polymer is the most likely cause. The results for Percol 140 is described below.

Figure 4.8. shows that there is no flocculation at a dosage of 25 $\mu g/l$ in a salt-free solution. However, significant flocculation occurs when salt is present. The amount of adsorbed polymer required to destabilize the particles is less in the presence of added salt. The results also show that the lag period is reduced as the ionic strength is increased. As the particles are partly neutralized by the effect of added salt, the onset of flocculation takes place more

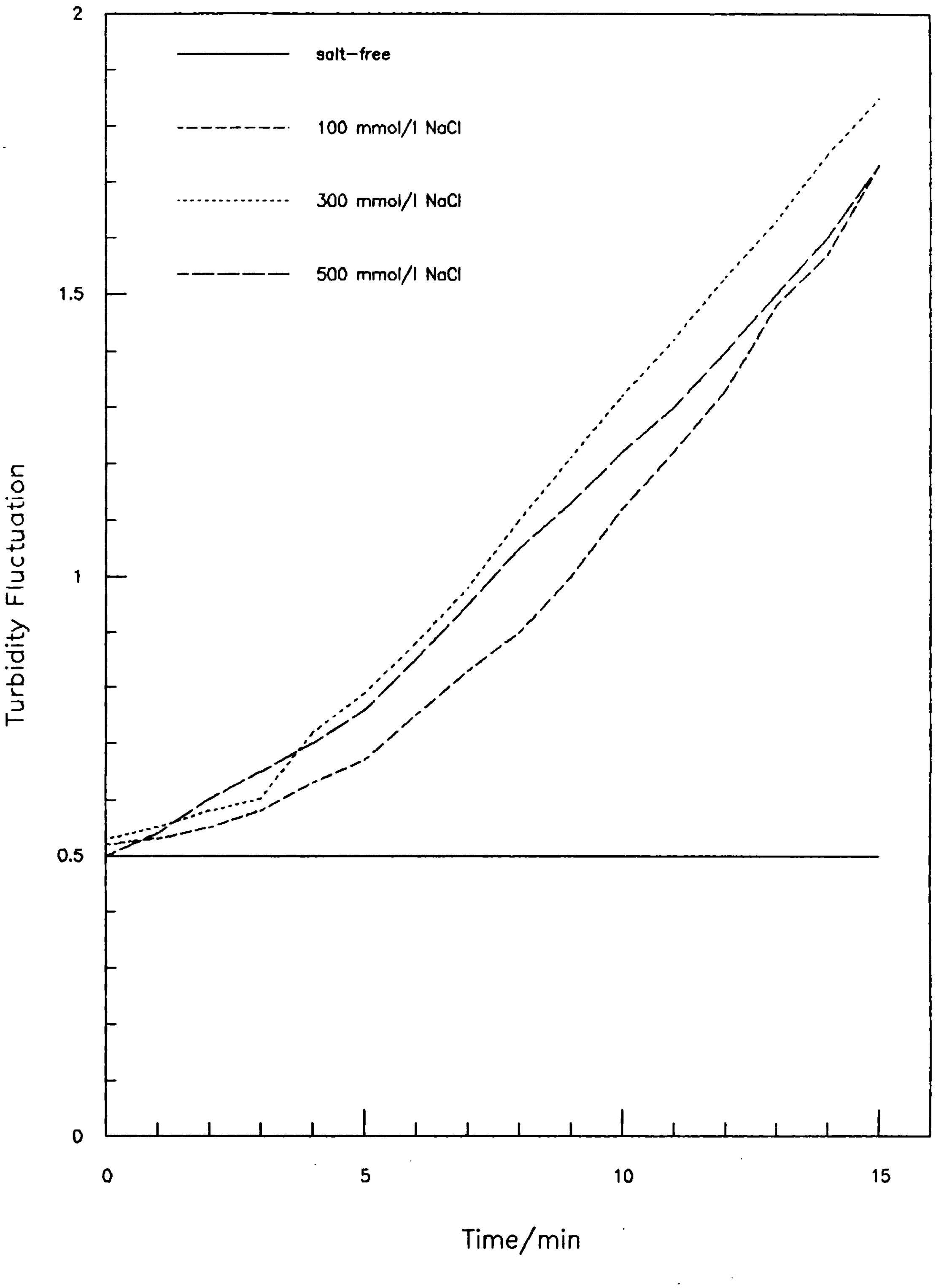


Figure 4.8. The effect of ionic strength on flocculation
(Percol 140) 25 μg/l

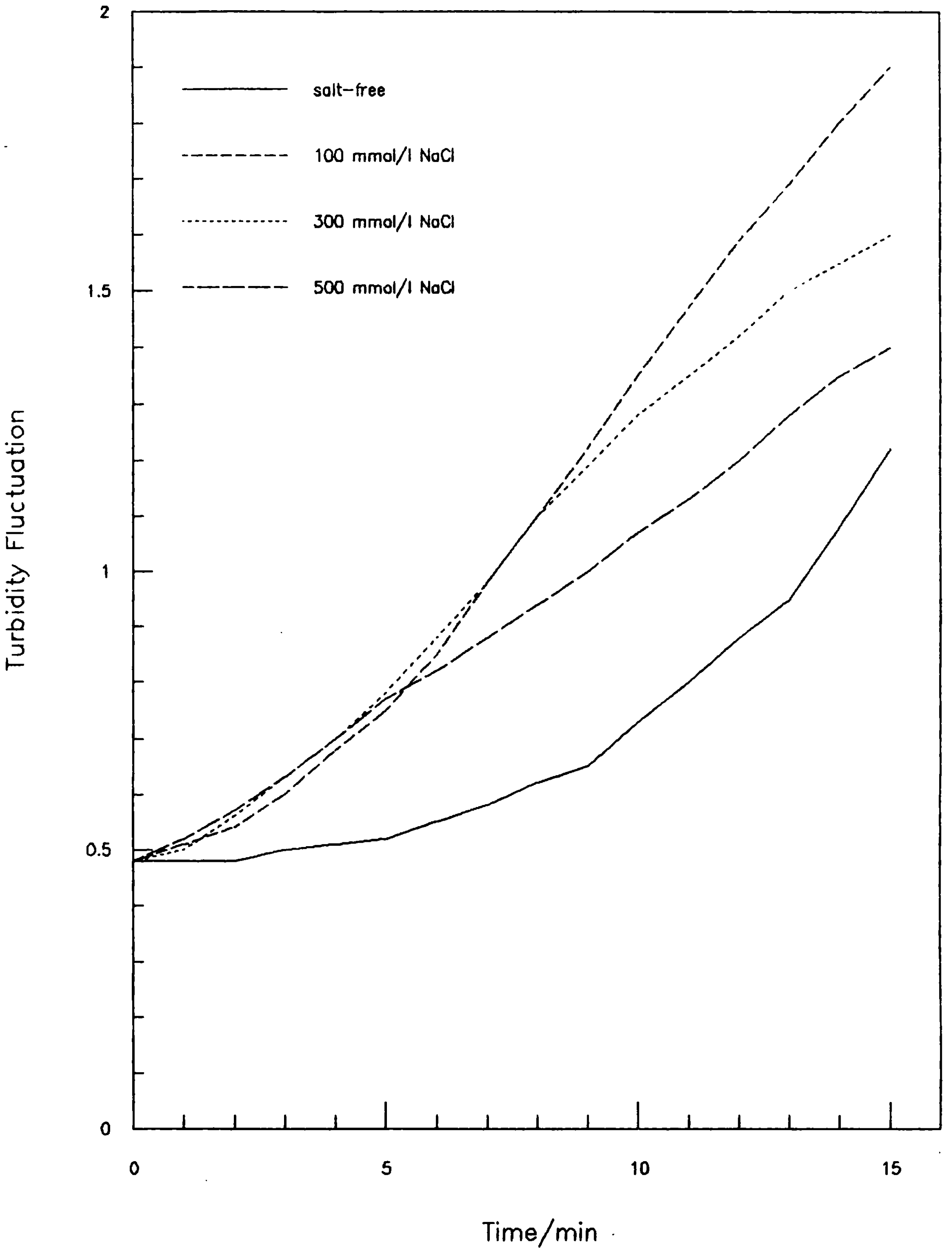


Figure 4.9. The effect of ionic strength on flocculation (Percol 326) 50 µg/l

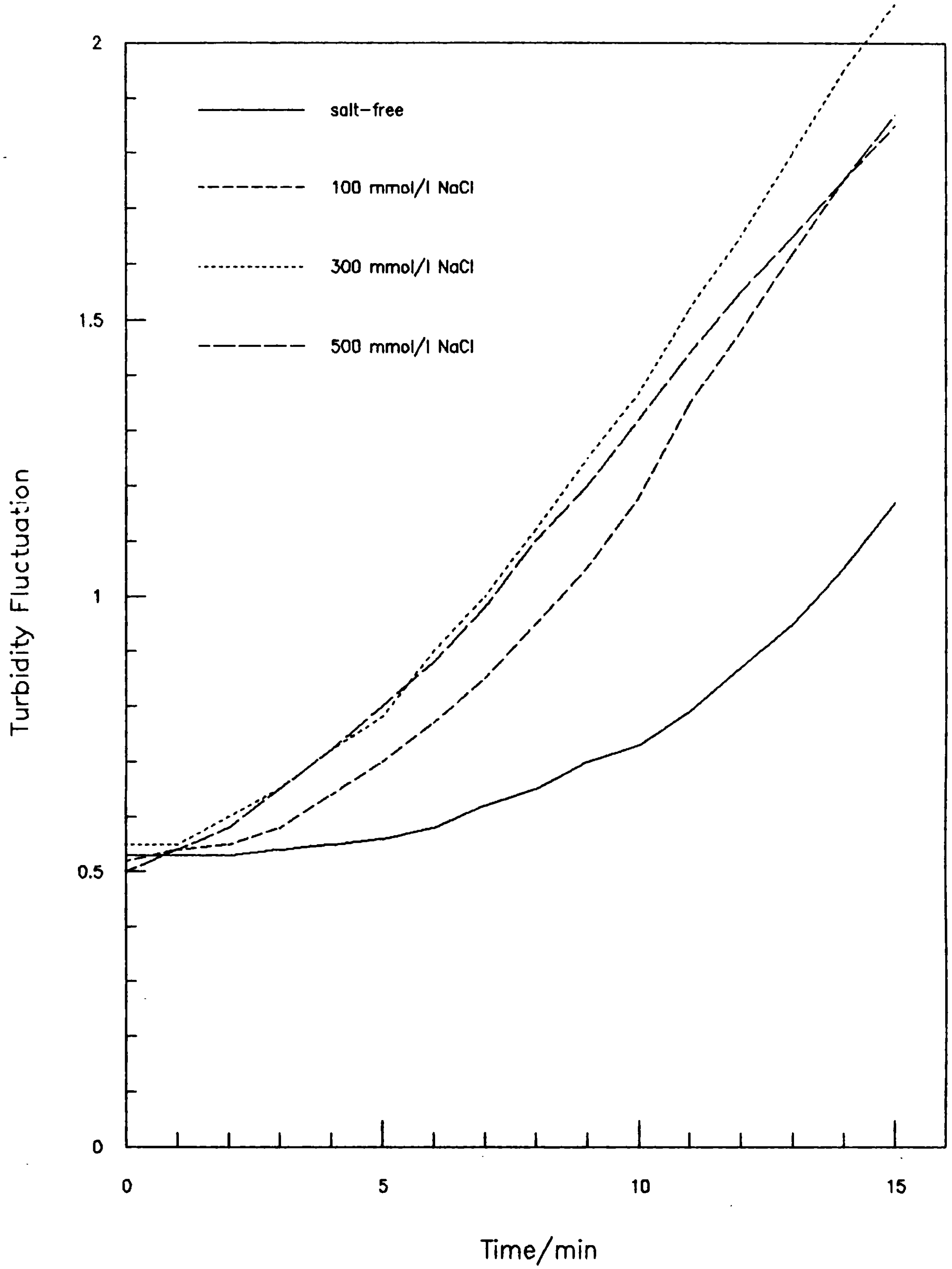


Figure 4.10. The effect of ionic strength on flocculation (Percol 292) 25 µg/l

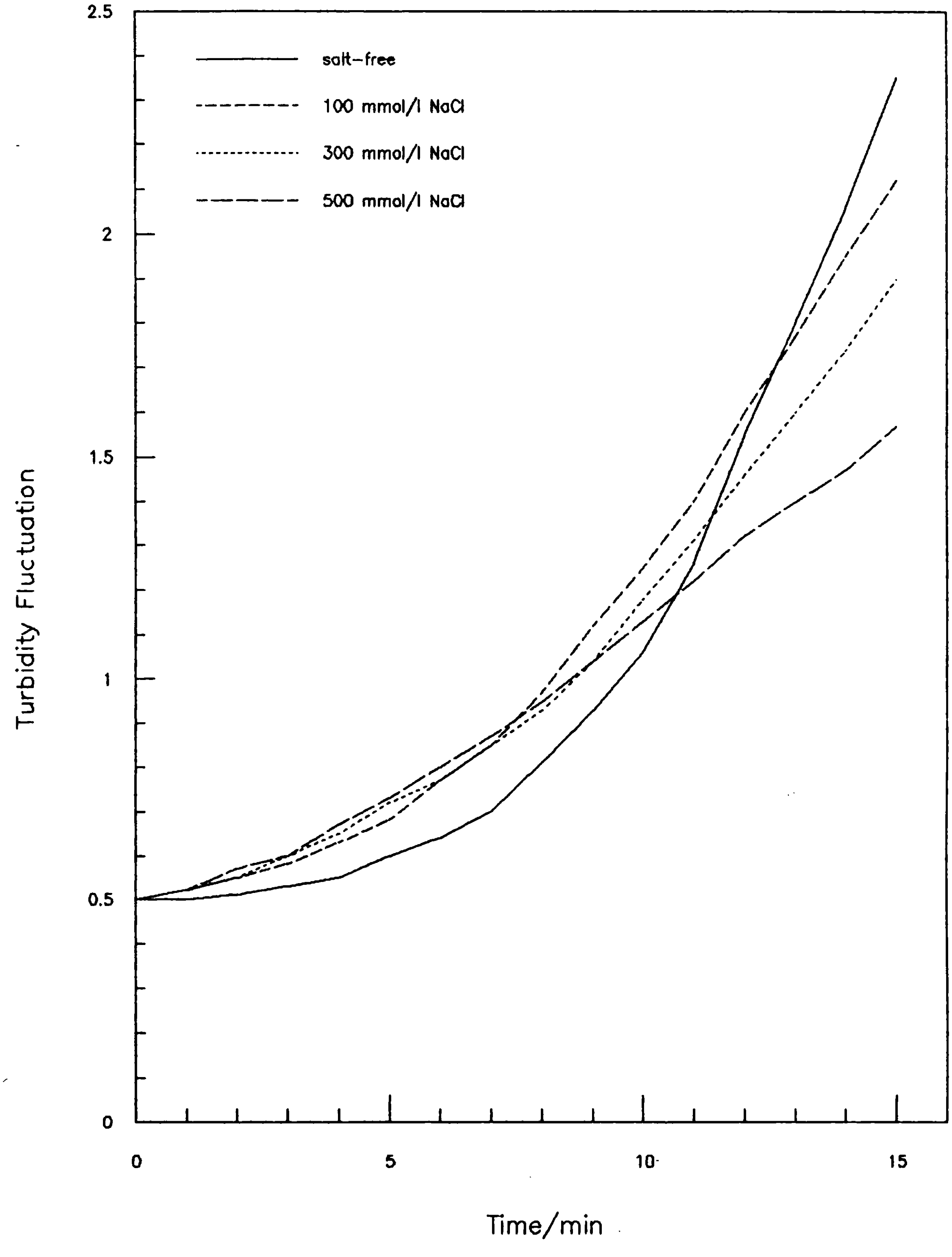


Figure 4.11. The effect of ionic strength on flocculation (Percol 63) 12.5 µg/l

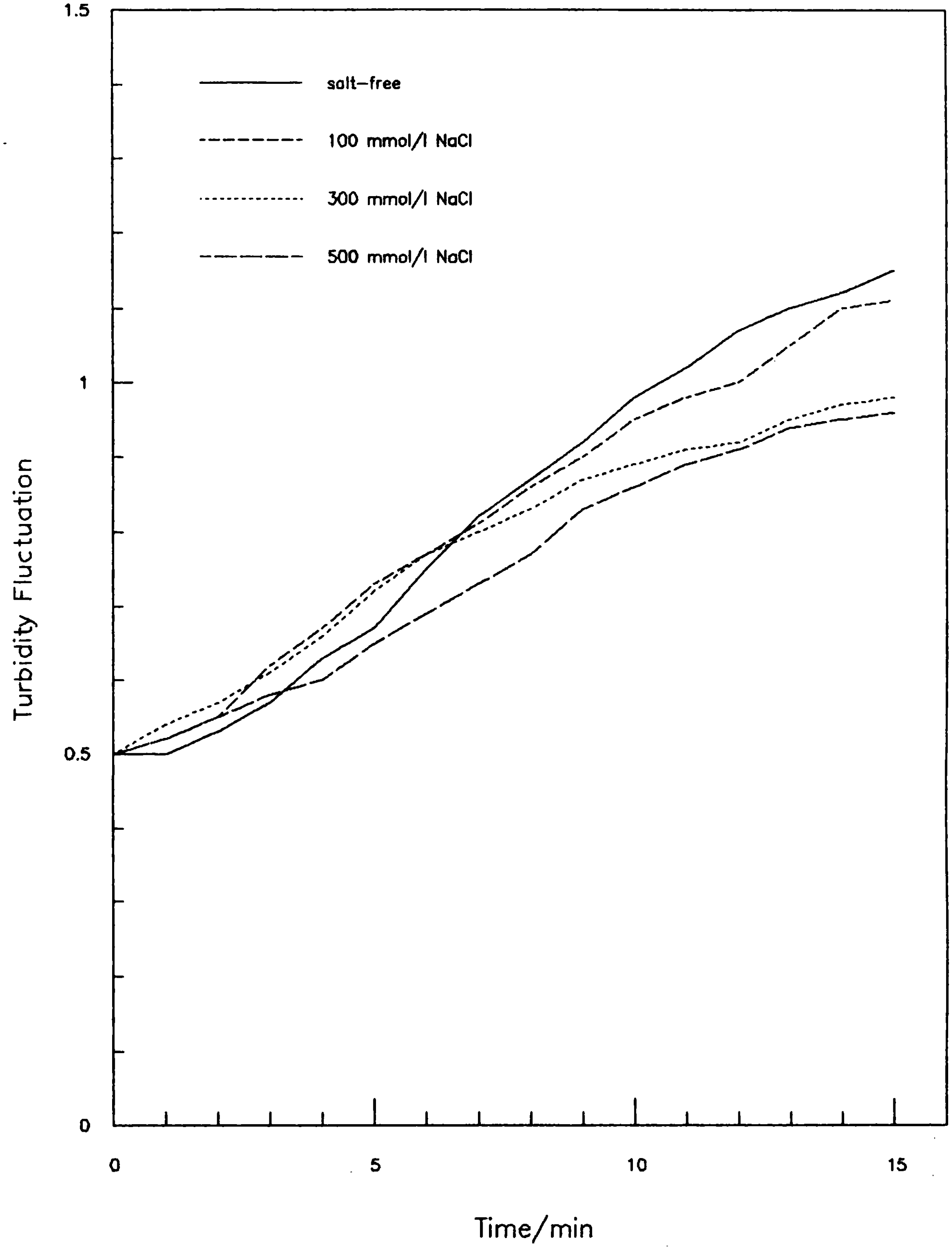


Figure 4.12. The effect of ionic strength on flocculation (P1597) 10 µg/l

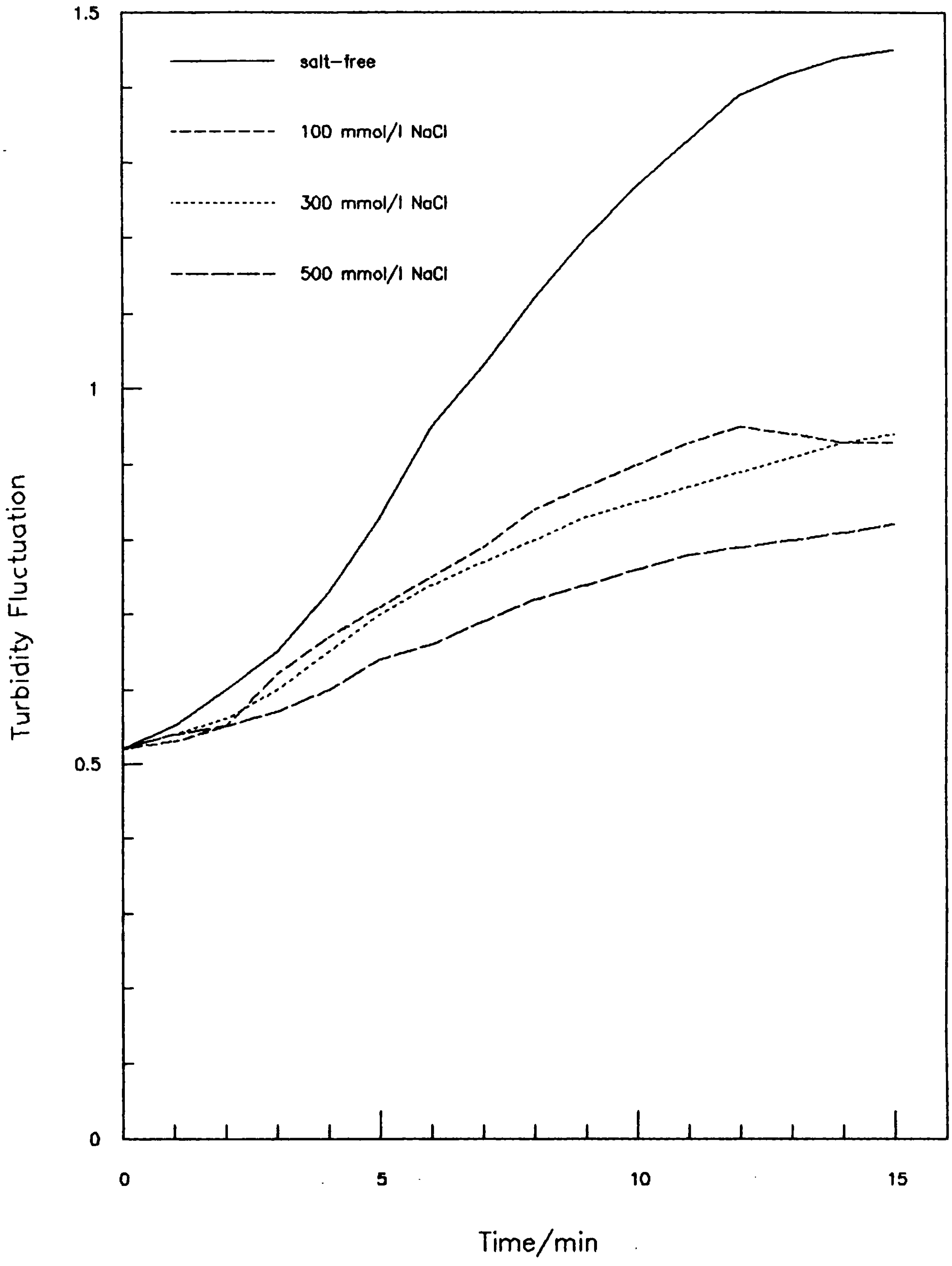


Figure 4.13. The effect of ionic strength on flocculation
(P1697) 10 µg/l

rapidly for a given dosage at a higher salt concentration as shown by the reduced lag time. Flocculation begins at a significant rate after a lag of about 4 min at 100 mM NaCl. The lag time is reduced to about 2 min at higher salt concentrations (300 mM NaCl and 500 mM NaCl). The rates of flocculation for the two higher salt concentrations are comparable to the maximum rate achieved at 100 mM NaCl. Once complete destabilization is achieved, the rate of flocculation, being transport limited, cannot be further increased. Hence, the flocculation rates are about the same at high salt concentrations. The highest value of Turbidity Fluctuation reached, at the end of a 15 minutes flocculation time, at 500 mM NaCl is less than that at 300 mM NaCl. This observation seems to suggest that 300 mM NaCl may be the optimum ionic strength for the conditions specified.

