FLOCCULATION BY POLY(ETHYLENE OXIDE):
MECHANISM AND APPLICATIONS

A thesis submitted for the degree of
Doctor of Philosophy in the University of London

By

JORGE RUBIO

Imperial College of Science and Technology
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ABSTRACT

The adsorption-flocculation reactions of a high molecular weight poly(ethylene oxide) on a number of silica surfaces have been investigated. Adsorption isotherms have been determined for the adsorption of poly(ethylene oxide) from aqueous solution on to a flame-hydrolyzed silica, a flame-hydrolyzed silica treated with dimethyldichlorosilane and a precipitated silica; the results are correlated with the varying degrees of flocculation produced.

The effects of pH and heat treatment, as methods of varying either the charge density or the structure of silica surfaces, have been studied. The extent of adsorption was found to vary markedly from one adsorbent to another, " plateau" adsorption values (expressed per unit area) being in the order flame silica ≈ treated flame silica > precipitated silica. There was complete correlation between flocculation and adsorption. In every case, efficient flocculation corresponded to virtually complete adsorption of the polymer. Partial dehydroxylation of the precipitated silica by heating to >450°C enhanced the adsorption of poly(ethylene oxide) but further heating to temperatures higher than 900°C greatly reduced the affinity of any form of silica for the polymer. Rehydration of such silicas in water is very slow.

On the basis of these measurements, the mechanism of adsorption of PEO on to silica was established; a combination of hydrogen bonding and hydrophobic interaction may be responsible for the attachment of the polymer. Any factor which favours the presence of water on the surface (in preference to organic compounds) tends to weaken the, already fragile, attachment of the solute.

Following studies of flocculation effects of poly(ethylene oxide) on different substrates, investigations on selective flocculation of non-sulphide copper minerals were undertaken. The initially weak flocculation characteristics of poly(ethylene oxide) for copper compounds were found to be greatly improved by addition of some reagents commonly used as flotation modifiers, namely, quebracho, sodium sulphide and tannic acid, as well as with typical xanthate type collectors. This feature provided an alternative principle for obtaining selective adsorption of a polymer on to these minerals.

The selective flocculation, by poly(ethylene oxide), of chrysocolla and malachite from their synthetic mixtures with either quartz, calcite or dolomite, following different pre-treatments of the copper mineral with sodium sulphide or potassium amyl xanthate was investigated in detail. Successful separations were obtained in most cases. Following the studies of flocculation and selective flocculation of separate minerals and synthetic mineral mixtures, a selective flocculation scheme consisting of gangue dispersion, with either sodium sulphide or xanthate, followed by treatment with poly(ethylene oxide), was tested on a natural non-sulphide copper ore.

Efficient separations were obtained only with special attention to the method of addition and the dosage of flocculant, and achievement of selectivity required strict control of the gangue dispersion characteristics as well as modulation of the adsorption of poly(ethylene oxide) ("depression") on to "self-activated" siliceous gangue material.

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FOREWORD

The present thesis is divided into two parts. The first part is devoted to a study of the mechanism by which a poly(ethylene oxide) flocculant is adsorbed at a solid/liquid interface. Special attention is paid to hydrophobic interactions influencing the adsorption of poly(ethylene oxide) onto various forms of silica. Correlation between the adsorption of polymer and the degree of flocculation produced is particularly examined. The flocculation properties of poly(ethylene oxide) on various other substrates are also studied.

The second part of the thesis is concerned with the use of poly(ethylene oxide) for the selective flocculation of non-sulphide copper minerals. A principle to promote the adsorption of PEO on to these copper minerals has been developed and tested.

PART I

THE SURFACE CHEMISTRY OF POLY(ETHYLENE OXIDE) SOLUTIONS

CHAPTER 1

INTRODUCTION : THE HYDROPHOBIC EFFECT IN ADSORPTION

Hydrophobic interactions have been extensively studied by physical chemists and biochemists for a number of years, principally with regard to the solubility of hydrocarbons in water and apolar group interactions between enzyme-substrates (1), protein-protein chains (2, 3) and polymer-surfactants (4, 5).

The low solubility of hydrocarbons in water is distinguished from that of " normal" liquid mixtures in that usually mutual solubility is mainly determined by enthalpic factors whereas the solubilities of hydrocarbons in water are mainly controlled by entropic effects. Thus the transfer of a simple hydrocarbon molecule into water is accompanied by a negative entropy of hydration. This observation led to the suggestion that inert solutes promote the structuring of the neighbouring water molecules (the " iceberg" effect (6)) so that, hydrophobic bonding (i.e., the association of apolar groups), could then be regarded as a partial reversal of the thermodynamically unfavourable process of solution. Kauzmann (2) has used the term " hydrophobic bond" to describe the gain in the free energy on the transfer of non-polar residues from an aqueous environment to the interior of proteins. This interaction has been responsible for the folding of proteins. This reasoning can be extended to other molecules, the only two requirements being substantial apolar residues and an aqueous environment. Thus the reversible aggregation of molecules or ions with long apolar chains or aromatic groups, as in the case of surfactant micellization, glycerides, dyestuffs, etc., is believed to depend mainly on the phenomenon of hydrophobic association (7).

The exact origin of the driving energy of the hydrophobic effect is still controversial (8) and despite its importance a quantitative description in terms of intermolecular forces has not been achieved for hydrophobic interactions. However, several advances have been made recently to quantify and characterize the hydrophobic effect (7b, 7c, 10). A priori, phenomenological aspects of the hydrophobic interaction has been intensively investigated, and the consensus view is that the driving force for contact between non-polar residues in water is entropic in nature (8). It is generally believed that such residues are solvated in a special way in water, a mode of solvation which involves the formation of short-lived cages composed of water molecules (7a). Association of apolar groups reduces the number of such perturbed water and hence leads to an entropy gain. Enthalpic effects are not responsible for this association, as can be verified by a comparison of the free energies, enthalpies, and entropies of transfer of hydrocarbons from the liquid state to water (8).

However, it should be noted that attraction of non-polar groups (such as hydrocarbon chains) for each other plays only a minor role in the hydrophobic effect. This effect actually arises primarily from the strong attractive forces between water molecules which, being isotropically arranged must be disrupted or distorted when a solute is dissolved in the water. Thus, if the solute is ionic or strongly polar, it can form strong bonds to water molecules, which more than compensate for the disruption of the bonds existing in pure water. Accordingly, ionic or polar substances are readily soluble in water. No such compensation however, occurs with non-polar groups, and their solution in water is therefore, resisted. It is then a loss of entropy rather than bond energy that leads to an unfavourable free energy change for the process.

The expression " hydrophobic bond" given by Kauzmann (2) to describe the association of apolar groups, was initially used by Némethy and Scheraga (9) in their attempt to quantify hydrophobicity on a molecular basis. They were able to calculate the free energy associated with the approach to pairwise contact of apolar residues, in terms of certain postulated changes in the aqueous environment and solute - solvent dispersion interaction. However, the term " hydrophobic interactions" seems to be more appropriate since it is not a bond in the accepted sense. Finally, it should be emphasized that the term " hydrophobic effect" used by Tanford (8) describes much better the entire phenomenon, thus assigning the predominant role to the properties of water per se and a minor role to the attraction of non-polar groups (hydrophobic interaction). Therefore, the term " hydrophobic effect" will be used here to describe the phenomenon as such, and the term " hydrophobic interaction" will be used to describe the association between apolar groups.

Hydrophobic interactions are also basic to the classical phenomena of adsorption of surface-active substances at the air/water (11, 12), oil/water (13, 14) and solid/water interfaces (15, 16). They are important in mineral processing and sometimes play a significant role in processes such as froth flotation, solvent extraction and thickening (16, 17).

The present work deals mainly with the solid (in its dispersed state)/liquid interface; the general aim being to obtain evidence of hydrophobic interaction accompanying the adsorption of a polymer flocculant (as hydrophobic as possible) at the solid/water interface. Thus the solid should be such that the surface carries hydrophobic sites and the polymer should be amphiphilic in character, i.e., should contain one part that has " sympathy" and another that has " antipathy" for water. Because the present work was ultimately aimed at developing selective flocculation, the study was concerned with fundamental analysis in conjunction with macromolecular adsorption-flocculation in a) a model system and b) a copper ore (Part II). The possibility of hydrophobic interaction influencing the adsorption of a polymeric flocculant will be investigated.

Several attachment mechanisms of macromolecules (surfactants and polymers) from water to solid surfaces have been suggested in the literature. Accordingly, the free energy of adsorption (ΔG_{ad}) can be described as:

$$\Delta G_{ad} = \Delta G_{e} + \Delta G_{chem} + \Delta G_{H-H} + \Delta G_{IE} + \Delta G_{M} + \Delta G_{HI} + \ldots$$

(i.e., the sum of several contributions assumed independent of each other) where:

ΔG_{e} = " electrostatic interaction" contribution

ΔG_{chem} = " chemical interaction" contribution (i.e., salt linkage through divalent counterion, interfacial precipitation, complexing, chelating, etc.)

ΔG_{H-H} = " Hydrogen bonding" contribution

ΔG_{IE} = " Ionic exchange" contribution

ΔG_M = miscellaneous contributions like dipole-dipole interaction, entropic (repulsion-attraction) contribution, etc.

ΔG_{HI} = " hydrophobic interaction" contribution.

Several of these contributions have already received attention. Several authors have measured the ΔG_{HI} contribution to the adsorption of surfactants at various interfaces (15). The values for transfer energy per CH_2 group for various phenomena such as micellization, emulsification, adsorption of surfactants at the solution/gas or solution/solid interfaces have also been calculated (15). In addition a few studies have been reported on the adsorption of surface active substances and polymers (4,145) on to solid substrates. Hydrophobic interactions occurring in solution between the surfactant and the polymer may be also responsible for the increased amount of polymer or surfactant which is being adsorbed under conditions where little or no adsorption occurred otherwise (4). However, an integral and systematic study of some factors, such as ΔG_m or ΔG_{HI}, possibly significant in several phenomena involving polymers, namely, dispersion, flotation and flocculation, has not been reported yet. In this respect, it was thought appropriate to design some experiments in order to evaluate at least semi-quantitatively the influence of the hydrophobic interaction term on polymer adsorption-flocculation effects. Therefore, the problem was centred upon the search for a suitable experimental system. The use of hydrophobic silica (silica (AEROSIL) treated with dimethyldichlorosilane) was found to be the most suitable solid substrate since it consisted of very small unitary spherical particles, fairly uniform in size and well characterized (18). Its dispersibility in water, however, is due to some residual silanol groups present on the surface. These groups seem to be responsible for several properties of hydrophobic silica including its negative surface potential (60). Its differences with respect to hydrophilic silicas are constantly examined.

Poly(ethylene oxide) (PEO) was chosen as the flocculant for a number of reasons which are given below. Its behaviour in aqueous solution and its interfacial characteristics largely fulfill the primary need of the present study.

CHAPTER 2

THE ADSORPTION CHARACTERISTICS OF POLY(ETHYLENE OXIDE) AT VARIOUS INTERFACES

A general understanding of PEO as a polymeric flocculant implies knowledge of its properties in solution as well as its adsorption characteristics at different interfaces. A review of its chemistry is given in this Chapter.

2.1. The Solution Properties of Poly(ethylene oxide)

Poly(ethylene oxide) is a crystalline, thermoplastic, water soluble polymer with the general composition of the molecule $X\!-\!(\!-OCH_2CH_2\!-\!)_n\!-\!Y$, where n refers to the number of monomer units in the polymer chain and X and Y represent the end groups of the molecule (these are known to be OH only for low molecular weights). Unlike most polymer systems, PEO is commercially available with a wide range of molecular weights; from ethylene glycol and diethylene glycol to polymers that have molecular weights of several millions.

" Polyox coagulant" (BDH-Union Carbide), a poly(ethylene oxide) with a molecular weight of over 5×10^6 (19), was chosen for the present study. It has several interesting properties. Possibly the most important feature for the understanding of its, sometimes unusual behaviour is that the monomer contains hydrophobic regions, ($-CH_2-CH_2-$) and hydrogen-bonding sites (-O-). For example, the configuration (or conformation) of the PEO chain will be mainly influenced by the hydrophobic nature of the interaction between the ethylene groups and the polar solvent molecules and by the electron donor action of the ether oxygens. Ultrasonic attenuation measurements (20) show that there is a single relaxation time in aqueous solution. This is attributed to a polymer/solvent interaction involving hydrogen bonding of the water molecules to ether oxygen atoms along the chain, modified by hydrophobic interaction within the polymer and by water clusters near the hydrophobic groups. The data also imply that a minimum molecular size of the solvent macromolecule structure, of the order of 75 units is required before cooperativity is displayed. The requirement of a minimum molecular size has also been demonstrated in the case of helix-coil transition in polypeptides (45).

The conformation properties of the polyoxyethylenic chain. Studies of neutron inelastic scattering (21), i.r., n.m.r. (22) and laser-Raman spectroscopy (23) have shown that water molecules promote a more ordered conformational structure in PEO than is found in chloroform and benzene solution. All four physical measurements suggest that the conformation of PEO in aqueous solution retains, to a high degree, the TGT (trans, gauche trans) sequence of crystalline PEO. The helical form of this polymer is constructed with a succession of trans (CCOC) gauche (OCCO) and trans (COCC) conformers along the chain, with bond angles of 192^o, 60^o and 192^o respectively. Such an "ordered arrangement" of PEO in aqueous solutions would not, however, be the helical type conformation noted in DNA molecules; consequently, PEO in water should be referred to as a highly ordered structure (21, 22, 23, 24).

A more recent study on the conformation of PEO in the solid state, melt and solution measured by Raman scattering (25) has shown that the PEO molecule (high molecular weight) forms a hydrogen bonded complex in aqueous solution in which three water molecules are involved with one repeat unit. (Another author (26) interpreted viscosity data in terms of three water molecules associating with each ether oxygen). In addition, the helical structure of the crystal is lost in aqueous solution, as in the melt (and also in chloroform solution). In the melt, the structure seems to move towards the random coil configuration with an increase in trans conformation of the (C-C) bond. However, both of the solution spectra studies (water and chloroform) exhibited some retention of ordering; the difference between the chloroform and aqueous solution spectra can be explained by the hydrogen bonded water perturbing the ethylene rocking modes and the backbone stretching modes. There is, therefore, very little difference between the conformational structures for the two solutions. The hydrogen-bonded structure in aqueous solution is lost above the melting point of the pure polymer (the structure becomes that of the melt).

Solubility. According to Rattee and Breuer (27), " dissolution of the non-polar solutes in water depends upon the existence of structure in the neighbourhood of the non-polar solute and consequently the solubility will fall with increasing temperature. Dissolution will be exothermic (hydrogen-bond) and accompanied by a loss of entropy. The precipitation process, as the temperature is raised, results from a drive to regain entropy. In other words, the non-polar solute molecules are driven to interact with another by an entropic force within the water. This is known as a hydrophobic interaction and operates as a bonding force between non-polar solute molecules as well as non-polar regions or residues of large molecules e.g., polymers and dyes" .

PEO is the simplest-structured common synthetic polymer which is water soluble. The very fact of its water solubility is rather remarkable when we consider that for the general class of polyethers $-\!\left(-[CH_2]_m - O -\right)\!_n$ neither with m = 1 (polyformaldehyde, polyoxymethylene) nor with $m \geqslant 3$ poly(trimethylene oxide, etc.) is the polymer appreciably water soluble. It is also notable that for the methylated derivative of PEO, poly(propylene oxide), $-\!\left(-CH_2CH(CH_3)O-\right)\!_n$, only the oligomers are water soluble. Solubility or insolubility is much more of an all-or-nothing phenomenon with polymers than with small-molecule compounds; in addition, as with small-molecule compounds, solubility involves an equilibrium entailing not only the solute in solution but also the pure solute (or, in the case of polymers the more or less swollen polymer) which is in contact with it. In particular, the forces within the crystalline regions of an expectedly more hydrophilic polymer such as polyoxymethylene will also be an important factor in determining its solubility.

The unexpected solubility of PEO in water has led to suggestions that the polymer may be able to fit better into the water lattice than the other polyethers (28).

PEO is completely soluble in water at high concentrations. Its aqueous solutions show " stringy" or visco-elastic character at concentrations of less than one per cent. Its solution viscosity decreases with increasing shear stress and therefore is usually classified as pseudoplastic. On the other hand, PEO exhibits a negative solubility-temperature coefficient. The polymer precipitates from its aqueous solutions if the temperature is increased to near the boiling point of water. The upper consolute temperature depends on polymer concentration and molecular weight. " Polyox coagulant" in diluted concentrations forms a cloudiness rather than a precipitate at temperatures between 95^{o} and 100^{o}C.

Lyophilicity-lyophobicity transition has been postulated by Doolittle (29) as the main mechanism to interpret the inverse solubility-temperature relationship of other related systems. The different effects are reflected in the heat and entropy of dilution factors of the polymer-solvent interaction. Thus the dependence on temperature is such that the solvent becomes a non-solvent at a critical temperature and correspondingly an increase in the hydrophobic character of the polymer should result in a lowering of the polymer precipitation temperature. In the case of PEO, the hydrophobic and hydrophilic character are given by the alternate ethylenic units (hydrophobic) and ether oxygens (hydrophilic) of the polymer chain. Evidence of the hydrophilic character of the ether oxygens in PEO is apparently more obvious than for the hydrophobic nature of the ethylenic $-CH_2-CH_2-$ groups (mainly because of the problem of measuring this phenomenon in short molecules). So far, several authors have reported different degrees of association between water molecules and the ether groups of the chain (25, 26). Similarly, however, many pieces of evidence of the hydrophobic nature of the ethylenic groups in PEO have arisen and several examples of the relatively non-polar character of the molecule will be reported throughout this work. Bailey and Callard (30) used copolymers of ethylene oxide and propylene oxide (enhancing the hydrophobic character of PEO) to test the hydrophilic-hydrophobic effect on the solubility-temperature characteristics when compared with linear PEO. At a given concentration, the precipitation temperature decreased linearly with increasing propylene oxide contents (decreasing with increasing hydrophobic character of PEO).

Another way to explain the inverse solubility-temperature relationship of PEO would be through a disordering of " bound water" or " icebergs" that exist around the polymer molecule - specifically around the ethylenic groups of the chain (21, 22, 23). These " icebergs" correspond to a layer of highly oriented water which surrounds the polymer in aqueous solution. Increasing temperature could cause a disruption of this water and allow relatively strong polymer-polymer interaction. Such a mechanism would be mainly entropic in nature and can be comparable with the solubility characteristics of non-polar solutes as defined previously by Rattee and Breuer (27).

Using salting-out data and temperature solubility measurements on PEO in aqueous solutions, Bailey and Callard (30) estimated the heat and entropy of dilution of the polymer. According to Fox and Flory (31) from the temperature dependence of the intrinsic viscosity both the heat of dilution and the entropy of dilution of PEO in water must be negative. They concluded that many of the unusual characteristics of aqueous PEO solutions are entropic in origin and that the negative heat and entropy of dilution for high molecular weight polymers implies not only a high degree of polymer-solvent interaction but also an orientation of water molecules with respect to the poly(ethylene oxide) chain. Their result are in good agreement with those of Malcom and Rowlinson (32) who reported the most extensive thermodynamic study of the water - PEO system so far. They determined vapour pressures, heats of mixing, phase separation and other properties of this system at different temperatures and over wide ranges of composition. They also concluded that the entropy and the enthalpy of dilution of PEO in water are negative.

Solution viscosity. Commercial poly(ethylene oxide), such as " Polyox coagulant" has a broad molecular weight distribution and the bulk viscosity of their dilute aqueous solutions is often taken as a measure of the average size. " Polyox coagulant" is reported by the manufacturers (19) to have an approximate average molecular weight of 5×10^6 and a viscosity for a 1 wt. % aqueous solution of about 4×10^3 centipoises (19). In water at 30°C, the equation $[\eta] = 1.25 \times 10^{-4} \times M^{0.78}$ (from the classic Mark-Houwinck relation $[\eta] = K \times M^a$) appears to hold over a very wide range of high molecular weights.

It is noteworthy, however, that dependence of viscosity on shear rate results in low values of reduced or intrinsic viscosities. Correct values, therefore, should be extrapolated to zero shear conditions. Data on reduced viscosity of PEO with a molecular weight of 5.7×10^6 in water at various shear rates were obtained (33) with the use of an Ubbelohde type, multibulb capillary viscometer. Results indicated that they behave in a manner which allow them to be classified as pseudoplastic. Again, the unusual hydration of PEO in water, and the possible existence of a layer of structured water around the molecules, has been postulated to explain the marked dependence of the viscosity on the low rates of shear encountered in capillary viscometry (34). In addition, moderate high shearing forces can cause severe degradation of the polymer which may result in a lowering of the viscosity. Therefore, the mode of solution preparation (agitation, time, etc.) becomes important and must be controlled when reproducible solutions are required.

Salts or electrolytes cause a lowering of the absolute viscosity of aqueous solutions. The effect of K_2SO_4 (0.45 M, water 35°C) on the structural viscosity of a 2% aqueous solution of a high molecular weight poly(ethylene oxide) has been studied by Bailey and Callard (30). Marked differences in the shear rate dependence of viscosity between water solutions and salt solutions were reported only near the theta-temperature, (which is the condition with 0.45 M K_2SO_4 at 35°C). In the theta solvent, the molecular coil is in a relatively compact form. As the shear forces are increased on such molecular configurations, the molecules are elongated and an increase in structural viscosity results from increased intermolecular interaction. The increase in viscosity continues with increasing shear rate until a point is reached where the molecules in the salt solution attain a configuration that is similar to that of the expanded molecules in water solution. After this point, the molecules in salt solution begin to behave in a manner that is similar to the behaviour of the molecules in water alone under shear.

Friction reduction effect. " Friction reduction" is the phenomena where under turbulent conditions, a dilute polymer solution requires a smaller energy expenditure to maintain a given flow rate (through a pipe for example) than pure solvent. This phenomenon is sometimes termed the Toms Effect (31) and has been confirmed for a number of polymer/solvent systems (36, 37). PEO has been shown to be particularly effective as a friction reduction agent in water at very high dilutions. For example, the addition of only 30 p.p.m. Polyox coagulant to water resulted in about an

80% reduction in the frictional resistance through fire hoses. Although this effect has been related to " structural turbulence" in dilute solution of high polymers (the onset of a rise of apparent viscosity with increasing shear rate while flow is still below that of the critical Reynolds Number) the mechanism responsible for the Toms effect has not yet been clearly established. However, several explanations have been advanced, namely, the possible development of anisotropic viscosity by polymer molecules under shear stress (38); the transition from laminar to turbulent flow " delayed" by the polymer molecules stabilising the flow (36, 39); the induction of slip by a mobile oriented layer of polymer molecules near the pipe wall (35, 40) and finally the possible viscoelastic interaction between polymer molecules and turbulence (36, 40).

Association complexes : Poly(ethylene oxide) of either low or high molecular weight shows a tendency to form association complexes, especially in water, with other organic macromolecules (41, 42, 43). Both enthalpic and entropic factors are believed to be important. A decrease in entropy is usually the driving force in the complex formation when low molecular weight compounds are involved. However, the increased tendency of association complex formation observed with high molecular weight polymers seems to correspond to an entropic contribution only, because in the case of these large molecules, the degrees of freedom are considerably reduced. In addition, the enhanced tendency of complex formation in water is favoured by an increase in entropy from disruption of water structure. Examples of association complexes of PEO and PEO derivatives with various compounds are given below:

a) phenolic and polyphenolic substances; e.g., tannic acid (44), quebracho (44), phenol (46).
b) surfactants : sodium dodecyl sulphate (47); quaternary ammonium compounds (48, 4), sodium hexadecyl sulphate (4), carboxylate soap mixtures (49).
c) polymeric substances; acrylic and methacrylic polymers (41, 33), polyvinyl alcohol (44), maleic polymer derivatives (50), cellulose ethers (50) etc.

Hydrogen-bonding and hydrophobic interactions seem to be responsible for complex-formation of PEO with the substances cited above.

2.2. The Adsorption of Poly(ethylene oxide) At Various Interfaces

Many of the principal applications of poly(ethylene oxide) involve its use at or on surfaces. Most of the studies of polymers at interfaces have been concerned with the solid/liquid interface and relatively little is known about the interfacial characteristics of adsorbed macromolecules at the liquid/liquid or liquid/air interface. However, studies have been reported concerning the physical chemistry of PEO at various interfaces (24, 51). Results of these studies are briefly summarized below.

Adsorption at the aqueous/air interface. " Agitated PEO solutions are frothy in nature" (52). The driving force for the physical adsorption of macromolecules at the aqueous/air interface is mainly entropic in origin. Associated with the adsorption process is a loss of conformational entropy which is outweighed by the gain in entropy due to liberation of water from the air/water interface as well as from the water associated with the polymer (33).

Glass (51) measured the adsorption characteristics of various PEO and PEO derivates at the aqueous/air interface as a function of polymer molecular weight, concentration and temperature. The data indicated that the polymer is not adsorbed at the interface in a flat, zig-zag conformation but rather in portions of the polymer which are oriented out of the interfacial region. This polymer conformation is such that a molecular weight-dependent percentage of the hydrophobic segments are adsorbed at the interface. Contraction in the hydrodynamic volume of a polymer molecule could be expected to favourably affect the entropy of adsorption and provide a higher interfacial segment density in an interfacially adsorbed looped structure. The addition of inorganic electrolytes to aqueous solutions of PEO has been shown to decrease the hydrodynamic volume; monovalent electrolytes are least effective. For example : 0.36 M K_2SO_4 results in a 2 dyn/cm increase in π (initial π = 10.57 [dyn/cm]) of a 2.4×10^6 molecular weight PEO (0.1 wt. % at 25^oC). Equivalent amounts of KCℓ did not give such an increase (51).

Below a molecular weight of about 10^4 the surface activity of PEO solutions decreases with increasing molecular weight. Above this value, up to several millions, interfacial adsorption properties remain almost constant. The larger polymers exhibit a slightly positive temperature coefficient of surface activity, whilst smaller polymers with a molecular weight of ca. 400, exhibit a slightly negative coefficient (51). The results can be interpreted in terms of the dominance of entropic factors in the high polymer adsorption contrasted with a greater importance of enthalpic factors in the case of the lower molecular weight species. Frisch and Simha (72) have postulated that π generally decreases with decreasing molecular weight. This suggestion is based upon the increasing significance of a configurational entropy loss with decreasing molecular weight. The theoretical thermodynamic data determined by extrapolating values representing equilibrium adsorption (from a modified Gibbs equation (54)) clearly give support to this hypothesis.

Glass (51) has described the adsorption of PEO at the aqueous/air interface as occurring in two stages:

(1) diffusion from the bulk of the solution to the sub-surface phase

and (2) movement from the sub-surface phase to the surface layer with possible orientation of the adsorbing species.

As a result a new surface is created and adsorption of the water-soluble polymer at this interface is measured over a period of time. The surface activity of high PEO was found to be time dependent. Using the drop-weight method 14 hours was required to obtain equilibrium with dilute PEO solutions of molecular weight 2.4×10^6 (51).

Adsorption at the liquid/liquid interface. " PEO emulsifies a benzene-water mixture" (52). Adsorption of PEO at aqueous/organic liquid interfaces is of considerable interest. Adsorption characteristics of PEO, as studied by interfacial tension measurements (volume-drop and pendant drop techniques) have been investigated by Glass (24) at various aqueous/organic liquid interfaces. As mentioned before, PEO possesses a random conformation in bulk benzene solutions and a partially ordered structure in aqueous solutions. The conformational behaviour of PEO at the benzene/water interface was discussed following pendant-drop studies of PEO adsorption at that interface. Despite the different conformation in the two media with different solvating characteristics, equivalent interfacial pressures were observed. Interfacial pressure equilibrium was attained more rapidly from the more " ordered" aqueous phase. Equilibrium was attained surprisingly rapidly in comparison with the slower approach to equilibrium at the air/water interface; less than half an hour is required for equilibrium from either liquid phase (24). Studies at the hexane/-water interface (where PEO is soluble in the water phase but not in the hexane) showed equilibrium attainment from the water phase with a time dependence similar to that observed in interfacial adsorption from the benzene phase of a water/benzene boundary. The results were interpreted in terms of the ability of the benzene phase to rapidly orient interfacial polymer segments rather than to conformational effects (a role in which a non-solvent such as hexane cannot readily play). Finally, because the interfacial pressure equilibrium is obtained more rapidly from the " ordered conformation" (i.e., from water in the water/benzene system), it has been inferred that the adsorbed species is ordered rather than random. The interfacial configuration is supposedly equivalent from whichever phase the polymer was adsorbed, as no different equilibrium interfacial pressures were noted.

In relation to the use of PEO as a protective colloid, there are studies of the partial coalescence of liquid drops at the liquid/liquid interfaces (55). Drop coalescence at interfaces of aqueous PEO and 1,4-dichlorobutane and diethylmalonate was determined and related to adsorption of the polymer at the liquid--liquid interface. It was found that the amount of polymer adsorbed determines the number of coalescence steps.

Adsorption at the solid/liquid interface. The change in free energy for the adsorption of polymer molecules at the solid/-liquid interface can be described as: $\Delta G = \Delta G_1 + \Delta G_2$, where ΔG_1 arises from polymer-adsorbent (and solvent-adsorbent) interactions, and ΔG_2 is the contribution due to changes in internal configuration entropy on adsorption (this is a simplified version which excludes the contribution of heat of mixing and exclusion volume effects).

Thus, the free energy of an adsorbed polymer, ΔG, is equated to the sum of two parts:

$$\Delta G = E_i - T\Delta S_s$$

where E_i is the surface interaction energy and ΔS_c is the configurational entropy. As a difference from smaller molecules, with polymer molecules the flexibility is very important and the conformation of polymer molecules at an interface is a key feature in polymer adsorption; this magnifies the contribution of the second term in the equation given above, especially in non-polar media. In addition, these conformations largely determine the configurational entropy and enthalpy of adsorbed polymers and these, in turn, are needed to calculate the extent of adsorption, experimentally the most easily accessible parameter. Indeed, the problem is to calculate the most probable configuration or configurations of the adsorbed polymer molecules and hence their chemical potential. Equating this potential to the chemical potential of the polymer molecules in the bulk solution gives the adsorption isotherm. However, in aqueous media the surface interaction energy factor, E_i, will be of major importance and the extent of polymer adsorption from solution is determined by the balance of three interactions: polymer with solvent, polymer with surface, and solvent with surface. Necessarily, any modification in surface chemistry, any alteration in polymer structure or change to a different solvent medium will affect at least two of the three interactions. In addition, in many systems of interest in mineral processing, the interaction between a macromolecule (a polymer or a surfactant) and the surface is of major importance and the understanding of attachment mechanisms is then the key problem. Thus, for PEO adsorption, the free energy, ΔG_{ads}, can be described as:

$$\Delta G_{ads} = \Delta G_{H-H} + \Delta G_{HI} + \ldots\ldots$$

i.e., the addition of several contributions among ΔG_{H-H}, the " hydrogen bonding" contribution and ΔG_{HI}, the " hydrophobic interaction" contribution are recognised to be the dominant factors. Of course, the relative importance of these two contributions will be a function of the nature of the surface; but in water the hydrogen bond term is open to dispute. However, there are a number of studies claiming hydrogen bonding between ether oxygen on the polymer and surface site electron acceptors (56, 57, 58). Then, PEO should be adsorbed on to a solid surface if it satisfies at least one of these two interaction mechanisms.

Solids are commonly classified as hydrophobic or hydrophilic with respect to their affinity for water but the terms are used rather loosely in different circumstances - notably in wetting phenomena, vapour adsorption and colloid stability. For example, hydrophilic substances form thermodynamically stable aqueous dispersions and those described as hydrophobic do not. On the other hand, it is believed that adsorption of any polymer must be contingent upon the ability of the polymer molecules to displace water molecules from the " hydrated surface" . Hence, it is suggested that hydrophilic substances because of their high surface energy, would be refractory for PEO adsorption and only a reduction of this hydrophilic character would allow adsorption to take place. So far, a number of studies on flocculation of aqueous dispersions by PEO seem to give support to this hypothesis (59, 53a, 53b). The majority of the solid suspensions amenable to flocculation by PEO may be referred to as hydrophobic (53a, 53b, also Chapter 4).

On the basis of the properties of PEO discussed here, it appears that PEO fulfils the requirements of a polymeric flocculant, the adsorption of which is dependent on hydrophobic interactions. This principle has been tested on a model system (silica) and applied subsequently to other mineral systems.

CHAPTER 3

THE ADSORPTION-FLOCCULATION REACTIONS OF POLY(ETHYLENE OXIDE) AT THE SILICA/WATER INTERFACE

3.1. Introduction

The role of non-ionic polymers such as poly(ethylene oxide) (PEO) in adsorption and flocculation phenomena has already been mentioned. In addition to the nature of the forces of adsorption operating between PEO and an interface (possibly non-specific hydrogen bonding and hydrophobic interactions) an entropic effect should favour the interaction of a PEO molecule with a surface by a gain in free energy due to the water molecules released from the multiple solute (PEO)-water (" ordered") conformations in solution. In other words, there will be an increase in the total entropy of water favouring the adsorption of the solute at the solution/interface (i.e., hydrophobic effect). In addition, the loss in entropy by the polymer in the adsorbed state will be minimum, if its attachment is by relatively few groups (as in bridging flocculation).

The present chapter is concerned with the interaction of PEO at the silica/water interface. A considerable amount of information regarding the adsorption and flocculation behaviour of polymers on silica has been accumulated (4, 62, 63, 64). However, it is essential to consider some of the general principles governing polymer adsorption and its effect on dispersion stability (flocculation). The discussion will therefore be mainly concerned with the behaviour of non-ionic polymers, although some reference will be made to the action of polyelectrolytes on flocculation studies.

3.2. The Adsorption of Polymers at Interfaces

The main problem in polymer adsorption is the investigation of structure and conformation of the adsorbed polymers. The conformation is of particular interest in connection with the influence of adsorbed polymer on dispersion stability. Special attention will be given here to the adsorption characteristics of the polymer at the solid/liquid interface.

When a polymer adsorbs at a liquid/solid interface, the adsorbed molecule adopts a conformation consisting of an alternating arrangement of two-dimensional totally adsorbed trains and three dimensional loops (and tails) projecting out into the bulk solution. Such a conformation represents a compromise between the usual three-dimensional random coil configuration in bulk solution (not precisely so in the case of PEO) and a totally adsorbed randomly twisted two-dimensional molecule. The existence of loops of segments not in contact with the surface of the adsorbent is a consequence of the loss of configurational entropy experienced by the polymer molecule on adsorption.

These considerations account for the following phenomena.

1. The ease with which polymers adsorb at most interfaces. Because of the large number of repeating units in each molecule, polymers adsorb (to some degree) onto nearly any surface. Even if the gain in free energy (i.e., a decrease in the total ΔG) due to adsorption of one unit is small, the decrease in free energy per adsorbed molecule can become very high because of the multiplicity of points of attachment.

2. The " irreversibility" of the adsorption process. Because of the large number of segments in contact with the surface, it is statistically very unlikely that desorption of all the segments will occur simultaneously. However, this fact does not mean that the polymer cannot be displaced. By change of conditions, such as pH or addition of a high concentration of a surface competitor, it is generally possible to displace a polymer that would be completely immune to washing with pure water. In addition, factors tending to make the solution phase a " better solvent" for the polymer will tend to desorb it. Obviously, in all cases, the polymer molecule is gradually eased off by displacement of segments in a random order (65).

3. The adsorption of more than one equivalent monolayer. The mass in excess of an ideal, close-packed monolayer, is accommodated in loops and tails projecting out from the surface. These conformations, which are of great importance in the control of stability-flocculation of dispersions, are somewhat different from its conformations in bulk solution, and, moreover, vary with the

extent of adsorption.

Improved understanding of polymer adsorption can be obtained by comparison with the adsorption characteristics of small molecules. The adsorption of polymer molecules can be expected to differ from that of ordinary low-molecular weight compounds in several ways:

a) The unique physical properties of polymer molecules in solution (or adsorbed at a solid surface) are the direct result of their flexibility, which arises from the freedom of rotation of one chemical bond about another at a constant angle. Thus a long polymer chain containing many hundreds of bonds in the backbone can assume an enormous number of different configurations. Consequently, it possesses, even after adsorption on to a surface, a great deal of mobility which is not typical for small molecules. Indeed, these conformations largely determine the configurational entropy and enthalpy of adsorbed polymers and subsequently influence the extent of adsorption.

b) An individual polymer molecule possesses a greater number of possible adsorption sites than small molecules. The existence of a large number of potentially active groups which may adsorb on the surface leads to a situation where the formation of an attachment between a segment of a polymer molecule and a surface enhances the probability of the adsorption of neighbouring groups of the same molecule to that surface (hence, favouring the formation of " trains").

c) The polymer molecules are relatively bulky (a few hundred to a few thousand Angstrom units in molecular diameter) and they cannot penetrate at all or, at least, penetrate only very slowly (by slow diffusion) into regions of the adsorbent which are partially shielded from the surrounding solution by surface irregularities (or pores). Rate studies on the adsorption of polymer on to porous substrates demonstrates the importance of this factor (66).

Theoretical models. A considerable amount of information on the adsorption of polymers from solution onto solid surfaces has been accumulated since systematic study first began about 30 years ago. The major progress made in recent years has been development of a theoretical treatment of polymer adsorption. Reviews of the major aspects of the theories are available in a number of articles (67, 68, 69, 70). Three main approaches have been adopted. Basically, they all aim to predict how certain thermodynamic and configurational parameters (namely, the mass adsorbed per unit areas (Γ), the fraction of segments in trains (p), and the thickness of the adsorbed layer (δ)) depend on the various variables of the system such as concentration, molecular weight, temperature, solvency, etc. They differ in the mathematical formulation of the problem; but most of them include the following assumptions:

1. The structure of the polymer is represented by a flexible string of monomer units (segments), all of which may adsorb at the interface. The models are restricted to the consideration of isolated polymer molecules adsorbed at an interface.
2. The interface is plane and structureless.
3. The system is in thermodynamic equilibrium (although true equilibrium is unnecessary in studies involving the use of Monte Carlo statistics (71)).

Historically, the different treatments may be classified as follows:

<u>The random walk model theory.</u> Frisch, Simha and Eirich (72), determined the changes in conformation occurring when a typical Gaussian coil was in contact with a reflecting barrier. They calculated the thermodynamic properties of the adsorbed layer, and hence described the adsorption isotherm (in the absence of polymer-polymer interactions):

$$\theta = \beta K c (1 - \theta)^{\beta}$$

where β is the number of adsorbed segments per molecule,
θ is the fraction of sites occupied,
c is the equilibrium solution concentration of polymer, and
K is the adsorption constant.

It may be seen that when $\beta = 1$ (i.e., one adsorbed segment per molecule) the equation reduces to a Langmuir equation:

$$\theta = Kc(1 - \theta)$$

This treatment of polymer adsorption was later modified by Di Marzio (73) and by Di Marzio and McCrackin (74) to account for the correct statistical weight to the monomer units. Di Marzio and McCrackin (74) and later Rubin (75) were able to use the lattice walk model to calculate some of the conformational characteristics of adsorbed polymers.

The statistical mechanical theory. Silberberg (76) and later Hoeve (77) calculated the most probable configuration or configurations of the adsorbed polymer molecules and hence, their chemical potential, on the basis of the concept that polymers are adsorbed in trains loops and tails. Equating this potential to the chemical potential of the polymer molecules in the bulk solution gives the adsorption isotherm. This analysis involved the derivation of the partition function of a macromolecule adsorbed at the surface assuming a quasi-lattice model for the macromolecular surface phase.

In general, the main discrepancy between the Frisch, Simha and Eirich model and the early Silberberg model (1962) was that the latter predicted much higher values of P, the number of equally probable states of an adsorbed polymer. However, there is now considerable agreement concerning this point. These theories have now now been expanded to cover more realistic conditions. Recent work for example, has extended the theory to account for lateral interactions on the surface i.e., at high surface coverages (78, 79). It is in this region of high surface coverage where polymer-polymer interactions are important. They comprise at least two parts : a repulsive interaction arising from excluded volume effects, and an attractive force arising from the van der Waals attractions between atoms. Progress has also been made in analysing the adsorption of polymer in multilayers, the adsorption of polyelectrolytes (80) and the adsorption of polymer molecules, either in slits, or pores, (66) and between parallel plates (81). However, application of these theories to practical systems is not always successful, mainly because of the irreversible character of polymer adsorption leading to frozen-equilibrium states. In addition, there has been no satisfactory theoretical treatment of the kinetics of polymer adsorption.

The diffusion theory. This approach avoids the use of lattice or random walk model and makes use of the diffusion equation approximation (82, 83). Chang, *et al.* (84) have recently used this model to calculate the conformational properties of an adsorbed polymer as a function of the adsorption energy parameter w. An advantage of this approach is that it is more amenable to quantitative analysis than the lattice models. However, it has been observed that, whilst the diffusion equation is valid for polymers in bulk solution, the appropriate initial and boundary conditions are uncertain in the vicinity of boundaries (84, 85). More recently, Chan, Davies and Richmond (85) applied the continuum model to study the properties of an ideal (non-interacting) adsorbed polymer confined between two impenetrable flat surfaces with which it may interact. The segment-surface interaction determined by an adsorption parameter w, was studied to describe the pressure, fraction of segments adsorbed and number density of segments between the plates. Their results are in qualitative agreement with those obtained by Di Marzio and Rubin (81) who used a lattice model.

The major predictions of current theories of polymer adsorption are the following:

1. General predictions:

a) a polymer molecule adsorbs onto a solid surface in two-dimensional trains of segments and in three-dimensional large loops (and tails) protruding into the solvent away from the surface. There is a wide distribution of train and loop (and tail) sizes;

b) the adsorption isotherm has a very steep initial gradient at low solution concentrations and tends to level off, although no actual horizontal plateau is reached and the gradient remains positive.

2. Predictions relating to the adsorbent (i.e., adsorption energy). When the polymer segment interaction with the surface is high, smaller loops with longer trains results; with low adsorption energies, larger loops and shorter trains are favoured.

3. Predictions relating to the polymer:

a) polymer structure; high polymer flexibility favours shorter trains and loops; consequently the mean layer thickness should decrease. The total amount adsorbed should also increase with increasing flexibility;

b) polymer molecular weight; at low surface coverage, the amount of polymer adsorbed increases with molecular weight. The prediction for high surface coverages is similar but other factors, namely, chain interaction and solvency, may modify this behaviour.

4. Predictions relating to the medium.

a) solvency; the amount of polymer adsorbed and the layer thickness increase as the solvency power of the medium is decreased. The fraction of segments in trains, however, decreases with decreasing solvent power;

b) temperature; the prediction is that the temperature coefficient could be positive or negative depending on the way in which other parameters, such as solvency, flexibility, etc. vary with temperature.

In general, most of these predictions are in accord with the experimental results but a rigorous test of these sophisticated theories is lacking. However, it is expected that developments in analytical instrumentation techniques, will soon make possible direct observation of the adsorbed layers. So far, information about the fraction of segments in trains and loops (P) has been obtained by using spectroscopic methods, e.g., IR (86, 87), ESR (88) and NMR (89). Direct measurements of the force of interaction between particles with adsorbed layers, as a function of their distance of separation, have recently reported by Dorozskowski and Lambourne (90) using a surface balance and by Cairns and Ottewill (91) using a compression technique with a concentrated latex. Knowledge about the net interaction energy between the surface and the segments and between the surface and the solvent molecules has been obtained from microcalorimetry (92). Finally, the effective adsorbed layer thickness, a vital parameter which offers some insight into the structure of the adsorbed layer has been measured by a number of different techniques, namely, ultracentrifugation (93, 94), viscometry (95, 96, 97), ellipsometry (98, 99, 100), spectroscopic methods (101) and electrophoresis (101, 102, 103). Combination of the electrical double layer data from electrophoresis and direct surface charge measurements has led to information on the polymer segment distribution between trains and loops (103).

Nevertheless, classical measurements of adsorption isotherms still form the majority of the published experimental data on polymer adsorption. These isotherms are frequently incomplete since the sharp initial gradient makes difficult the measurement at low coverage and, furthermore, the isotherms are time-dependent. Therefore, it is not easy to deduce much about the state of the adsorbed layer. A combination of classical adsorption isotherms together with more direct observation of layer conformation is a more powerful approach. However, for many practical purposes such as the present study adsorption isotherms provide qualitative analysis of the distinct interaction forces governing the adsorption of the polymer on to a solid substrate. Thus, by modifying the adsorption sites, the different responses to polymer adsorption can be measured, permitting some deductions to be made of various attachment mechanisms which may be involved.

Despite all the advances in the theoretical treatment of polymer adsorption already mentioned, the formulation of a thermodynamic model describing the adsorption process still presents many problems, especially in the case of aqueous systems. These arise partly from the difficulty in identifying and defining the various processes involved in the adsorption process (for example, the role of the solvent has often been ignored), and partly because of the lack of reliable experimental data.

A priori, the adsorption of a polymer segment from aqueous solution on to a surface can be written as

$$P + S_{(H_2O)_n} \longrightarrow PS + n(H_2O)$$

where P is the polymer segment, S the adsorption site and n the number of coordinated water molecules around the solid site. Therefore, the free energy of adsorption per segment will formally be:

$$\Delta G_{ads} = (\Delta H_{S-P} - n\Delta H_{S(H_2O)}) - T(\Delta S_c - S_{(H_2O)})$$

where $(\Delta H_{S-P} - n\Delta H_{S(H_2O)})$ is the enthalpic contribution to the adsorption process (commonly referred to as E_i, the surface interaction energy); ΔH_{S-P}, the enthalpy of polymer-adsorbent interactions and $\Delta H_{S(H_2O)}$ the enthalpy of solvent-adsorbent interaction.

ΔS_c is the configurational entropy, which arises from the entropy loss in passing from a three-dimensional random coil to a completely two-dimensional random coil and is of the order of

$$k \ln \frac{C_s}{C_B}$$

where k is Boltzman's constant and C_s and C_B are the surface and bulk quasi-lattice coordination numbers. If $C_B = 2C_s$ this results in an increase in free energy of the adsorbed molecule of approximately 0.7 kT per segment.

$\Delta S_{(H_2O)}$ is the change in entropy due to release of water and T is the temperature in ^{o}K.

It should be noted that polymer-water interactions are assumed unchangeable. This may not be a general case, especially for those sparingly soluble polymers (in water). As mentioned previously, it is believed that polymer adsorption is largely an entropic effect but only a few studies (104, 105, 106) account for the entropy change associated with the displacement of solvent molecules. In addition, the role of solvent-adsorbent interactions in determining polymer adsorption has been ignored. Most of the studies, however, were carried out in non-aqueous solvents where such an interaction may well be negligible. But in many practical systems that make use of polar solvents (e.g., water), adsorbents interact strongly with the solvent molecules.

Finally, in addition to the different approaches concerning the adsorption of polymers at interfaces, in particular the solid/liquid interface, attempts have been made to evaluate the effect of adsorbed layers on colloid stability (107, 108). These theories have been mainly concerned with the calculation of the repulsive force generated when the adsorbed polymer layers on two approaching particles overlap. However, direct testing of these theories is lacking due to the absence of adequate experimental methods for measuring many of the parameters involved. Recent experimental developments (143) give promise that this will soon be possible.

3.3. The Flocculation by Polymers

Terminology. It is desirable to make a distinction between the different terms that define the destabilisation of dispersed particles because confusion is common with respect to the terms coagulation, sensitization, flocculation, etc. In the present study the following nomenclature will be used:

coagulation	to describe the compression or reduction of the electrical double layer thus resulting in particle aggregation.
† flocculation	to describe aggregation by means of polymer bridging mechanism.
sensitization	to describe aggregation of particles by polymers with the aid of small amounts of electrolytes (salts).
aggregation	to describe destabilisation of dispersion by hydrolyzing electrolytes such as ferric or aluminium sulphate. This process can be considered composite in that the polyvalent ions destabilise the dispersion and the precipitated hydroxides provide bonding. Alternatively, surfactants may adsorb at the solid/liquid interface rendering the solid hydrophobic, thus favouring particle-particle adhesion and destabilisation by the attraction between the hydrophobic coatings on the particles and also by the reduction in the area of the hydrophobic solid/water interface.

† It should be noted that certain polymers (polyelectrolytes) destabilise dispersions by means of charge neutralization only (see below).

There has been an increasing interest in the flocculation of dispersions by polymers in the last two decades (106, 67). The interest arises from the many technological processes which make use of polymeric reagents. Their main use is to facilitate the separation of colloidal suspended solids from the liquid phase. Water treatment, disposal of industrial effluents and mineral processing are processes that currently utilize flocculation by polymers for solid/liquid separations either for water purification, recycling of water to the plant, cleaning aqueous effluents before disposal to a water-course, or recovery of solids.

The reason for the use of polymeric flocculant instead of electrolyte coagulants in solid-liquid separations is that the process of flocculation is far more effective than ionic coagulation in giving stronger, faster settling floc and more permeable filter--cakes. Thus the practical aggregation rate is faster and the resultant aggregate (floc) size in a stirred system is far larger and more resistant to shearing than coagula. To a first approximation, sedimentation velocity is proportional to the square of the aggregate radius, and therefore clarification rates are conveniently large for flocculated systems.

The water-soluble polymers used as flocculants include natural products such as starch, proteins, gum guar etc., derivatives of natural products (dextrin, sodium alginate, etc.) and synthetic polymers, such as non-ionic polymers (PEO, polyvinyl alcohol) and polyelectrolytes (ionic polyacrylamides, polyethyleneimine).

Because of the scope of the present study, flocculation of charge-stabilised dispersions by polymers will be considered.

A number of comprehensive reviews of polymer flocculation are available (65, 67, 109) so only a brief description of the main general mechanisms of flocculation will be given here.

Flocculation by ionic polymers. Flocculation on oppositely charged polymer and surfaces. A great number of studies have been made on the destabilisation and restabilisation of negative particles by cationic polymers (110, 111, 112). However, the mechanism or mechanisms of flocculation by polymer have proved to be somewhat controversial (110, 112, 113) and sometimes are not necessarily mutually exclusive; charge neutralisation or bridging (or both) have been proposed as the main factors. It can be said that the neutralisation factor has been mainly supported by the electrophoretic data (111, 112) and the bridging theory by the dependence on the degree of polymerization (110, 113).

a) Charge neutralisation mechanism. Basically, it includes both compression of the electrical double layers due to the added polyelectrolyte (i.e., an ionic-strength effect) and the loss of part or whole of the electrical double layer by specific interaction of the surface charge with the polyelectrolyte. Optimum flocculation would occur when a definite amount of positive charge has been adsorbed by the particles, irrespective of the length of the polymer chain carrying the charge. This mechanism has been postulated to be exclusive, for instance, for the flocculation of negative latex particles by cationic polymers (112, 114). The cationic polymers, differing only in molecular weight, have the same optimum flocculation concentration regardless of molecular weight. In this case, therefore, the bridging mechanism may not be significant.