Figure 4.14. shows the effect of ionic strength when the polymer dosage is high, (500 $\mu g/l$) - Percol 140. The lag period is not observed in the absence of added salt. The destabilization of the particles due to adsorbed polymer is rapid when the polymer dosage is high. The initial flocculation rates (2 minutes after polymer addition) are roughly the same for the range of salt concentrations studied. It is noteworthy that during the initial 6 minutes flocculation time, the values of Turbidity Fluctuation for the salt-free suspension is higher than those suspensions with added salt. Six minutes after polymer addition, the Turbidity Fluctuation for the salt-free suspension are comparable to the 300 mM NaCl but they are lower than those of the 100 mM NaCl and higher than those of the 500 Mm NaCl. These results show that 100 mM NaCl is the optimum ionic strength for the experimental conditions. In fact, the leveling-off of the flocculation rate took place sooner for the higher salt concentration. The highest Turbidity Fluctuation was achieved in 100 mM NaCl at the end of the flocculation time. The results show that for the same polymer dosage, in particular when the dosage is high, restabilization of particles is possible at high salt concentration. For the same degree of destabilization, the amount of adsorbed polymer needed is probably less at a higher ionic strength solution.

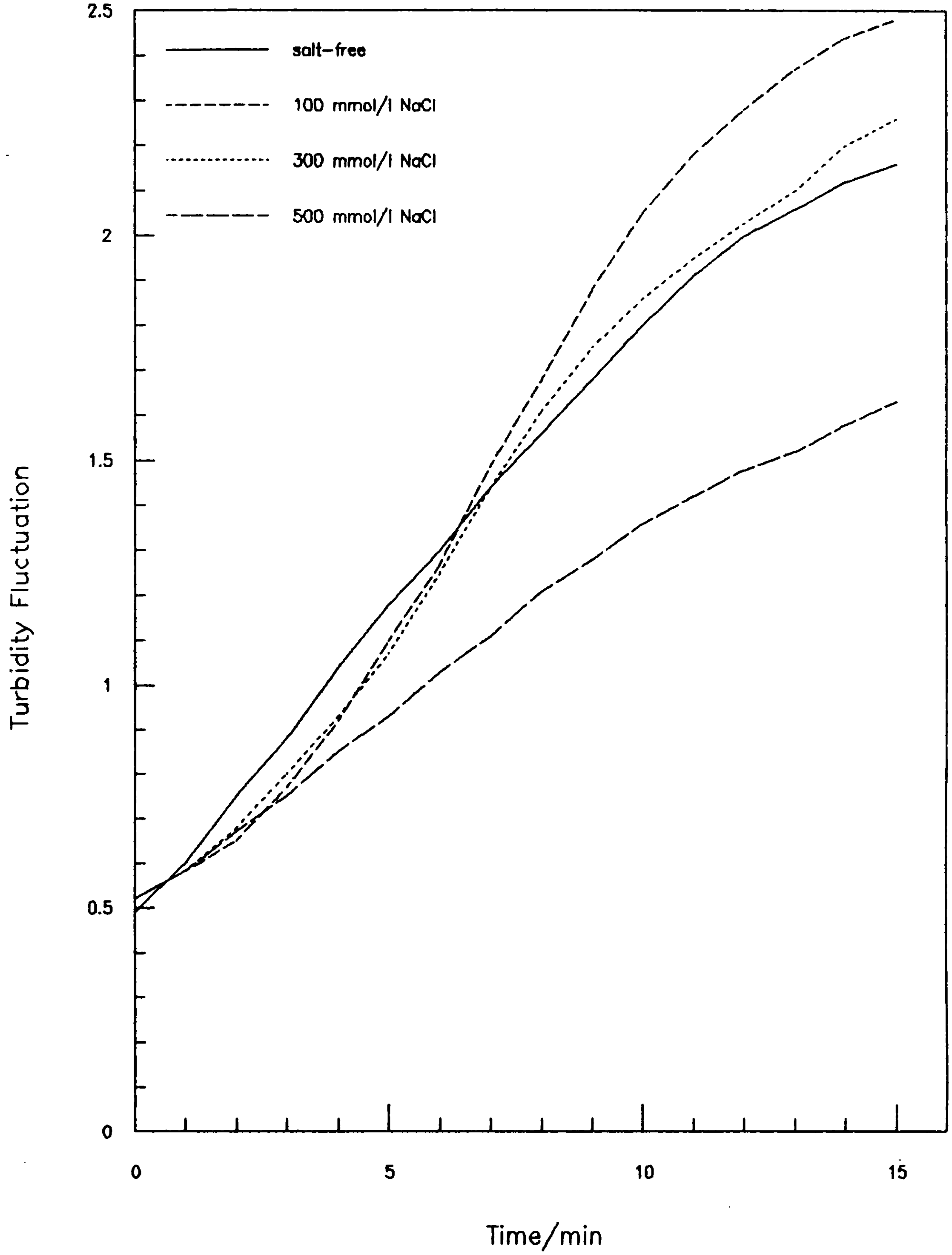


Figure 4.14. The effect of ionic strength on flocculation
(P140 at high dosage – 500 μg/l)

The ionic strength effects depend on the characteristics of the polymer. The charge density of the polymer is an important parameter as the destabilization is essentially due to charge neutralization. The flocculation curves for Percol 63 at a dosage of 12.5 $\mu g/l$ are shown in Figure 4.11.. There is a considerable degree of flocculation at this dosage in salt-free solution. On the other hand, there is no flocculation for Percol 140 at a dosage twice as much (see Figure 4.8.). The results are different because of the difference in charge density of the two polymers. The interaction between oppositely charged particles and polymer is expected to be higher for the polymer of higher charge density. This will result in a more effective particle destabilization. The effects of charge density is discussed in more details in Section 4.1.3. The effects of ionic strength on flocculation in using polymer of different charge density is considered below.

The reduced lag time in the presence of inorganic electrolyte observed with Percol 140 is also found with Percol 63. In the case of Percol 140, the lag time continues to reduce with each increase in ionic strength. Whereas with Percol 63, the reduction in the lag time observed in the presence of sodium chloride is independent of the ionic strength in the concentration range studied. That is the flocculation rates are about the same for all the salt solutions during the first five minutes. Previously, it has been mentioned that flocculation rate cannot be further increased once complete destabilization is achieved. The observation with Percol 63 at 12.5 $\mu g/l$ suggests that particles are sufficiently destabilized in 0.1 mM NaCl and therefore further increase in ionic strength has no effect on the initial flocculation of the suspension. Figure 4.11. also reveals that the flocculation rates for different ionic strengths begin to differentiate after 7 minutes flocculation time, the higher ionic strength shows a lower flocculation rate. The value of Turbidity Fluctuation at the end of the 15 minutes flocculation time is lowest for the highest ionic strength solution. It is interesting to note that the faster flocculation rate and the highest value of Turbidity Fluctuation are achieved in the salt-free condition, despite the longer initial lag time.

These results demonstrate that the polymer application rate as well as the characteristics of the polymer used determine the optimum ionic strength.

4.1.3. Effect of charge density

In dilute suspension, particles may undergo several collisions with other particles before acquiring sufficient amount of adsorbed polymer to be able to form stable aggregates. With increasing charge density, less polymer is required to neutralize the particle charge. The adsorption time needed to achieve a certain degree of destabilization is less for a polymer of higher charge density. The flocculation curves obtained with six polymers at the same dosage (50 $\mu g/l$) in salt-free medium are shown in Figure 4.15., to compare the effect of cationic charge density of the polymers. The polymer of the lowest charge density (Percol 140), 5%, gives almost no flocculation. With increasing charge density (up to 30% cationicity), flocculation becomes more pronounced and the lag time is reduced.

The degree of flocculation with Percol 1597 and Percol 1697 (both 100% charged) during the initial six minutes is more significant than with Percol 140 (5%), Percol 326 (10%) and Percol 292 (10%), but not with Percol 63 (30%). There is virtually no "lag time" with these two polymers. This indicates the destabilization of the particles are rapid and reinforces the idea that the amount of adsorbed polymer molecules required to destabilize the particles are less for a polymer of higher charge density. At first sight, the result obtained with Percol 63 seems to be irregular. However, a careful inspection of the data reveals the flocculation of the suspension, with Percol 1597 and Percol 1697, is overdosed at the given dosage. The values of Turbidity Fluctuation has remained constant after 8 minutes flocculation time. However, it must be pointed out that the use of either Percol 1597 or Percol 1697 generally gives a relatively poor degree of flocculation. This knowledge comes to light when the highest values of Turbidity Fluctuation reached by different polymers, during the 15 minutes flocculation time are examined. The highest Turbidity Fluctuation recorded by Percol 1597 and Percol 1697 do not exceed

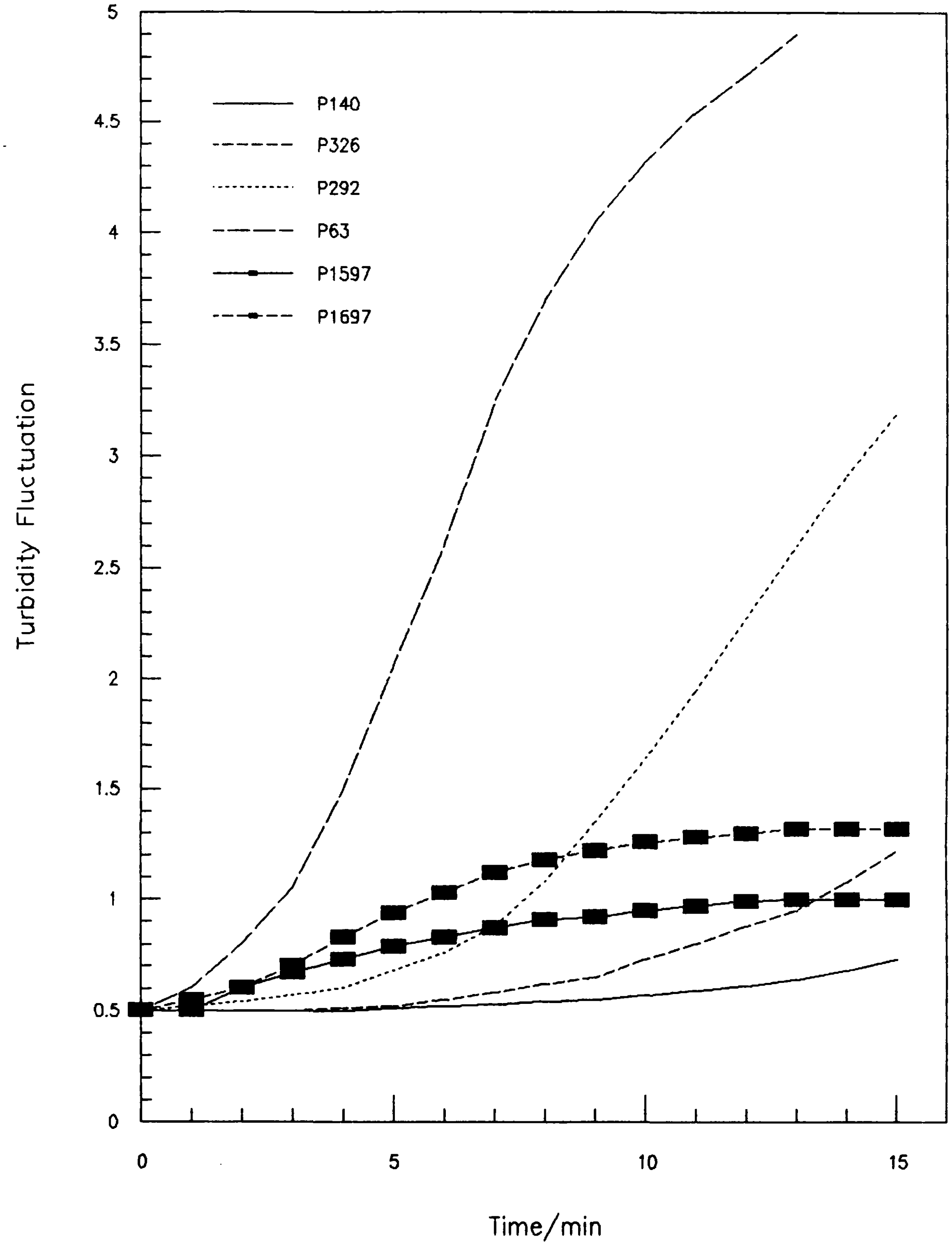


Figure 4.15. The effect of charge density on flocculation (50 µg/l)

2 Turbidity Fluctuation units (TFu). The Turbidity Fluctuation unit are reported in an arbitrary scale where the unaggregated suspension measured 0.5 TFu. The highest Turbidity Fluctuation recorded by other polymers are mostly greater than 2.5 TFu. In the case of Percol 63, it can be as high as 4 TFu. The empirical flocculation rates of the Percol 1597 and Percol 1697 are also lower, see Figure 4.17. in Section 4.1.5.. A combination of factors, such as the low molecular mass, high charge density and different chemical nature of the polymers, can contribute to the relatively low flocculation activity of Percol 1597 and Percol 1697.

As mentioned in Section 2.3.3.c., the rate of polymer molecules re-conformation on particle surface may be more rapid with a higher charge density polymer. The attraction between oppositely charged polymer and particles may be stronger for a polymer of high charge density because the number of charges per polymer molecule will be higher. As a result, the loops and tails of the flattened adsorbed polymer molecules become too short to bridge the "gap" between colliding particles. It is generally observed that Percol 63 is a more effective flocculant than Percol 1597 and Percol 1697. The size of Percol 63 is considerably larger than those of Percol 1597 and Percol 1697; the molecular mass of Percol 63 is about one hundred times higher. The effect of molecular mass on polymeric flocculation is discussed in the next section. Another consideration is the effect of the size of the adsorbed polymer patches on the attraction between colliding particles. The important feature of the "Electrostatic patch" flocculation mechanism is that it is not possible to physically neutralize each of the surface charges individually by the adsorbed polymer molecules, even under conditions of overall neutrality of the particles. The excess positive charge resulting from the adsorption of cationic polymer on negatively charged particles is more significant with the higher charge density polymers. The electrostatic attraction between positive and negative surface regions on different particles becomes strongly dependent on the orientation of the colliding particles. The possibility of the colliding particles to repel each other because of the excess positive charge of the adsorbed polymer is higher with a higher charge density polymer. Very little can be said about the effect of the chemical nature of the polymer on polymeric flocculation. The effect can be specific to the nature of the suspended particle, as well as being easily influenced by the chemical composition of the solution.

Although the degree of flocculation with Percol 140 and Percol 326 is not significant at the end of the 15 minutes flocculation time, the curves in Figure 4.15. show that the flocculation is about to progress. The lag time for Percol 140 and Percol 326 is relatively long, it is clear from Figures 4.2. and 4.3. that 50 $\mu g/l$ is an underdose for these polymers.

Percol 326 and Percol 292 have the same charge density but Percol 292 shows a shorter lag time and a higher degree of flocculation, see Figure 4.17. The discrepancy can be attributed to their different molecular size. The effect of molecular mass is discussed in Section 4.1.4..

4.1.4. Effect of molecular mass

The molecular mass of a polymer can affect polymer adsorption and particle flocculation in several ways. In general, the polymer/particle collision rate is higher for the smaller polymer molecules by the perikinetic collision mechanism, as indicated by Equation (2.19). On the other hand, the rate is higher for the larger polymer molecules by the orthokinetic collision mechanism, as shown by Equation (2.22). The size of the polymer can also affect the rate of successful particle collisions. It is conceivable that the length of the loops and tails of adsorbed polymer molecules may be longer for the larger molecules and this will enhance the capture of particles. The formation of more loops of adequate length to bridge the "gap" between colliding particles may also lead to a stronger bridging effect between aggregating particles as discussed in Section 2.3.3.c.. The length of the loops and tails are particularly important in the flocculation of suspended particles in low ionic strength solution where the range of electric double layer can be considerable (typically, the closest distance of separation between two colliding particles is of the order of 60 nm in 0.1 mM NaCl). Another consideration is the size of the

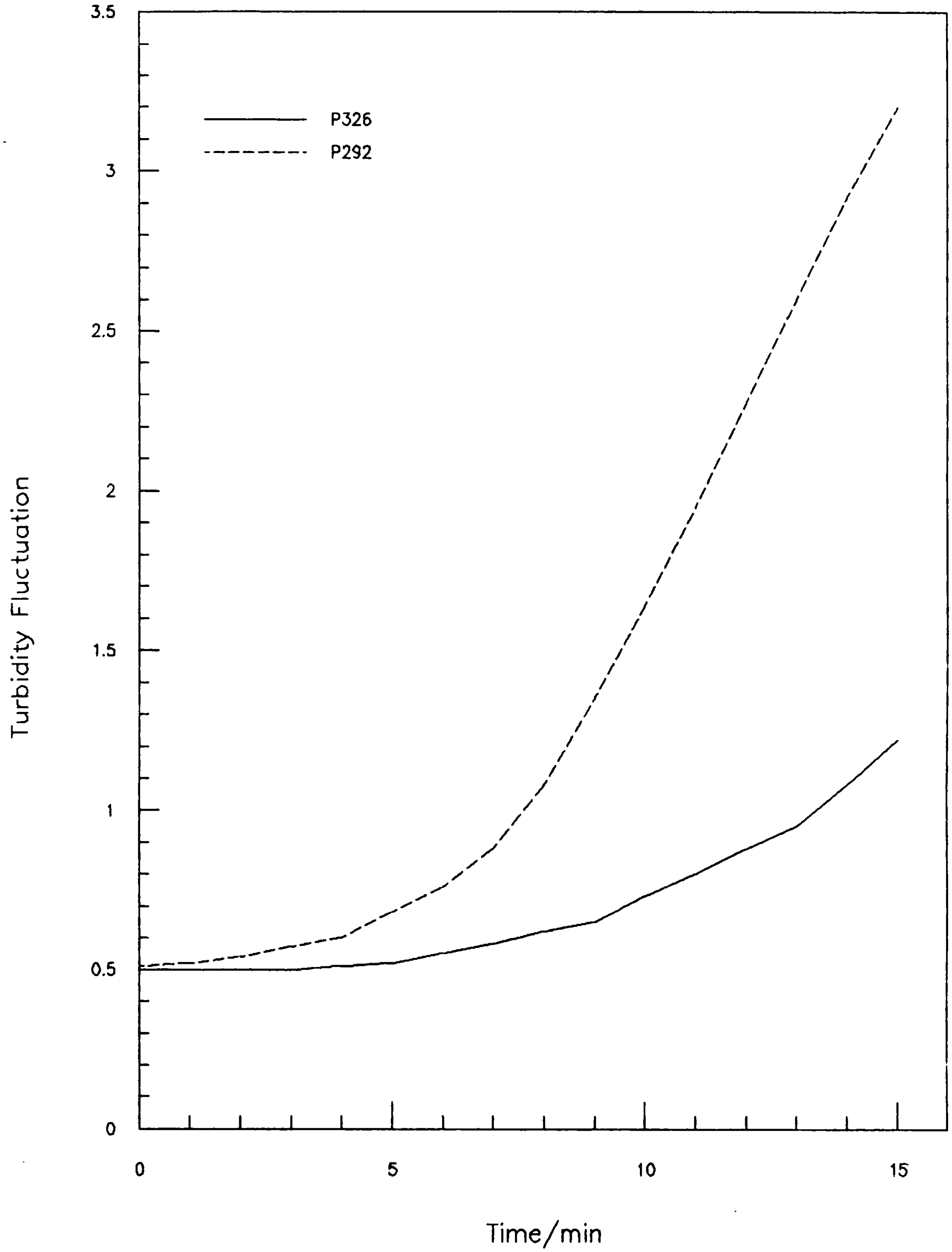


Figure 4.16. The effect of molecular mass on flocculation
(50 μg/l)

adsorbed polymer patches. The patches are larger for the polymer of higher molecular mass, giving a more "patchy" adsorption. As a result, the electrostatic attraction between positive and negative surface regions on different particles is stronger. The work of Treweek and Morgan (1977) seems to support this view.
Graham (1981) has also pointed out that increasing the molecular mass of a polymer of a given charge density would increase the uneveness of the surface charge distribution which would give rise to a greater "electrostatic patch" attraction and the number of polymer loops of adequate length to allow interparticle bridging.

The effect of molecular mass has been studied using two polymers, Percol 326 and Percol 292, which differ in molecular mass by a factor of about six but have the same charge density. The results presented in Figure 4.16. show that Percol 292 is the more effective flocculant, giving a shorter lag time and a more rapid flocculation. Less number of adsorbed polymer molecules is needed to initiate flocculation, Pelssers *et al* (1990). The sizes of Percol 326 and Percol 292 of 0.5 M NaCl are 60 nm and 110 nm respectively (Table 3.1. in Section 3.1.3.). Although, the polymer molecules in salt-free water are expected to adopt a more extended conformation and be larger than the values quoted in Table 3.1.. Nevertheless, Percol 292 would still be larger in size than Percol 326. The shorter lag time for Percol 292 indicates the polymer adsorption rate is faster than that for Percol 326. Considering the experiments were carried out under the stirring conditions where the orthokinetic collision mechanism is predominant, the larger polymer (Percol 292) are expected to adsorb faster. The results also show that Percol 292 give a more rapid flocculation. The larger molecular size polymer is able to bring about a greater bridging effect or a stronger electrostatic attraction. It was found that the same optimal dose was estimated for these two polymers (see Figure 4.17. and Table 4.1. in the following section). However, Percol 292 give a better flocculation rate. It has to be pointed out that the true optimal doses of the given polymers may not be the same as those estimated in Table 4.1.. Relatives flocculation rates were estimated for several dosages. The actual optimal dose may occur at a dosage somewhere between the experimental points shown. A more accurate estimate made on a new set of suspension dosed with a narrower range of polymer concentrations covering the rough estimate determined previously may be able to differentiate the optimal dose for the two polymers.