A possible explanation for the charge neutralisation mechanism has been advanced by Gregory (112) and also by Kasper (115). They have reported that when adsorbed on negative particles, polycations rapidly adopt a flat two-dimensional (patches) configuration because of the strong interaction between oppositely charged groups on the particle surface and along the polymer chain. Kasper (115) has proposed the patch model and derived a mathematical model for flocculation of suspensions by polymers having the opposite charge to that on the particle surface. According to this theory flocculation occurs when a polymer patch on one particle comes in contact with a " fresh" surface on another. These polymer patches have a high charge density of opposite sign to the particle surface and therefore adsorb on contacting the " fresh" surface. Finally, the particles are then held together by the polymer patch adsorbed on to both of them. It is then suggested that although particles end up " bridged" by polymer, the main factor causing aggregation is electrostatic attraction. However, the equilibrium configuration of an adsorbed polymer chain is achieved at some finite time after initial contact, and during this time, the distribution of polymer segments from the particle surface is more extensive than in the equilibrium state, so that bridging may be possible. Moreover, it is worth pointing out that the concepts of " patchwise" adsorption and the flat configuration of adsorbed polycations are applicable only to particles which are larger than the polymer molecules. Clearly, with long polymers (high molecular weight) and very small colloidal particles, these assumptions would no longer apply.

b) Polymer bridging mechanism. The concept of bridging between particles is well established in non-ionic polymer systems (see below) but has also been applied in systems of particles and polymer of opposite sign (110). Lindquist and Stratton (116) studied the flocculation of silica by polyethyleneimine and found that the relative importance of polymer bridging and charge neutralisation was pH-dependent. Thus, at pH 9 and above, polymer bridging is the dominant mechanism (due to the low cationic charge of the polyethyleneimine). However, at pH less than 9, charge neutralisation between the polymer and silica is the dominant factor.

Other investigators (117, 111, 118) have found that the mechanism of action of polyelectrolytes is a combination of polymer bridging and charge neutralisation.

As may be seen, systematic analysis of the data is complicated and no generalizations can presently be made. The polyelectrolyte charge and particle charge on aggregation have not been properly evaluated and, therefore, the information given has never been sufficiently complete to allow a satisfactory physical interpretation of the results.

Flocculation of similarly charged polymer and surface. The adsorption of negatively charged polymeric groups on to negatively charged surface is a common phenomenon in colloid science (119, 120). All that is needed for polyelectrolyte adsorption onto a surface of the same sign is for the Coulombic repulsion to be counteracted by another interaction of chemical or electrical origin. Mechanisms for the attachment of polyanions onto anionic surfaces that have commonly been considered (121) are van der Waals forces, hydrogen bonding, anion interchange with adsorbed anions (such as OH^-), or the interaction with cation on the surface.

Slater, Clark and Kitchener (122) studied the flocculation of quartz (negatively charged) by an anionic polyacrylamide in the presence of copper sulphate as a function of pH. They reported that for any given concentration of copper there is a limiting pH above which cupric hydroxide precipitates and the particles of $Cu(OH)_2$ being positively charged, mutually coagulate with the quartz and the system then become strongly susceptible to flocculation by anionic polyacrylamides. Actual " activation" by Cu^{++} ions occurred over a narrow range of pH and copper ions. Thus, they ion-exchange with the quartz surface and may also form complexes with the carboxylate groups of the polyelectrolyte. Kuz'kin and Nebera (123) have postulated that the presence of electrolyte is to act to screen the Coulombic repulsion between the particle surface and the polyelectrolyte, rather than act as a " bridging" link between two charged particles. Somerauer, Sussman and Stumm (121) investigated the flocculation of negatively charged silver bromide sols by negatively charged poly(acrylic acid), polyacrylamide and poly(styrene sulphonate). They concluded that flocculation occurred only in the presence of a suitable electrolyte (e.g., a calcium salt) which acts as an electrostatic bridge promoting the adsorption of the polymer through complex formation with its functional groups at, or near, the surface. The polymer chains themselves finally form bridges between the colloid particles (polymer bridging flocculation). Sarkar and Teot (124) studied the flocculation of polystyrene lattices by Na-polystyrene sulphonate, in the presence of multivalent cation at low pH. They suggested that the flocculant is a " neutral" complex of the cation/polyelectrolyte, but that a minimum excess cation concentration is required before flocculation occurs. Contrary to Sommerauer, <u>et al.</u> for their closely related system, they excluded the bridging mechanism as the operating mechanism. Indeed, several mechanisms may be operating along with polymer bridging, but generally bridging is the dominant mechanism in flocculation by polymer of the same sign as the particles and many features correspond to those occurring in flocculation by neutral polymers.

<u>Flocculation by non-ionic polymers.</u> As already mentioned the concept of polymer bridging offered by La Mer and co-workers (64) is well established in non-ionic polymer systems. Basically, it is postulated that the flocculant interferes with the free movement of the particles, either by adsorption of a number of particles on a polymer network, or by the formation of long bridges between particles which otherwise might not meet so readily by diffusion or free, or forced, convection. The considerable extension into solution of the adsorbed polymeric molecules, which results in the formation of such large, polymerically bridged aggregates (flocs), renders consideration of surface charge and potential repulsion almost unnecessary. This is because particles can be polymerically bridged while they are still at sufficiently large separation distances that the interparticle forces are negligible. Consequently, in certain systems it is possible to flocculate a well stabilised dispersion without the need to eliminate the electrical double layer (65). Bridging

occurs at low surface coverages because only then is free surface readily available on which adsorption of loops of molecules attached to other particles may occur.

Understanding of the mechanisms by means of which a polymer molecule becomes attached to a surface is of fundamental importance. Non-Coulombic interactions are obviously particularly important with non-ionic flocculants and protective colloids such as starch and gums, but no detailed study has been reported on the different adsorption forces which may be operating. Fleer and Lyklema (125) have studied the flocculation of silver iodide sols with polyvinyl alcohol (PVA) and found that adsorption of PVA on the surface of the particles was irreversible. No mechanism of adsorption was advanced but it is believed that the hydrocarbon chains of the polymer are probably held to the hydrophobic surface of the silver iodide by hydrophobic interactions. Accordingly, the hydroxyl groups should be oriented toward the aqueous solution. A similar mechanism may be responsible for the adsorption of poly(ethylene oxide) (PEO) on AgI (126). The adsorption isotherm was shown to be at high affinity type, reaching a plateau at high PEO concentration.

Tadros (4, (1974)) studied the adsorption of PVA alone and in combinations with cationic and anionic surfactant on the surface of precipitated silica (BDH). He reported that the adsorption of PVA on silica is reversible and that it occurs mainly at low pH where the hydroxyl groups of PVA apparently form hydrogen bonds with uncharged silanol groups on the silica surface. On the same basis, Mountvala, et al. (127) reported that when PVA is adsorbed on the hydroxylated surface of alumina, it may displace the hydrogen-bonded water layer so that a monolayer of polymer is held directly to the hydroxyl surface by hydrogen bonding with the hydroxyl group of PVA.

However, no systematic study has been made to elucidate the mechanisms by which a non-ionic polymer become attached to the oxide/water interface. Accordingly, on the basis of the reasons stated in Chapter 1, the present study is aimed at identifying the mechanism by which a typical non-ionic polymer, poly(ethylene oxide) behaves at the silica/water interface. The role of the structure of the silica surfaces and pH on the adsorption-flocculation by PEO are the main variables to be studied.

3.4. Experimental Materials and Techniques

Experimental materials. Reagents. All standard reagents used in this study were of analytical grade. All solutions were prepared with double distilled water having a resistivity of less than 1 x 10^6 ohm.cm. The pH of the water, however, was approximately 5.5 ± 0.1, indicating the presence of some dissolved CO_2. All pH measurements were made with a combined glass calomel electrode in a Pye Unicam, PW 9418 pH meter (Philips). The glassware was cleaned with NH_4OH, chromic acid, tap water in that order. Pipettes were rinsed for some hours with tap water. Finally, all glassware was rinsed thoroughly with distilled water.

Poly(ethylene oxide) : The poly(ethylene oxide) used in this study was " Polyox-Coagulant" , a commercial product from Union Carbide, supplied by B.D.H.. The polymer solutions of this product were prepared with water free of CO_2 and O_2 (distilled water boiled and purged with N_2) and kept in a refrigerator to prevent bacteria growing during its storage period of one week. Solutions were randomly checked for polymer activity using the analytical procedure based on tannic acid (see Appendix 1). Potentiometric titrations showed that the poly(ethylene oxide) did not contain acid or basic groups and, therefore, did not acquire charge due to dissociation. Therefore, poly(ethylene oxide) should be referred to as strictly non-ionic.

Silicas. Hydrophobic silica. The material used was Aerosil R-972 supplied by Degussa, Frankfurt. According to the manufacturers (18) the diameter of the primary particles is 10-30 Å, the SiO_2 + ($-CH_3$) content is > 99.8% and the carbon content 1.1% ± 0.2%. The carbon content arises from the methylation (with dimethyldichlorosilane) of almost 70% of the silanol groups in the ordinary silica surface.

" Flame Silica" (" Cab-O-Sil M5" from Cabot Corp.). This Cab-O-Sil is stated by the manufacturers to consist of 99.9% SiO_2, with an ultimate particle size of 30-150 Å. The Cab-O-Sil M5, like other Cab-O-Sil (128) is non-porous and has according to Hair and Hertl (129) a value of 1.7 OH groups/100 $Å^2$ (when fresh), based on reaction of Cab-O-Sil with methanol. This corresponds to about 25% of a fully hydroxylated surface (7.9 OH groups/100 $Å^2$). Thus, the

Cab-O-Sil M5 surface consists of both siloxane (Si-O-Si) as well as silanol (Si-OH) groups.

Precipitated silica. The silica sample was BDH " precipitated silica" . The exact preparative technique is unknown, but it is believed that is produced by the addition of acid to sodium silicate under controlled conditions to give a hydrated silica, followed by washing and drying. The structure of the BDH silica has been studied (130, 131) by gas adsorption, tritium exchange, and dissolution rate methods. It has been found that BDH silica does not present physical porosity when studied by gas adsorption (131) but once in water, the interface appears to be permeable to proton and counterions (131). It has been suggested that this fact indicates the presence of a surface gel layer of polysilicic acid (131). Further details on the surface characteristics of BDH precipitated silica will be examined and related to its behaviour towards adsorption and flocculation by PEO.

Experimental techniques. Preparation of silica stock dispersions.

a) Hydrophobic silica. A reproducible well-stable colloidal dispersion could be obtained by applying ultrasonic vibration in an aqueous dispersion of Aerosil R-972 with a little ethanol which was added as a wetting agent (3 ml in 1 ℓ). The role of the ethanol was to get the powder amenable for wetting and further dispersion. As the alcoholic content is quite low, its influence on the surface properties of the silica it is assumed to be negligible, and its possible effect on colloidal stability was checked. Table 1 shows the effect of different concentrations of ethanol on the dispersion stability of silica as a function of time. The suspensions contained 0.05 wt. % silica. The stability of the dispersion was measured by the optical absorption as a function of time. Apparently the dispersions were unaffected by changing from 0.2 to 0.4 g/100 ml of alcohol.

Table 1

Transmittance of hydrophobic silica dispersion as a function of the alcohol content

T is the optical transmission at λ = 540 μm after 5 minutes or 24 h standby.

Test No.	C_2H_5OH (g/100 ml)	% T (5 min)	% T (24 h)
1	0.4	89	89
2	0.4	89	89
3	0.3	88	88
4	0.3	88	88
5	0.2	88	88
6	0.2	88	88

The silica prepared with the lowest alcoholic content (0.2 g/100 ml, test 6) was used in all the experiments which follow.

b) Hydrophilic silicas. Flame and precipitated silicas were dispersed by the same procedure described above without addition of ethanol. In addition to silicas, some experiments were made with a fractionated sample of high purity powdered quartz (< 27 μm). In part of the work the various silicas were pre-treated by heating or " ageing" in water, as detailed later.

Surface areas were determined by the dynamic one-point BET method, using a " Monosorb" surface area analyzer (Quantachrome Corp.). Values were reproducible to about 1% and differ from full N_2-BET values by less than 5%. The results are summarized in Table 2 .

Adsorption measurements. Carefully stoppered flasks containing known amounts of adsorbents and polymer solution were shaken for 4 hours at room temperature and the silica then separated from the

Table 2

Specific surface areas of silicas and influence of heat treatment (24 h)

Form of Silica	Temp. of Heating (^{o}C)	Surface Area (m^2g^{-1})
Flame silica (Cab-O-Sil M5)	-	171
	500	167
	700	156
	880	115
	930	103
	1030	94
Hydrophobic silica (Aerosil R-972)	-	98
Precipitated silica (BDH)	-	73.3
	350	72.4
	500	69.2
	700	61.1
	800	49.1
	940	9.6

supernatant by centrifugation at 900 g. Supernatants were analyzed for polymer concentration by a nephelometric method based on tannic acid--PEO product in the presence of sodium chloride (44). All isotherms were found to be of the typical form for polymers, having a steep initial rise in polymer adsorption followed by a nearly (but not quite) level " plateau" region.

Flocculation measurements. Flocculation tests were carried out by an arbitrary, but standardized, routine. The very dilute flocculant solution (also, the electrolyte and surfactant solutions when used) was run into a well-stirred silica suspension which was then left to stand for 1 h. The optical absorbance of a sample of the supernatant liquid was then determined and compared with that of a blank to which no flocculant was added. A E.E.L. absorptiometer at 450 μm was used in all the experiments. Results are then reported as

$$\text{" relative adsorbance" } (A_r) \equiv \frac{\text{absorbance of test sample}}{\text{absorbance of blank}}$$

Thus a relative absorbance of 1.0 indicates that the added reagent did not affect the stability of the suspension, whereas strong flocculation is indicated by a low value of A_r, approaching zero, because flocs have formed and settled out (102, 125).

3.5. Results and Discussion

The stability of aqueous hydrophobic silica dispersions. The stability of hydrophobic silica dispersions was compared with that of hydrophilic silica.

Coagulation studies. The effect of pH and NaCℓ on the stability of hydrophobic silica was studied. A spectrophotometric determination (absorbance) of the supernatant after addition of reagent was used, the tests being made in cylinders of 50 ml. Figure 1 show the effect of pH on the stability of silica. In the same Figure, results on the ζ-potential values as a function of pH for a hydrophobic crystalline silica, obtained previously (60), are inserted to establish qualitative correlation. As expected according to previous results (132), the methylation of silica restores the theoretical relation of stability on pH, the hydrophobic sols being " stable" only in the zone where at least a " minimum" surface potential is found (between 25 and 35 mV). Figure 2 represents the critical coagulation concentration (ccc) values obtained for NaCℓ at different pH values according to the previous method. In this case, a ccc value means the minimum concentration of NaCℓ required to promote coagulation, determined by the spectrophotometric method, considering A_r 0.7 as the minimum value for coagulation. In the same Figure, similar values previously reported (133, 134) on hydrophilic silicas (a flame-hydrolyzed silica (AEROSIL) (133) and colloidal silica (Ludox) (134) are included for comparison. Thus, it is seen that contrary to hydrophilic silicas, the stability of hydrophobic silica increases with pH and decreases with the concentration of NaCℓ. It is therefore concluded that hydrophobic silica follows a DLVO colloid

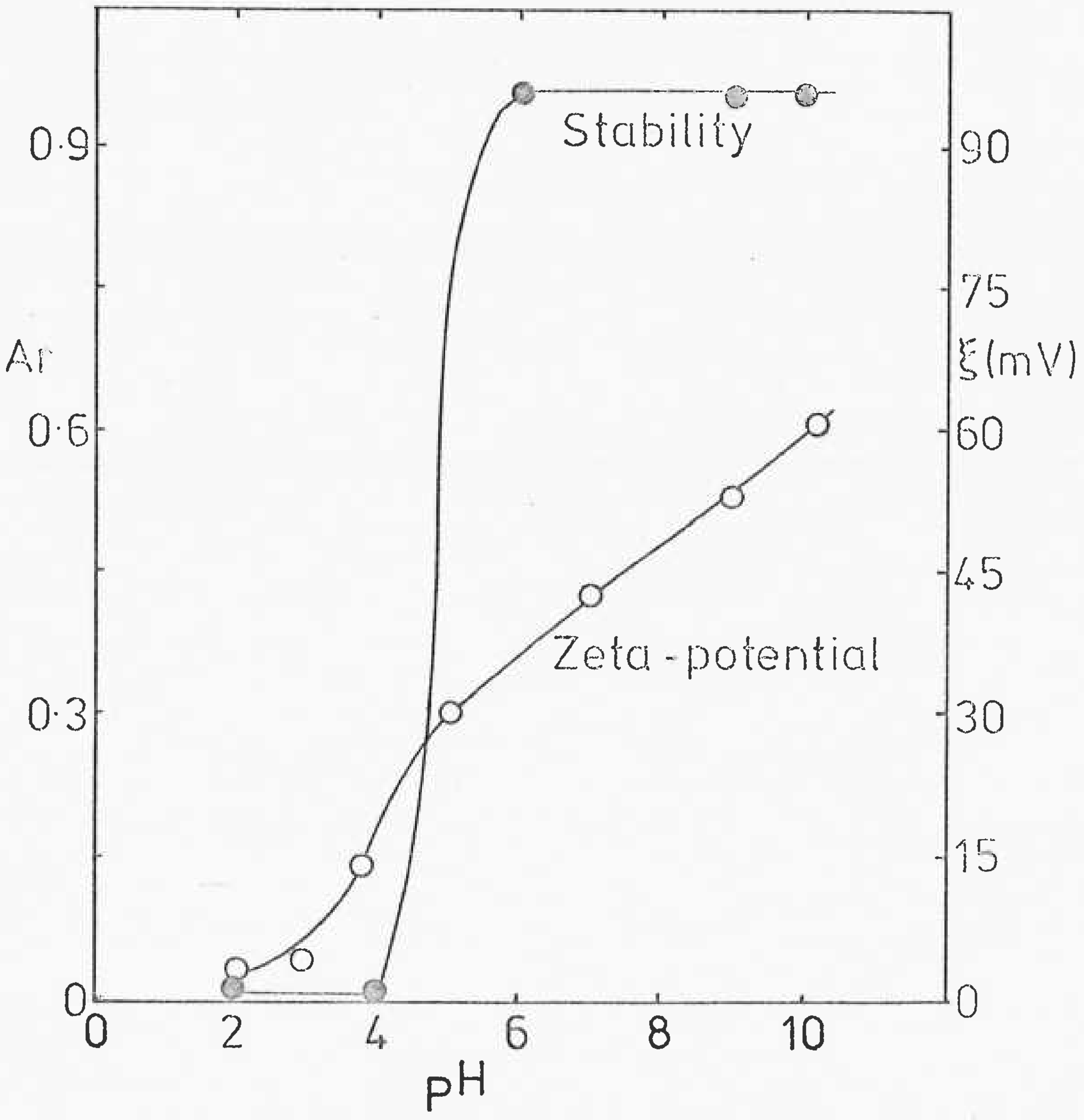

Figure 1

Correlation between stability and ξ potential in aqueous dispersions of hydrophobic silica as a function of pH (A_r = relative absorbance of dispersion after 1 h)

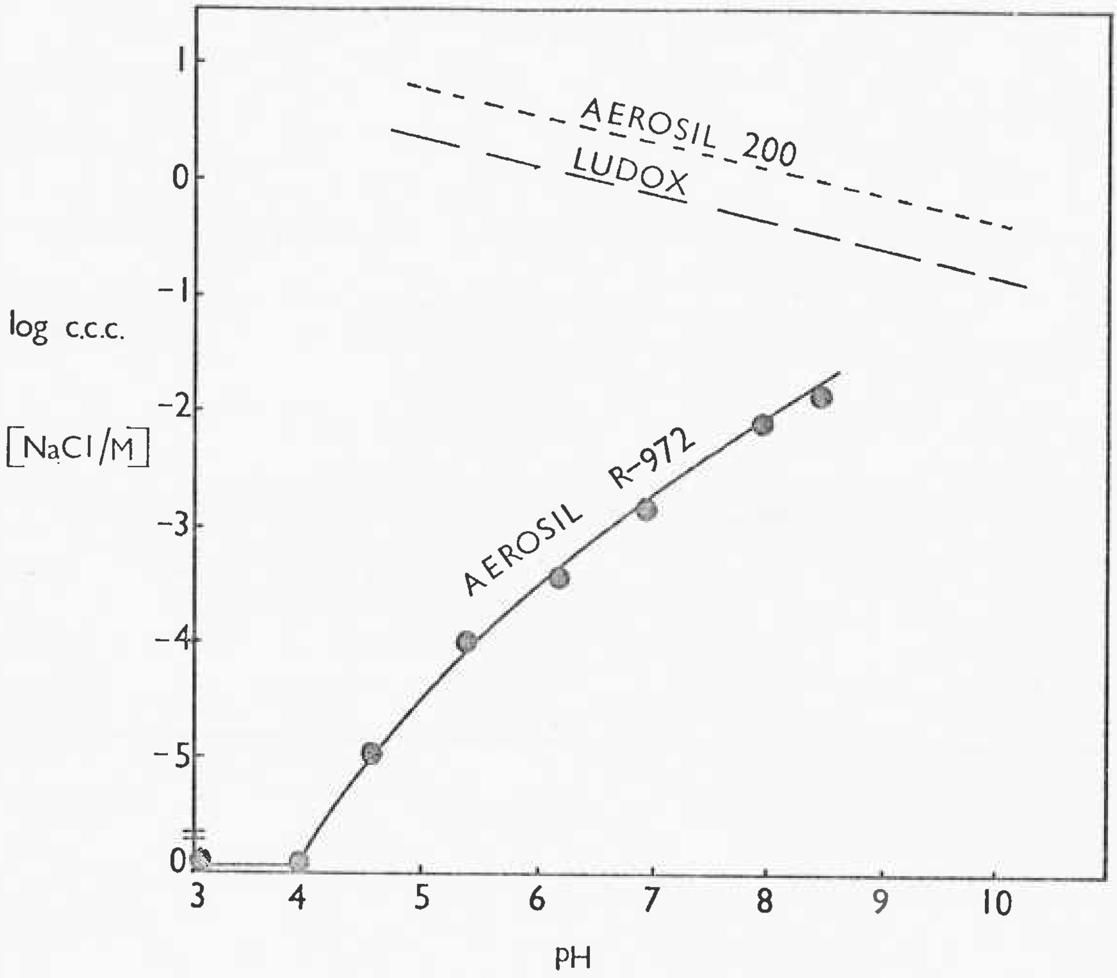

Figure 2

Critical coagulation concentration (c.c.c.) of silicas in the presence of NaC*l* as a function of pH.

behaviour and hydrophilic silicas do not.

As stated by Kitchener (135) there have been endless confusion in the literature concerning the extraordinary stability of silica sols towards electrolytes. The mechanism of coagulation by salts has been investigated for about 60 years and is not yet fully understood. However, several theories have been advanced recently and they are briefly discussed here:

1. The hydrophilic-hydrophobic transition theory. Allen and Matijević (134, 136) have examined the coagulation of colloidal silica (prepared by acidification of sodium silicate) in the pH

range of 6 to 11 and found that the cation of coagulating salt ion-exchanges with the silanol surface proton. The coagulating effect of various electrolytes was correlated with the number of ion equivalents that are ion-exchanged, rather than the valence of the ion. They proposed that with every cation adsorbed, the silica surface loses one silanol site for hydrogen bonding with water, and in that sense is " dehydrated" , It is proposed that this increasing " hydrophobic" character renders the silica strongly susceptible to coagulation by electrolytes. On this theory, hydration is reduced by ionization, the latter being a function of solution pH and salt concentration. However, there is evidence that the opposite may occur. A priori, ionized groups are always more hydrophilic than non-ionized and as general phenomenon, ionization of any solid surface reduces the contact angle at the solid/liquid/air interface and at the solid/liquid/liquid interface (60, 61).

2. Direct " interparticle" bonding instead of dehydration has been proposed by Depasse and Watillon (137) as the mechanism of " coagulation" of amorphous silica by simple electrolytes. They proposed temporary acid-base bonds between particles represented as ——Si—OH----OSi—— instead of direct Si-O-Si (siloxane) because the coagulate redissolves when acidified. At pH 7 to 11 and above certain critical concentration of various electrolytes, coagulation occurs because the particles become initially linked together by acid-base bonds. However, above pH 11, sodium and lithium salts continue to cause coagulation but potassium, rubidium and cesium salts do not. Depasse and Watillon have proposed that sodium or lithium may act as interparticle bonding agents because at this pH value the particles fully covered with basic groups, would not be able to form acid-base bonds. A somewhat different hypothesis has been postulated by Iler (138). He proposed that all the univalent cations are adsorbed and can act as bonding agents but above pH 11, the larger K, Rb and Cs form a complete double layer of sufficient thickness around each particle to cause dispersion and prevent aggregation.

3. The bridging mechanism. It has been suggested by Iler (138) that the adsorbed cations of simple univalent electrolytes may act as " bridging factors" in the coagulation of silica in a

similar way as the larger polycations such as those of basic ferric or aluminium salts. Thus when a sodium ion is adsorbed on the surface of a silica particle, one or more of the oxygen atoms of the water of hydration can be displaced by the oxygen of the surface silanol groups which become linked directly to the sodium ion. The positive charge of the sodium ion neutralises the negative charge of the adjacent adsorbed hydroxyl ion which is responsible for the surface charge and a neutral adsorption complex is formed, i.e., a type of Stern layer. At a certain electrolyte concentration, a second silanol groups on the surface of a second colliding particle displaces the water associated with the outwardly disposed side of the sodium ion and thus the bridging between two silica particles is established. Coagulation takes place when more than one such bridge per particle occur. As the bridging distance of the sodium atom is only one or two Å units, with smaller similar particles the bridged contact area should be a larger fraction of the total silica surface area. Thus the critical amount of sodium ion-exchange in milliequivalents per unit area at the c.c.c., should be greater with smaller particles. Therefore it is assumed that for this bridging mechanism to occur, the amount of adsorbed or " ion-exchanged" coagulating cation per unit surface area of silica should decrease with increasing size of the silica particles. However, no experimental data have been reported in support of this theory. Rather, a recent work of Iler (139) on the mechanism of coagulation of colloidal silica by calcium ions showed that the c.c.c. of calcium ions in solution required to coagulate, increases with decreasing particle size, but for coagulation to take place, a critical number of calcium ions must be adsorbed per square unit area of silica surface, independently of particle size. Thus according to this author, to attain this degree of adsorption, a higher concentration of calcium must be maintained in solution when the particle are smaller. It is noteworthy, however, that reported coagulation results on a flame-hydrolyzed silica (132) showed that larger silica particles, that is, 50 μm (diameter), behave in accordance with the double-layer theory, but the behaviour of the small particles (12 μm) cannot be explained by the conventional theory and showed the usual anomalous resistance to coagulation by electrolytes.