4.1.5. Empirical flocculation rates

The value of Turbidity Fluctuation always increases as the aggregation of a suspension proceeds. The rate of increase in Turbidity Fluctuation can be considered to correspond to an empirical rate of flocculation. Hence, an empirical flocculation rate can be obtained from a flocculation curve such as the one depicted in Figure 4.1., by determining the gradient of the steepest part of the curve. As mentioned in Section 2.5.4. that the values of Turbidity Fluctuation depend on the settings of the instrument. Therefore, the units of the empirical flocculation rates, in units of Turbidity Fluctuation/min, are arbitrary defined. However, it is adequate for the purpose of comparing relative flocculation ability of each polymer under given conditions. Figure 4.17. shows the flocculation rates for polymers tested in salt-free medium over a range of concentrations. As discussed in Section 4.1.1., it is difficult to define the operational optimum dosage unambiguously, since it is closely related to the specific operating conditions of the process. The dosage giving the maximum flocculation rate is regarded as the optimum dosage in the present discussion. The optimum flocculation dosages estimated for salt-free medium are given in Table 4.1.

The results presented in Tables 4.1. indicate a strong inverse correlation between the optimum dosage and the charge density. The higher charge density polymer corresponds to a lower optimum dosage. However, Table 4.1. also shows that the amount of cationic charges added at the optimum dosages are comparable for all polymers tested. The predominance of charge effect is reinforced by the electrophoretic mobility data shown in Section 4.2.

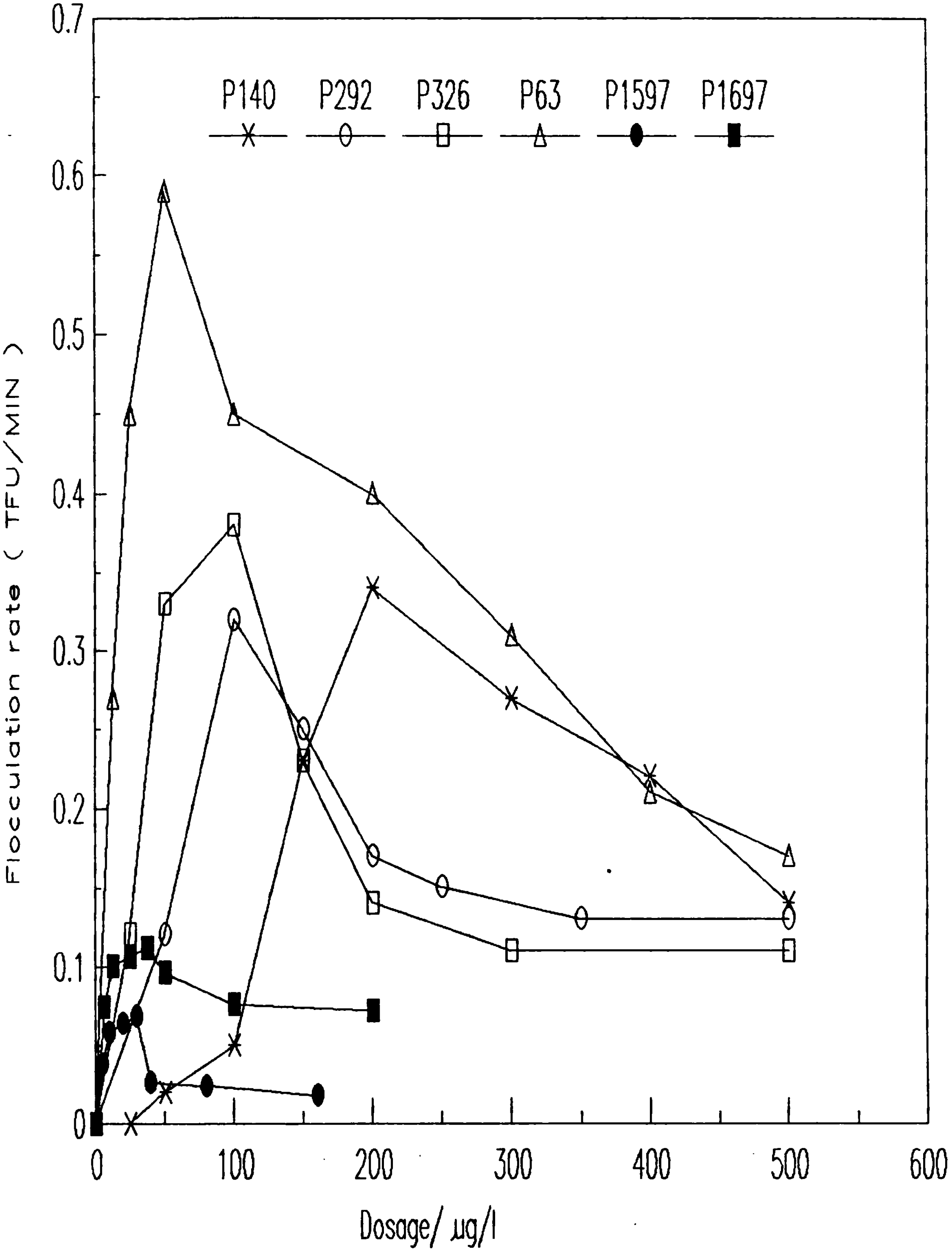


Figure 4.17. Flocculation rates as a function of dosage in salt-free solutions

Flocculation is found to occur over a narrow range of polymer concentrations, in agreement with the previous findings that the range of polymer dosages to bring about flocculation is critical (Black and Vilaret, 1969). They established that optimum dosages required were proportional to the surface areas of the particles in the systems. Gregory (1973) has shown that the range of polymer dosages was dependent on the characteristics of the polymer. The range became slightly broader with increasing molecular mass for a fixed ionic strength. In the present work, the range of polymer dosages giving rise to flocculation in salt-free medium is found to be dependent on the cationic charge density of the polymer. The optimum dosages of each polymer carry approximately the same amount of cationic charge. The results indicate the importance of charge neutralization in the flocculation of the suspension.

Table 4.1. Optimum flocculation dosage

Polymer	Optimum flocculation dosage	
	application rate $\mu g/l$	positive charge added $\mu eq/l$
P140	200	0.13
P326	100	0.18
P292	100	0.18
P63	50	0.15
P1597	30	0.22
P1697	35	0.22

The range of electrical repulsion is extensive in a salt-free medium. A slight excess of positive or negative charge is sufficient to gain stability. Hence, flocculation occurs over a very narrow range of polymer concentrations. When inert electrolyte is added, the range of electrical repulsion is reduced through the screening effect of counter ions. According to Equation 2.8. $\sigma_o = \epsilon\kappa\psi_o$, an increase in ionic strength either increases the surface charge density, or decreases the surface potential, or both. In the presence of added salt, either less polymer is needed to neutralise the surface charge of particles, or more polymer loops and tails become "active" in bridging interacting particles, or both. Particles may flocculate at lower polymer dosages in salt solutions. Similarly, the excess positive charge of the adsorbed cationic polymer is screened by the counter ions to the polymer. Particles are not restabilized until a considerable excess of polymer has been adsorbed. Consequently, the breadth of the flocculation region may be increased because of the screening effect of the added electrolytes.

Figures 4.18.-4.23. show the flocculation rates in salt-free medium, 100 mMol NaCl and 300 mMol NaCl. The range of polymer dosage to bring about flocculation is less critical in salt solutions. The reduction in flocculation rates at dosages slightly above or slightly below the optimum dosage is quite noticeable in salt-free medium but it is less prominent in salt solutions. None of the flocculation rates in salt solutions is higher than the maximum flocculation rate in salt-free medium, except the maximum flocculation rates for Percol 292 which are roughly the same in both salt-free medium and 100 mMol NaCl. The reasons for the observation that the highest flocculation rate always occurs in salt-free medium have not been established. The presence of salt can affect the conformation of polymer molecules (both as free polymer in solution or as adsorbed polymer at particle surface), and the adsorption of polymer. Pashley and Israelachvili (1984) have shown that there is a short range repulsion, due to adsorbed cations at salt concentrations above about 1 mMol. The adsorption of polymer inevitably involves the desorption of adsorbed counter ions (sodium ions for the negatively charged particles and chloride ions for the cationic polymer). The need to displace these weakly adsorbed ions for aggregation to take place may be responsible for the lowering of flocculation rates in salt solutions at the dosage which corresponds to the optimum dosage in the salt-free solution. The influence of the salt effects on flocculation rates remains to be elucidated.

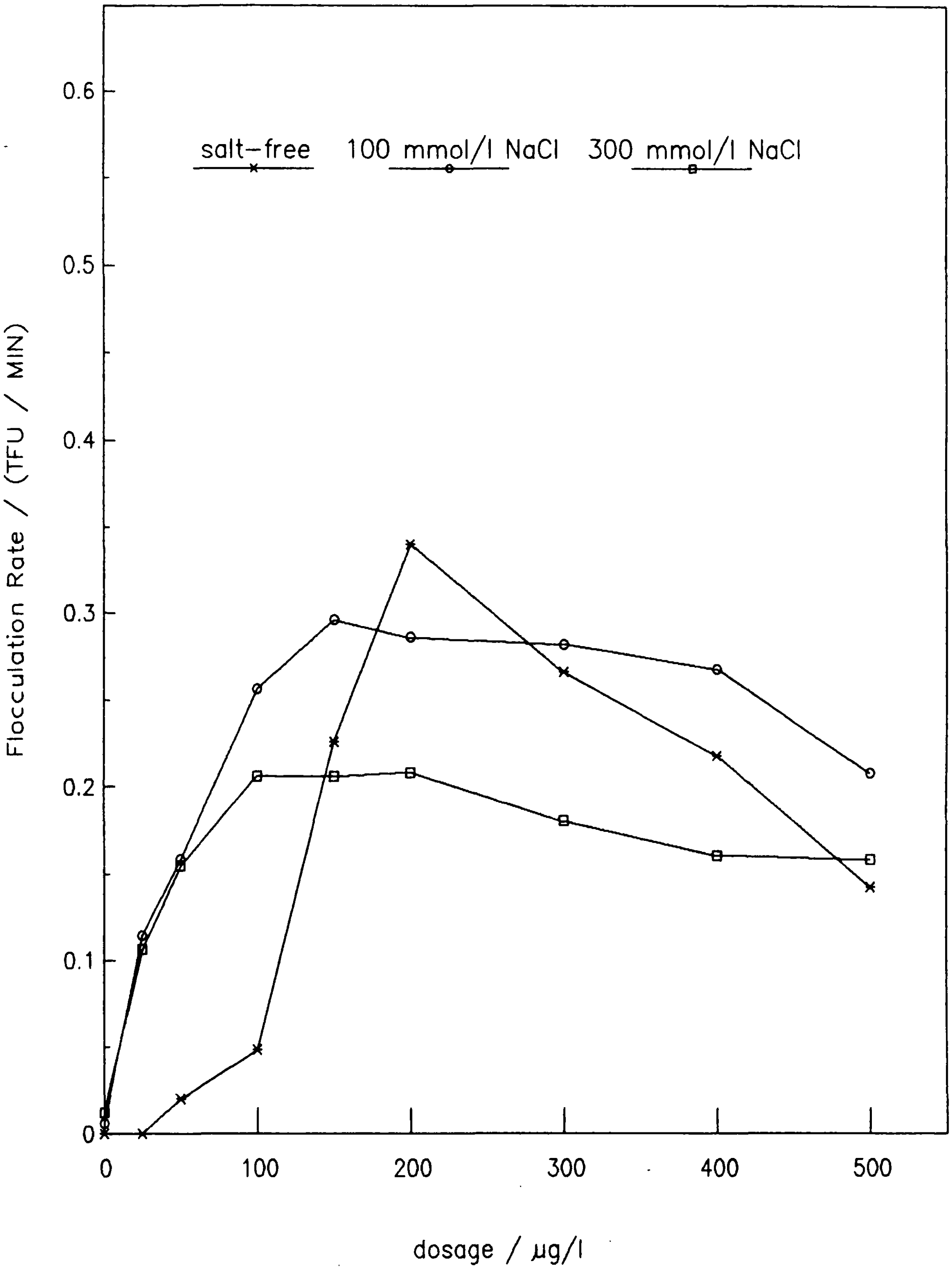


Figure 4.18. Flocculation rates at different salt concentrations (P140)

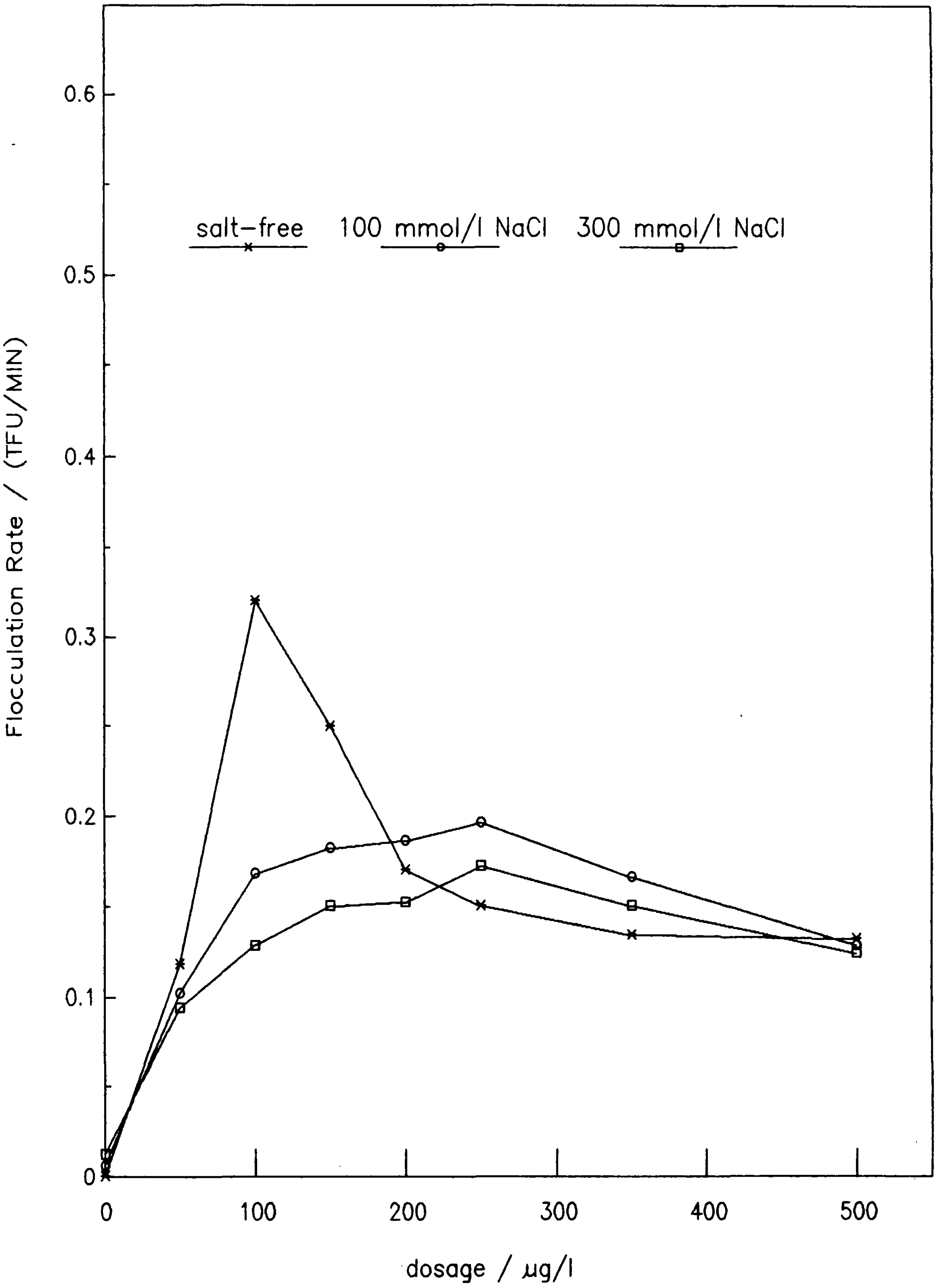


Figure 4.19. Flocculation rates at different salt concentrations (P326)

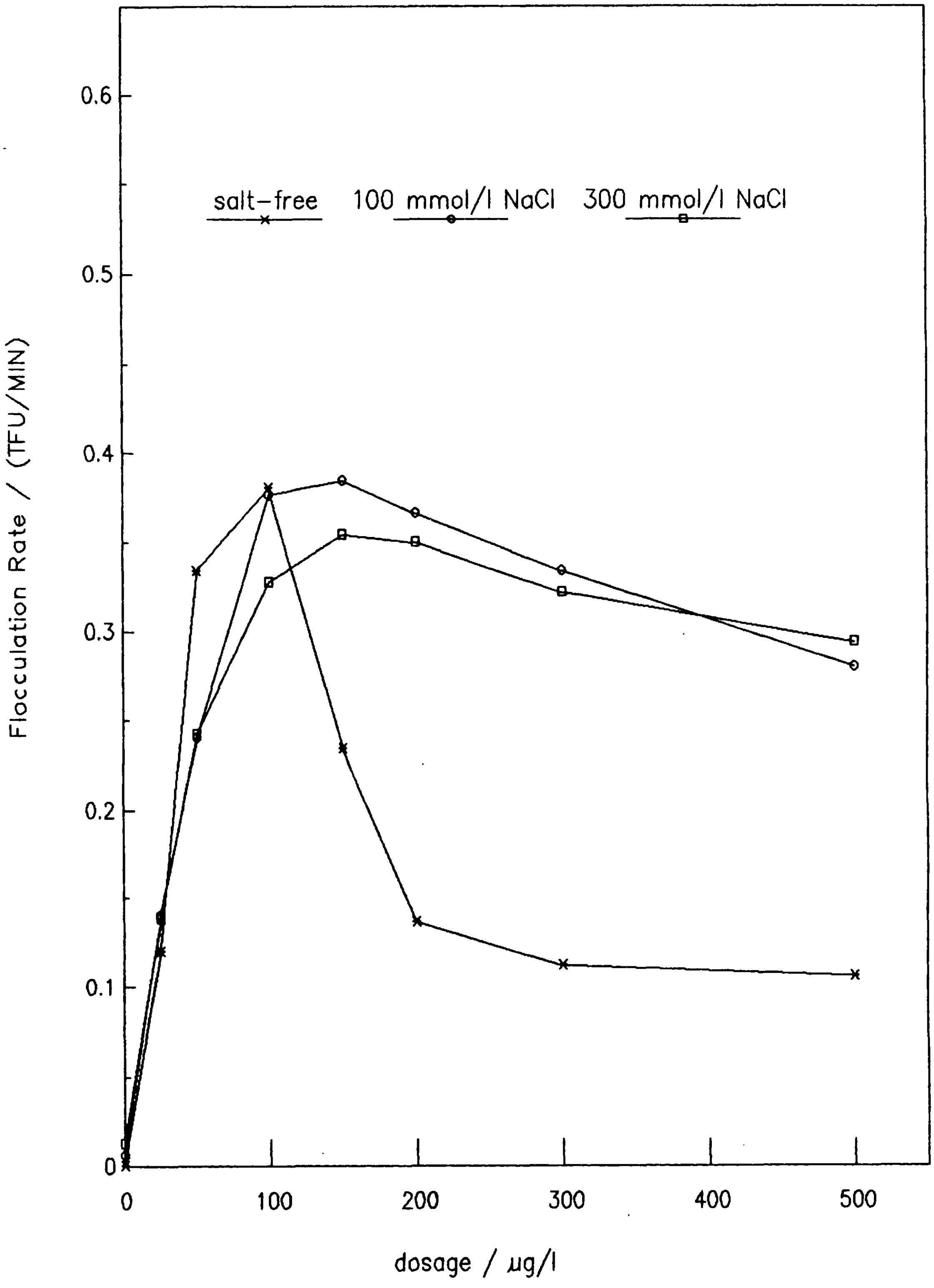


Figure 4.20. Flocculation rates at different salt concentrations (P292)

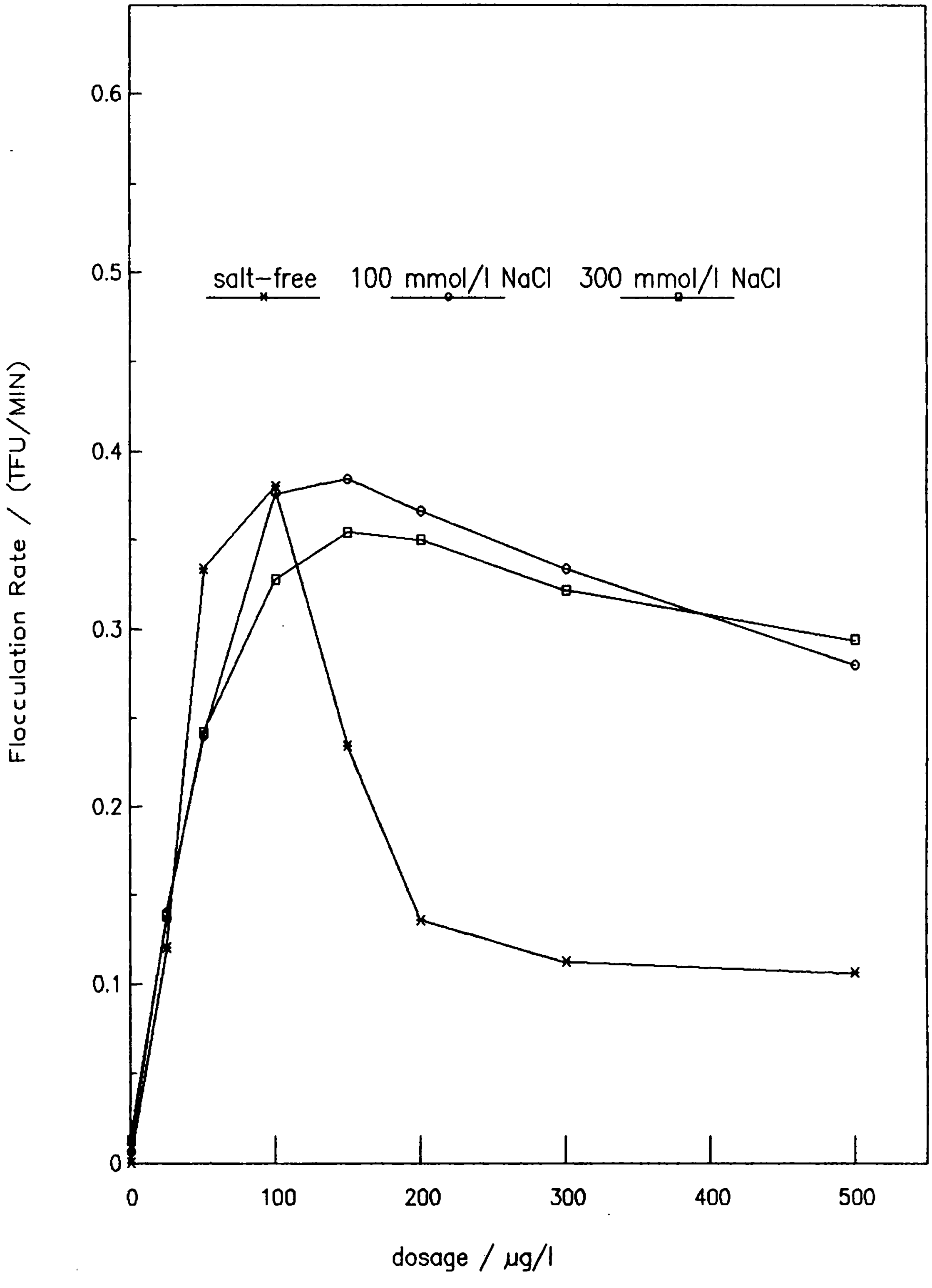


Figure 4.21. Flocculation rates at different salt concentrations (P63)