4. The gelation mechanism. When silica is precipitated from aqueous solution at ordinary temperature it behaves as an open, random network of partially cross-linked chains which is incapable of condensing by dehydroxylation into quartz (for kinetic reasons). Thus the swollen gels will have extended chains of polysilicic acid branching out into the medium (135). It was suggested by Kitchener (135) that coagulation of colloidal silica is brought about by adhesion of the polysilicic acid chains, through chemical condensation, which is catalyzed by OH^- ions. As a result, polysilicic acid chains can join together, forming interparticle bridges. This theory seems to explain qualitatively several facts which are not very well understood, namely, pH effects, peptization, cation specificity. Thus several items of experimental evidence give general support to this theory:

i) Quartz suspensions with the same chemical composition of silica are readily coagulated by electrolytes, i.e., it behaves as lyophobic systems at high and at low pH (135, 140). However, a quartz which is " aged" in water is significantly more stable towards coagulation by electrolytes (135, 140). This is believed to be due to the formation of a coating of silicic acid over the quartz; the silicic acid is derived from active fragments generated by grinding. In addition, stability of the quartz at low pH is promoted by sufficient addition of sodium silicate to generate super--saturated silicic acid.

ii) The BDH precipitated silica exhibits a very stable foam when shaken in water (131). This foam was not observed on samples heated above 500°C (131). On the other hand, it is suggested that a gel layer of incompletely condensed polysilicic acid is present at the surface of the same silica (131). Correspondingly, there was found no evidence of a gel layer on the heated samples (131). In the present work, it was found that BDH precipitated silica which was heated at 880°C for 24 hours behaves as a classical DLVO colloid with respect to coagulation by electrolytes as a function of pH, and the untreated sample do not. Similarly, Tschapek and Torres-Sanchez (140) have reported that amorphous (AEROSIL) silica behaves contrarily to the predictions of the DLVO theory of colloid stability whereas the heated sample (at 1100°C, no time recorded) behaved accordingly.

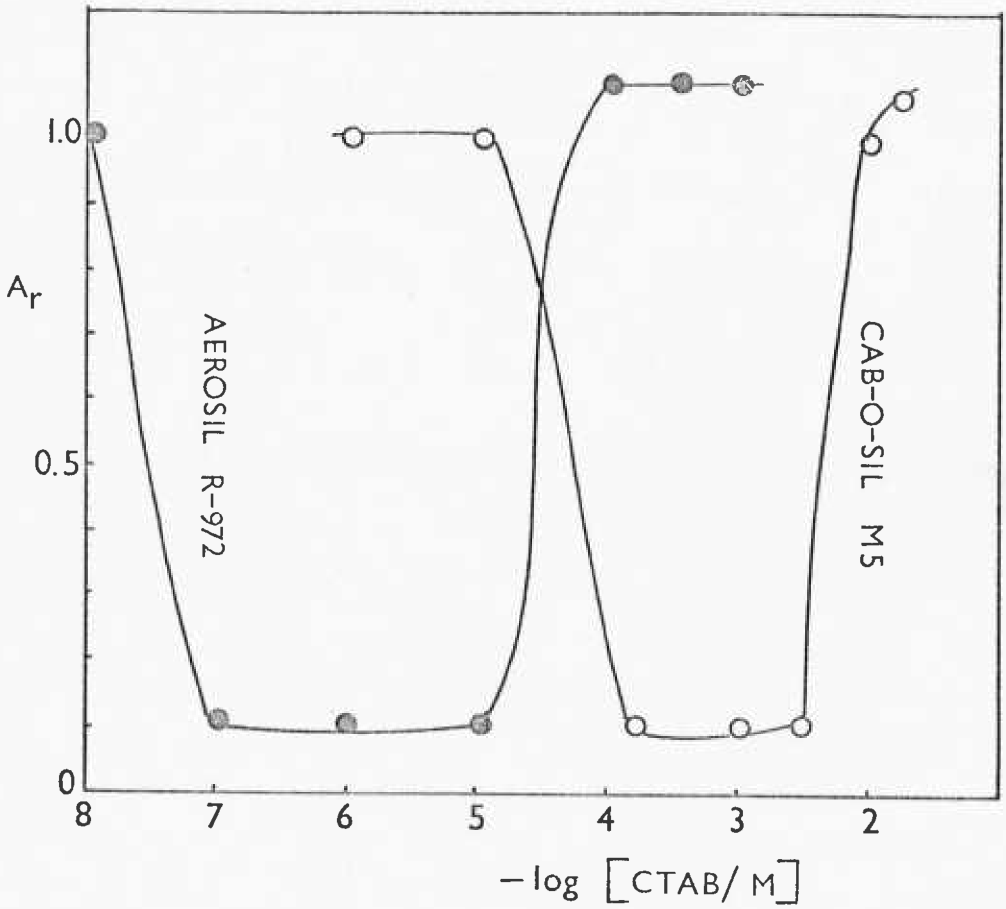

Figure 3

Stability of silicas in the presence of CTAB at pH 5.5

Aggregation by surfactants. CTAB (cetyltrimethylammonium bromide) was chosen as an example of a cationic surfactant. Results obtained using the same method as before are shown in Figure 3. The destabilisation concentration is smaller by a factor of a thousand or more than those obtained with NaC*l* and after a certain concentration no more aggregation is observed. Results obtained with Cab-O-Sil M5 are included in the same figure for comparison. Destabilisation--restabilisation have been found for both forms of silica. Aggregation was obtained at smaller concentrations for hydrophobic silica by a factor of about a thousand. Besides, just where hydrophobic silica is restabilised, aggregation of hydrophilic silica begins. Nowadays, there is no doubt that aggregation occurs when the detergent is adsorbed on the silica with the polar group oriented toward the surface, so that the outwardly disposed hydrocarbon chains make the surface hydrophobic. The silica particles may then be aggregated by hydrophobic interactions (133, 141); however, if more surfactant is present at a concentration near the c.m.c., then a two-fold layer is formed, so that the outwardly disposed cations render the surface hydrophilic again (142). The picture for hydrophobic silica can be rather different in terms of the concentrations required, i.e., hydrophobic silica needs only a few CTA^+ adsorbed molecules to render the surface completely hydrophobic. This fact could explain the very low concentration needed for aggregation of the particles and the earlier restabilisation.

Sodium lauryl sulphate was used as example of an anionic surfactant. No aggregation was observed at any concentration between 10^{-5} and 5×10^{-5} M. This phenomenon is probably due to the electrostatic repulsion between the sol and the surfactant. However, Ruppretch (57) has found adsorption of sodium lauryl sulphate on to hydrophobic silica, the adsorption probably being through the alkyl chain of the detergent and the methyl groups on the silica. Thus, for the concentration used here, the surface becomes more hydrophilic even and no aggregation of the particles takes place.

Flocculation by polymers. PVA (125,000 mol. wt.), PAM (non-ionic pure polyacrylamide) 10^6 mol. wt. and PEO (Polyox--coagulant) of about 5×10^6 mol. wt. were the polymers tested. Results are shown in Figures 4 and 5. As may be seen in Figure 4, PEO is the most effective flocculant for hydrophobic silica, PVA and PAM showing effect only in the presence of NaC*l* (see Figure 5). Particular attention has been paid on the PEO-silica system. A priori, it would seem that because PEO contains strong electron donor groups, namely, the oxygen of the ether group, these may be held to the silica surface by hydrogen bonds, the reaction occurring with the silanol groups still present on the surface. But, in addition, a further contribution may be obtained, i.e., a hydrophobic interaction between the surface CH_3 groups and the CH_2 groups of the polymer. The very hydrophobic character of the flocs which float on the air/water interface and remain on the oil/water interface offers experimental evidence supporting this idea.

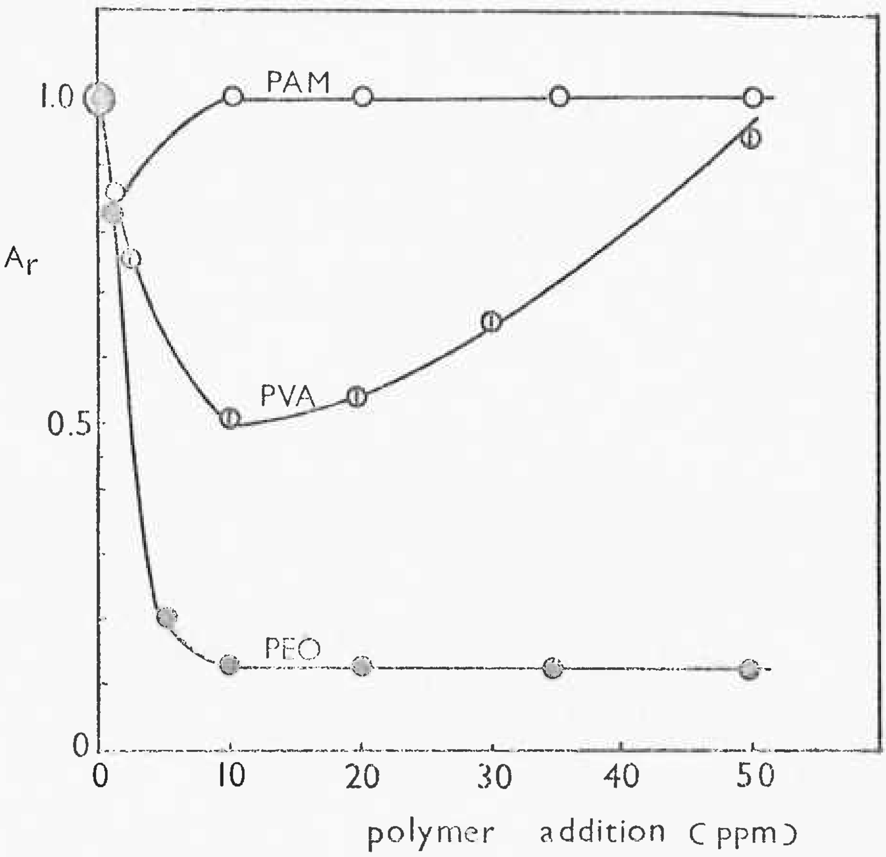

Figure 4

Flocculation of hydrophobic silica by polymers (pH 5.5)

The performance of hydrophobic silica and the differences in behaviour with respect to hydrophilic silicas toward the adsorption and flocculation reactions by PEO will be extensively studies here.

Silica dispersions present an especially suitable substrate for study because it is known that small changes in the surface condition of the silica can greatly affect the adsorption. A connection therefore must be sought between the strength of the adsorption of polymers and the chemical structure of the surface of the adsorbent. Thus Griot and Kitchener (62) reported that high molecular weight polyacrylamide (PAM) is a good flocculant for fresh suspensions of " Aerosil" (a flame-hydrolysed silica) but not for " aged" suspensions or for precipitated silica. Nevertheless, it was shown

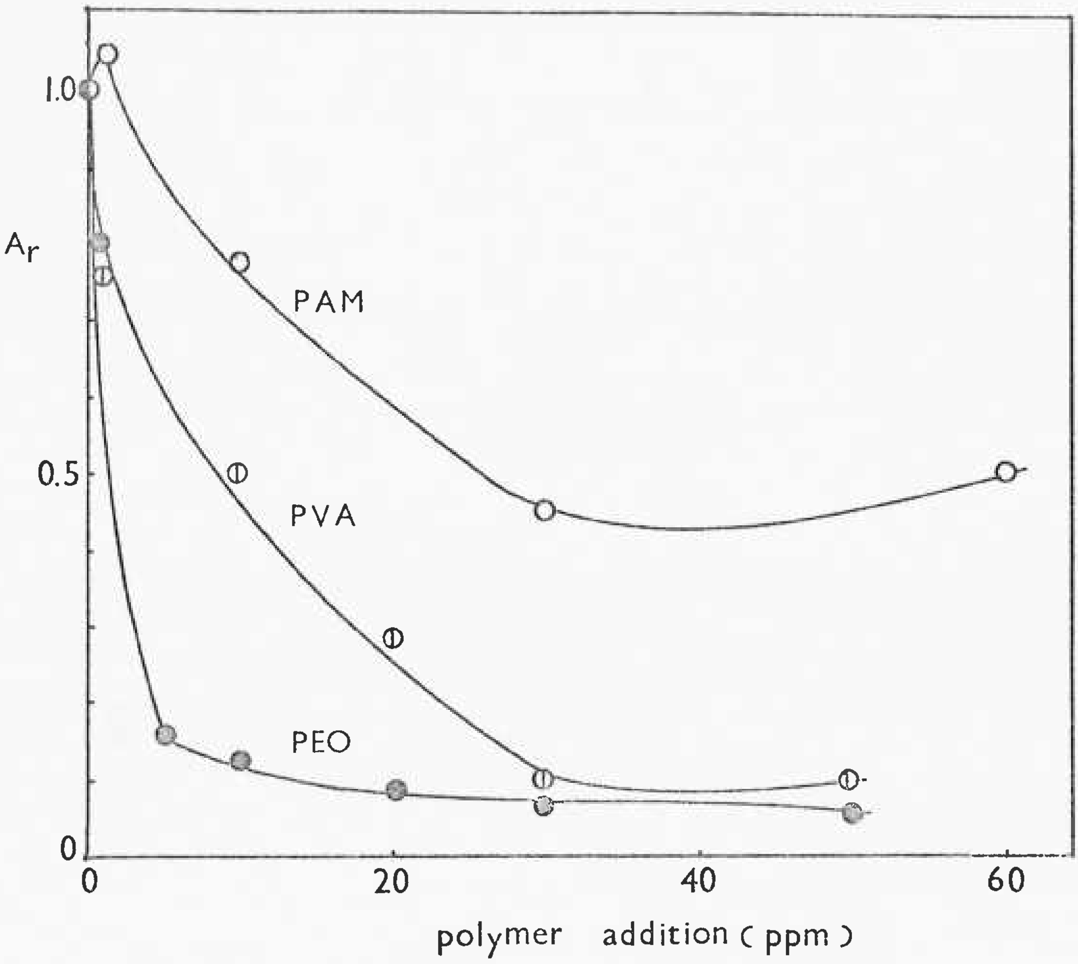

Figure 5

Effect of 10^{-4} M NaCl addition on the flocculation of hydrophobic silica by polymers (pH 5.5)

that precipitated silica became sensitive to flocculation if it was first subjected to heat treatment (e.g., at 730°C) before the flocculation test. These results were correlated with changes in the adsorption of the polymer and with alterations in the infrared spectra of the silicas. A somewhat similar phenomenon was reported by Greenland (63) with polyvinylalcohol (PVA) and hydrophilic silica, and this system was subsequently studied by Tadros (4) who recorded its dependence on pH.

The poly(ethylene oxide) chain, $(CH_2-CH_2O)_{\overline{n}}$, is usually considered as the hydrophilic, non-adsorbed, unit in conventional non-ionic surfactant; clearly, the ether groups are responsible for the solubility of the PEO, operating as hydrogen-bond acceptor to water.

But as discussed in Chapter 2, the $-CH_2CH_2-$ groups in PEO are sufficiently hydrophobic to lead to physical adsorption at various interfaces. In an aqueous medium, the bonding between surface silanol groups and ether groups, i.e., $-SiOH\cdots O(CH_2CH_2)=$ (hydrogen bonding), will be reduced by competition from water molecules. Thus the extent of adsorption of PEO on to silica will be a function of the relative adsorption affinity of sites for water or $O(CH_2CH_2)=$ units. The effects of methylation, pH ionic strength and heat treatment (as methods for varying the structure of silica) on the extent of flocculation and adsorption by PEO were studied.

The silica-PEO system. Flocculation results. Figure 6 indicates that whereas flame silica and hydrophobic silica in distilled water are strongly flocculated by PEO, precipitated silica is only weakly affected. All three silicas are restabilised by an excess of polymer. In Figure 7(a) flocculation results are given for a constant dosage of 11.4 ppm of PEO, over a range of pH values. All three silicas are strongly flocculated at pH 2 (which is the accepted pzc); but each has a critical pH above which it begins to lose sensitivity to the flocculant. Precipitated silica is seen to be virtually non-flocculable at pH > 8. A sample of precipitated silica, which was flocculated at pH 2, deflocculated when the pH was raised to pH 6. Analysis confirmed that the PEO was simultaneously desorbed in approximately quantitative agreement with the direct adsorption isotherm. This provides some evidence for reversibility of the polymer adsorption. The broken line in Figure 7(a) shows that in presence of 0.02 M $NaCl$ flocculation of precipitated silica is enhanced, but the general effect of pH remains. This proves that the pH effect is distinct from any ionic strength effect, and must be a true acid-base reaction of the silica surfaces.

Nevertheless, the flocculation is improved by increase of ionic strength, as shown by Figure 8 for precipitated silica at pH 5.9, with 11.3 ppm of PEO. Under these conditions, complete flocculation of precipitated silica was obtained by adding 0.09 M $NaCl$ (or more), 0.003 M $MgSO_4$ or 0.0009 M $LaCl_3$.

Adsorption results. Figure 9 shows adsorption isotherms for conditions comparable with those used in the flocculation measurements

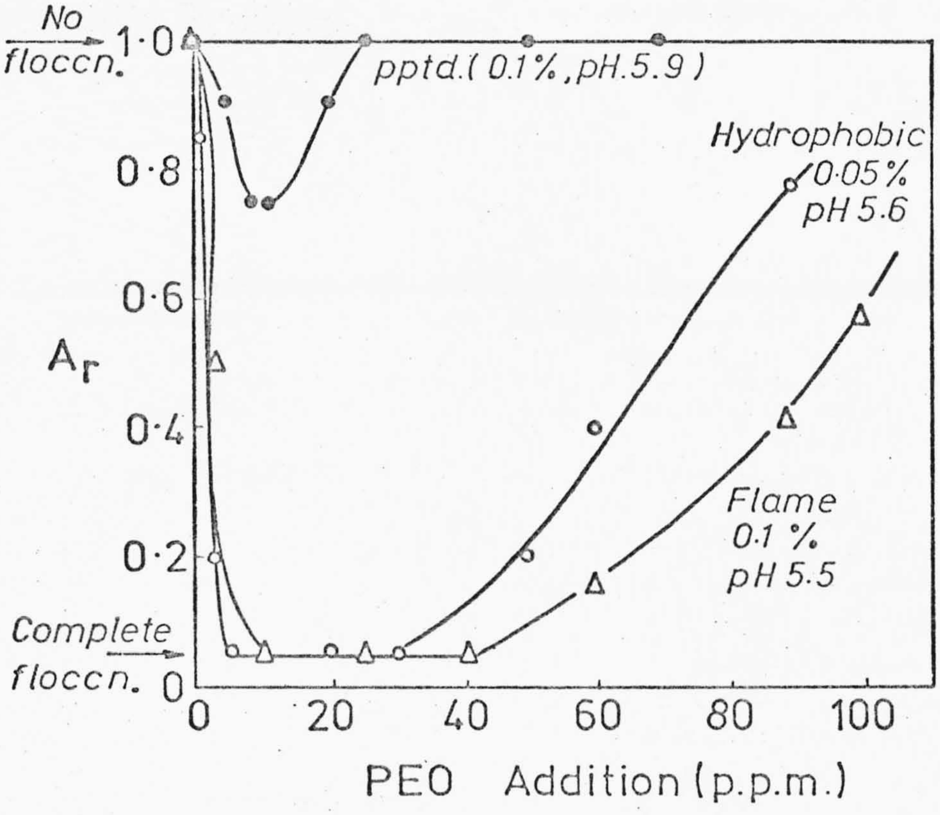

Figure 6

Flocculation of suspensions of precipitated silica (BDH), hydrophobic silica (Aerosil R972), and flame silica (Cab-O-Sil M5) by PEO.

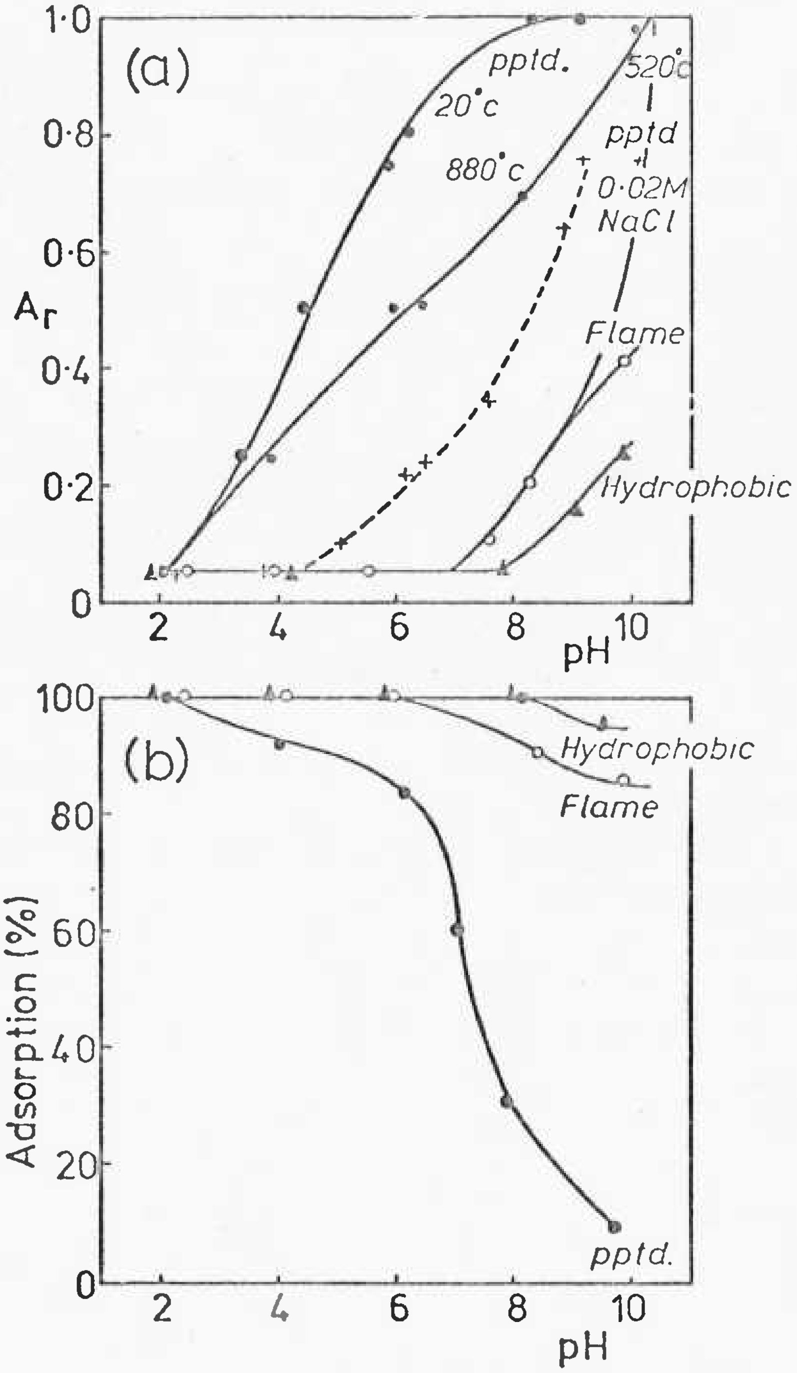

Figure 7

Effect of pH on flocculation (a) and adsorption (b) of PEO.

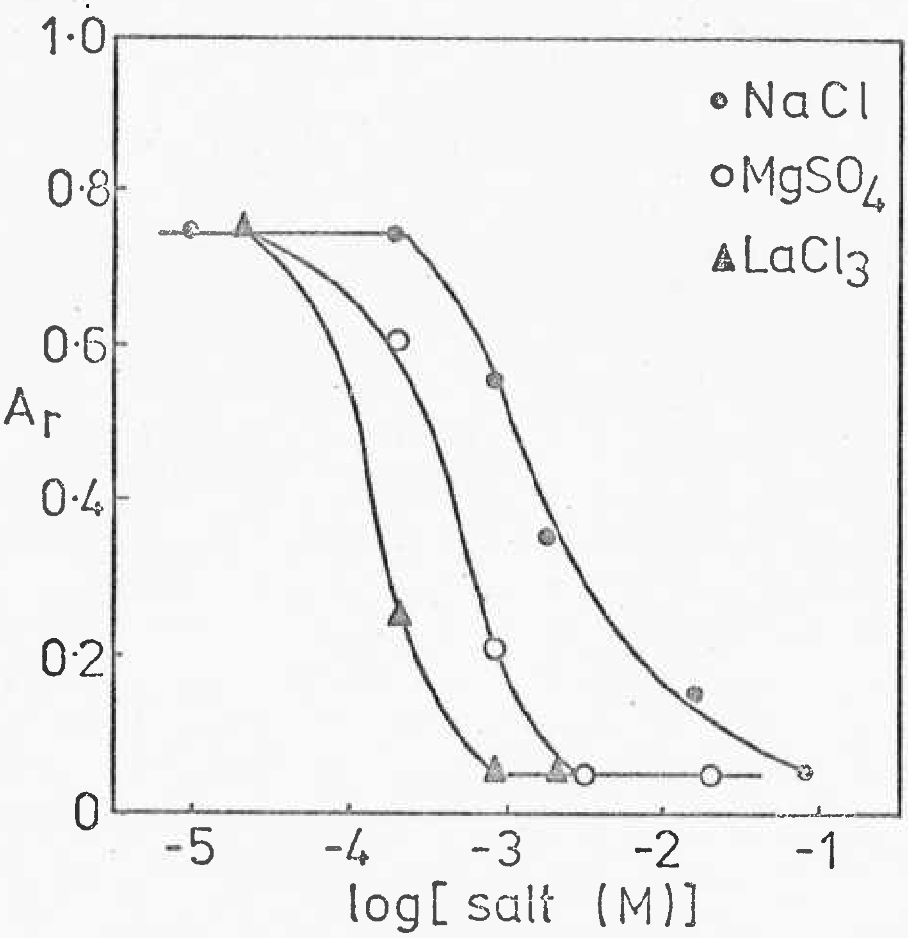

Figure 8

Influence of electrolytes on flocculation of precipitated silica by PEO (11.3 ppm) at pH 5.9.

of Figure 6. The amount of PEO adsorbed per gm of silica has been divided by the BET surface area. On this basis, it appears that the adsorption density lies in the order flame silica $\approx$ hydrophobic silica > precipitated silica, which corresponds to the order of sensitivity of the silicas to flocculation (Figure 6). The correlation between adsorption and flocculation is also clearly seen in Figure 7. Figure 7(b) shows the percentage of PEO adsorbed in the flocculation experiments of Figure 7(a), as a function of pH. In every case, strong flocculation ($A_r \sim 0.05$) corresponds to practically complete removal of the polymer (> 99% adsorbed) and, for each silica, gradations of flocculation correspond to gradations of strength of adsorption. Zero flocculation of precipitated silica corresponds to weak adsorption (> 20%). Under these conditions, addition of 11.4 ppm of PEO already constitutes an " overdose" for precipitated silica at pH 8. Although it is the " optimum" dosage at about pH 6 (Figure 6), the flocculation is imperfect and about 15% polymer remains in solution.