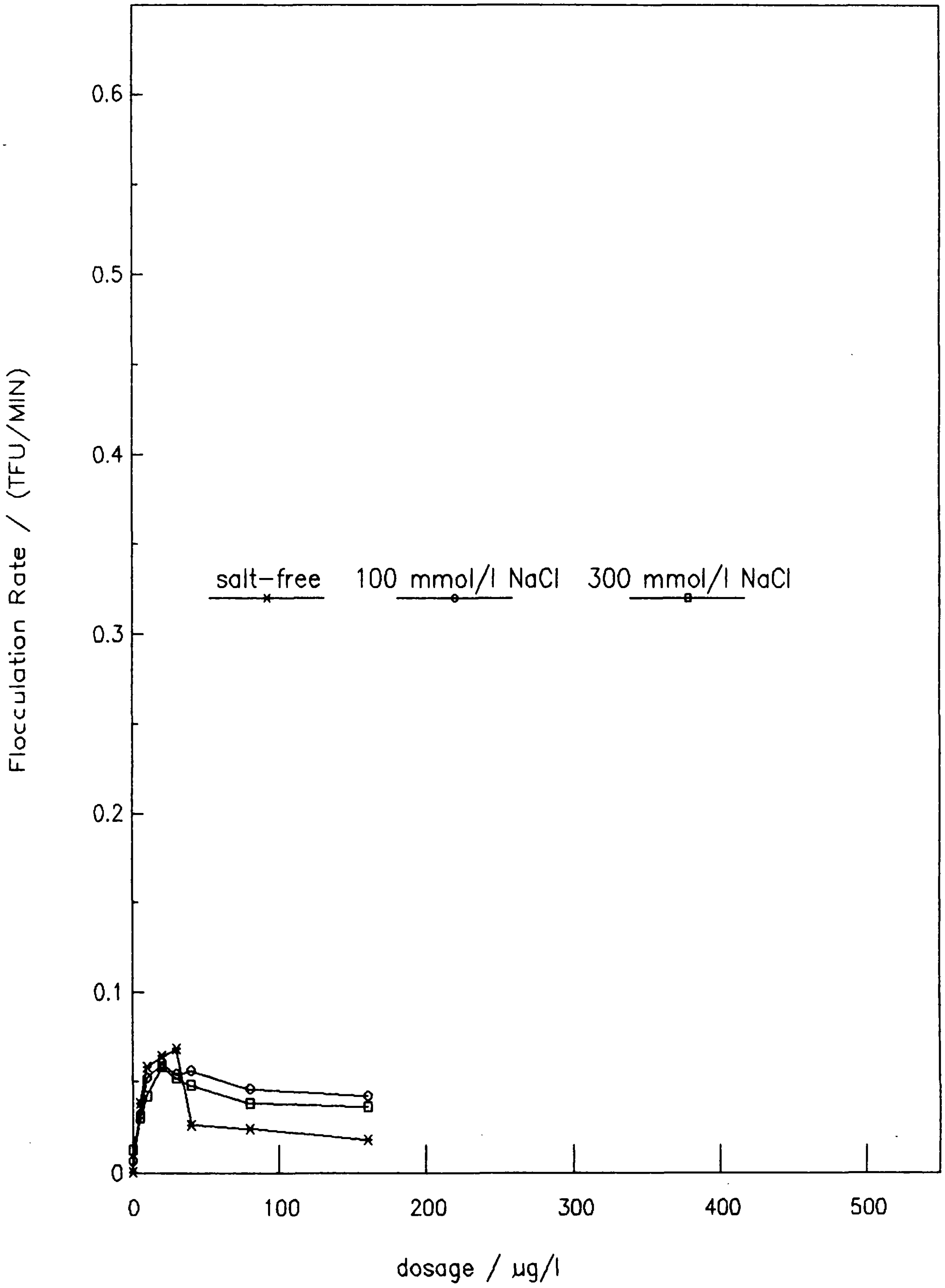


Figure 4.22. Flocculation rates at different salt concentrations (P1597)

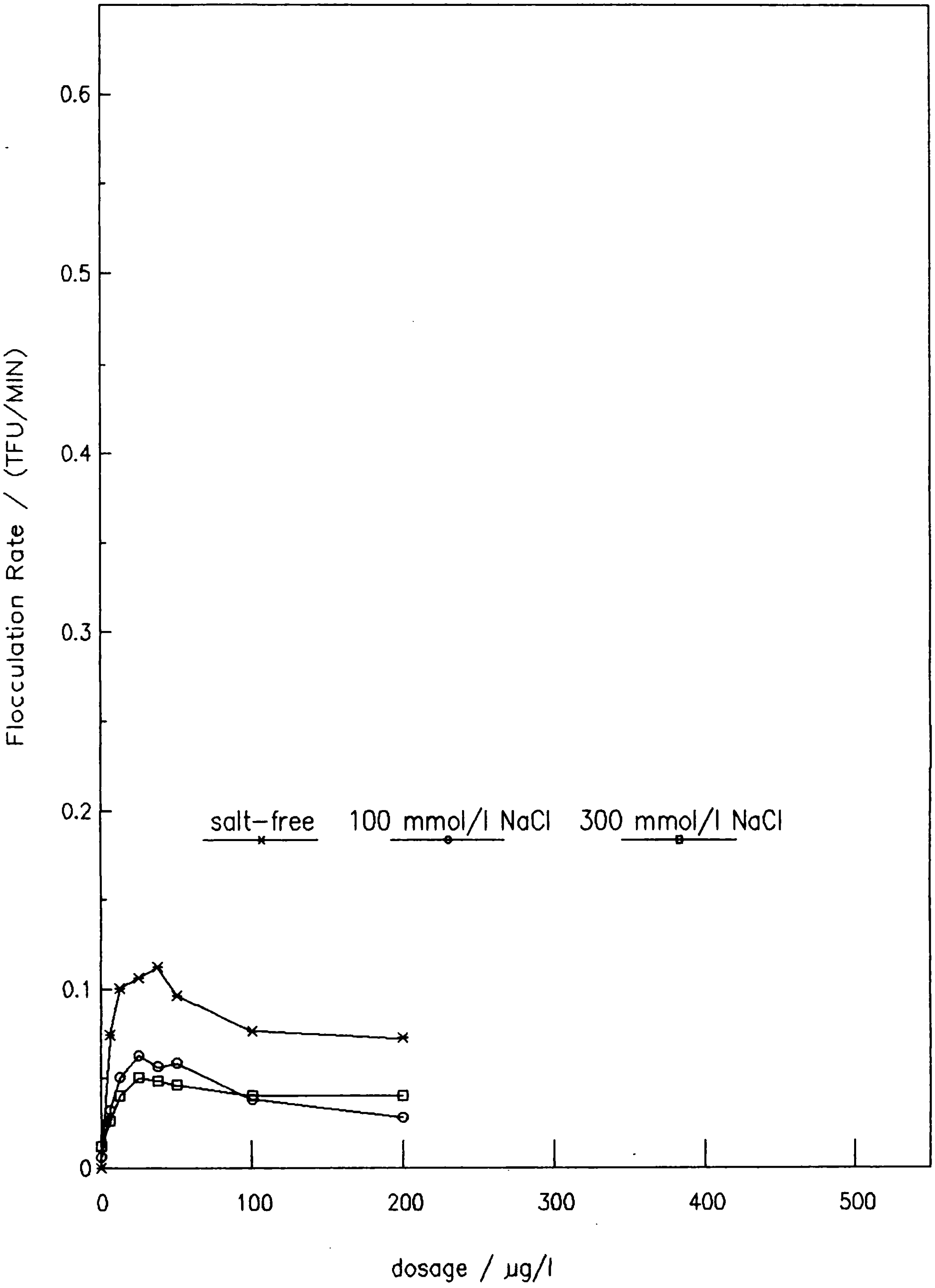


Figure 4.23. Flocculation rates at different salt concentrations (P1697)

For Percol 1697, the flocculation rates achieved in salt-free medium are higher than the corresponding flocculation rates achieved in salt solutions for the complete range of polymer doses. No reason has been found to explain the lowering of flocculation rates in salt solutions for this polymer. The adsorption of polymer and the aggregation of particles may be affected by the screening effect of inert electrolytes in many ways. The repulsion between charged segments of the polymer is reduced in the presence of electrolyte and this enables different segments to come closer to one another. Consequently, the collision diameter of polymer molecules becomes smaller. The reduction in particle size may lead to a reduced polymer adsorption rate, depending on the collision mechanisms. In practice where moderate shear rates are applied, orthokinetic collision will be dominant and polymer adsorption will be slower for the smaller polymers. The rate of polymer re-conformation will be more significant than the rate of polymer adsorption, especially for polymers of low molecular mass and high charge density. For these polymers, the loops and tails may become too short to bridge the "gap" separating the particles, despite the range of electrical repulsion in salt solutions can be considerably lower than in salt-free solutions. In addition, the screening effect of inert electrolyte may weaken the electrostatic attraction between oppositely-charged patches of different particles. Finally, the adsorption of polymer and the aggregation of particles may involve the desorption of the weakly adsorbed counter-ions (cations for the negatively charged particles and anion for the cationic polymer). The extent of the displacement of adsorbed counter-ions depends on the characteristics of the polymer and of the particles, such as how strongly are the respective counter-ions adsorbed and the degree of the polymer/particles interaction. It is possible that the counter-ions to Percol 1697 interact very strongly with the polymer. Therefore, the adsorption of the polymer is restricted and the aggregation of the particles is hindered.

However, destabilization of particles due to screening of charge can enhance flocculation rates for low charge density polymer. For low charge density polymer, such as Percol 140, higher flocculation rates are achieved in salt solutions at dosages which correspond to either suboptimal dosages or over-dosed conditions in salt-free solutions (See Figure 4.18). Whereas for polymers of higher charge density, higher flocculation rates are achieved in salt solutions only at dosages which correspond to over-dosed conditions in salt-free solutions but not at dosages which correspond to the suboptimal dosages in salt-free medium.

At low polymer dosages, particles are partly destabilized by the added salt and partly by the adsorbed polymer. It is, therefore, not surprising to observe the enhanced flocculation rates for Percol 140 in salt solutions. The low charge density polymer may required a longer polymer adsorption time to acquire sufficient polymer to destabilize the particles. The adsorbed polymer molecules are likely to adopt a rather "flattened" conformation. The flattened polymer molecules may not be able to bridge the "gap" separating the particles, especially, in salt-free medium where the range of repulsive forces is high. The excess positive charge of a low charge density polymer is expected to be less significant than that of a high charge density polymer. As a result, the electrostatic attraction between oppositely charged patches of different particles are weaker for a low charge density polymer. Even though the polymer may adopt a more coiled conformation in the salt solution (the effect may be negligible for a low charge density polymer), the range of repulsion forces is reduced and the amount of polymer required to bring about flocculation is reduced. The net effect is an enhanced flocculation rates in salt solutions. The empirical rates for Percol 140 at a dosage of 25 $\mu g/l$ in salt solutions are about 0.5 and the same dosage in salt-free solution is zero. Although, high charge density polymer may be expected to "flatten" more quickly, less number of polymer molecules is required to bring about flocculation. Particles may acquire enough polymer for flocculation to proceed before the loops and tails of the polymer become too short to form bridges. The more uneven distribution of negative and positive charges on the particle surface is the stronger the attraction at a lower polymer coverage. It has to be pointed out that these empirical flocculation rates are determined by taking the gradient of the steepest part of the flocculation curve. These empirical flocculation rates correspond to the maximum flocculation rates achieved in the 15 minutes flocculation time. It is possible that particles are destabilized more quickly in the presence of added salt but the ultimate flocculation rates may be higher in salt-free solutions. Figures 4.9.-4.12. show that the degree of flocculation in salt solutions are higher at the early stages of flocculation which indicates that destabilization of particles is more easily achieved in the presence of added salt. However, a higher degree of flocculation is observed with Percol 63 (Figure 4.11.) and Percol 1597 (Figure 4.12) in the salt-free medium after a few minutes of flocculation time. As a result, the flocculation rates in salt-free medium are higher after about 10 minutes flocculation time. Hence, the observed flocculation rates in salt solutions at dosages which correspond to the suboptimal dosages in salt-free solutions are higher for the low charge density polymer and lower for the high charge density polymer. The higher flocculation rates in salt solutions at dosages which correspond to the over-dosed conditions can simply be explained by the screening effect of the electrolyte. A larger amount of polymer can be adsorbed before the particles become restabilized, a higher flocculation rate can be maintained at a higher polymer dosage or at the same dosage in a higher ionic strength solution.

The optimum ionic strength for a polymer of a given cationic charge density is difficult to establish. This is because the molecular mass and the chemical nature of the polymer, as well as the charge density should be taken into account. However, some generalisations can be made for the results in the present work. The flocculation rates in 300 mM NaCl are lower than those in 100 mM NaCl unless when the polymer dosage is very high. It is rather interesting that none of the flocculation rates for Percol 1697 in salt solutions exceeds those in the salt-free medium (see Figure 4.23.). This behaviour is not observed with Percol 1597. Although, the molecular mass of Percol 1597 and Percol 1697 are similar and the charge density of both polymers are 100%, the two polymers are synthesized from different type of monomers. Flocculation rates in salt solutions are found to be faster than the corresponding rates in salt-free medium, over a wide range of polymer dosages, for Percol 326 (Figure 4.19.), Percol 63 (Figure 4.21.) and Percol 1697 (Figure 4.23.). From these results, it can be said that flocculation is overall better in the absence of salt when the cationicity of the polymer is 30% or greater, or when the molecular mass is less than about 4 x 10^5. However, Figure 4.22. shows that Percol 1597 (a 100% charged polymer of molecular mass in the region of 3-4 x 10 ^{4}) does not fit in with the above generalisation. The flocculation rates of this polymer is sharply reduced for dosages exceeding the optimum flocculation dosage in salt-free medium. On the other hand, a more gradual reduction in flocculation rates is shown in salt solutions. Therefore, a wide range of polymer dosages in salt solutions gives higher flocculation rates. As a result, flocculation is generally better in salt solutions for Percol 1597. The above results illustrate how the flocculation of a suspension can be influenced by a subtle balance of the characteristics of the polymer and the ionic strength of the solutions.

4.2. Electrophoretic mobility measurements

Electrophoretic studies have been used successfully to gain useful information in many investigations on the stability of colloids. They can be used to give an indication of the double-layer repulsive forces between particles. Electrophoretic mobility of silica particles dosed with each of the six cationic flocculants in a salt-free medium, 5 mMol NaCl and 10 mMol NaCl solutions were determined. The results are presented in Figure 4.24-4.29. The adsorption of cationic polymer may neutralise the surface charge of the negatively charged particles. Those particles which are electrically neutral will remain stationary under the influence of an electric field and the mobility of these particles will be zero. A reversal of particle charge will occur if an excess amount of polymer is adsorbed. The dosages required to give zero mobility in a salt-free medium are estimated and are given in Table 4.2.. These data show that the reversal of the particle charge from negative to positive occurs at a polymer dosage very close to the estimated optimum flocculation dosage. The results reinforce the importance of charge neutralization in flocculation, as discussed in Section 4.1.5..

Table 4.2. Optimum flocculation dosage and zero mobility dosage (in a salt-free medium)

Polymer	Optimum flocculation dosage μg/l	Dosage to give zero mobility μg/l
P140	200	235
P326	100	140
P292	100	110
P63	50	65
P1597	30	27
P1697	35	33

Figures 4.24-4.29 show that with an excess amount of polymer the mobility eventually reaches a plateau value which represents the maximum positive charge attained by the particles. Maximum positive electrophoretic mobility is primarily determined by the amount of cationic charge residing on polymer in the adsorbed state when the coverage of the particle surface is completed. The ultimate amount of adsorbed polymer is independent of the molecular mass but dependent on the surface available. These plateau mobility values in salt-free solutions are shown in Table 4.3.. These results show that the amount of positive charge gained at complete surface coverage depends quite strongly on the charge density of the polymer. Percol 63, a 30% charged polymer, gives a positive mobility about five times higher than Percol 140, a 5% charged polymer. Percol 326 and Percol 292, both polymers are 15% charged, give a positive mobility about three times higher than Percol 140. The respective maximum positive mobility of these polymers shows a good correlation with the ratio of their charge densities. The maximum positive mobility for the 100% charged polymers, Percol 1597 and Percol 1697 are lower than expected. The

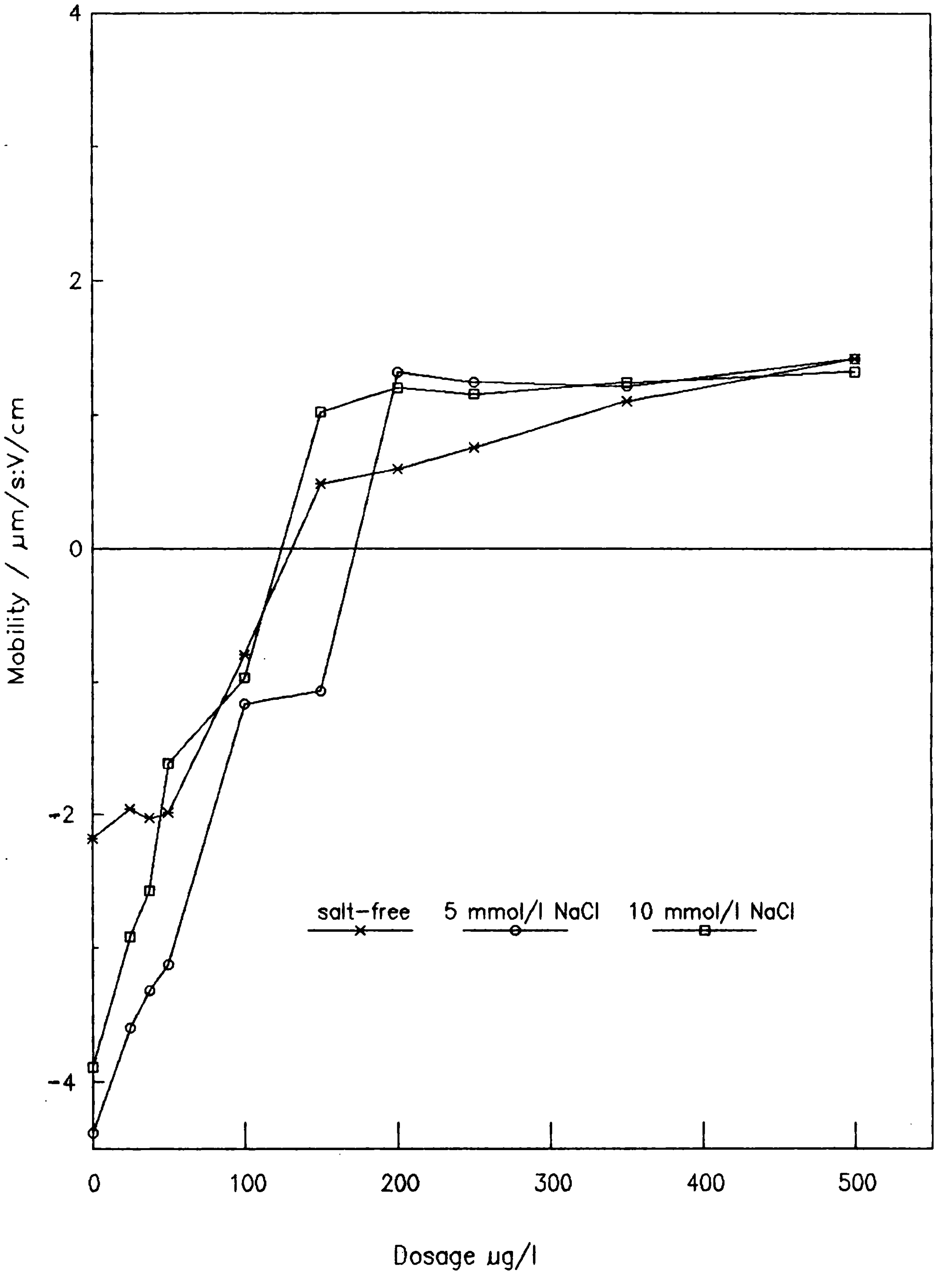


Figure 4.24. Electrophoretic mobility as a function of polymer dosage (P140)