Figure 10 shows sets of complete isotherms for the three silicas, at a range of pH values. The striking feature of these results is that the isotherms are all of the same form, but are more expanded along the concentration axis as the affinity for the surface decreases. This appears in the height of the (apparent) intercept on the ordinate axis (note that (a) and (b) have a suppressed zero) and the level of the (apparent) " plateau" .

The correlation between flocculation and adsorption is complete. In every case, perfect flocculation corresponds to virtually complete adsorption of the polymer; any measurable excess of PEO left in solution corresponds to some degree of restabilisation. Optimum flocculation was generally obtained with a dosage (which was wholly adsorbed) corresponding to about 20-30% of the maximum adsorption capacity of the silica.

Heat treatment of silicas. Figure 11(a) shows that pretreatment of flame silica in a furnace (in air) for 24 h, at any temperature up to 800°C, does not affect its flocculation or the adsorption of PEO (virtually complete). Above 800°C, however, adsorption and flocculation are progressively reduced and above 1000°C, both are zero.

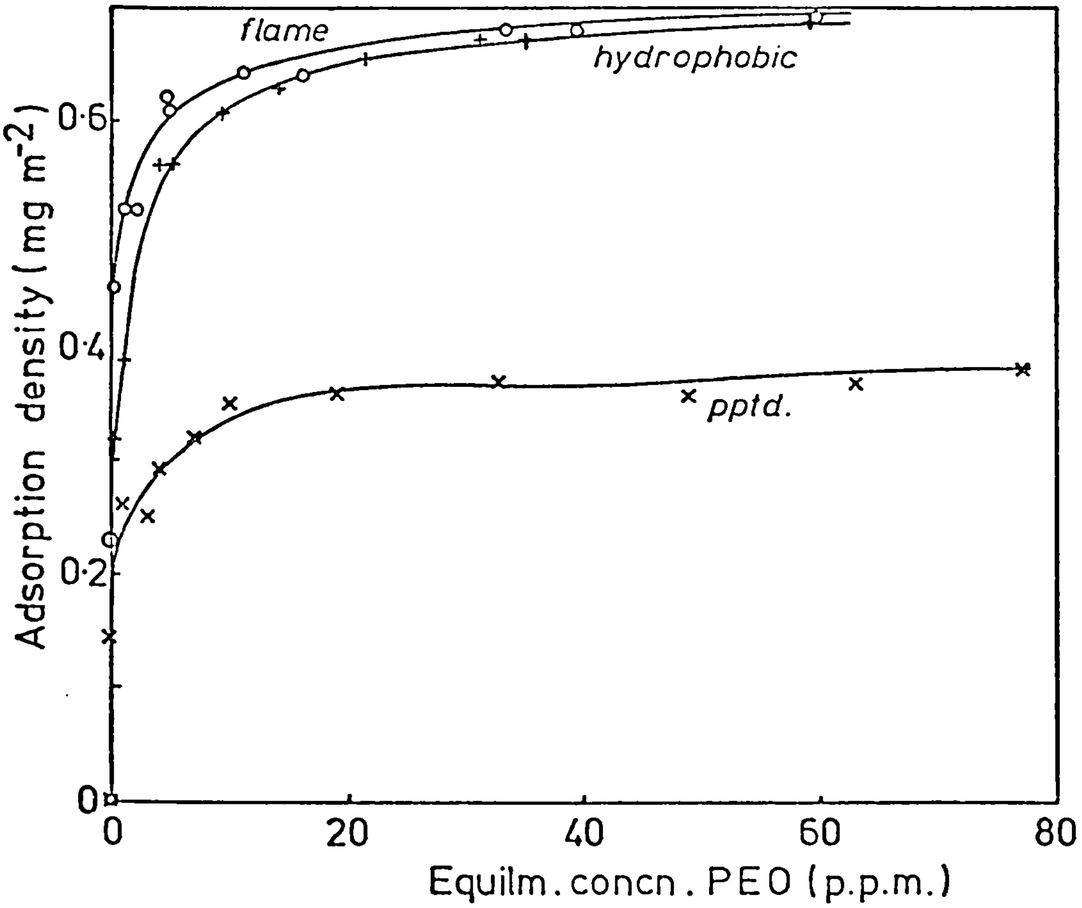

Figure 9

Adsorption isotherms for PEO on different silicas at pH 5.7.

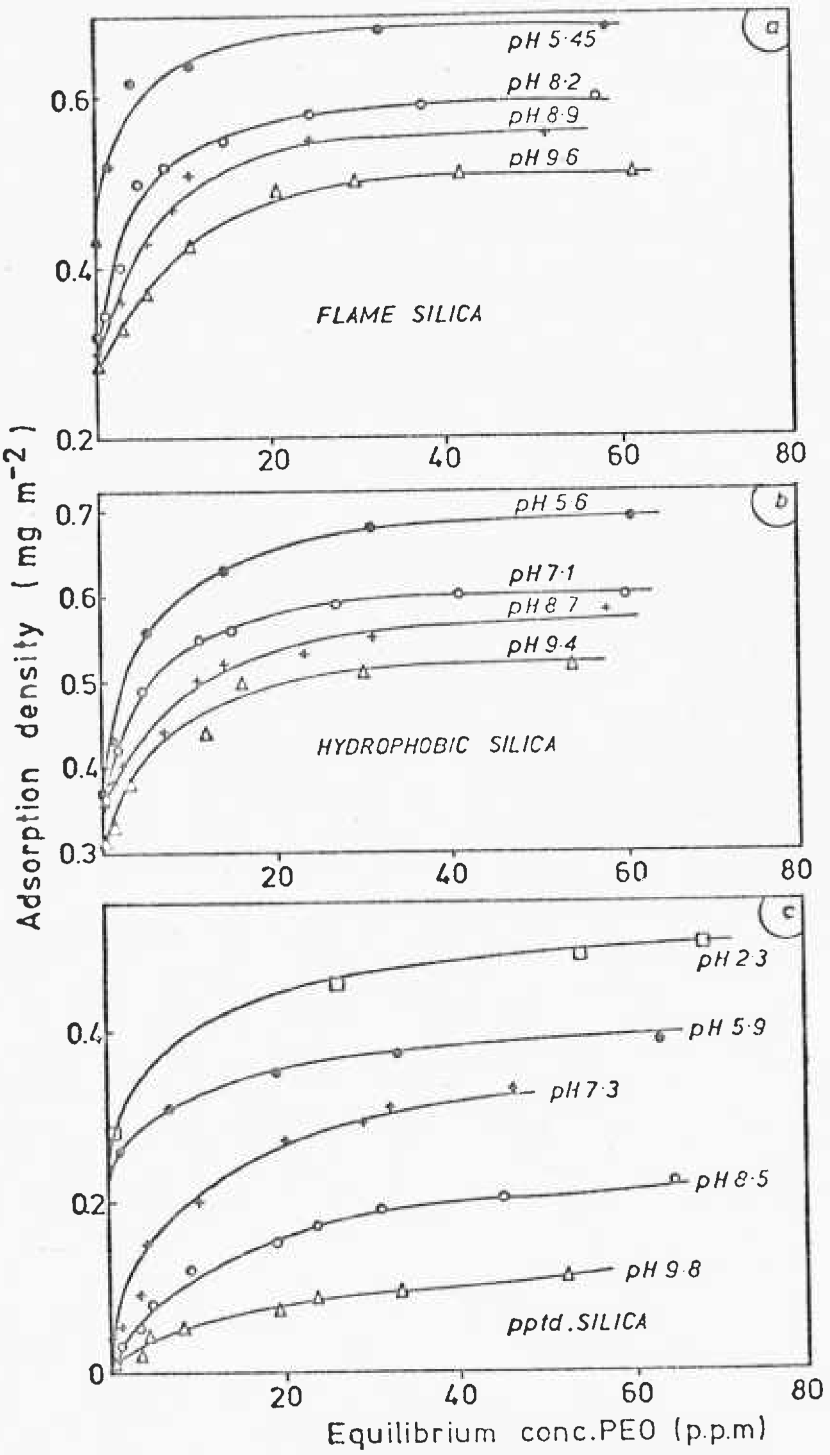

Figure 10

Adsorption isotherms for PEO on different silicas at various pH values

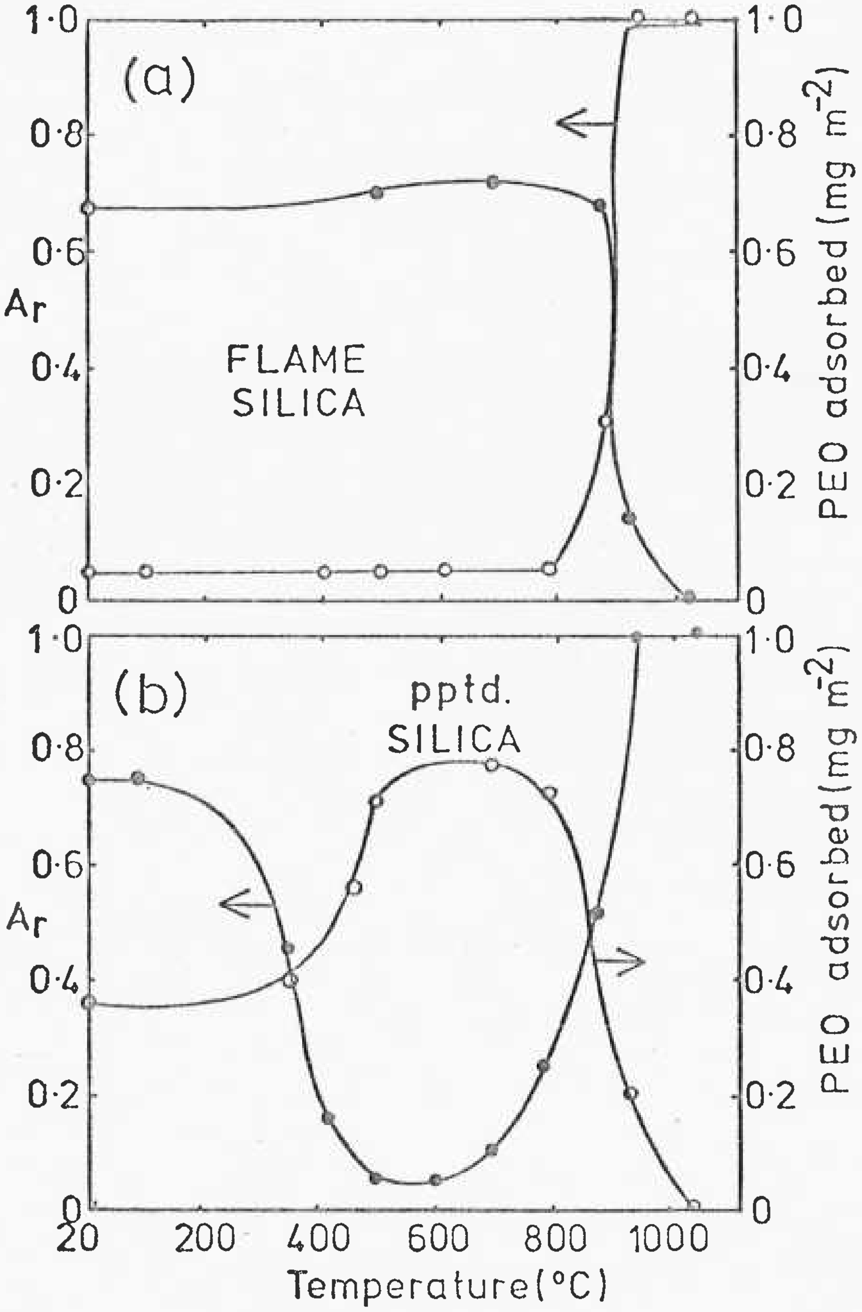

Figure 11

Effect of heat treatment of silicas on flocculation and adsorption by PEO (11.5 ppm) at pH 5.9.

Figure 11(b), on the contrary, shows the " activation" effect of moderate heating, mentioned earlier, with precipitated silica. Maximum sensitivity to the polymer is obtained by heating to about 600°C. At temperatures higher than 800°C adsorption and flocculation fall off exactly as with the flame silica.

Figure 12 gives adsorption isotherms for the same heat-treated silicas. Heating of flame silica slightly increases the adsorption density from 20 up to 700°C, but higher temperatures then produce progressive reduction, until virtually zero adsorption results if the silica is heated above 1000°C (Figure 7(a)). Similarly (Figure 12(b)) heating of precipitated silica above 350°C causes a very marked increase of adsorption density, up to a maximum of 700°C, followed by a fall to zero at the highest pretreatment temperature.

Figures 12 and 13 show that flame silica and precipitated silica become practically identical in adsorption properties towards PEO, provided both are pre-treated to 500°C or more. This fact suggests that after heating to temperatures about 600°C the two silicas have similar accessibility to PEO.

Heat treatment at above 350°C is well known to cause dehydroxylation of silica. It is obvious from the changes of colloidal properties that the treated silicas did not fully rehydrate when put into water for the flocculation and adsorption tests. That these effects were not due to loss of porosity was confirmed by similar experiments on a microcrystalline quartz powder; heat treatments lowered the adsorption isotherm in the same way as with flame silica. In addition, no physical porosity was found for precipitated silica (BDH) before and after heat treatment (500°C for 36 hr) (131). The influence of pH on heat-treated precipitated silica is also marked, as shown in Figure 7(a).

Rehydration after heat treatment. It is recognized that flame silicas such as Cab-O-Sil M5 are not fully surface-hydrated. In water at room temperature and ordinary pH, the hydroxylation process is very slow (> 72 h, see Figure 14). Treatment in a Soxhlet extractor in condensing steam for 96 h produced a marked reduction of adsorption, and boiling in water for 96 h was more effective (Figure 14), the adsorption being about halved, and comparable with that of precipitated silica. It is assumed that the accessible surface area has not been reduced correspondingly.

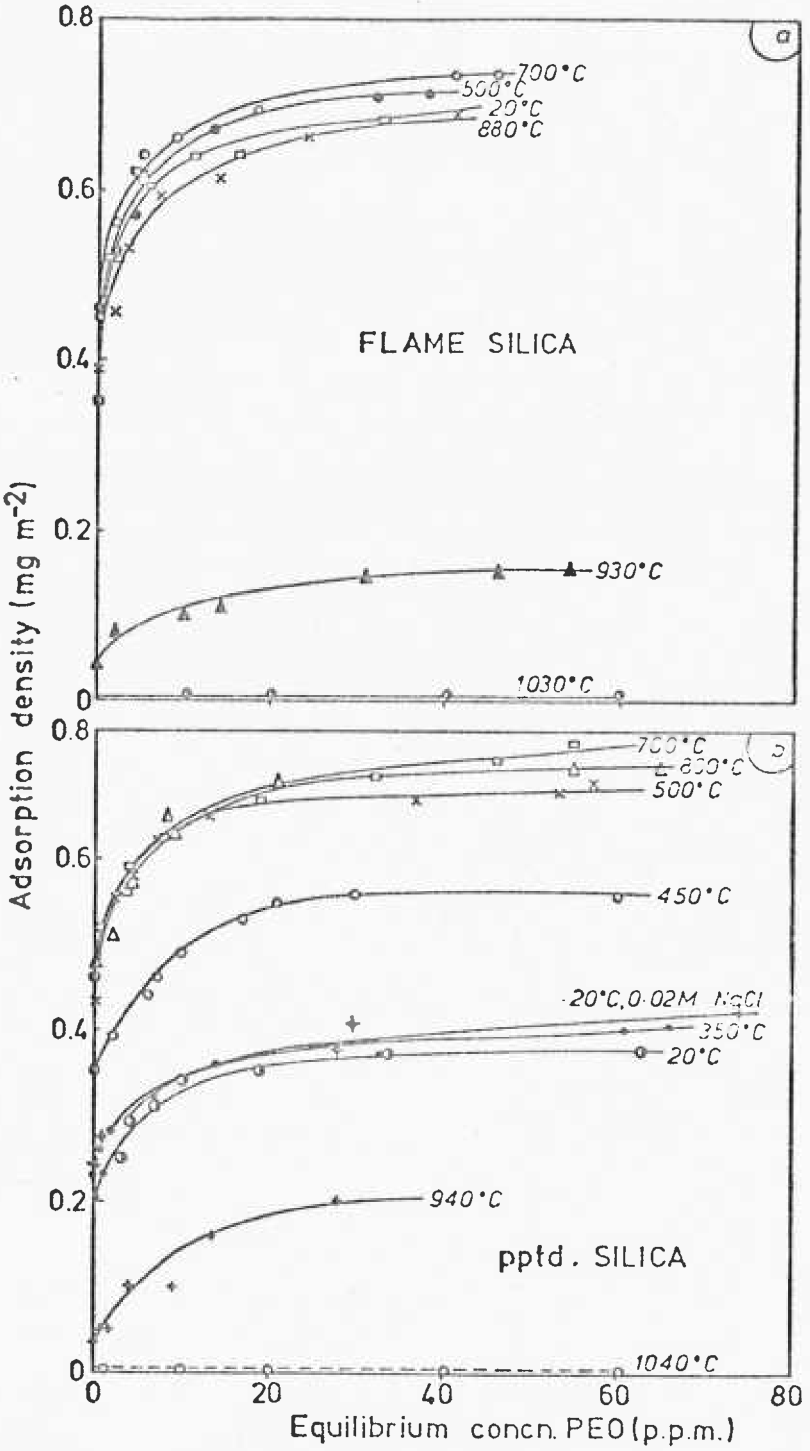

Figure 12

Adsorption isotherms for PEO on silicas
heat treated to various temperatures (pH 5.9)

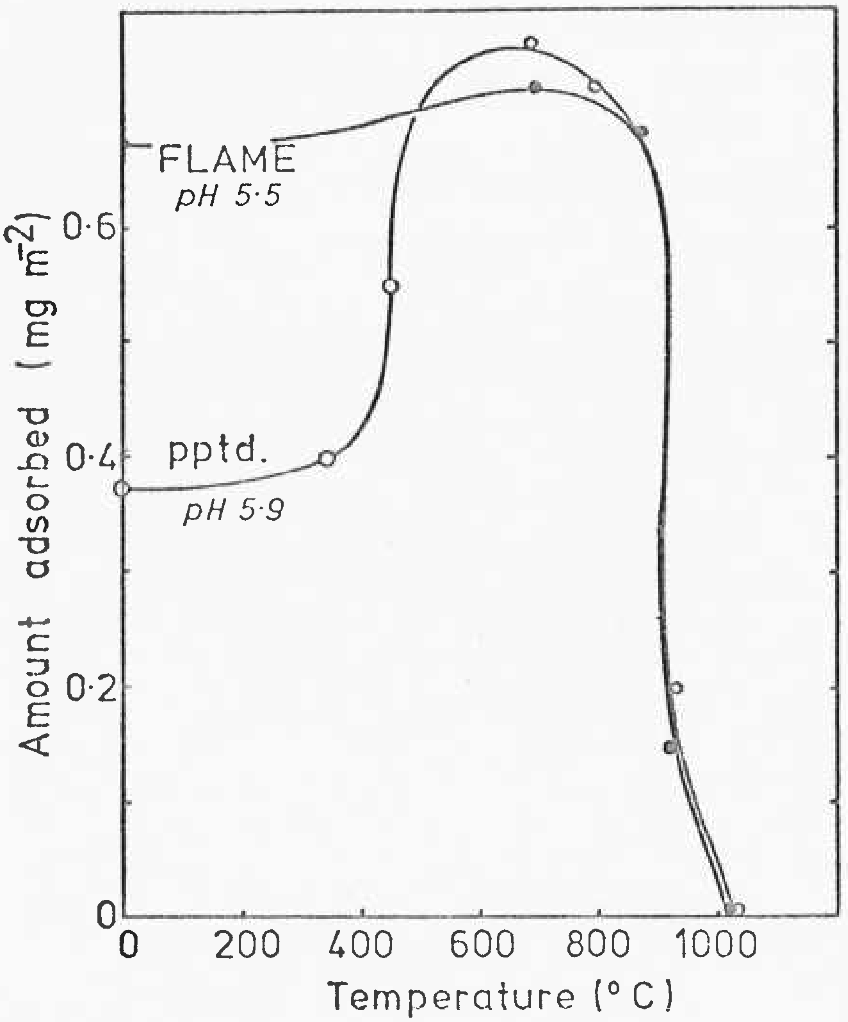

Figure 13

Effect of heat treatment (24 h) of silicas on the plateau adsorption of PEO

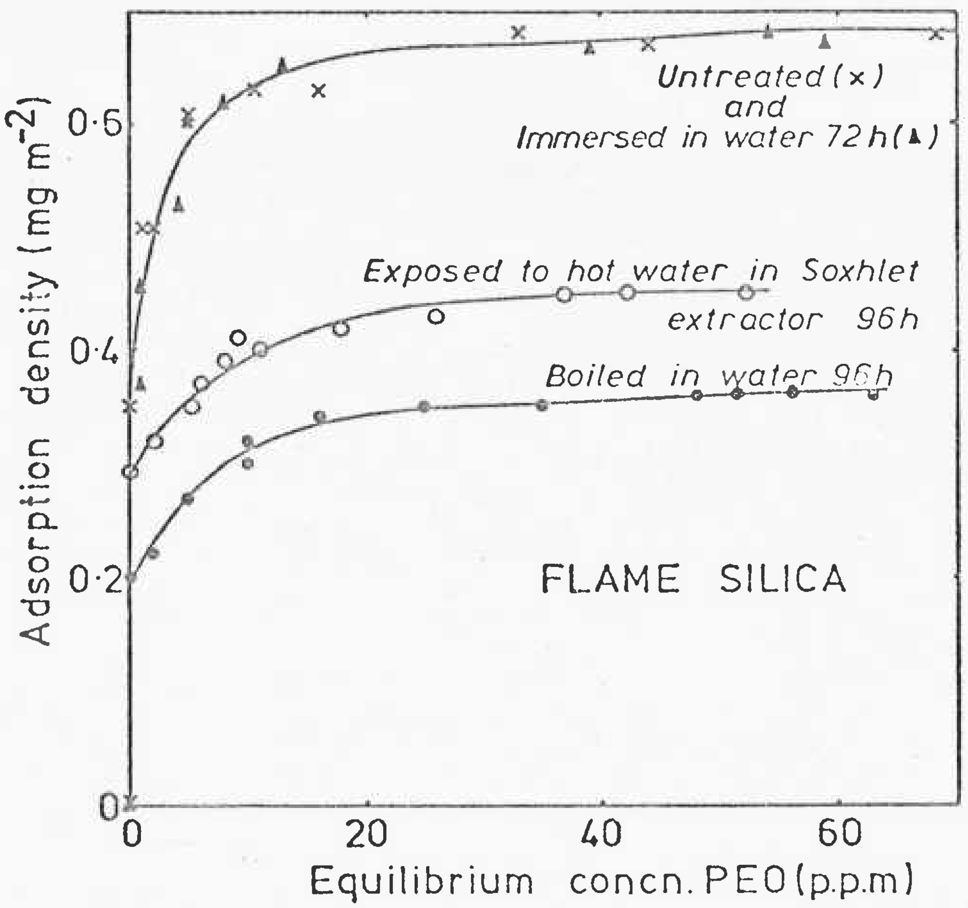

Figure 14

Effect of hydration treatments on the adsorption isotherms of PEO on flame silica (pH 5.5)

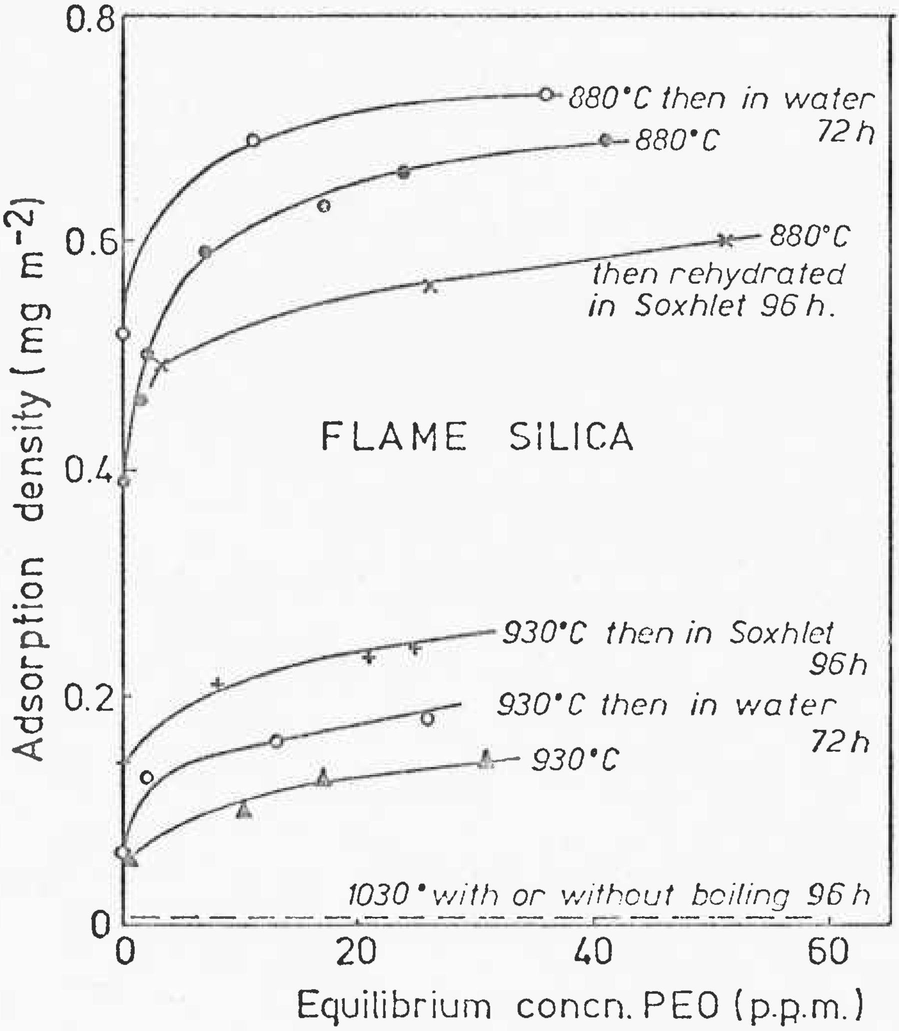

Figure 15

Effect of rehydration treatments of heated flame silicas on adsorption of PEO (pH 5.5)

Figure 15 give isotherms for flame silica pre-heated to 880, 930 or 1030°C and then partially rehydrated. These results show that moderate rehydroxylation increases the adsorption affinity; but an optimum is reached and thereafter further rehydration reduces the adsorption of PEO. After the strongest heating, recovery of adsorption affinity was barely detectable after 96 h in boiling water.