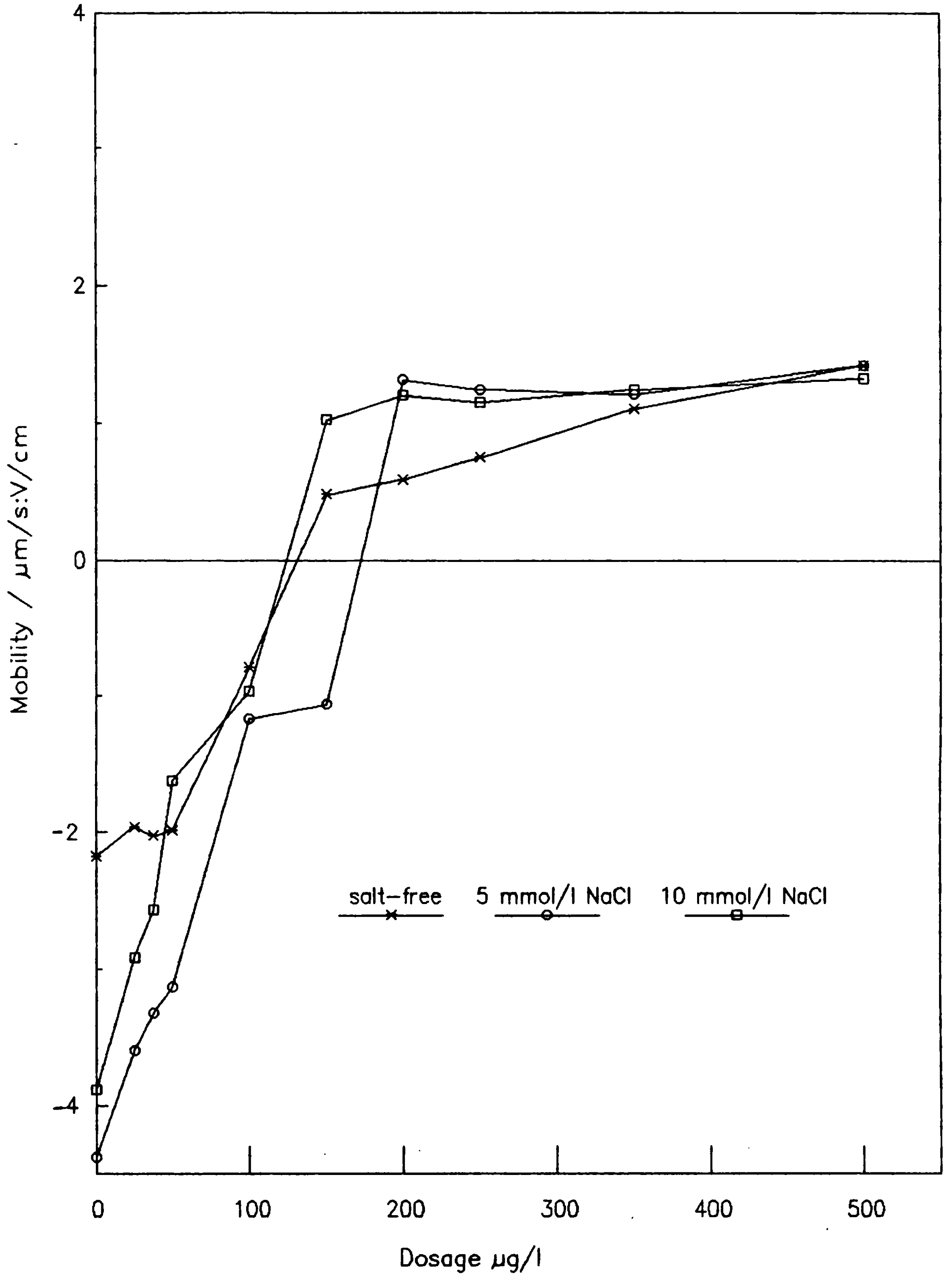


Figure 4.25. Electrophoretic mobility as a function of polymer dosage (P326)

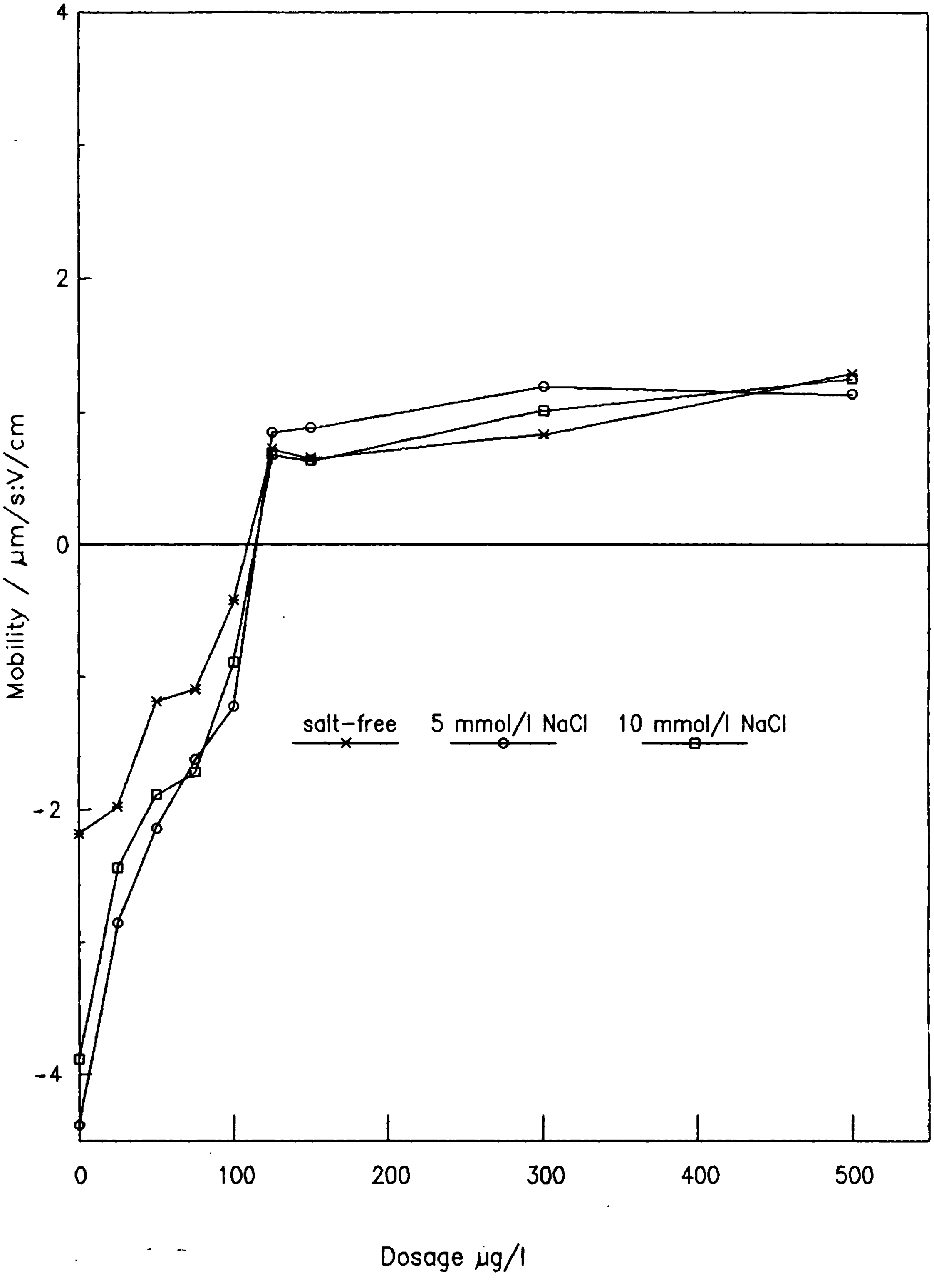


Figure 4.26. Electrophoretic mobility as a function of polymer dosage (P292)

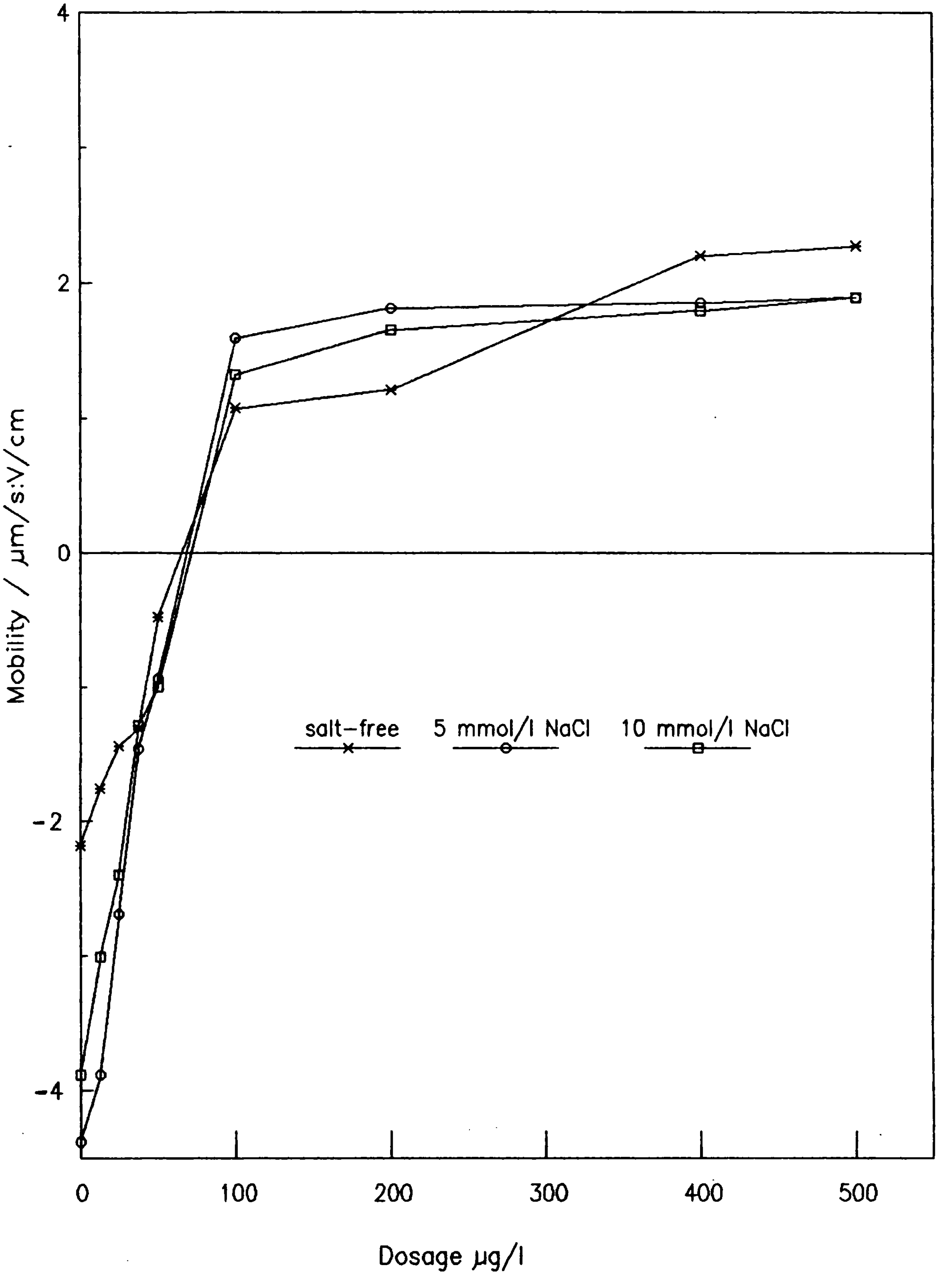


Figure 4.27. Electrophoretic mobility as a function of polymer dosage (P63)

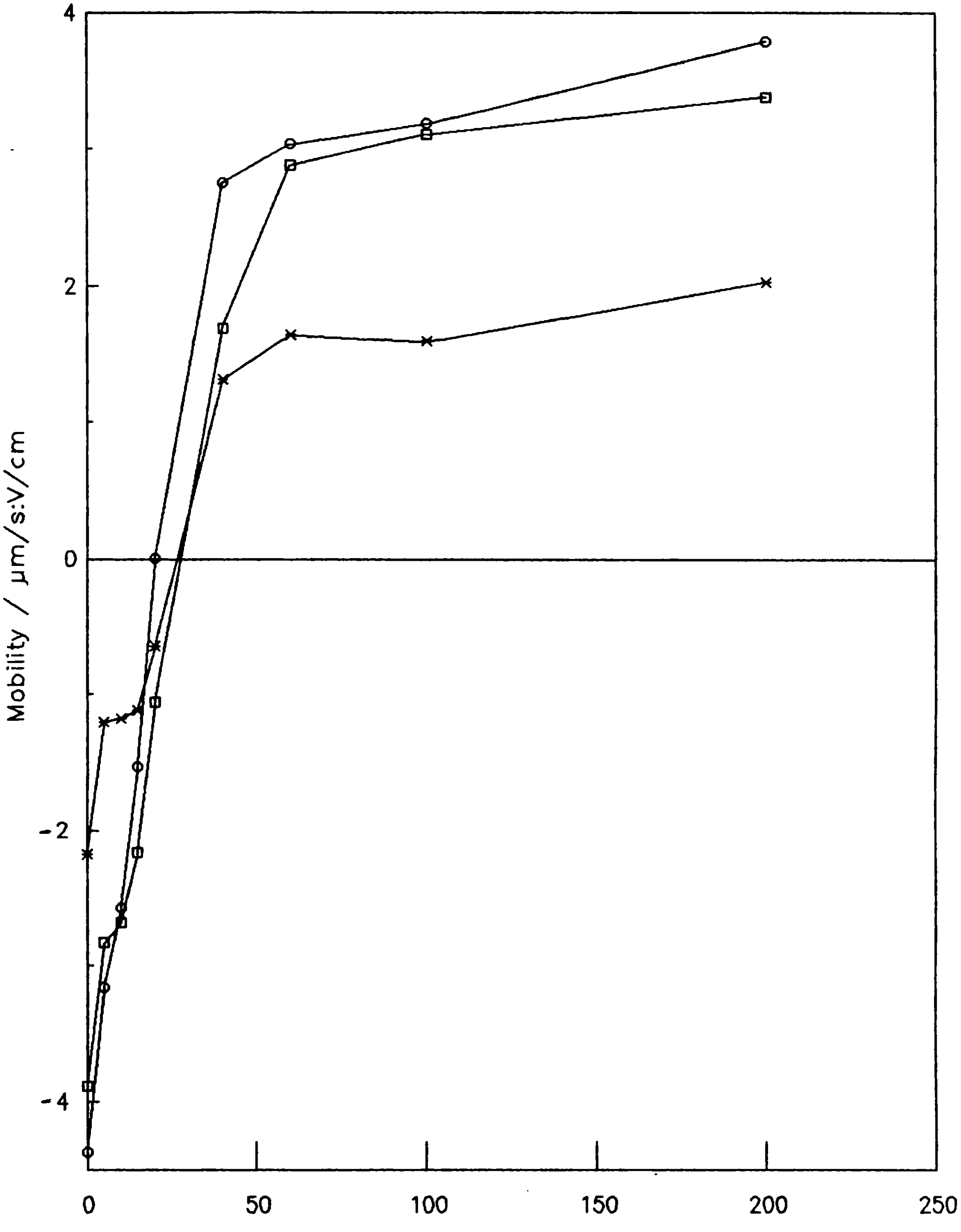


Figure 4.28. Electrophoretic mobility as a function of polymer dosage (P1597)

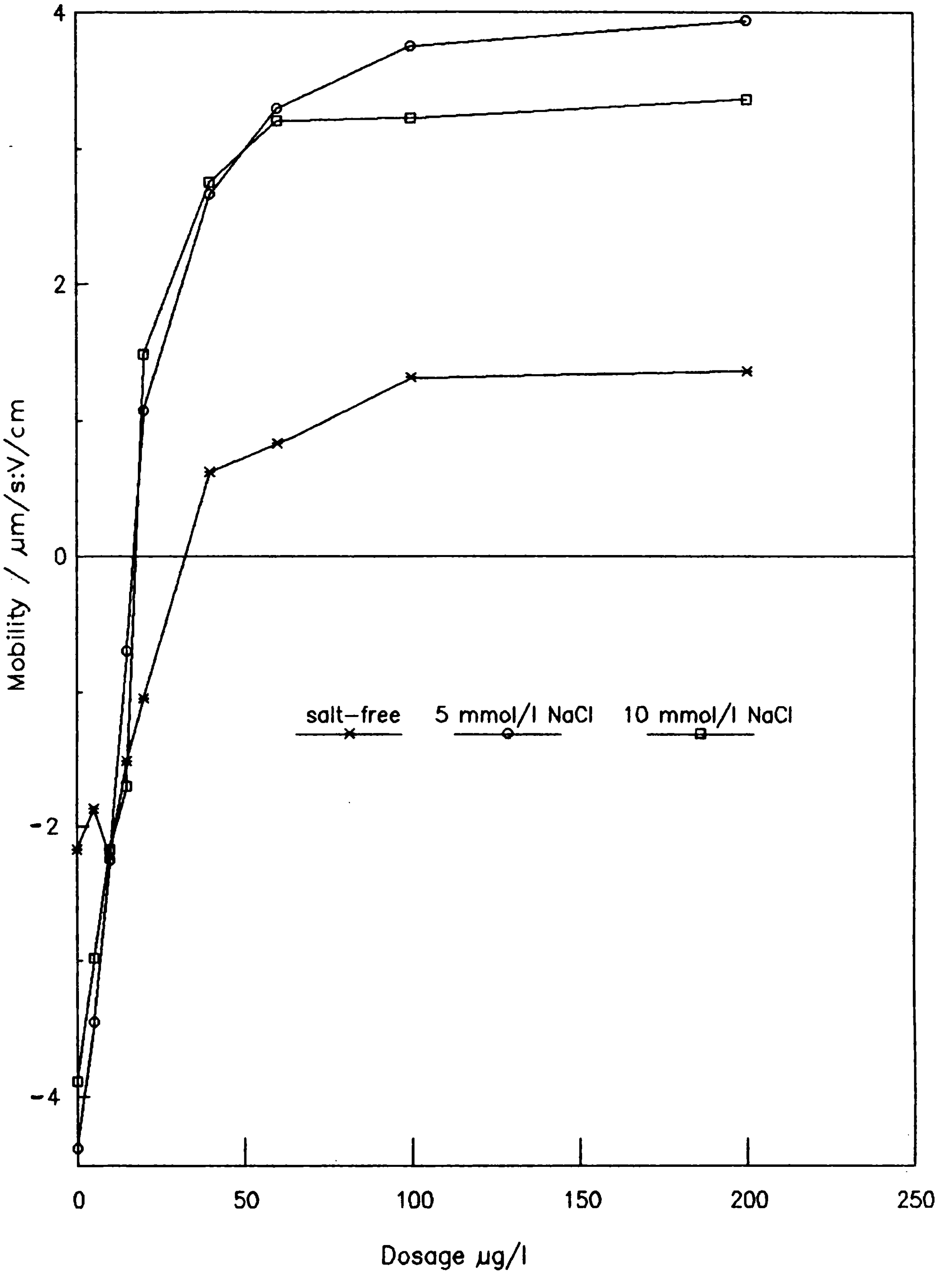


Figure 4.29. Electrophoretic mobility as a function of polymer dosage (P1697)

values for Percol 1597 and Percol 1697 correspond to those of a 30% and 15% charged polymers respectively. It is possible that lateral repulsion among charged segments of polymer molecules for the 100% charged polymers is higher than that for polymers of lower charge density. This may prevent the adsorption of polymer at sites close to other adsorbed polymer. Also, Percol 1597 and Percol 1697 are expected to adsorb in a rather "flattened" conformation because of the high charge density and low molecular mass of the polymers. Therefore, the amount of polymer adsorbed at full polymer coverage is less for Percol 1597 and Percol 1697 than for those polymers which can adsorb in a more extended conformation. As a result, the amount of excess positive charge remaining is also less, giving a lower maximum positive mobility than expected. It should also be mentioned that care should be taken when comparing the results of Percol 1597 and Percol 1697 with other polymers because these polymers are made from different types of monomers. Meaningful comparison can be made only on Percol 140, Percol 326, Percol 326 and Percol 63.

Table 4.3. Maximum positive electrophoretic mobility

Medium	Maximum positive mobility ($\mu m/s:Vcm$)					
	P140	P326	P292	P63	P1597	P1697
Salt-free	0.51	1.41	1.29	2.27	2.03	1.36
5 mM NaCl	0.34	1.41	1.25	1.89	3.79	3.94
10 mM NaCl	0.32	1.32	1.19	1.89	3.38	3.36

It is interesting to note that an increase in the values of maximum positive mobility in salt solutions is observed for Percol 1597 and Percol 1697, whereas a decrease is observed in other polymers. The screening effect of charged surface in salt solutions is expected to give a lower maximum positive mobility. The reason for a higher positive mobility in salt solutions for Percol 1597 and Percol 1697 is difficult to explain. Electrostatic repulsion among polymer segments can be reduced in a moderate amount of salt, such that a denser packing of polymer is possible. The salt effect may be more pronounced with highly charged polymers because lateral repulsion between high charge density polymers is more significant. It is possible that for Percol 1597 and Percol 1697, the amount of polymer adsorbed in 5 mMol NaCl is higher than that in salt-free medium, giving a thicker layer of adsorbed polymer. As a result, the amount of excess positive charge on the particles is higher in salt solutions for these two polymers. On the other hand, the amount of excess positive charge becomes slightly less as the salt concentration is increased to 10 mMol NaCl. The lower maximum positive mobility at 10 mMol NaCl is expected because of the screening of surface charge. Indeed, this lowering of mobility at 10 mMol NaCl is also observed with other polymers. Since, there is no information available on the polymer segment density distribution for the system studied, it is not possible to verify this point.

4.3. Specific effects of flocculating ions

It is known that apart from the valency of the counter ions, the specific nature of the added salts also has a certain influence on the stability of colloid, (Overbeek, 1952). In the Gouy-Chapman treatment of the diffuse double layer, ions are treated as point charges. This will not give rise to any specific effects of ions. The Stern theory takes the finite size of the ions into account and thus specific effects can be explained.

If the double layer is treated as two capacitors in series, then the capacity of the diffuse part of the double layer can be calculated from Equation 2.8., $\sigma_0/\psi_0=\epsilon\kappa$. It can be seen that a diffuse double layer has the same capacity as a parallel plate condenser with a distance $1/\kappa$ between the plates. The inner part of the double layer, the Stern plane, can be treated as a molecular condenser. The capacity of the Stern layer does not depend on electrolyte concentration except in so far as the permittivity of the Stern layer is affected. The potential ψ_0 depends on the thickness of the molecular condenser, other things being equal. The thickness of the molecular condenser will be determined by the size of the counter-ions. The adsorption of counter-ions lowers the potential across the Stern plane. The Stern plane. The Stern correction results in a lower potential drop in the diffuse double layer. The surface potential ψ_o decreases first linearly with distance in the Stern plane and then exponentially in the diffuse layer (See Figure 2.1.). When considering the electric double layer interaction of two approaching particles, it is applicable to replace ψ_o with the Stern potential ψ_d. The size of the adsorbed counter-ions to the particles determines the ψ_d. Therefore, the adsorption of larger counter-ions is expected to give rise to a lower ψ_d and a lower stability.

The second feature in Stern's theory is the specific adsorbability. When the counter-ions are strongly adsorbed, a sharp reduction in potential will result across the Stern layer which lead to a lower stability. The adsorption of electrolyte will be more pronounced, the higher the charge number of the ion. Indeed, the critical coagulation concentration of an indifferent electrolyte, (i.e. the concentration of the electrolyte which is just sufficient to coagulate a lyophobic sol to an arbitrarily defined extent in an arbitrarily chosen time) always shows a strong dependence upon the charge number of its counter-ions. The electrostatic attraction between the charged particles and the oppositively charged ions is expected to be stronger with ions of higher charge number. For a series of ions, the greater polarizability of the larger ion will be expected to increase their adsorbability and thus leading to a lower stability.

A further consideration of the specific effects of flocculation ions is the hydration effects of ions. As mentioned in 2.1.3.c., the short-range repulsion due to adsorbed hydrated ions increases with the degree of hydration. The molecules of hydration water are orientated and immobilized by the ion-dipole forces, forming a hydration sheath around the ion. Large ions such as caesium, iodide and tetramethylammonium show the effective number of bound water molecules to be nearly zero. The field force which aligns the water dipole decreases as the ionic radius increases. A larger ion has a greater tendency to lose its water of hydration, therefore, it can adsorb onto a charged surface more easily. The repulsion arising from the adsorbed hydrated ions is less for a larger ion. Consequently, aggregation of colliding particles occurs more readily, leading to a lower stability.

In summary, it can be said that the important parameters in a consideration of the specific effects of flocculating ions are the size and the charge of the ions. These two parameters determine the adsorbability of ions, the polarisability of ions and the degree of hydration. These factors are interdepenent and they in turn give rise to the specific effects of ions on the stability of colloid.

An electric double layer is made up of the charged surface and a neutralising excess of counter-ions over co-ions distributed in a diffuse manner in the aqueous medium. The nature of the co-ions can affect the stability of the sol, although to a lesser extent than that of the counter ions. The smaller co-ions, being more highly hydrated, have a greater tendency to remain in the bulk aqueous medium. This further the preferential tendency of charged particles to adsorb counter-ions. As a result, co-ions of smaller size leads to a lower stability.

Cations and anions can be arranged in the following lyotropic series of approximately decreasing degree of hydration:

$Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$
$> Li^{+} > Na^{+} > K^{+} > NH_4^{+} > Rb^{+} > Cs^{+}$

and

$\text{citrate}^{3-} > SO_4^{2-} > Cl^{-} > NO_3^{-} > I^{-} > CNS^{-}$

Flocculation tests have been carried out to investigate the specific effect of flocculating ions. The empirical flocculation rates over a range of polymer dosages in salt-free, 0.5 M NaCl, 0.5 M KCl and 0.5 M $NaNO_3$ solutions are determined as described in Section 4.1.5.. The results are presented in Figures 4.30-4.33.. It has been discussed in Section 4.1.5. that flocculation occur over a wider range of polymer concentrations in the presence of added salt. The results can be generalised that flocculation rate is less sensitive to polymer dosage in these salt solutions at a concentration of 0.5 M. Higher flocculation rates are found in 0.5 M $NaNO_3$ over the complete range of polymer dosages studied. On the other hand, 0.5 M KCl always gives the slowest flocculation rates.

The larger K^+ is expected to be more effective than the Na^+ in destabilising the negatively-charged silica particles. Similarly, the smaller Cl^- ions should lead to a lower stability of the silica suspension. However, the results presented in Figures 4.30-4.33 for the four cationic polymers are in contradiction to the concept of specific effects of flocculating ions mentioned above. Lower flocculation rates are observed with the larger counter-ions and the smaller co-ions to the charged particles. The above concept is applicable to the destabilization of a hydrophobic salt by addition of indifferent electrolyte alone. In the present work, the particles are partly destabilized by the salt effect and partly by adsorbed polyelectrolytes.

Very little information is available on the specific effects of inert electrolyte on the adsorption of polyelectrolyte on oppositely-charged particles. The adsorption of cationic polymer on a charged surface involves the desorption of the weakly bounded counter-ions to the charged surface of the particles and perhaps those to the charged segments of the polymer as well. The more strongly adsorbed counter-ions to the particles are more difficult to displace by the cationic polymer. Therefore, the flocculation ability of the polymer is reduced to a greater extent by the larger, more strongly adsorbed ions. This idea is supported by the experimental results shown in Figures 4.30.-4.33., flocculation rates with the larger counter-ions to the particles, K^+, are found to be lower than those with Na^+.

The flocculation rate is expected to be higher in the presence of the smaller, more highly hydrated ions which are co-ions to the particle and also counter-ions to the polymer. The more hydrated ions may compete with the charged segments of the polymer for its water of hydration. This may lead to a stronger polymer adsorption and, subsequently, higher flocculation rates. On the other hand, these highly hydrated ions also have a greater tendency to remain in the bulk liquid. Therefore, they are likely to be away from the

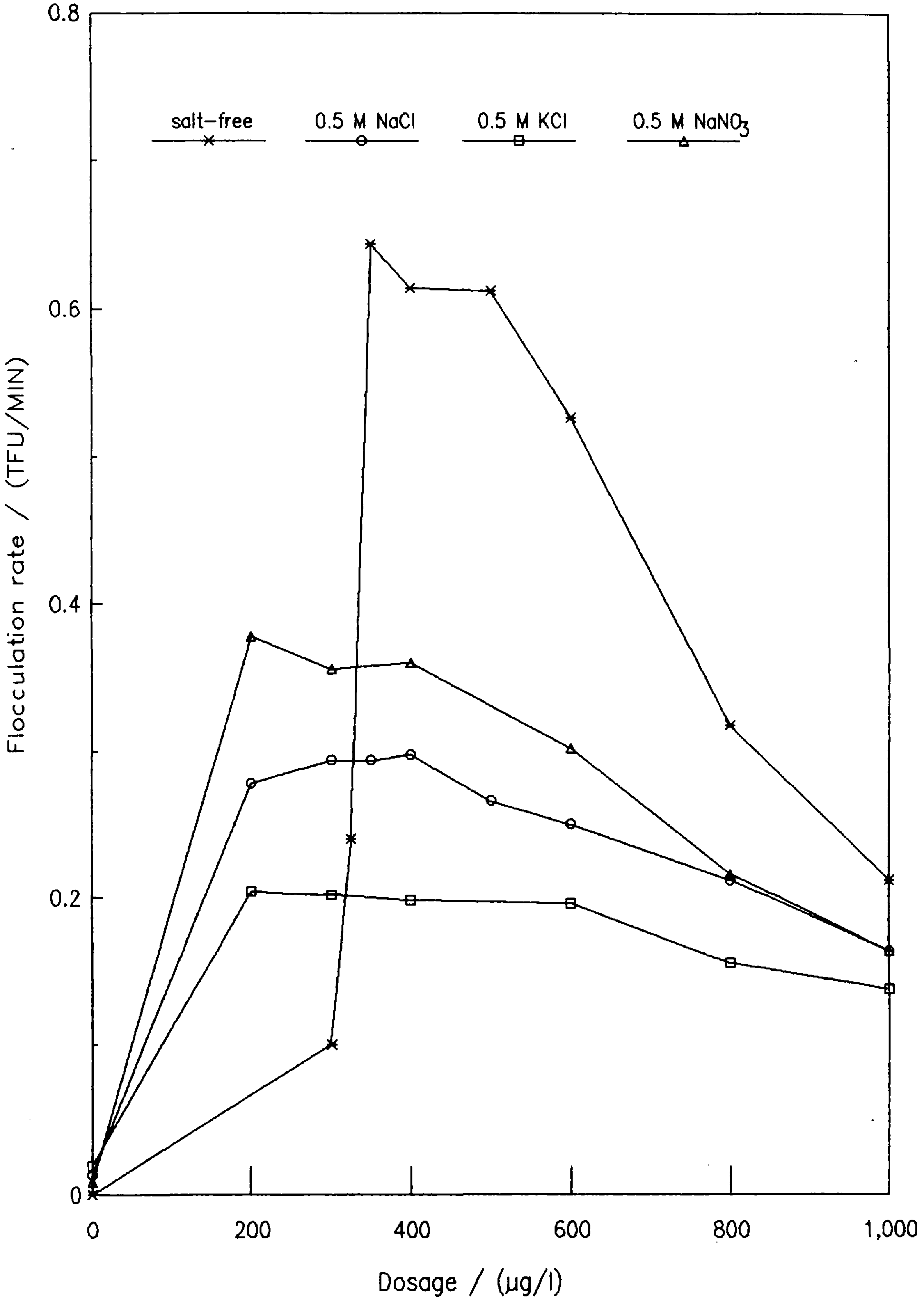


Figure 4.30. Comparison of flocculation rates (P140)

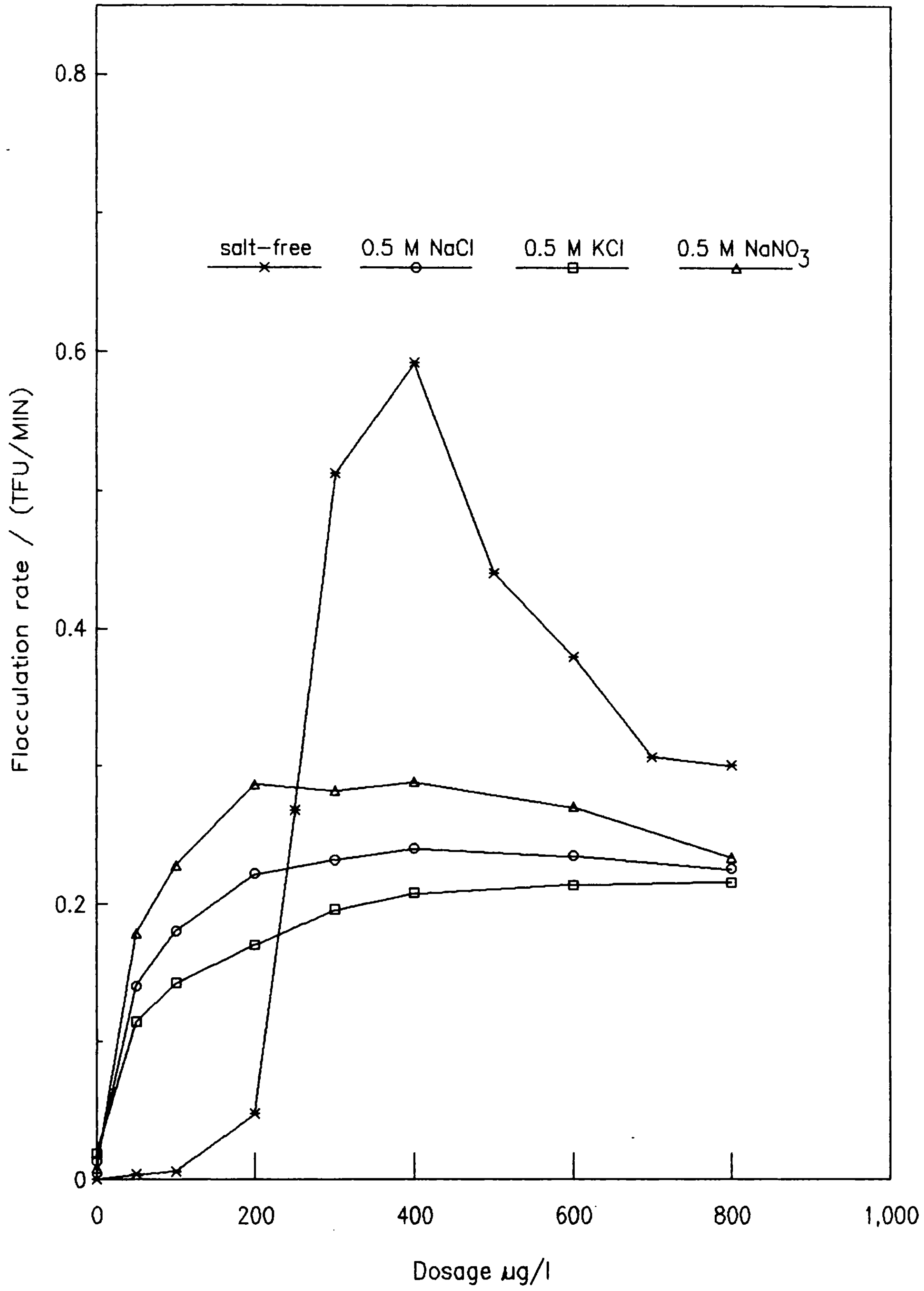


Figure 4.31. Comparison of flocculation rates (P326)

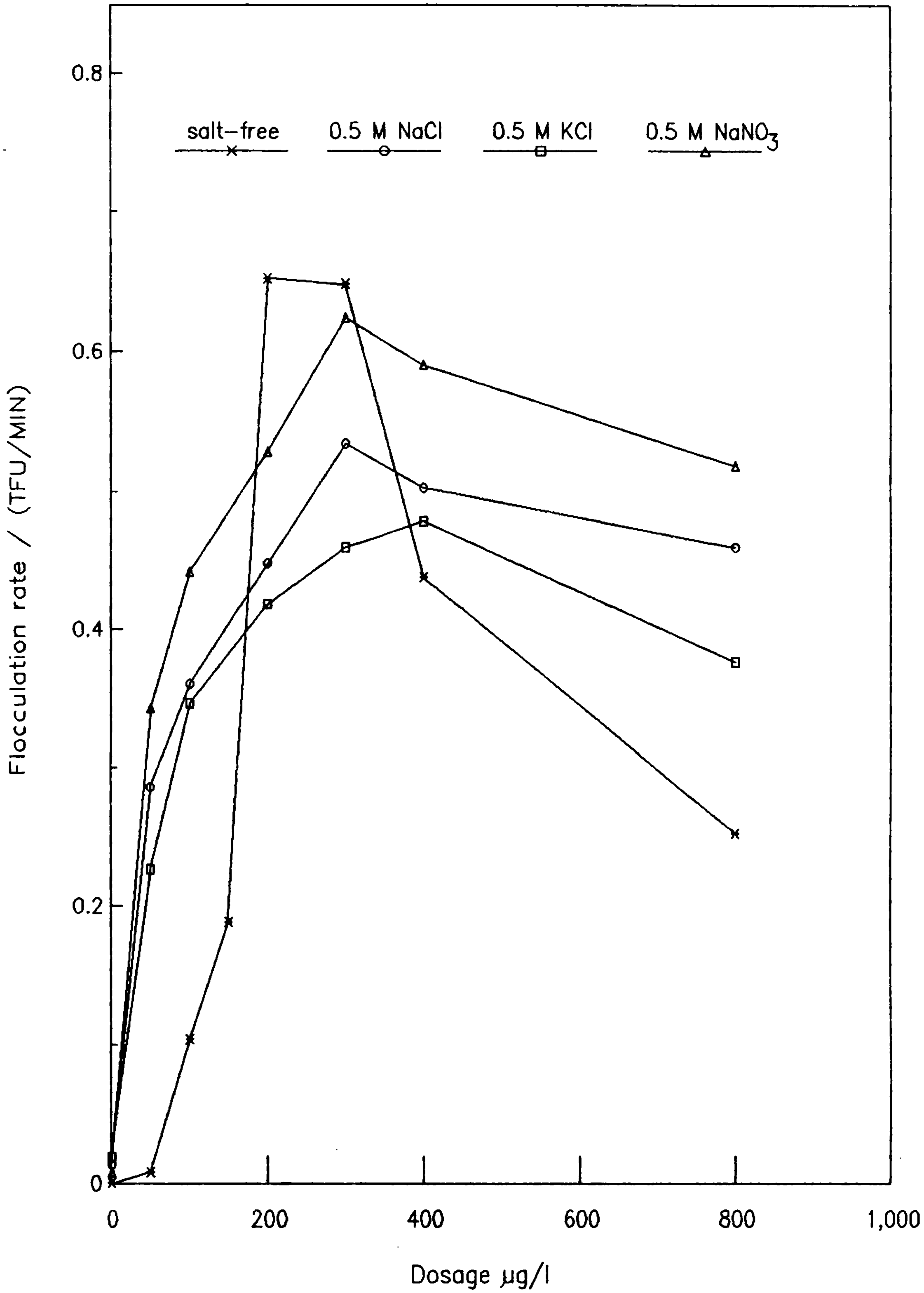


Figure 4.32. Comparison of flocculation rates (P292)

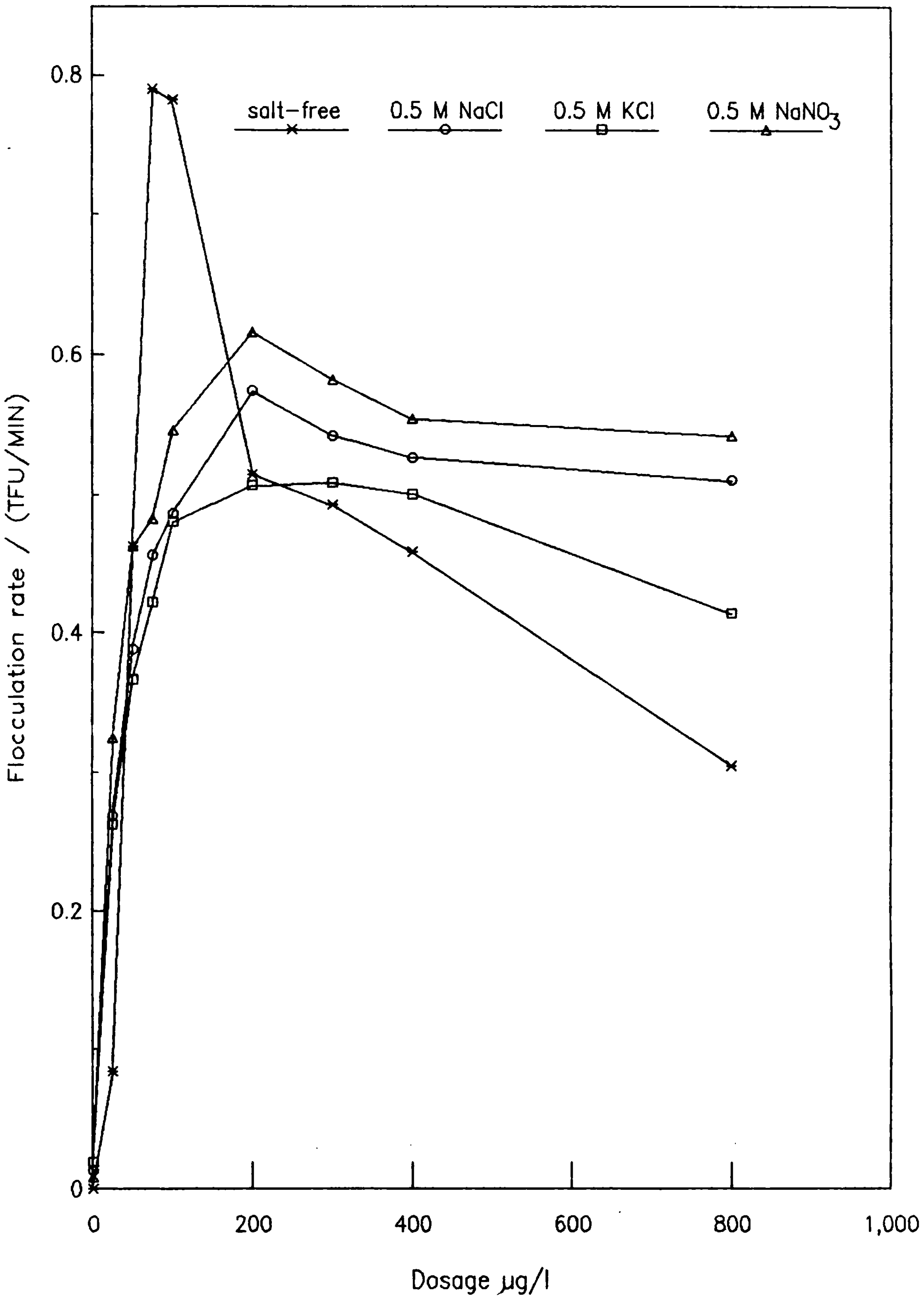


Figure 4.33. Comparison of flocculation rates (P63)

particles and away from the polymer. As a result, they have little influence on the flocculation rates. The experimental results show that the flocculation rates with the more hydrated Cl^- ions are lower than the NO^3-. These results clearly show a specific effect of the counter-ions to the polymer. However, competition for water of hydration contradicts the lower flocculation rates observed with Cl^-. Some unknown factors must be present to give this effect but the reasons are still unclear. Nevertheless, it can be said that the adsorbability of the counter-ions to the particles may be responsible for the specific effects on the flocculation of particles by polymer.

4.4. Effect of mixed electrolytes

The flocculation rates over a range of polymer dosages in a range of salt solutions have been determined and the results are shown in Figures 4.34-4.41.. As mentioned in Section 4.1.5., the flocculation rate is less sensitive to polymer dosage in the presence of added salt. Figures 4.34-4.37 show the flocculation rates in salt-free, 0.5 M NaCl, 0.01 M $CaCl_2$ and a mixture of 0.5 M NaCl/0.01 M $CaCl_2$. The flocculation rates for all the polymers tested in 0.01 M $CaCl_2$ are consistently higher than those in 0.5 M NaCl and in a mixture of 0.5 M NaCl/ 0.01 M $CaCl_2$. Despite the ionic strength of the 0.01 M $CaCl_2$ solution is lower than that in the 0.5 M NaCl, the higher valency of the calcium ion is able to bring about a lower stability and hence the higher flocculation rates. Similarly, in Figures 4.38-4.41 the flocculation rates in 0.05 M $MgCl_2$ are consistently higher than those in the 0.5 M NaCl and in a mixture of 0.5 M NaCl/0.05 M $MgCl_2$ for the same reason.