The hydrophilic/ether-philic character of silicas. Since adsorption of PEO involves a " competition" between H_2O and $\mathrm{-\!\!\left(CH_2CH_2\text{-}OCH_2CH_2\right)\!\!-}$ units for surface sites, some correlation is to be expected with the free energy of immersion of silica in water or in diethyl ether, $C_2H_5OC_2H_5$ (which could be regarded as the precursor of PEO). More simply, the relative affinities of silica for water or ether should be shown by the 3-phase contact angle, and hence the partition behaviour of finely divided silicas in a (mutually saturated) ether-water mixture.

When variously treated silica powders were shaken with equal volumes of water and ether, they were observed to either remain in the water or stick at the ether/water interface or (in the case of hydrophobic silica) pass wholly into the ether phase. The qualitative observations are indicated by + in Table 3 for the location of the silica.

As may be seen in Table 3 , it is clear that fully hydrated silica " prefers" water to ether; but partial or complete dehydroxylation or methylation reduces the hydrophilicity and thereby favours the ether-silica interaction. The development of hydrophobicity on strong heating of silica is well established and White (144) has presented air/water/silica contact angle data. Furthermore, Howard and McConnell (56) have suggested a greater affinity of heat-treated silicas for non-polar solvents to explain the decrease of adsorption of polyethers on to heat-treated from benzene and chloroform and an enhancement from methanol. Although there is a broad correlation between wetting characteristics and adsorption of PEO, it is not universal. For example, numbers 5 and 12 (Table 3) passed into ether, but 12 showed strong adsorption of PEO whereas 5 showed weak adsorption.

In general, the present results demonstrate that differences in

Table 3

The partition of silicas between ether, water, and interface

Test No.	Form of Silica	Pretreatment	Particles Present In		
			Water	Interface	Ether
1	Precipitated	Untreated (pH 6 or pH 2)	+	-	-
2		Heated 24 h, 450°C	+	+	+
3		500°C	-	+	+
4		700°C	-	+	+
5		880°C	-	-	+
6	Flame	Untreated (pH 6)	+	++	+
7		Heated 24 h, 500°C	-	+	+
8		700°C	-	-	+
9		930°C	-	-	+
10		No. 6 boiled in water 96 h	+	-	-
11		No. 9 steamed for 96 h	-	-	+
12	Hydrophobic	Untreated (pH 6)	-	-	+
13		(pH > 8)	+	-	-
14		No. 13 then acidified to pH 2	-	+	+
15	Ground Quartz	Untreated (pH 6)	-	++	+
16		Heated 24 h, 800°C	-	+	++
17		900°C	-	+	++

response of various samples of silica to flocculation by PEO arise from differences in the strength of adsorption of the polymer and are related to the nature of the surface groups on the silica. Numerous papers have been reported on the nature of the functional groups present on the surface of silica (146). Among others, the salient points for the present discussion are the following:

1. Precipitated silica is a fully hydrated form in which the surface is densely covered with silanol groups, the majority of which are " adjacent" or " hydrogen-bonded" (Type B). It has also been suggested that a gel layer of incompletely condensed polysilicic acid is present at the surface of precipitated silica (131).
2. Heating above 400°C begins to cause some irreversible dehydroxylation, eliminating first the Type B groups, which are virtually all removed at 500°C. Type A " isolated" or " single" silanol groups remain, to the extent of about 1.4 groups per 100 $Å^2$.
3. Type A groups begin to be lost above 700°C but dehydroxylation is not complete until above 1000°C.
4. After total dehydroxylation the surface is covered by siloxane ($\equiv$Si-O-Si$\equiv$) groups.
5. Flame-hydroxylated silica is broadly comparable to precipitated silica that has been dehydrated to about 500°C.
6. Hydrophobic silica corresponds to a flame silica that has been methylated in a proportion of about 70% of the total silanols; the rest, about 0.9 OH per 100 $Å^2$ are believed to be " isolated" (Type A) (147).

The present results show that adsorption of PEO is strongest on flame silica or on precipitated which has been heated to about 600°C. A priori, a plausible explanation is that isolated silanol groups provide the best adsorption sites, acting as proton donors in hydrogen bonding to ether oxygens.

$$-SiOH\cdots O(CH_2CH_2)_2=$$

This hypothesis has been previously suggested for the case of PAM (62) and for low molecular weight PEO by Howard and McConnell (56), by Fontana (148) for a copolymer of ethylene oxide and methyl methacrylate and recently by Iler (149) for poly(ethylene glycol) of various molecular weights. Complete dehydroxylation leaves siloxane groups, which are hydrophobic and incapable of providing a proton;

consequently, adsorption of PEO is nil (from dilute solutions). Accordingly, the Type A silanols left on hydrophobic Aerosil R-972 would be also available for hydrogen-bonding, as this silica is only a little less sensitive to PEO than flame silica.

A scale molecular model of PEO showed that it is impossible to arrange the chains with all the -O- atoms in contact with a plane. Arranging alternate -O- atoms on opposite sides, it is possible to bring half of them close to a plane, with an O-O distance of about 7.5 Å. In this configuration, two of the CH_2 groups between the O-atoms are in contact with the plane. Thus, the hydrogen bond acceptors are separated by a significant hydrophobic section, possibly matching the spacing of the hydrophobic groups, either methyl or siloxane, present on the silica.

The main problem is now to explain why precipitated silica has a low affinity for PEO. The possible influence of basic impurities in the commercial material can be dismissed as a result of the following test. A sample of precipitated silica was boiled with dilute HCl and then washed and tested for adsorption of PEO; its affinity was unchanged by this treatment, which would certainly have eliminated any exposed cations such as Na^+, Ca^{2+}, Al^{3+} etc. Thus, the lower affinity of hydrated silica for PEO is a consequence of its silanol surface, not its impurities. It should be noted, however, that precipitated silica is not deficient in affinity at pH 2 (Figure 7).

These observations are concordant with other facts concerning the interaction of PEO and silica. For example, colloidal silica is almost quantitatively precipitated by PEO at about pH 2 but not from alkaline media (pH > 7). Similarly, PVA behaves as a precipitant at low pH values (150) and not at higher pH (4, 150). Colloidal silica is also known to form complexes at pH 2 with non--polymeric analogues of PEO, namely ethylene glycol diethyl ether, $CH_3CH_2OCH_2CH_2OCH_2CH_3$ (151).

Therefore, the problem which particularly needs an explanation is the effect of pH on the adsorption of non-ionic polymers, which is shown by all forms of silica, quartz (the flotation of which by PEO type surfactants is also drastically cut by pH > 5.5 (152)), and even the surface-methylated hydrophobic silica (Table 3 , Nos. 12-14). Previous work has shown not only that some silanol groups are inaccessible to methylation but also that they continue to ionize, giving a zeta-potential close to that of non-methylated silica (60, 132).

Effects of pH. As the pH is raised above 2, silica begins to take up bases by cation exchange. Tadros (4) has suggested that loss of adsorption (e.g., of PVA) with rise of pH is due to reduction in the number of silanol groups available for hydrogen bonding. However, the number of groups ionized at about pH 6 in absence of salts is very small compared with the total number present on hydrated silica. Therefore it is suggested that either (1) there is a certain minority type of silanol group which is the important one for both hydrogen bonding and base binding, or (2) the effect of surface ionization is through general electrical double-layer phenomena (rather than loss of sorption sites). It should be noted that these hypothesis are not mutually exclusive and all might be operative. However, some of the evidence seem to point to (1) and some to (2), as follows:

(1) Several authors have concluded that the hydroxyl groups on silica have a range of (Bronsted) acid strengths (153, 154) in the presence of water. Strazhesko and co-workers (155) have proposed an electronic valence theory to explain the acidity of silica gel in the pH range 3-6 (which they consider is not consistent with the accepted pK value of monosilicic acid). Ethers, on the other hand, are known to form oxonium salts and hydrogen-bonded complexes with strong acids. It is, therefore, suggested that the most readily dissociable silanol groups are also the important ones for adsorption of PEO.

(2) Reduction of adsorption of polyethers by ionization of the silica might be caused by non-specific " salting out" due to the electrostatic field near an ionized surface. At pH 2, $\Psi_o = 0$, while at pH 6, $\zeta \approx - 100$ mV and the Ψ_o-potential operative for adsorption must be even more strongly negative. In support of this hypothesis is the observation that addition of neutral salts improves the flocculation (Figure 8) and is also needed to permit interaction of hydrated silica with simple ethers (151). Since addition of salts, at constant pH, actually increases the degree of cation exchange, this effect is clearly electrostatic rather than a question of the

number of undissociated silanol groups. In fact, the adsorption of PEO was slightly increased by adding 0.02 M NaCℓ (Figure 12(b)).

In addition to hypothesis (1) and (2), it is suggested that the hydrated counter ions, which are associated with ionized sites, may also prevent PEO from approaching the surface. Therefore, since methylated silica or partially dehydroxylated silicas carry a lower surface density of silanol groups than does precipitated silica, the former two would have to be carried to a higher pH to reach a given cation density. On this view, charge density would be more important than surface potential (hypothesis (2)) in repelling the PEO. In fact, for BDH precipitated silica, potentiometric acid-base titrations (131) showed that an exceptionally high surface charge density could be readily developed. Also, the effect of heat treatment caused a substantial reduction in the surface charge density (almost 70% after heating at 500^{o}C for 23 h (131)). However, the difference in σ_o (surface charge) values between pH 2 and 6 is very small indeed (130, 131) and would not explain the drastic fall observed in the adsorption of PEO between these two pH values. In addition, the fact that addition of neutral electrolytes increases the adsorption of PEO also seems to favour the potential hypothesis. Also, increase of ionic strength has a marked effect on the flocculation of silicas (see Figure 8) and quartz (see Chapter 8) by PEO. It is suggested that since the salt concentrations (e.g., 0.02 M NaCℓ) are not high enough to produce electrolytic coagulation of hydrated silica at pH 6, the ionic strength effect can be ascribed to reduction in the long-range double layer repulsion between silica particles; the double-layer thickness (under these conditions), $\frac{1}{K} \approx 22$ Å, is then small enough to allow PEO molecules to bridge the gap.

Finally, it is concluded that whichever the mechanism, it is clear that rise of pH increases the hydrophilicity of any form of silica (even methylated, cf. Table 3, Nos. 12-14), and a stronger silica-water interaction correlates with reduced adsorption of PEO from solution.

3.6. Conclusions

The experimental results presented in this Chapter can be summarized with the following generalizations.

1) In line with other reported studies on silica, the methylation of the silica surface to form hydrophobic silica, restored the theoretical relation of stability to pH, the hydrophobic silica sols being " stable" only in the zone where at least a minimum surface potential is found (pH > 5).
2) Aggregation of hydrophobic silica by a cationic surfactant occurred at concentrations of about a thousand smaller than those required to aggregate the hydrophilic silicas. Restabilisation occurred at concentrations where aggregation of hydrophilic silica begins.
3) The best conditions for adsorption-flocculation of PEO on the silicas are when physically adsorbed water and Type B silanols are removed from the surface and free silanol with vicinal, either siloxane or methyl groups are present. Accordingly, a combination of hydrogen bonding and hydrophobic association may be responsible for the adsorption of PEO.
4) The adsorption of PEO is disfavoured if the regions between the adsorption sites are hydrated, and particularly disfavoured if the surface is appreciably ionized. Ionization of the silica surface reduces its affinity for PEO by a general " salting out" mechanism.
5) Dehydration of hydrophilic silicas by heating at $t^o > 400^oC$ and $< 900^oC$ enhances their affinities for PEO but further dehydroxylation (> 900^oC) decreases the adsorption of PEO which becomes almost negligible at temperatures over 1000^oC. Rehydration in water is an extremely slow process.

CHAPTER 4

THE FLOCCULATION PROPERTIES OF POLY(ETHYLENE OXIDE)

4.1. Introduction

Recently, poly(ethylene oxide) (PEO) has been finding increasingly wide use in various processes occurring in aqueous suspensions. One of the basic characteristics of PEO is its ability for flocculating certain aqueous dispersions. Table 4 summarizes published examples. In addition to these examples, the trade literature reports (19) that PEO is an effective flocculant of coal washery suspensions, uranium ore slimes, phosphate slimes, and a variety of clays such as kaolin, montmorillonite and bentonites. Also, in the field of mineral processing PEO is being used as a collecting polymer in a new process (" floto-flocculation") of clarification of water and purification of waste water (156). This process consists essentially of a " hydrophobization" of the surfaces of the suspended particles by polymers, followed by flotation of the particles which are now flocculated.

With regard to the mechanism (or mechanisms) by which PEO become attached to a specific substrate, very little information is, unfortunately, available at present. Nevertheless, it is noteworthy that the majority of the solids amenable for flocculation by PEO can be referred to as hydrophobic. Rubio and Kitchener (59) have recently reported that a combination of hydrogen bonding and hydrophobic interaction may be responsible for the adsorption of a high molecular weight poly(ethylene oxide) on to various silica substrates. According to their theory, the ether groups of the polymer operate as hydrogen-bond acceptors to silanol sites present at the surface and the ethylene, $-CH_2-CH_2-$ groups are sufficiently hydrophobic to interact with either methyl sites (hydrophobic silica) or siloxane (flame-hydrolyzed silica). Birkner and Edzwald (157) suggested that hydrogen bonding occurs between the ethylene groups in the polymer chain and oxygen atoms on the Kaolin surface, although $-CH_2$ groups are not usually considered to act as proton donors.

Solomentseva et al. (158) suggested that the " recharging" of

Table 4

Recent studies on the effect of added PEO on the stability of various model aqueous systems

Dispersed Solid	PEO, Molecular Weight	Flocculation Details	Initially Reported
Au	$10^3 - 10^6$	sensitization	Baran et al., 1976 (161)
AgI	$10^3 - 10^6$	sensitization	Solomentseva et al., 1973 (158) Baran et al., 1976 (53b)
polystyrene latex (after Matsumato and Ochi (159))	$10^5 - 10^6$	sensitization	Ash and Clayfield, 1976 (53a)
polystyrene latex (after Ottewill and Shaw (160))	$10^3 - 10^6$	flocculation	Evans and Napper, 1973 (162)
SiC	10^6	flocculation	Egorov et al., 1975 (163)
SiO_2	10^6	flocculation	Rubio and Kitchener, 1976 (59)
SiO_2	$400 - 2 \times 10^4$ (polyethylene glycols)	aggregation	Iler, 1976 (149)
SiO_2 (quartz)	10^6	flocculation	Ethimakov, 1973 (164)
C (bitumen)	10^7	flocculation	Bortel and Lamot, 1973 (165) ibid, 1974 (166)
C (graphite)	10^6	flocculation	Afenya, 1975 (167); Rubio, 1976(168)
C (activated)	10^6	adsorption	Susuki et al., 1976 (169)
SbS	$10^3 - 10^6$	adsorption	Eremenko et al., 1975 (170)
talc	10^6	flocculation	Mukai, 1968 (171)
limonite	10^6	flocculation	Mukai, 1968 (171)
kaolin	10^6	sensitization	Birkner and Edzwald, 1969 (157)
" Laponite"	10^6	sensitization	Wright and Kitchener, 1976 (145)

a positive AgI sol and the sensitization of the negative sol with respect to univalent cations, observed in the presence of small PEO additions, are attributable to the dipole nature of adsorbed polymer units. Conversely, Erlander (172) suggested the formation of a " pseudo-polyectrolyte" by the interaction of the A-regions of hydrated cations with the polyethers. The " cationic" pseudo-electrolyte molecules would adsorb at the particle surface and so create regions of reduced or even reversed charge. This last mechanism has been used by Ash and Clayfield to interpret their negative values of log W_{sp}, the stability ratio term, for collisions in the early stages of flocculation between a polymer (PEO)-covered particle and a bare particle. Thus, interaction between regions of opposite charge would lead to an attractive force. Such a mechanism has been invoked for the flocculation of polystyrene latices by PEO in the presence of $BaCl_2$ (or $Ba(NO_3)_2$) but not for the flocculation in the presence of KNO_3, because K^+ ions contain no A-regions and are not complexes by polyethers.

Flocculation experiments with PEO on those suspensions which are relevant to the present study were undertaken. Characterization of PEO in terms of its flocculant properties was studied on several mineral suspensions.

4.2. Experimental

Definitions. Because of the importance of the process of dispersion in flocculation studies, dispersibility of a number of minerals before flocculation has been studied here under controlled conditions by measuring supernatant dry-weight after agitation has ceased for a definite period.

The dispersibility of a given powder in a liquid will be defined here operationally in terms of the concentrations of solids which remain in suspension after stirring of the system has stopped. Since dispersions usually show a variation of concentration with height, dependent on the time of settling, both variables have to be specified. Hence, the dispersibility (D) will be defined as:

$$D = (C_x/C_o)_{h_x, t_x} \qquad \ldots\ldots(1)$$

where C_o is the calculated concentration as total weight of solid in the system over the total volume of solvent; C_x is the concentration measured at time t_x of a sample taken up to a distance h_x from the liquid level.

The solid particles present at heights equal to or greater than h_x will have radius smaller than or equal to a " critical equivalent radius" r_c, given by:

$$r_c = (h_x/Kt_x)^{0.5} \qquad ......(2)$$

where K is the constant of the sedimentation equation which is applicable (whether free or hindered settling).

It may be shown that the percentage dispersibility, as defined above, may be expressed as:

$$\% D = 100 \sum_{i=1}^{c} f_i[1 - (\frac{t_x}{h_x})v_{(r_i)}] \qquad ......(3)$$

where f_i represents the weight fraction of particles of radius r_i whose sedimentation velocity is $v_{(r_i)}$. Within this definition, dispersibility will be dependent on the size and relative densities of the final kinetic units formed in the dispersion process (whether agglomerates, aggregates or unitary particles). Thus, with a given system, 100 percent dispersibility means that the particles formed are all small enough to remain in suspension without appreciable settling within t_x. The ratio h_x/t_x may be chosen or varied according to the practical implications of the dispersion studies. For instance, in most cases it is relevant whether or not the solid remains suspended for more than an hour, and the time t_x must be chosen shortly after agitation is stopped.

The dispersibility criteria above will be used to describe the effectiveness of flocculation. It is convenient to define a flocculation index as:

$$\% F = 100(D_1 - D_2)/D_1 \qquad ......(4)$$

where % F is the fraction of solids which sediment out and do not remain dispersed because they have been flocculated. D_1 is the percentage dispersibility of the mineral in the absence of polymer and D_2 the dispersibility obtained after flocculation has taken place.

Normally, it is more practical to define a value which considers all the fraction of solids which have been settled and do not remain dispersed either because of their coarse size or because they have been flocculated by polymers or coagulated (as a result of ortho--kinetic collisions). Hence, for the present case, it is useful to define quantity settled as

$$\% S = 100 - \% D_2 \qquad \ldots\ldots(5)$$

where % S is the total amount of solids being settled.

Methods. Dispersibility measurements : Known weights of powder in contact with given volumes of solution (200 ml) were dispersed with the aid of ultrasound during 3 minutes. (" Soniprobe" , type 7530A, Dawe Instrument Ltd.). Then the dispersions were placed in a cylindrical glass tube (Figure 16); after given periods of stirring and settling, samples were withdrawn from a side outlet and the amount of solid in the sample analyzed directly from dry-weights. The percentage dispersibility was calculated as $\% D = 100(C_x/C_o)_{h_x,t_x}$.

Flocculation measurements. Subsequently, flocculation experiments were carried out in the same cylindrical glass tube described above. The samples which were withdrawn from the side outlet after predetermined periods of stirring and settling were measured for solids content from dry-weights. Highly dispersed suspensions (after the ultrasonic treatment) were introduced to the cylindrical glass tube and stirring was maintained at 1900 r.p.m. for 5 minutes. Finally, the flocculant was slowly added from a 1 ml. pipette, while stirring continued. The suspension was stirred for a fixed period of 90 s at 1980 r.p.m. to allow uniform distribution of the flocculant and also to promote floc formation. Contrary to usual experience with flocculant such as polyacrylamide, in most cases, it was found that the extent of aggregation and the size of the flocs increased the faster the suspension was stirred. Moreover, the further period of slow shear rate which is normally provided was, in

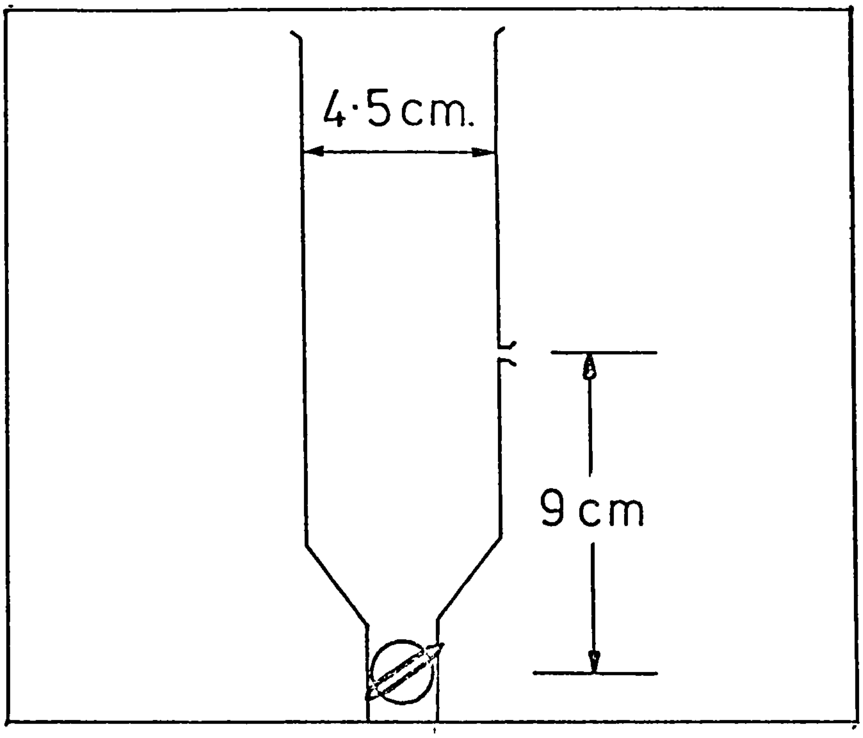

Figure 16

The cylindrical glass tube
used on dispersibility and flocculation
experiments.

some cases, found to unnecessary.

Results. Dispersion and flocculation measurements. Comparative results of dispersibility and flocculation of typical minerals are shown in Table 5. The dispersion medium was a dilute, alkaline (pH 10) solution of sodium hexametaphosphate (" Calgon"), which is well known to favour dispersion of many oxide silicate and salt-type minerals because of the well-developed negative charge produced by the alkalinity and by the adsorption of the polyphosphate.

As may be seen in Table 5, high dispersibility values were found for those solids normally recognized as hydrophilic. On the other hand, flocculation of those called hydrophobic solids (Group C) by PEO was noticeable. Accordingly, there is a broad correlation between these results and those reported in the literature (Table 4).

Weak flocculation of " non-sulphide" copper minerals (classed as A in Table 5) by PEO was observed as compared with " sulphide" copper minerals (classed as B) with the exception of chalcocite. (Bortel and Lamot (166) reported that chalcocite was not flocculable by PEO). The " sulphides" are recognized to be less hydrophilic and evidence can be found on the differences in contact angle values at the solid/liquid/air interface between sulphide and non-sulphide copper minerals.

Similarly, strong flocculation by PEO was found for highly hydrophobic substances such as graphite and talc (classed as C in Table . 5) and weak flocculation for these very hydrophilic compounds, namely, rutile, quartz, calcite and dolomite (D in Table 5).