The interesting point is the flocculation rates in a mixture of electrolytes. The flocculation rates in the 0.5M NaCl/0.01M $CaCl_2$ mixture are lower than those in 0.5M NaCl at low polymer dosages but become higher at high polymer dosages. The transition takes place near the optimum flocculation dosage in the salt-free solution. This trend is observed for all four polymers tested. The flocculation rates in a 0.5M NaCl/0.05M $MgCl_2$ mixture are consistently higher than those in 0.5M NaCl for all dosage with Percol 140, but are consistently lower with Percol 326, Percol 292 and Percol 63. These results indicate the

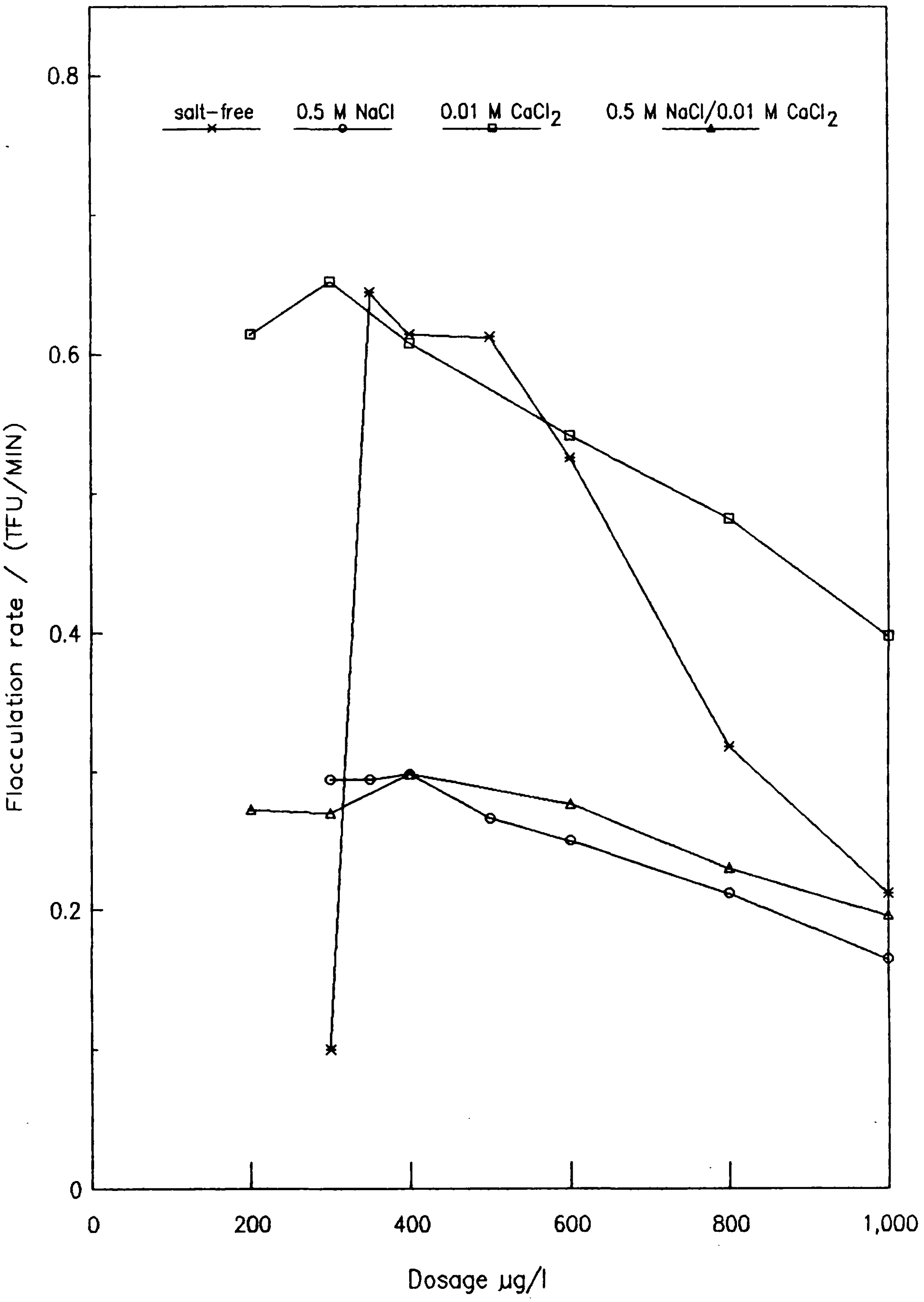


Figure 4.34. Comparison of flocculation rates (P140)

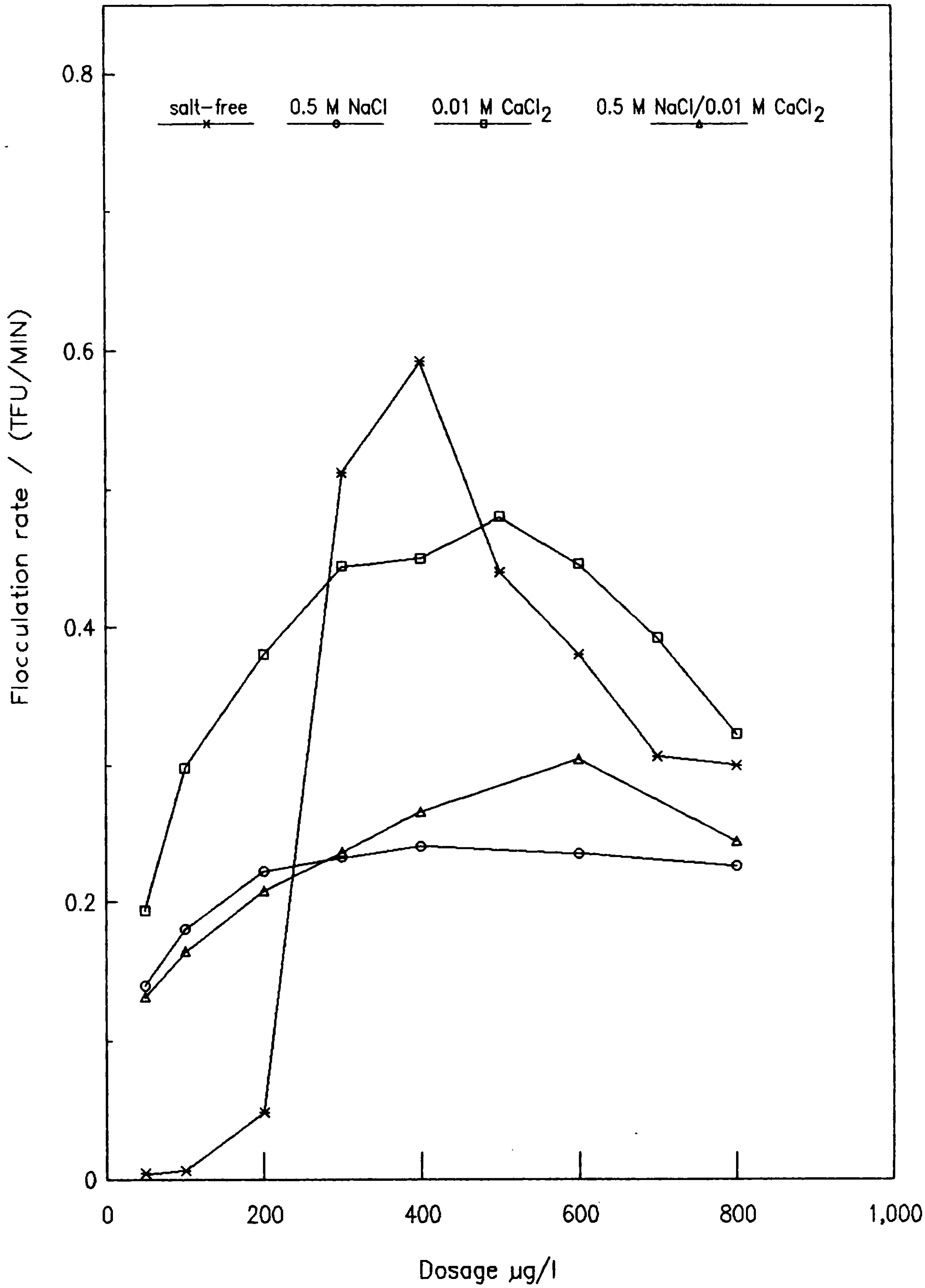


Figure 4.35. Comparison of flocculation rates (P326)

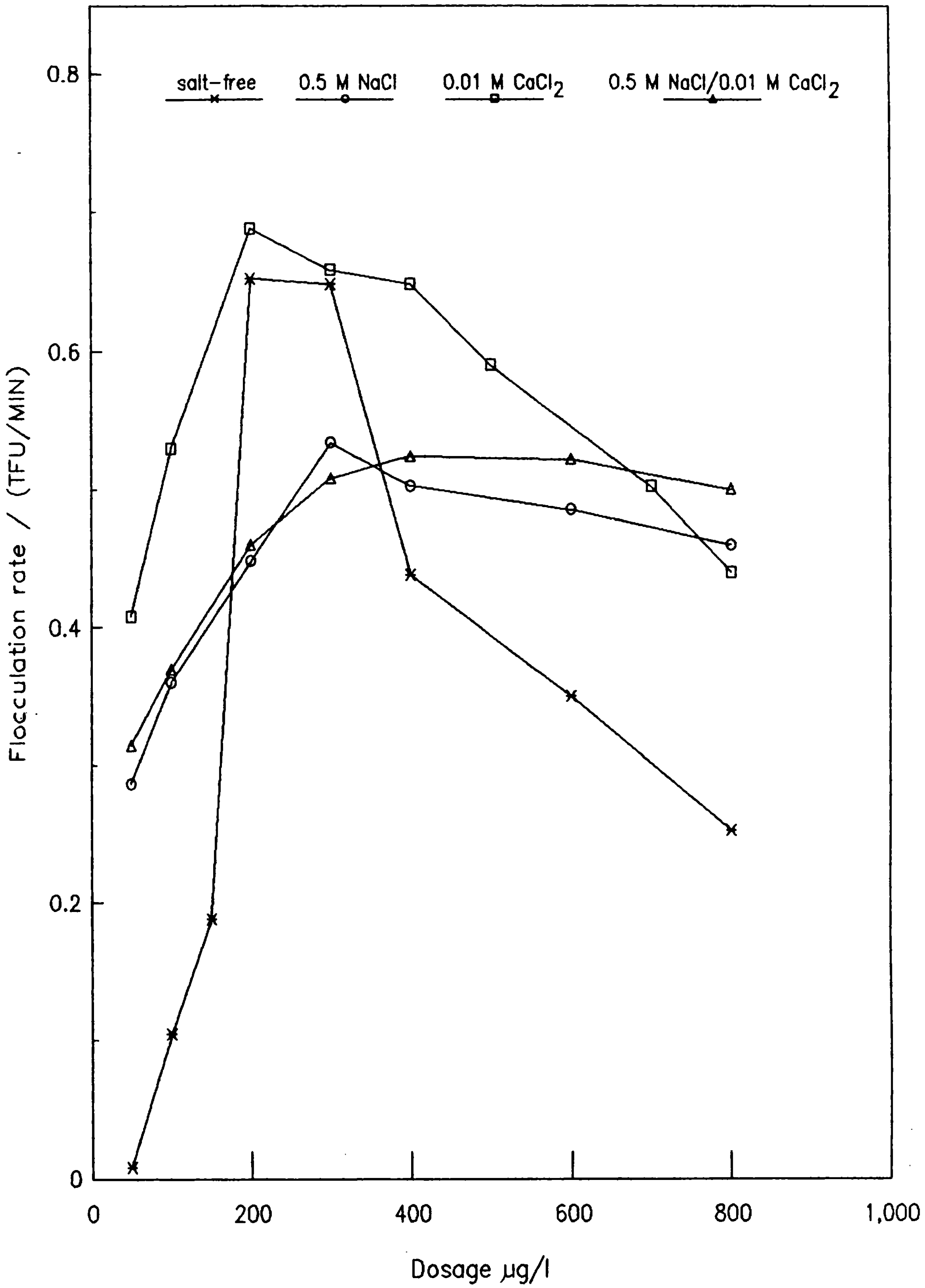


Figure 4.36. Comparison of flocculation rates (P292)

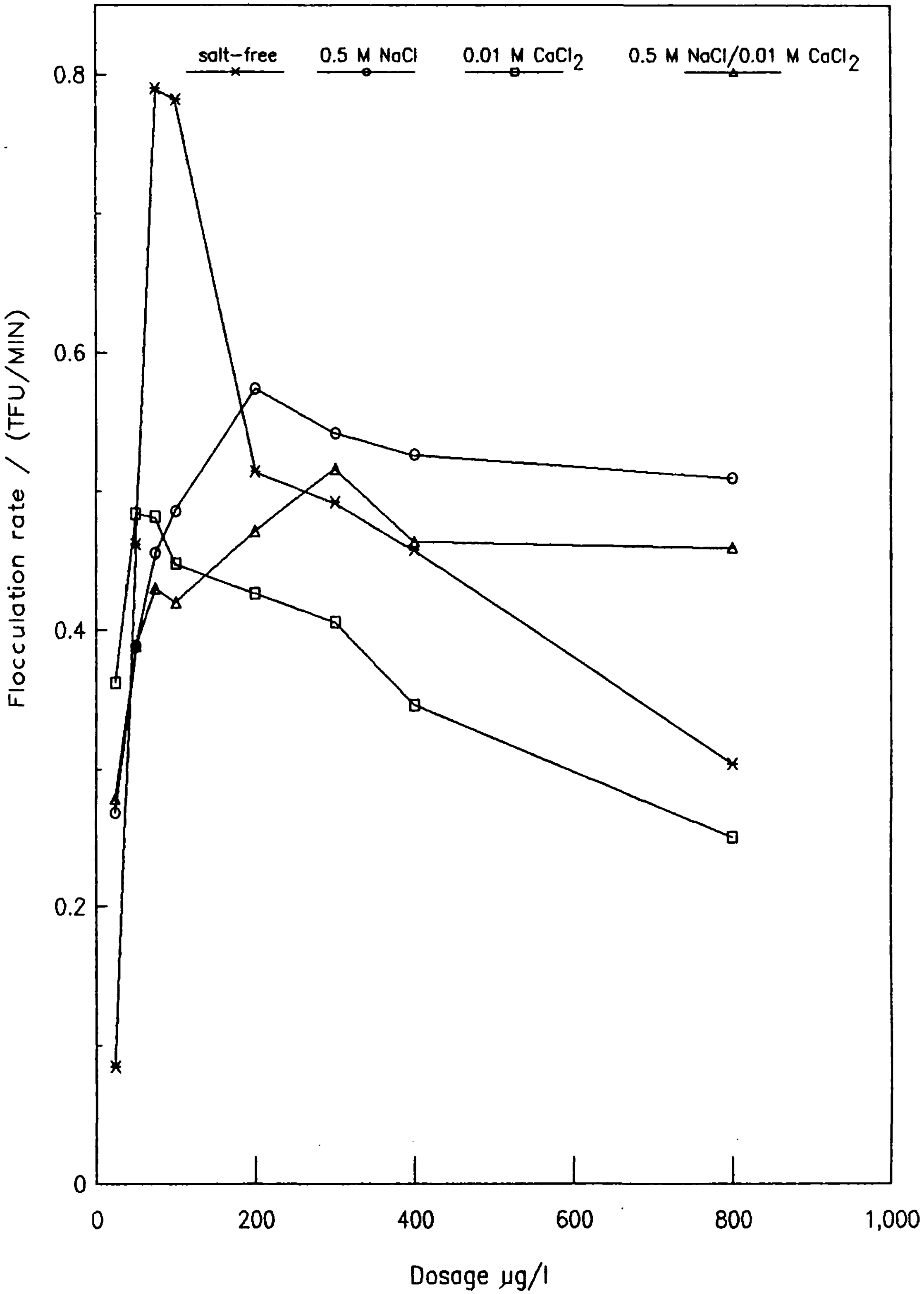


Figure 4.37. Comparison of flocculation rates (P63)

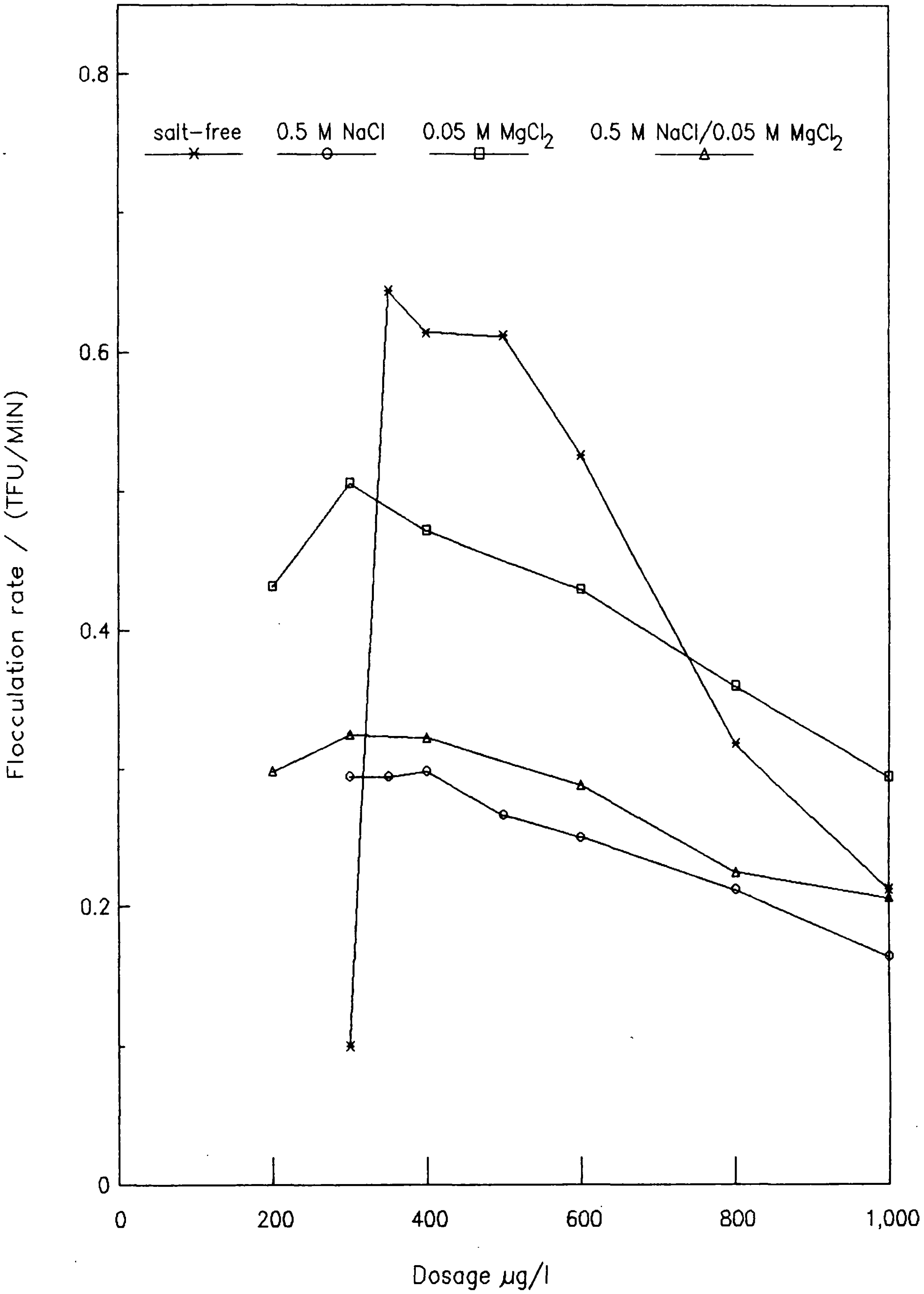


Figure 4.38. Comparison of flocculation rates P140)

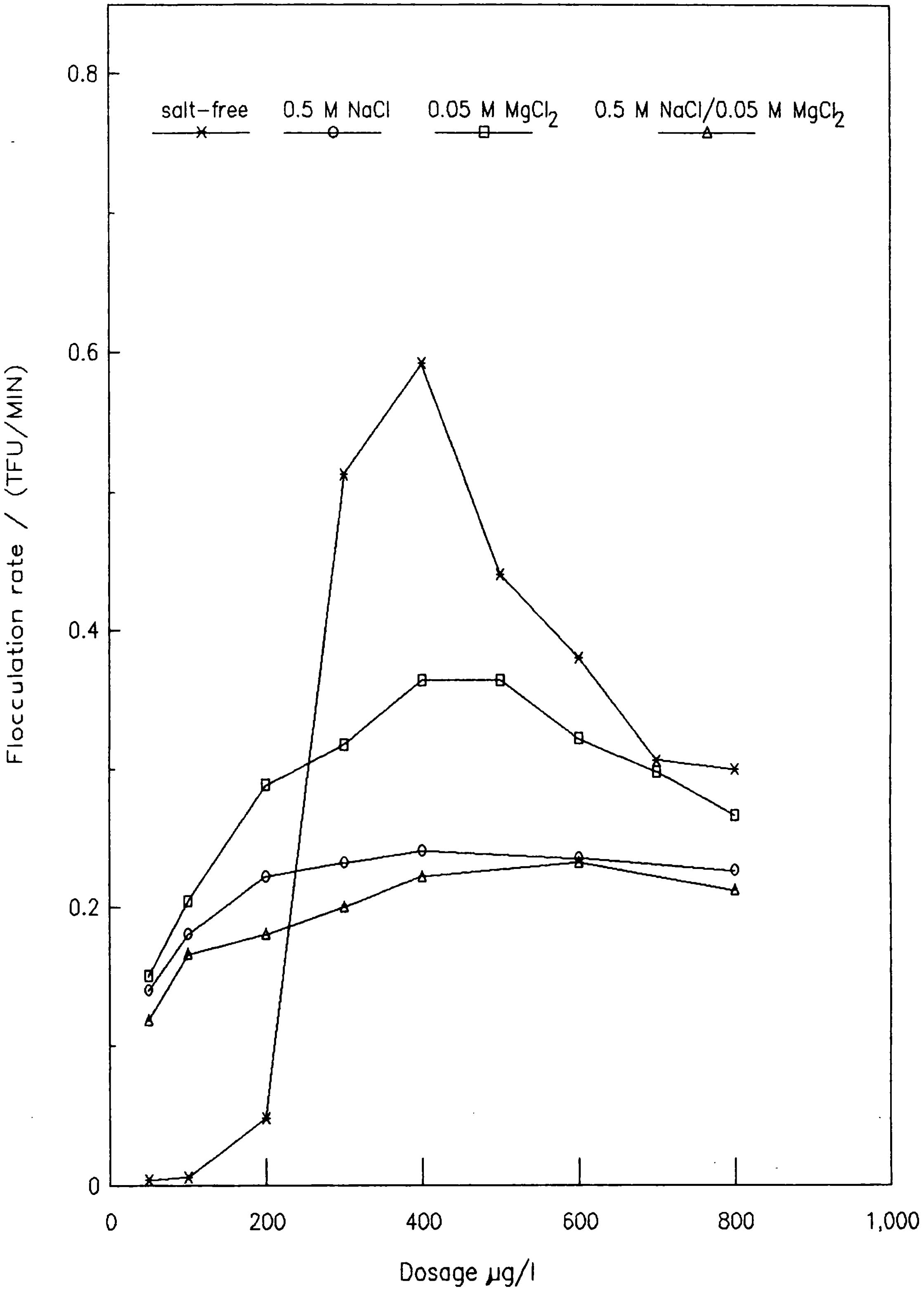


Figure 4.39. Comparison of flocculation rates (P326)