In the light of the observations obtained here and those already published, it was concluded that PEO can be characterized as a good flocculant for dispersions of those solids classed as hydrophobic and a weak flocculant for those usually recognized as hydrophilic.

Table 5

The flocculation of minerals by PEO. Dispersibility measurements of minerals in the absence of PEO $\% D_1$ (pH 10; 50 p.p.m. Calgon; $C_o = 1\%$; $V = 200$ ml; $h_x = 9$ cm; $t_x = 6$ min) and in the presence of PEO, 6 p.p.m., $\% D_2$ (same as for $\% D_1$); Flocculation values, % F calculated as $100 (D_1 - D_2)/D_1$; Settled solids, $\% S = 100 - \% D_2$. † is for $t_x = 30$ sec; In all cases the average size of the particles was less than 37 μm.

Mineral Sample		Formula (ideal)	$\% D_1$	$\% D_2$	% F	% S
tenorite	A	CuO	68	67	1.5	33
chrysocolla		$CuSiO_3.2H_2O$ (approx.)	33	17	45	83
cuprite		Cu_2O	86	79	8	21
malachite		$Cu_2(OH)_2CO_3$	64	65	none	35
chalcocite	B	Cu_2S	23	18	22	82
covellite		CuS	15	7.4	51	93
chalcopyrite		$CuFeS_2$	26	8	69	82
talc	C	$Mg_3Si_4O_{10}(OH)_2$	24	2	92	98
graphite		C	34†	0.5	98	99.5
rutile	D	TiO_2	99.5	98	1.5	2
quartz		SiO_2	99	99	none	1
calcite		$CaCO_3$	90.5	89	1.6	11
dolomite		$MgCaCO_3$	92	91	1.1	9
shale		(clays)	76	57	25	43

CHAPTER 5

CONCLUSIONS

The following conclusions can be drawn from the data presented in Part I.

1. " Hydrophobic silica" , namely silica treated with dimethyldichlorosilane, behaves as a typical DLVO colloid insofar as its response to coagulation by electrolytes is concerned. The untreated silicas, i.e., " hydrophilic silicas" behave contrarily to the postulates of the classical theory of colloid stability and the mechanism of their coagulation by electrolytes as a function of solution pH is not well understood yet. Hydrophobic silica sols are very sensitive to aggregation and restabilisation by a cationic surfactant (CTAB). The " critical" concentrations for aggregation and restabilisation of hydrophobic silica are of the order of a thousand less than those necessary to destabilise or restabilise hydrophilic silica.
2. Poly(ethylene oxide) was shown to be a better flocculating agent for hydrophobic silica than polyvinyl alcohol or non-ionic polyacrylamide. The last two polymers require the addition of electrolytes to sensitise the silica sols.
3. Poly(ethylene oxide) (PEO), a strictly non-ionic polymer is able to interact with different interfaces through its two main chemical groups. The ether groups which are responsible for the aqueous solubility of the PEO and presumably operate as hydrogen-bond acceptors to water molecules, are also capable of acting as links to hydrophilic substrates. Secondly, the $-CH_2-CH_2-$ groups in PEO are sufficiently hydrophobic to lead to physical adsorption at the air/water, the oil/water, the mercury/water and also at the solid/liquid interface. In addition, they are capable of reacting in solution with the corresponding hydrophobic portions of other macromolecules. Particularly relevant to this work is the reactivity of PEO with surfactants where hydrophobic interactions are recognized to be the chief factors responsible for interaction.
4. The studies on the adsorption and flocculation reactions of PEO at the silica/water interface led to the following conclusions:

a) PEO has a high affinity for those silicas which are not fully hydrated. A silica such as precipitated (BDH) silica, which is highly hydrated (possibly as a result of a layer of chemisorbed water plus a layer of polysilicic acid coming from dissolution-polymerization products), behaves as a refractory surface for PEO adsorption when the silica is ionized. Moderate adsorption is only possible for this silica in its recognized zpc (pH 2).

Adsorption is most marked with silicas which carry " isolated" silanol groups and hydrophobic groups (either methyl or siloxane).

b) PEO adsorption corresponds with good flocculation in most silicas. Thus the extent of adsorption of PEO lies in the order; flame silica $\approx$ hydrophobic silica > precipitated silica, which corresponds to the order of sensitivity of the silicas to flocculation. Furthermore, in every case, strong flocculation ($A_r \sim 0.05$) corresponds to practically complete removal of the polymer (> 99% adsorbed) and, for each silica, gradations of flocculation correspond to gradations of strength of adsorption. Perfect flocculation corresponds to complete adsorption of the polymer. If any measurable PEO is left in solution, there is some degree of restabilisation.

c) Partial dehydroxylation by heating (at temperatures > 450°C) of the precipitated silica and flame silica enhances the adsorption of PEO; but heating to temperatures higher than 900°C greatly reduces the affinity of any form of silica (including quartz) for the polymer. A maximum was obtained when the silicas were heated to temperatures between 600 to 700°C. The composition of functional groups on the surface of the different silicas after treatment at these temperatures are broadly similar and explains their similar affinities towards PEO. Rehydration of silicas heated at temperatures over 900°C is very slow.

d) A considerable decrease in adsorption (and consequently flocculation) of PEO by all forms of silica was observed on raising the solution pH. Ionization of silicas reduces their affinity for PEO by a general non-specific " salting-out" effect, presumed to be due to the electrostatic field near an ionized surface. In addition, the rise of pH increases the hydrophilicity of any form of silica, and stronger silica-water interaction causes reduced adsorption of PEO from solution.

e) According to the arguments expressed in (a), (b), (c) and (d), it is concluded that a unified qualitative explanation of all the observed phenomena may be summarized as follows:

i) A combination of hydrophobic interaction and hydrogen bonding is responsible for the attachment of PEO to the silica surfaces. Thus, in line with other reported studies on adsorption of polymers on standard and modified silicas, the " free" surface silanol site act as the main adsorption sites for polyethers such as PEO; but, in addition, hydrophobic interaction between the surface methyl or siloxane groups and the non-polar sites of the polymer is also present.

ii) Any factors which favour the presence of water on the surface (in preference to organic compounds), namely ionization, or polysilicic acid coatings, will have a marked negative effect on adsorption and flocculation of silica (and possibly other substrates) by PEO.

5. A comparison with reported flocculation studies of different dispersions by PEO shows that the results of flocculation obtained in this work with PEO are in good qualitative agreement. PEO is a good flocculant for those solids which may be referred to as somewhat " hydrophobic" and a weak flocculant for those which are strongly hydrophilic.

PART II

THE PROCESSING OF NON-SULPHIDE COPPER ORES BY SELECTIVE FLOCCULATION

CHAPTER 6

INTRODUCTION

6.1. The Treatment of Non-sulphide Copper Ores

Copper minerals are normally found in small proportions and in various forms, varying in composition and structure, associated with other minerals. The most common types of copper mineral are usually divided into " sulphides" and " oxides" ; the latter are often termed " oxidized" copper minerals and imply all non-sulphide minerals - mainly the basic carbonate (malachite) and silicate (chrysocolla).

The practical methods of separating and extracting the copper minerals differ between sulphide or non-sulphide minerals. Whereas copper sulphides are readily separable from the ore by froth flotation, the response of non-sulphide copper ores to this process is usually ineffective and presents many practical problems (173). Nevertheless, the reasons for the different floatabilities of oxides, sulphidized oxides and sulphides are not yet clear (174). Only two basic flotation procedures have been used commercially to treat non-sulphide (mainly malachite) copper ores. They utilize different collector systems, the first (175) uses fatty acid collectors which can provide good recoveries but poor selectivity. The second (176) utilizes sulphidization with sodium sulphide prior to flotation by xanthates. In spite of the fact that this system is far more selective than the first one, it is costly in terms of reagents and also difficult to control, especially the consumption of the sodium sulphide, as the malachite slimes consume too much, whilst on the other hand, an excess can lead to flotation depression (177).

Several methods for the flotation of chrysocolla have previously been examined on a small scale and some degree of success has been claimed (178). The most promising possibilities in the flotation of chrysocolla are the use of organic chelating agents as collectors and the use of sulphidization as a preliminary step followed by flotation by a xanthate type collector (178, 179). Hydrometallurgical methods are currently more commonly applied instead of froth flotation or other physical methods for the processing of non-sulphide copper minerals. Acid leaching of copper carbonates and silicates, however, can only be employed where the copper grade is high enough or in cases where the consumption of acid by the gangue is relatively low. The rejection of non-sulphide copper minerals is common practice in some operations where the extraction of mineral value does not meet minimum economic requirements (180).

The processing of finely divided non-sulphide copper ores is even more complicated and the design of new processes would be valuable. Among several methods proposed for the treatment of these " slimes" , the selective flocculation appears to be one of the most promising for use in the future.

6.2. The Selective Flocculation Process in Mineral Separations

The depletion of much of the high grade mineral resources of the world and the consequent necessity for more efficient beneficiation of low grade ores has added new emphasis to the development of new separation processes for finely divided minerals. In recent years various advances have taken place in the recovery of mineral particles in the very fine size range. The various aspects of the slime problem have been reviewed by Collins and Read (181) and by Fuerstenau, Chander and Abouzeid (17).

Mineral particles of diameters less than ca. 20 μm are generally termed by mineral processors as slimes or ultrafines and occur as a result of the inefficiency of the comminution process or due to the natural fine liberation size of the mineral in the orebody. Standard physical separations are made in mineral processing plants utilizing differences in the physical properties of desired mineral and gangue minerals. Obviously, the chemical nature of the mineral may directly determine or affect the physical properties being utilized. These separation processes are limited by the average size of the ground mineral particles. The upper size limit is essentially governed by the dominance of gravitational forces which begin to interfere with the separation process at coarse sizes. The lower size limit, however, is determined by the principles of separation on which the process under consideration operates. For example, down to particle sizes of 20 μm, the froth flotation process achieves such separations quite efficiently but the presence of finer particles leads to progressive deterioration of the process efficiency. In addition, the presence of ultrafine particles is also pernicious in flotation because they usually adsorb onto the coarser particles (slime coating) spoiling the efficiency of the process. The floatability of very fine particles has recently been reviewed by Trahar and Warren (182).

The reasons why slimes are difficult to treat are numerous and have been discussed many times elsewhere (181). Many of the difficulties, however, can be attributed to two main characteristics which begin to dominate : the specific surface area becomes large and the mass of the particle becomes very low. From the former phenomenon results that the surface and interfacial properties of these particles dominate their behaviour, and the separation therefore ought to be based on differences in surface and interfacial properties of the materials to be separated. On the other hand, when particles become sufficiently small the Brownian movement begins to dominate and gravitational forces become negligible. In aqueous media, where nearly all of the operations dealing with very fine particles are carried out, they tend to follow the motions of the fluid (rather than move relative to it) under the influence of any external force applied to achieve a separation.

A priori, promotion of aggregation of the valuable mineral in the multi-mineral slime-sized ore into larger units might be expected to overcome hydrodynamic and surface physicochemical limitations, allowing subsequently a further separation by conventional methods. Aggregation of the particles from a dispersed system may be promoted by different mechanisms by means of altering the dispersion medium or by modifying the surface physicochemical properties of the dispersed phase. Hence, destabilization of a stabilized aqueous dispersion leading to aggregation of particles can occur by at least the following mechanisms:

6.2.1. Physical Mechanisms

1. Mechanical aggregation.

Certain colloidal dispersions, especially colloidal dispersions of hydrophobic particles such as synthetic lattices, are perfectly stable if left undisturbed and are known to aggregate on stirring or shaking (they are known to develop very thin films of solid matter at the liquid/air interface). Heller (183), has found that mechanical coagulation produced by stirring or shaking of colloidal solutions (sterically stabilized polystyrene latex) resulted primarily in surface coagulation - bulk coagulation resulting from turbulence representing an additional coagulation process of minor importance. Yet the phenomenon is not well established; however, it is believed that these particles may aggregate under mechanical shear if the repulsive forces between the particles become ineffective or if there are forces, in addition to those causing collision due to Brownian movement, which are greater than the forces of repulsion between the particles, that can bring the particles into the sphere of attraction of the dispersion forces. If the latter is true, such forces acting under mechanical shear will have to overcome a potential barrier; otherwise the particles will not unite and aggregate (184). A similar phenomenon to that of mechanical aggregation has recently been reported by Warren (185) where very fine particles of scheelite ($CaWO_4$) which had previously been treated with sodium oleate but still having a high surface potential were stably dispersed only under low shear conditions but formed very stable aggregates under high shear conditions. This phenomenon has been described as " shear-flocculation" and has been found to occur in several systems (186).

2. Magnetic aggregation

Magnetic aggregation (using a steel matrix to cause deposition) occurs with those paramagnetic materials such as magnetite, hematite, etc. when they are subjected to magnetic fields. There have been several attempts to use this procedure to selectively separate these minerals from the non-magnetic gangue (187) and considerable work is proceeding on the use of a superconducting magnet system to achieve selective aggregation of para-magnetic minerals (188).

6.2.2. Chemical Mechanisms

1. Ionic coagulation

(i) Coagulation by simple uni-univalent salts. Electrolyte additions generally decrease the effective surface potential and the range of action of the electrical double layers resulting in instability and subsequent aggregation in accordance with the well-known DLVO theory.

(ii) Coagulation by hydrolyzing electrolytes such as ferric or aluminium sulphate can be considered different from simple coagulation (i) in that the polyvalent ions destabilize the dispersion and the precipitated hydroxides provide a further useful degree of bonding; but the aggregate units are weaker and less elastic than those obtained with linear polymers of high molecular weight (see (3) below).

2. Aggregation by surfactants

This results from the adsorption of surface-active agents at the solid/liquid interface, rendering the solid hydrophobic. Particle/-particle adhesion is then favoured due to the interactions between the hydrophobic coatings on the different particles and the resultant reduction in the area of the hydrophobic mineral/water interface.

3. Flocculation by polymers

This results from a process of adsorption and aggregation brought about by means of a multi-bonding agent (flocculant) that ties the particles together through a bridging mechanism. Flocs formed by the " bridging" mechanism with suitable polymeric flocculants yield larger, faster settling units than those formed by inorganic salts. They are also strong enough to be capable of withstanding moderate shear forces without rupturing (65).

It is also noteworthy that in some cases a distinction can be made depending on the flocculation mechanism, i.e., the term " flocculation" can be reserved for the process of aggregation of particles by a polymer only and " sensitisation" to the flocculation process by a polymer with the assistance of small amounts of salt.

All these forms of aggregation have been used selectively to concentrate or separate mineral components from mixtures. Selective coagulation has been performed in a number of examples to separate off mineral values or contaminants from clays (189). Also, examples of separation of rutile from quartz (190) and of hematite from quarts (191). have been reported. They have followed the theoretical analysis based on the classical DLVO theory of colloid stability to establish the possibilities of the selective coagulation process. The method has been described as based on differences in surface hydration and on zeta-potential properties of sub-micron sized particles (192). It is therefore, believed that the process will be applied essentially to separations of sub-micron material because of the slow settling rates involved (coagula sizes being an order of magnitude lower than those obtainable with high molecular weight flocculants), and also because the secondary minimum phenomena can cause difficulties in the treatment of 1 to 10 µm particles.

The aggregation of the mineral particles to be floated by collectors has long been considered to be a sign of floatability. This aggregation, which undoubtedly must be of selective character, has not been fully utilized on the separation of slimes. Gaudin and Malozemoff (193) emphasized the advantage to be gained by aggregating very fine particles of galena with xanthate type collectors before flotation, but no attempt was made to investigate the possibility of separating off the aggregate material without froth flotation. However a successful laboratory separation of a lead-zinc ore from the gangue by selective aggregation with potassium amyl xanthate has recently been described by Hollick and Read (194).

The selective aggregation by polymers or selective flocculation has become, however, the more efficient method for use in mineral separations. The advantages of the use of polymer selective flocculation are mainly concerned with the characteristics of the aggregate units formed with these macromolecules. These flocs are larger and stronger than coagula or " hydrophobic" aggregates. Thus, floc units are large enough to secure preferential sedimentation (relative to the unflocculated component) and strong enough to overcome mechanical abrasion and disruption by moderate shear forces.

6.3. Selective Flocculation : Previous Work and Main Features

6.3.1. Previous Work

In principle, the selective flocculation process has been known for many years and it has been found empirically by several authors that various polymeric flocculants exhibit some degree of specificity when applied to mixed dispersed systems (195). However, attention has been directed in the present decade towards the testing of its separation potentiality in the processing of finely divided minerals. Most of the work has involved only laboratory scale experiments (194), but the process has recently been incorporated in two large plants

(196, 197).

A review of a number of separations by selective flocculation and the feasibilities of its use on binary, ternary and multi--mineral systems has been presented by Read and Hollick (194). However, the upgrading values obtained with this process are far from meeting commercially acceptable concentrate specifications, but the method can be efficient enough to be used for the selective rejection of slime gangue as a preliminary step for another concentration process. Most of the work has been concerned with the treatment of clays, iron minerals, phosphates and potash (198, 199). The best concentration ratios have been obtained from laboratory trials only in optimum conditions of low solid content, high feed grade and high specific gravity of the component to be flocculated, etc. For example, Yarar and Kitchener (200) have successfully separated all the galena from a synthetic mixture with quartz when galena amounted to 25% of the mixture and the solids content was 5% w/v. Read (201) has succeeded in separating hematite from a siliceous gangue with polyacrylamide type flocculants only after strict control of the suspension medium and the ionic character of the polyacrylamide. However, other non-magnetic taconites have proved unresponsive to polyacrylamides (194). The separation of chrysocolla (89% recovery and a concentrate grade of 77%) from quartz with a non-ionic polyacrylamide has been readily performed with a 10% chrysocolla feed and 1.1% w/v solids content; but a decrease in the proportion of chrysocolla in the feed (2% chrysocolla) and an increase in the feed solids content (7.5% w/v) resulted in decreases of about 70% in both grade and recovery (202).

6.3.2. Basic Principles

The basic features governing the efficiency of the process are not adequately elucidated for the design of current selective flocculation schemes but some advances, however, have been made in the development of polymer flocculants for selective flocculation (200) and also considerable effort has been given to the design of separators for the removal and cleaning of the flocs after the selective flocculation stage (203). The chief factors involved in the process of selective flocculation can be summarized as follows:

1. Chemical and surface physico-chemical factors

(i) Factors relating to the suspension : prefloculation stability. Good dispersion is a primary condition; homocoagulation of the component to be separated may enhance the incidence of particle capture for one particle species but unselective coagulation (i.e., heterocoagulation) should be avoided. The stability of the suspension can be increased either by adjusting the concentration of the intrinsic potential-determining ions of the suspension or by addition of dispersing agents such as inorganic polyphosphates or polyacrylates of low molecular weight. The use of these deflocculant agents also offers the possibility of masking the ions produced from the partial dissolution of the minerals (200).

(ii) Factors relating to the polymer. The selectivity of the polymer flocculation is largely dependent on the nature of the polymer. These macromolecules are known to be good, poor or weak flocculants for certain mineral dispersions depending on the adsorption affinity of the polymer molecule for the substrate under predetermined conditions. This inherent selectivity can adequately be exploited to make use of the polymer in the process of selective flocculation. In addition, this natural selectivity can be enhanced by chemical modification of the polymer skeleton, incorporating ligands with the property of complexing to a specific cation in a mineral (204).

The promotion of selective polymer adsorption by the use of modifying agents before the addition of the polymer, has also received some consideration. The use of some divalent and polyvalent electrolytes has promoted the adsorption of the polymer and subsequently the flocculation of the valuable mineral (200). Untreated mineral particles were not amenable to flocculation at all with the same polymer.

(iii) Miscellaneous factors relating to modifying reagents. The action of modifying agents by analogy with froth flotation may be centred either in the bulk solution by, for example, masking ionic products from mineral dissolution or affecting the polymer activity coefficient and changing its solution properties such as end-to-end dimensions, degree of ionization, etc., or they may also alter the surface potential of the mineral, or, simply as a result of adsorption, prevent or promote the co-adsorption of the polymer on certain mineral surfaces (200).

2. Physical factors

(i) Factors relating to the separation process

a) The entrainment process arises when the solids content (pulp density) of a mixed slurry is increased or when the flocculation of the major component causes entrapment of the other. It has been found that this problem can be partially surmounted by mild agitation of the flocculated sediment; gentle working of the flocs releases much of the entrapped material (205).

b) The removal of the flocs after having achieved the selective flocculation implies the actual separation of the flocculated material from the dispersed phase and sometimes this process is followed by a further floc-cleaning stage to free flocs from occluded particles. Since flocs are rarely strong enough to be collected with screens or hydrocyclones (205), elutriation would seem to be the most logical separation method. Efficient elutriation has been reported by Read (203) with the use of an elutriation column. The wash water was introduced through a series of jets at the bottom of the column. The process requires a uniformly rising flow of water and the use of a very high column. Friend, Iskra and Kitchener developed a modified elutriation device where the wash water was introduced through a porous plastic base. It performs the functions of gently agitating the flocs and of elutriating off the freed particles in separated zones of a quite shallow unit without moving parts (203).

c) Flotation of the flocs has also been performed for the removal of the flocs from the dispersed unflocculated material (206, 207) Clement (206) managed to selectively flocculate fine-grained barite and float these flocs by small additions of anionic reagents at around a pH value of 9.5, corresponding to only a 20% monolayer coverage on the barite. Gogitidze and co-workers (207) floated the manganese carbonate flocs which formed after addition of polyacrylamide. Similarly, Usoni, et al. have found that flocculants improved the flotation yields of zinc minerals (208).

(ii) Limiting factors

a) The feed grade (or the initial concentration of the valuable mineral to be flocculated with respect to the gangue) and the solids content of the slurry are recognized to be limiting parameters of the process of se-ective flocculation. Thus the flocculation of a mineral component in a very low concentration with respect to the gangue is significantly decreased mainly because the formation of flocs is greatly hindered by the presence of a large proportion of non-flocculable components. The probability of effective collisions between polymer coated particles becomes very low and, as a result, the flocculation of the minor component is almost negligible. It also follows that with a high solids content the probabilities of flocculation of the minor component will be dictated by the same considerations. Flocculation under a turbulent regime will be effective only in those cases where the adsorption forces of the polymer on the mineral surface are favoured under turbulence and the floc units formed are strong enough to resist the disruptive action of the shear forces.

The efficiency of the process of selective flocculation will, in one manner or another, be dependent on all the factors given above. However, among all the problems which are involved, the selectivity still remains the fundamental key to the process.

Selectivity versus effectiveness The selectivity of the process arises mainly from a differential adsorbability (or affinity) of the polymer on the various minerals. For example, a polymer may strongly adsorb onto copper minerals but be weakly held on quartz or dolomite, but in all cases it could cause flocculation. However, by introducing another reagent strong enough to compete with the polymer for surface sites on quartz or dolomite, the flocculant would then be able to adsorb on the copper mineral only. Consequently, a polymeric flocculant can have an inherently high sensitivity to a particular mineral species, i.e., a polymer molecule operating under specified conditions may preferentially adsorb onto suitable sites of certain mineral species. But the existence of very weak non--selective forces of electrostatic or hydrophobic nature, for example between the individual surface-segment interactions, can be sufficient (since each polymer molecule possesses a large number of segments) to make the net adsorption free energy per molecule quite large and, therefore, the polymer may well adsorb and flocculate the undesired material.

The complete inhibition of these adsorption forces may theoretically be almost impossible to achieve but a substantial reduction in the degree of adsorption of the polymer to protect a suspension from flocculation is a very well known process. It follows then that depression of the material not to be flocculated from polymer adsorption-flocculation by suitable depressants should be essential. The latter is certainly so in the treatment of real ores when cross-contamination during grinding, the intrinsic " self-activation" to flocculation of the gangue material (quartz normally carries iron in the matrix) and the adsorption of dissolution products from other components in the system render some operations which are successful in the laboratory inoperable on the plant scale. Hence, the effectiveness of the separation of a mineral value from the gangue by selective flocculation is not exclusively dependent on the inherent affinity of the polymer for the mineral to be separated but also depends on the control of the adsorption of the same polymer on the material not to be flocculated.

Therefore, improvement in the efficiency of the process may be accomplished in at least two different ways:

A. Increasing the natural selective character of the polymer for a specific mineral. Incorporation of chemical groupings into the polymer chains with a strong affinity for ions in the minerals minerals to be flocculated may lead to an increase in selectivity (204). An alternative principle for getting selective adsorption of a polymer on the mineral may be by the use of flocculation " activators" as in the case of selective froth flotation.

B. Inhibiting the adsorption of the polymer flocculant on the surface of the material not to be flocculated. Flocculant adsorption may be inhibited by different mechanisms:
    i) increasing the electrostatic repulsion between particles by altering the surface potential of the minerals: anionic polyelectrolytes will not adsorb on to highly negatively charged surfaces (200).

ii) pre-adsorbing species : competition between the modifying reagent and the flocculant for surface sites on the minerals : for example, a low molecular weight polyacrylate, " Dispex" (Allied Colloids, Bradford) prevented the adsorption of an anionic polyacrylamide flocculant on calcite (209).

iii) removing the free hydroxyls from the surface of quartz by " ageing" or alkali treatment (200).

iv) by the use of selective depressant agents with complexing action for specific ions in the gangue.

6.4. The Aim of This Work

The aim of this work was to illustrate a novel chemical origin of selectivity; namely to consider an alternative approach to obtain selectivity by promoting an association between a " flotation collector" (which must be specifically adsorbed and, therefore, is a highly selective reagent) and a polymer interacting with the collector--coated particles.

A further aim was to extend the knowledge obtained in the first part of this work on the fundamentals of the mechanism of the adsorption and flocculation of a high molecular weight poly(ethylene oxide) on different surfaces and apply all this, to the processing of typical " hydrophilic" non-sulphide copper minerals which were to be pre-treated with hydrophobizing agents before flocculation by the polymer.