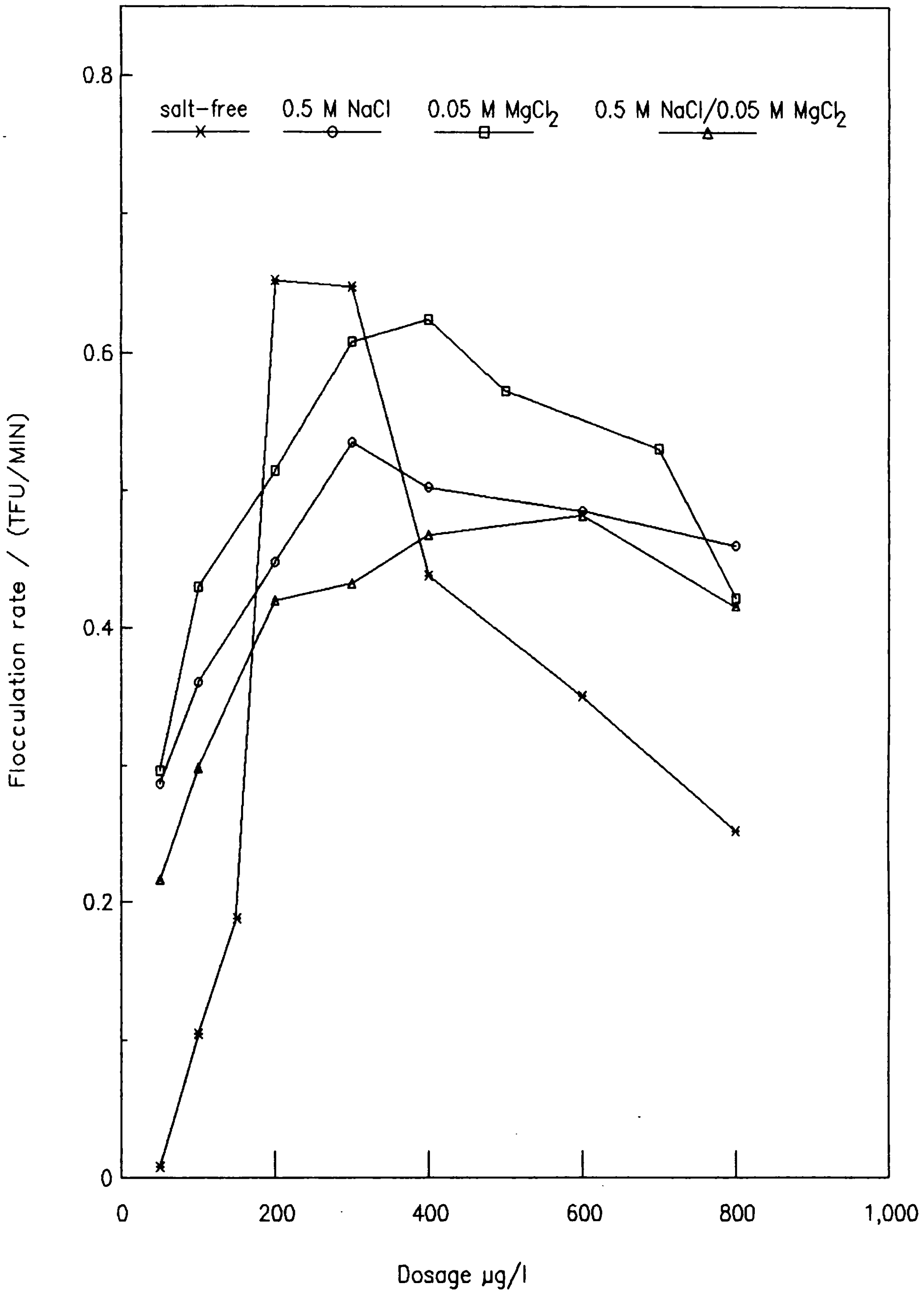


Figure 4.40. Comparison of flocculation rates (P292)

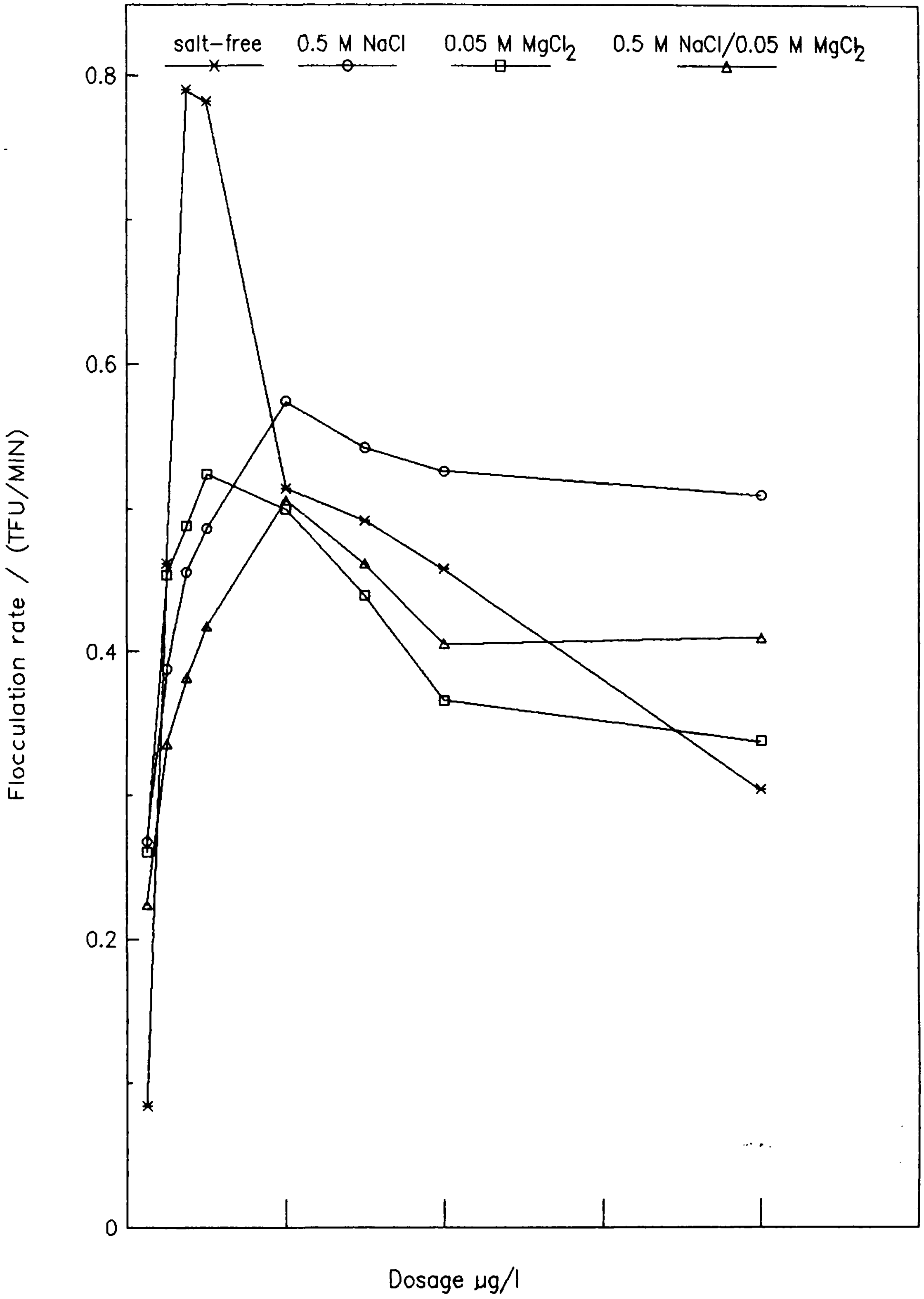


Figure 4.41. Comparison of flocculation rates (P63)

importance of charge effects on the stability of the suspension. The interaction of ionic strength, specific effects of flocculating ions and charge density of polymer is very subtle. Presently, there is no theoretical treatment on this aspect of flocculation. A detailed analysis of the results is not possible until information such as the amount of polymer adsorbed and the thickness of adsorbed polymer layer are known.

4.5. Verification of particle aggregation by Coulter counting and PDA 2000

The aggregation of a latex suspension in 10 mMol magnesium chloride has been monitored with a PDA 2000 and particle counts have been obtained with a Coulter Counter at intervals. The particle concentration decreases during the course of aggregation. Figures 4.42 shows the increase in Turbidity Fluctuation and the reduction of all particles greater than 1 μm with time. The values of Turbidity Fluctuation increase linearly with time. The "lag phase" observed in polymeric flocculation, as depicted in Figure 4.1., is not observed. This is expected for a suspension destabilized by electrolyte. A detailed analysis of the particle count data is very difficult to interpret unambiguously. The rate at which a suspension aggregates is not always constant during the course of aggregation. Factors such as particle collision frequency, the fraction of successful collisions and the change in particle size distribution can influence the aggregation rate. Polymeric flocculation is also complicated by the relative rates of polymer adsorption and particle collision. In a situation where the potential energy barrier to coagulation is reduced to zero by the presence of excess electrolyte to permit every encounter between colliding particles to form permanent aggregates, the aggregation rate can still be affected by parameters such as the influence of particles size on collision rate and the stability of the resultant aggregates.

The increase in Turbidity Fluctuation is found to correspond to a reduction in particle count. The inverse relationship between Turbidity Fluctuation and particle count confirms that the aggregation

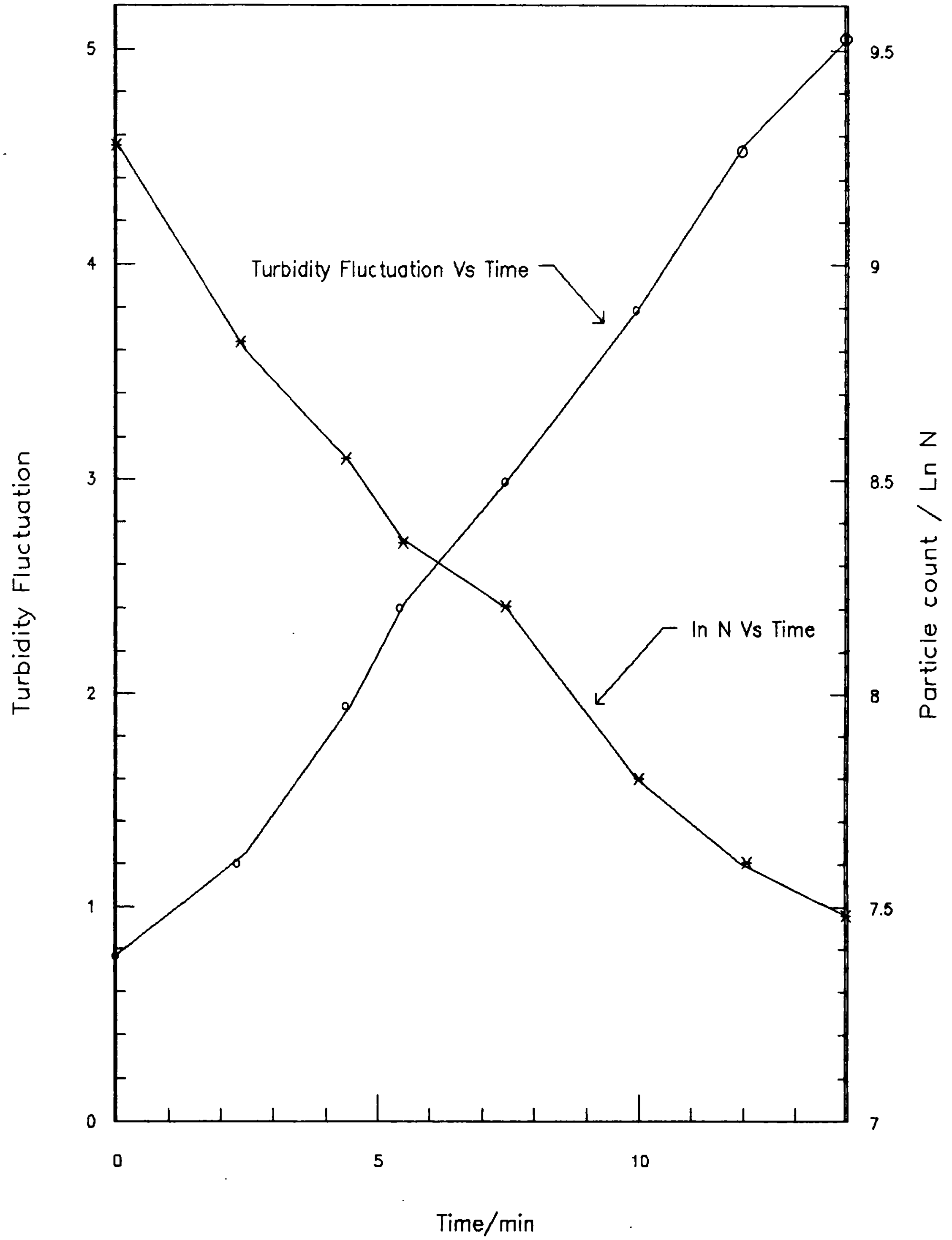


Figure 4.42. Correlation between Turbidity Fluctuation (Ratio) and particle count Vs Time

of particles can be followed by monitoring the light intensity fluctuations as described in Section 2.5.4. It is probably a coincidence that the results in Figure 4.42. show a 6-fold reduction in particle count corresponding roughly to a 6-fold increase in Turbidity Fluctuation. Generally, it is not possible to obtain a quantitative correlation of the particle concentration with the Turbidity Fluctuation since the scattering of light by aggregates is complicated by the various shapes that aggregates can adopt. Nevertheless, an overall measure of the state of aggregation can be adequately monitored by measuring fluctuations in the intensity of a light beam transmitted through a flowing suspension.

CHAPTER FIVE

CONCLUSIONS

The aggregation of particles by the use of polymeric flocculants involves several steps which may occur simultaneously. These steps include the adsorption of polymer molecules, the re-arrangement of adsorbed polymer and the collision of particles having an appropriate amount of adsorbed polymer. The adsorption of polymer molecules does not necessarily take place instantaneously. As a result, there may be an appreciable lag time between the addition of polymer and the onset of flocculation. The re-arrangement of adsorbed polymer also has an important significance on the aggregation process. The characteristics of the polymer, the composition of the solution, the particle concentration and the polymer application rates can have a major influence on the aggregation of suspended particles. These factors need to be carefully considered in order to understand the aggregation process better.

The aggregation of a suspension of silica particles by six cationic polymers has been monitored by an optical technique which measures the fluctuations of light intensity transmitted through the flowing suspension. An inverse relationship between the light intensity fluctuations and the particle concentrations has been established by monitoring the particle concentrations with a Coulter Counter. The destabilizing effects of cationic polymers on negatively charged silica particles have been found to be mainly charge related. The amount of cationic charge needed to give optimum flocculation in the absence of added electrolyte is about the same, despite the polymers used being different in molecular mass, charge density and even the nature of the monomer. The electrophoretic mobility data reinforce the charge effect of adsorbed polymer in the destabilization of dispersed particles. The dosages required to give zero mobility correlate well with the optimum flocculation dosages. An insight into the kinetic aspects of flocculation can be gained by considering the relevant factors involved.

In dilute suspensions, the adsorption of polymer may be the rate-limiting step if the polymer dosage is low. The time required for particles to adsorb adequate amount of polymer to form stable aggregates has been shown to be shorter at a higher polymer concentration. A high polymer application rate might be necessary in applications where rapid destabilization is required. Even though, a lower polymer dosage would lead, ultimately, to a faster flocculation. Rapid destabilization has also been achieved by using polymers of high charge density and/or high molecular mass. Less polymer is required to neutralize the particle charge with a high charge density polymer. Under the stirring conditions where orthokinetic collision mechanism is predominant, the larger polymer is expected to adsorb faster. Polymers of high charge density and high molecular mass are likely to give good flocculation.

As a result of the re-arrangement of adsorbed polymer, most adsorbed polymer has a tendency to flatten onto the particle surface unless the polymer coverage is high. The significance of polymer re-conformation on the flocculation of the suspension depends on the particle concentration of the suspension, the molecular mass, charge density and flexibility of the polymer, and the ionic strength of the solution. It is expected that the flattening of the polymer is more significant in dilute suspension, in cases where the concentration of polymer is low or the charge density of the polymer is high. The adsorption of polymer outweighs the re-conformation of polymer in dilute suspension or in low polymer concentrations. In the Interparticle Bridging Model, segments of polymer molecules have to attach to particles at many points. The "Electrostatic Patch" effect can be regarded as another form of "bridging" interaction, the difference being the thickness of the adsorbed layer. The crucial points are that the adsorbed polymers must be able to extend beyond the range of electrostatic repulsive forces between the colliding particles and become attached, and that the attachment must be sufficiently strong to withstand the shearing forces imposed by the shear conditions. Percol 63, a 30% charged, high molecular mass polymer is shown to give better flocculation than those polymers of lower molecular mass. The charge density of the polymer should be moderate, so that the excess cationic charge of the adsorbed polymer should not give rise to a repulsion between particles. In the presence of added salt, the range of electrostatic repulsive forces are reduced. Particles are able to come closer to one another giving a more effective flocculation.

The adsorption time to give a certain degree of destabilization is found to be shorter for a polymer of higher charge density. However, the results also show that up to 30% cationicity, flocculation becomes more pronounced with an increase in charge density. The 30% charged polymer is shown to give the fastest optimum flocculation rate and the highest degree of flocculation. The adsorption of the 100% charged polymers is more likely to give too much excess positive charge, which might lead to a repulsion between colliding particles. Even in an underdosed conditions, successful collisions can occur if suitable sites of different particles come into contact are matched up accurately. The interactions between particles destabilized by polymer of charge density less than 30% may be not as strong as those destabilized by the 30% charged polymer.

The flocculation of silica particles by two polymers of the same charge density but differ in their molecular mass by a factor of six has shown that the larger polymer (Percol 292) is more effective than the smaller polymer (Percol 326), giving a shorter lag time and a more rapid flocculation. In general, polymers of high molecular mass are able to bring about a more efficient flocculation. Percol 63, a polymer of high molecular mass 3.0×10^6, is found to be most effective. On the other hand, Percol 1597 and Percol 1697 (polymers of low molecular mass $3\text{-}4 \times 10^4$) are found to give poor flocculation.

The ionic strength of the solution can affect the polymer adsorption and flocculation efficiency. The range of polymer dosages to bring about flocculation is less critical in salt solutions and the highest flocculation rate always occurs in the salt-free medium. It is thought that the need to displace adsorbed ions may be responsible for the lowering of the optimum flocculation rate. As the particles are partly neutralized by the effect of added salt, the onset of flocculation has been shown to occur more rapidly for a low polymer dose in the presence of added salt. However, the maximum flocculation rate and the degree of flocculation attained at the end of the 15 minutes flocculation time for a given dosage in salt solutions may be lower than those in salt-free medium. Furthermore, restabilization of particles is possible at high salt concentrations when the dosage is high. A 5% charged polymer (Percol 140) gives higher flocculation in salt solutions at dosages corresponding to either suboptimal or over-dosed conditions in salt-free medium. For the higher charge density polymers, higher flocculation rates are achieved only at dosages which correspond to over-dosed conditions in salt-free medium. Results have demonstrated that both the polymer application rate and the charge density of the polymer determine the optimum ionic strength. The flocculation rates in 300 mmol/l NaCl are lower than those in 100 mmol/l NaCl, except for very high polymer dosages. In general, a higher degree of flocculation is obtained in the absence of salt for polymer of cationic charge density 30% or higher or for polymer of molecular mass less than about 4×10^5.

Flocculation rates has been found to be relatively lower in the presence of the larger counter-ions to the particles. The larger ions are less hydrated and more easily adsorbed onto the particles. The need to displace these more strongly adsorbed ions may lead to a lower flocculating ability of the polymer. The reason for the specific effects of the co-ions to particles on the flocculation of the dispersion by polymer remains unclear. The valency of the counter-ions to the particles is an important factor in the stability of the dispersion. Higher flocculation rates are found in the presence of ions of higher valency even when the electrolyte concentrations of the lower valency ions are higher. The valency and the size of the flocculating ions, the charge density of the polymer, and the concentration of the ions and polymer can influence the stability of a dispersion. Results obtained in mixtures of electrolytes indicate the destabilization of the particles is charge related. The stability of the dispersion is interdependent on the ionic strength, the type of electrolytes and the characteristics of the polymer.

SUGGESTIONS FOR FURTHER WORK

The present experimental investigation has provided an useful insight into the flocculation of a dilute suspension of silica particles (*size range* 1-3μm). The research is limited to one type of particle. Further work can be carried out on other particles to verify the general trend observed with silica particles. The influence of particle size and particle concentration can also be investigated.

The work has highlighted the behaviour of cationic polymers. The flocculation mechanisms by non-ionic and anionic polymers may be different from cationic polymers. There is a need to study the use of non-ionic and anionic polymers. The polymer flocculation rate can be the rate-limiting step when the polymer dosage is low or when the polymer is of low charge density and low molecular mass. A study on the effect of stirring rates can provide further information on the kinetic of the flocculation process.

More work is needed to verify the specific effects of inorganic electrolytes on flocculation by polymers. Other types of particles and polymers should be tested. During the 15 minutes flocculation time, the maximum R.M.S./DC Ratio has not been reached for most flocculation tests. It may be useful to allow the suspension to flocculate until the maximum Ratio value is reached for each tests. The results can be compared to investigate the maximum degree of flocculation each polymers can achieved and the relative strength of the flocs under specified conditions.

The use of polymers has great potential for the removal of suspended particles from waters of low particle concentration in direct filtration. The results of the presence investigation show that a polymer of high charge density and high molecular mass can bring about rapid destabilization of the particles. It would be useful to investigate the deposition of suspended particles aggregated to different degree of flocculation by using polymers of different characteristics.

Appendix I Size distribution of silica particles

The size distribution of the silica suspension was determined with a Coulter Counter, using a 50μm orifice tube. The concentration of the suspension for Sample A and Sample B were 6.5 g/l and 3.9 g/l respectively. 15μl of the suspension was diluted to 20.0 ml with 2% sodium chloride solution. The sample volume was 0.05 ml.

$$Particle\ concentration = \frac{total\ count\ x\ 20}{0.05\ x\ 0.015}\ particles/ml$$

Size range / μm	Number of count	
	Sample A	Sample B
0.95-1.00	1768	3316
1.00-1.50	3257	11915
1.50-2.00	2349	4271
2.00-2.50	2514	1867
2.50-3.00	1644	710
3.00-3.50	833	70
3.50-4.00	451	16
4.00-4.50	146	3
4.50-5.00	36	0
5.00-5.50	0	0
5.50-6.00	0	3
Average diameter	2.6	1.9

An average diameter was estimated by assuming the density of the silica particles to be 2 x 10^3 kg/m^3.

Average equivalent diameter / μm

$$= \left(\frac{solid\ content\ /\ g/dm^3}{\pi\ x\ \frac{4}{3}\ x\ density\ kg/m^3\ x\ particle\ count\ /\ dm^3} \right)^{1/3} x\ 2x10^6$$

Appendix II Size distribution of polystyrene latex particles

Size range / μm	Number of count
1.50-1.75	96
1.75-2.00	1495
2.00-2.25	3544
2.25-2.50	496
2.50-2.75	88
2.75-3.00	22
3.00-3.25	11
3.25-3.50	6
3.50-3.75	3
3.75-4.00	2
4.00-4.25	0
4.25-4.50	3
4.50-4.75	0
4.75-5.00	2
>5.00	1
Total count	5769

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