Selective flocculation and flotation are similar processes in that both exploit the differences of the surface-chemical properties of the minerals. In both systems the suspended particles have to be conditioned in such a way that functional groups of added molecules attach only to the surfaces of the particles to be removed. In selective flotation, the collectors used are organic molecules with appropriate functional groups linked to an alkyl chain of about 6 to 8 carbon atoms. In selective flocculation the high molecular weight polymeric flocculants used can have - even in their statistical coiled form - diameters as large as 100 nm in solution and they are selective only to a limited extent. For any given mineral suspension it can be simply demonstrated that a certain flocculant visibly functions much better than another. The efficiency of the selective flocculation process has lain mainly on this natural specificity and scope for improving this selectivity has always claimed to be something exclusive of the polymer flocculant.

The present work is concerned with the origin of selectivity in classical froth flotation and especially with the possibilities which stem from the well-known selectivity of xanthate type collectors for copper minerals. The principle was tested on separate copper minerals and on artificial mixtures. Pre-treatment with xanthates before flocculation by PEO was examined on typical copper minerals such as malachite, chrysocolla, etc. These studies should provide the basis then to establish the fundamental principles for the proper design for the selective flocculation process, as a method of separation for a finely divided non-sulphide copper ore. The general findings of this research should also apply to other types of ore.

CHAPTER 7

THE FLOCCULATION OF NON-SULPHIDE COPPER MINERALS

7.1. Introduction, Experimental Material and Techniques

The flocculation of non-sulphide copper minerals, namely chrysocolla and malachite, by synthetic polymers has been the subject of only a few, not very thorough, studies. Flocculation of suspensions of malachite and chrysocolla by a non-ionic polyacrylamide a cellulose xanthate polymer and a polyvinyl alcohol xanthate has been reported by Attia and Kitchener (204). They have also shown that modification of a polyacrylamide by treatment with glyoxal bis-2-hydroxyanil enhanced its flocculating ability for copper minerals, but decreased its effect on calcite, feldspar and dolomite. Other work (202) has shown that of the polyacrylamide type polymers, only those having non-ionic characteristics were effective in flocculating chrysocolla.

The present work deals with a different approach towards the flocculation of the non-sulphide copper minerals. The essence of the present approach is similar to that of the activation process in classical froth flotation, namely, modification of the surface before flocculation by a polymer.

The use of " regulating reagents" in the flotation process is well known from earlier years and it is recognized that the use of collector reagents alone is rarely sufficient for flotation selectivity unless the minerals differ sharply in their flotation properties. As a general rule, the process by which collection is increased is termed " activation" and that by which it is decreased is termed " depression" . Hence, the flotation modifiers are called activators or depressants. The same principle can be applied to promote or inhibit the process of flocculation of mineral suspensions; but, unfortunately, it has not been fully exploited. However, one example, which is well used in practice is sensitisation, the flocculation of dispersions by a polymer with the help of small amounts of common soluble salts (200). In addition, bivalent, trivalent or polyvalent ions are known to promote the flocculation of quartz (negatively charged) by anionic polyacrylamides (122). An alternative method for promoting flocculation may well be achieved with the use of other surface modifiers in conjunction with a polymer flocculant. The principle is to promote a hydrophilic-hydrophobic transition on mineral surfaces, as a preliminary step in order to influence the adsorption of a polymeric flocculant. Because the practical aim of this study is to make the adsorption of the polymer selective, special considerations will be given to those chemicals used in selective flotation . as collectors - this follows the flocculation of collector-coated particles, which is common practice in the flocculation of flotation concentrates. With regard to the polymer, the principle requires the use of a flocculant with poor action to hydrophilic substances and reasonably strong affinity to hydrophobic ones. A characteristic of PEO is that it is not significantly adsorbed onto any strongly " hydrophilic" surface unless a substrate modification to decrease this hydrophilicity is introduced. It should be emphasized that the terms " hydrophilic" and " hydrophobic" are being used here only in a relative sense; i.e., to distinguish between oxide surfaces which are not susceptible to wetting by organic solvents and those which are. The flocculation of malachite and chrysocolla and afterwards, the selective flocculation from synthetic mixtures with, either quartz, calcite or dolomite is to follow the general aim underlined here. Accordingly, it is to be expected that any reduction in the hydrophilic character of malachite and chrysocolla would eventually lead to flocculation by PEO. The latter is to be expected from the treatment of the copper minerals with either sodium sulphide (sulphidization) (210), thio-type collectors or other chelate-forming organic compounds before flocculation by PEO.

In addition, scope for flocculation by PEO with the aid of complex-forming organic macromolecules was also considered. This follows the chemical reaction of PEO with tannin-like structure molecules or with PVA (polyvinyl alcohol) or PAA (polyacrylic acid) type polymers in solution (the " anchor" effect of these flocculation promoters requires a further chemical reaction with the surface).

In this chapter investigation of the various aspects influencing the flocculation of pre-treated malachite and chrysocolla are to be considered to establish optimum flocculation conditions.

Experimental Material and Techniques:

Reagents. All standard reagents used in this study were of analytical grade. Solutions of either $NaC\ell$, Na_2CO_3, $CaC\ell_2$ were used for control of ionic strength, whilst NaOH and $HC\ell$ were used for pH adjustments. All solutions were prepared using the deionized and double distilled water already described in Part I of this work.

Potassium amyl xanthate. A commercial sample of potassium amyl xanthate was purified by recrystallization from acetone and precipitation with ethyl ether. It was kept under vacuum in a container and placed in a desiccator. In addition, it was periodically washed with ether to ensure its purity. Any solutions not used within two days were discarded.

Sodium sulphide. Analar grade sodium sulphide was also kept dry under vacuum and its solutions were prepared with distilled water which had been previously boiled for 10 min to reduce the amount of dissolved CO_2 and then purged with N_2 (free of organic matter by letting it to pass through an activated carbon column) for 3 hours to remove oxygen. Fresh solutions of sodium sulphide obtained by this procedure were made up every day to ensure the absence of oxidized species.

Poly(ethylene oxide). The polymer solutions of this commercial product (BDH-Union Carbide, " Polyox coagulant") were also prepared with CO_2 and O_2 free water and kept in the refrigerator to prevent bacteria growing during its " life-period" of one week. Solutions were randomly checked for polymer activity using the analytical method described in Appendix 1.

Materials. Chrysocolla from Arizona (hand-picked lumps) and malachite, either prepared by precipitation (BDH), i.e., basic copper carbonate or from a pure massive hand-picked sample from the Congo, were dry-ground in a laboratory agate mill to less than 37 μm. Aqueous dispersions of these materials were dispersed by ultrasonic treatment at high intensity for 3 minutes in the " Sono-probe" . The chrysocolla assayed 34.5% Cu, the precipitated malachite 56.1% Cu and the natural malachite 55.9% Cu.

Experimental procedure. The flocculation experiments were usually performed in the same cylindrical glass tube described in Part I of this study (occasionally, 400 ml baffled beakers were used when high shear rates were required). The dispersed chrysocolla or malachite was introduced to the cylindrical glass tube and stirring was maintained at 1900 r.p.m. for 5 min (the dispersant having previously been added). Addition of modifying agents was followed by conditioning for 5 min at 1280 r.p.m.. Finally, the flocculant was slowly added from a 1 ml pipette. The suspension was stirred for a fixed period of 90 s at 1980 r.p.m. to allow uniform distribution of the flocculant and also to promote floc formation. The extent of aggregation and the size of the flocs increased with increasing suspension stirring speed. Surprisingly, the further period of slow shear rate which is normally provided was, in some cases, found to be unnecessary. The samples were withdrawn from the side outlet after predetermined periods of standing and were measured for solids content from dry-weights. The results are presented as flocculation indexes, % F as defined in Chapter 4.

7.2. Flocculation of Chrysocolla and Malachite Suspensions

The most important factors affecting the extent of flocculation are the hydrodynamics of the system and the amount and type of the flocculation promoter present. In addition, the influence of the nature and concentration of different salts on the flocculation extent will also be considered.

Before flocculation experiments, the dispersion characteristics of the suspensions were studied as a function of concentrations of sodium silicate and sodium hexametaphosphate (Calgon). Dispersibility, % D, of malachite and chrysocolla calculated as $\% \text{ D} = 100 \left(\frac{C_x}{C_o}\right)_{h_x, t_x}$ is shown in Table 6.

The flocculation experiments which are described below were always preceded (unless otherwise stated) by the addition of either Calgon or sodium silicate. The samples were taken within short periods (usually 1 min after flocculation conditioning) to ensure clear differences between flocculated and unflocculated states. In all cases, more than 90% of the initial material was fully dispersed.

Table 6

Dispersibility of malachite and chrysocolla as a function of dispersant addition

(t_x = 3 min; h_x = 9 cm)

Test Number						
	Calgon (p.p.m.)	0	25	50	100	300
1	% D, malachite	10	82	85	87	87
2	% D, chrysocolla	5	30	33	47	63(91)[†]
	Sodium silicate (p.p.m.)	500		1000		
3	% D, malachite	75		83		
4	% D, chrysocolla	53		68		

[†] t_x = 1 min.

The optimal hydrodynamic conditions. In the early stages of this study attempts were made to flocculate " sulphidized" or " xanthated" malachite suspensions by PEO in routine jar tests under predetermined shear conditions. Slight flocculation took place at some concentrations of PEO and Na_2S (or potassium amyl xanthate), but the results were not easily reproduced. The extent of flocculation was found to depend greatly on the fluid flow velocity gradient imposed on the system, because a certain minimum speed was required for nearly complete flocculation to occur. The results obtained with the use of standardised method given in Section 7.1. were, however, very easily reproduced. The random error incurred was less than 4% with identical test procedures. When the extent of flocculation was considerable, very large and sticky flocs were formed which settled readily within seconds. On the other hand, with incipient flocculation only very small aggregates were present, some of which remained in the supernatant even for quite long periods. In Fig. 17 the flocculation of sulphidized malachite as a function of the degree of agitation of the suspension is shown. It can be concluded from the type of the curve, that a minimum average energy of collisions between sulphidized particles should be reached before complete adsorption of PEO and subsequently flocculation can take place. This energy barrier is not removed by addition of indifferent simple electrolytes, such as NaC*l*, as may be seen also in the same Figure. Apparently, therefore, the barrier is not due to electric double-layer repulsion.

The differential adsorption of PEO onto malachite preconditioned under different pretreatments is given in Table 7. The flocculation values obtained under similar conditions are also included for comparison.

Table 7

The stirring effect on the adsorption (and flocculation) of PEO on sulphidized malachite.

Initial polymer addition, 0.75 mg PEO/g malachite.

Test No.	Sample	Stirring Speed r.p.m. (for 3 min)	Adsorption extent, mg PEO/g malachite	Flocculation extent, % F
1	malachite	280 - 2060	< 0.1	18†
2	sulphidized malachite	280	0.20	18
3	sulphidized malachite	450	0.30	20
4	sulphidized malachite	700	0.30	37
5	sulphidized malachite	900	0.40	83
6	sulphidized malachite	1280	0.50	87
7	sulphidized malachite	1680	0.50	92
8	sulphidized malachite	2060	0.70	89

† slow sedimentation

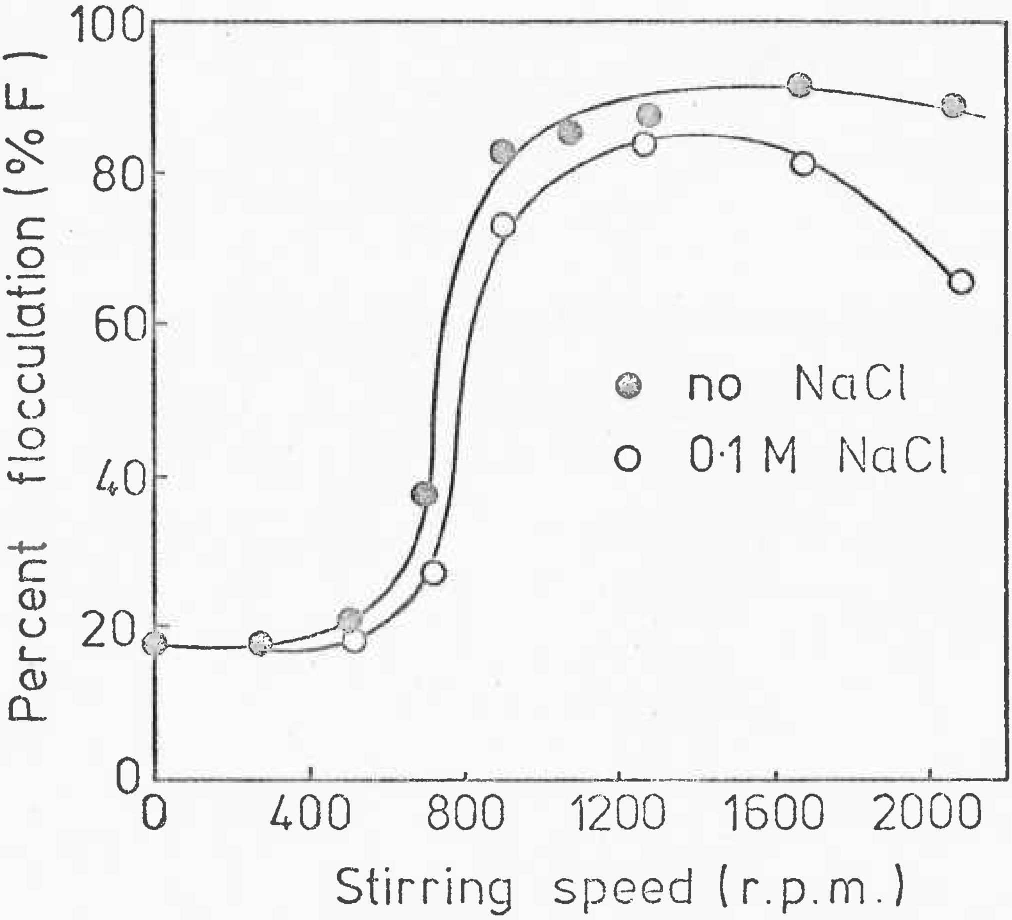

Figure 17

Effect of stirring condition (2 min at the given speed) on the flocculation of sulphidized malachite by PEO at pH 9.1 in the presence or absence of NaCℓ

Although there is a broad correlation between stirring, adsorption and flocculation, it is not universal. For example, test 2 and 3 compared to test 1, showed that adsorption of PEO by sulphidized malachite was not accompanied by an increase in flocculation. Between tests 3 and 4 and between 6 and 7, increases in the agitation of the system resulted in increases in the flocculation extent; however, here no differences in the strength of adsorption were observed (see Discussion).

The promotion of the flocculation of malachite and chrysocolla by PEO. The use of several surface modifying agents for malachite and chrysocolla was tested for flocculation by PEO. In their absence no flocculation of malachite or chrysocolla by PEO was observed. The flocculation promoters can be classified into two distinct categories according to their possible mechanisms of action.

I. Promoters (activators) with a hydrophobizing effect:

- a) sodium sulphide;
- b) surfactant collectors: sodium laurate, sodium lauryl sulphate, sodium oleate;
- c) chelate-forming organic compounds: alkyl xanthates; diethyldithiocarbamates, salicylaldoxime, diphenylguanidine, etc.

II. Promoters with surface and solution (with the polymer) chemical action. Examples are tannic acid and quebracho, which are known to form insoluble complexes in solution with PEO and adsorb at the non-sulphide copper / water interface.

Table 8 illustrates examples of flocculation of malachite and chrysocolla promoted by several chemical reagents.

The main features of the flocculation of malachite and chrysocolla by PEO with the use of these activators can be summarized as follows:

1. Aggregation of the dispersed particles before flocculation by PEO was observed with the use of modifying reagents of types I_b and I_c. The addition of PEO greatly enhanced the size and the strength of the aggregates.

Table 8

Flocculation effects of different activators on malachite and chrysocolla;

pH 9.5; values in brackets are concentrations (minimum) of activator in mg/g malachite or chrysocolla.

Flocculation Activator		Malachite % F	Chrysocolla % F	Activator Type
-		18	34	none
Sodium sulphide	(12)	95	98	I_a
K-amyl xanthate	(40)	94	98	I_c
Na-diethyl dithiocarbamate	(50)	91	95	I_c
Sodium oleate	(50)	92	91	I_b
Sodium laurate	(50)	89	93	I_b
Salicylaldoxime	(20)	68	81	I_c
Diphenylguanidine	(16)	90	97	I_c
Tannic acid	(12)	95	98	II
Quebracho	(13)	95	99	II

2. High shear rates were generally required to achieve floc formation and, in some cases a low shear rate following the higher was found to be unnecessary for floc building. Thus, these flocs were stable at high rates of shear.

For selective flocculation purposes, any of the flocculation promoters presented here could be used, in principle. However, in this study special attention has been given to those reagents classified in I_a and I_c, mainly because they offer a recognized high specificity for copper minerals; also, they are commonly used in practice because they are economical.

Flocculation of malachite and chrysocolla with sodium sulphide and K-amyl xanthate:

a) The effect of varying the concentration of Na_2S and K-amyl xanthate on the extent of flocculation of malachite and chrysocolla by PEO is shown in Figures 18 and 19 . Three main features are worthy of comment.

1. No flocculation at all (only slow coagulation) of either chrysocolla or malachite was observed in the absence of Na_2S or K-amyl xanthate.
2. Flocculation was brought about by the addition of very low concentration of Na_2S (less than 2.5 mg Na_2S/g chrysocolla; 12 mg Na_2S/g malachite).
3. An excess of Na_2S did not prevent malachite or chrysocolla from being flocculated by PEO.

b) The effect of pH and the use of tap water. The flocculation of sulphidized malachite by PEO was studied in distilled and in tap water as a function of pH (see Fig. 20). The flocculation was found to be independent on the pH value of the medium for dosages of sodium sulphide greater than 2 mg Na_2S/m^2 malachite. However, irreproducibility and a gradual decrease in flocculating power of PEO with a decrease in pH was found for sodium sulphide dosages of the order of 0.7 mg/m^2 malachite or less (a critical activation concentration).

The use of tap water showed the same general tendency but irreproducibility was very high in most cases. A possible explanation of this phenomenon may be given by the varying chemical composition of tap water (for example, the proportion of $CaCO_3$) with time (" ageing" and oxidation processes may also be different and dependent on time). The decrease in the flocculation extent observed, in many cases, with tap water may well be a result of the high amount of $CaCO_3$ present in the tap water (see below).

c) Effect of added electrolyte on the flocculation of sulphidized malachite by PEO. All the experiments discussed in the preceding sections were carried out without a constant electrolyte concentration. Since in all destabilisation phenomena the concentration and valency of the electrolytes are very important variables and since electrolytes are always present in mineral slurries, it was decided to determine

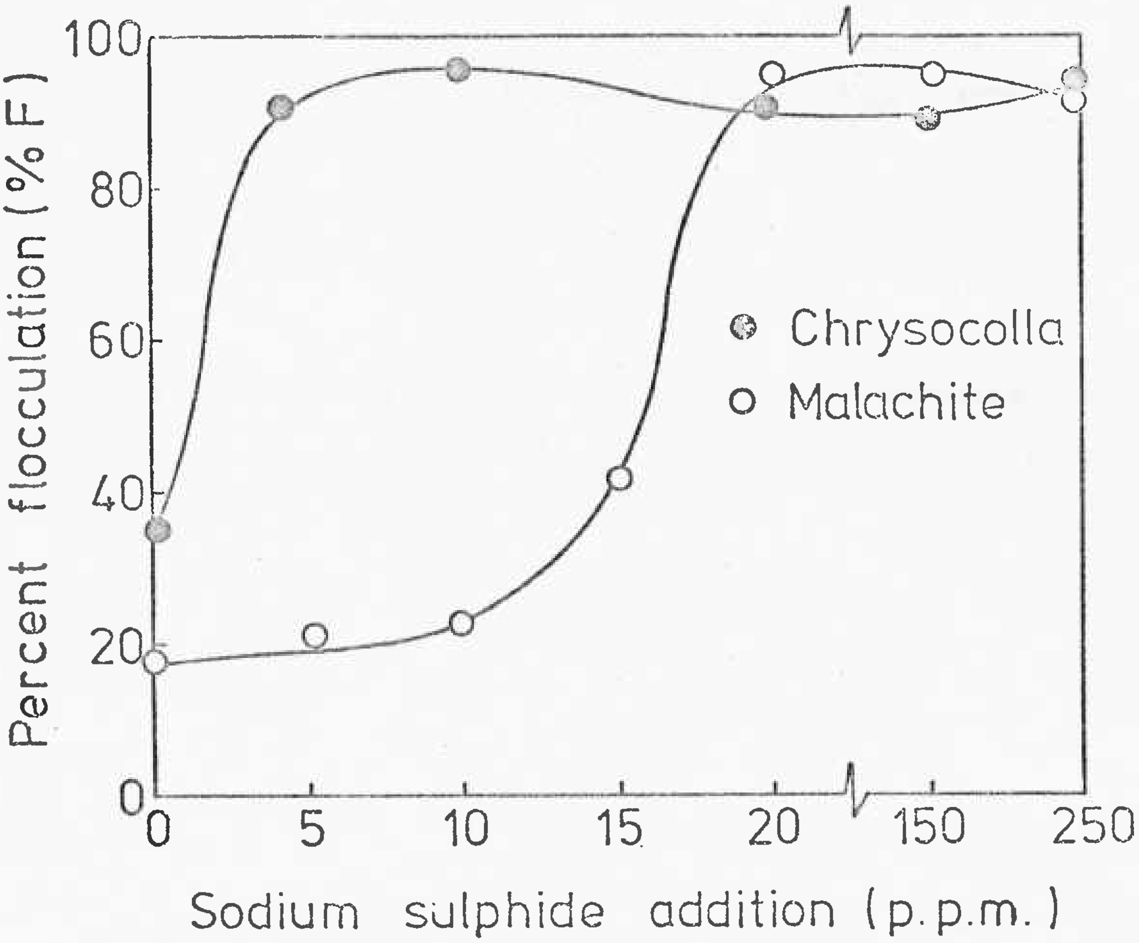

Figure 18

Effect of sodium sulphide on the flocculation of chrysocolla and malachite suspensions (0.2% w/w) by PEO (3 ppm); malachite dispersed in 25 ppm Calgon at pH 9.1; chrysocolla in 10^3 ppm sodium silicate at pH 10.9

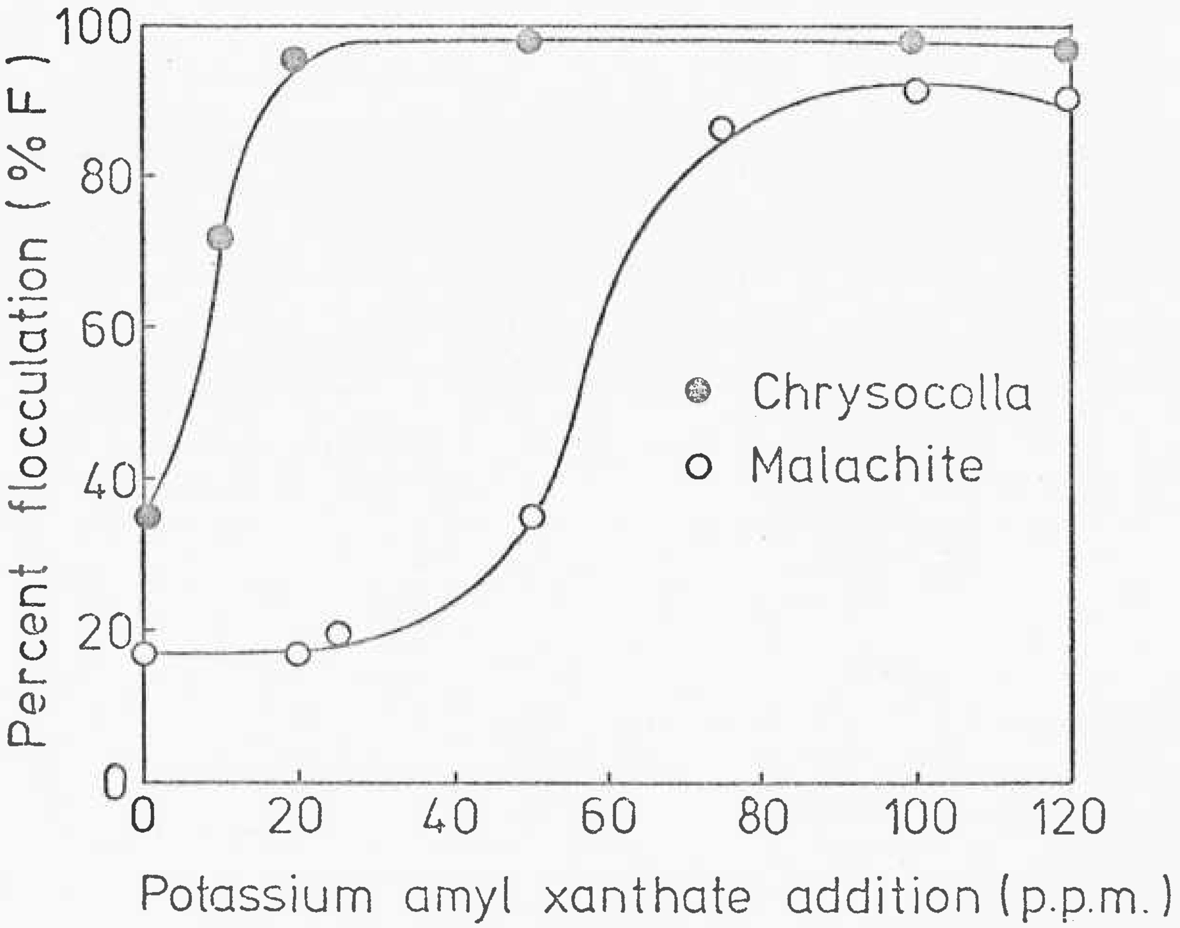

Figure 19

Effect of K-amyl xanthate on the flocculation of malachite and chrysocolla suspensions (0.2% w/w) by PEO (3 ppm), 25 ppm Calgon

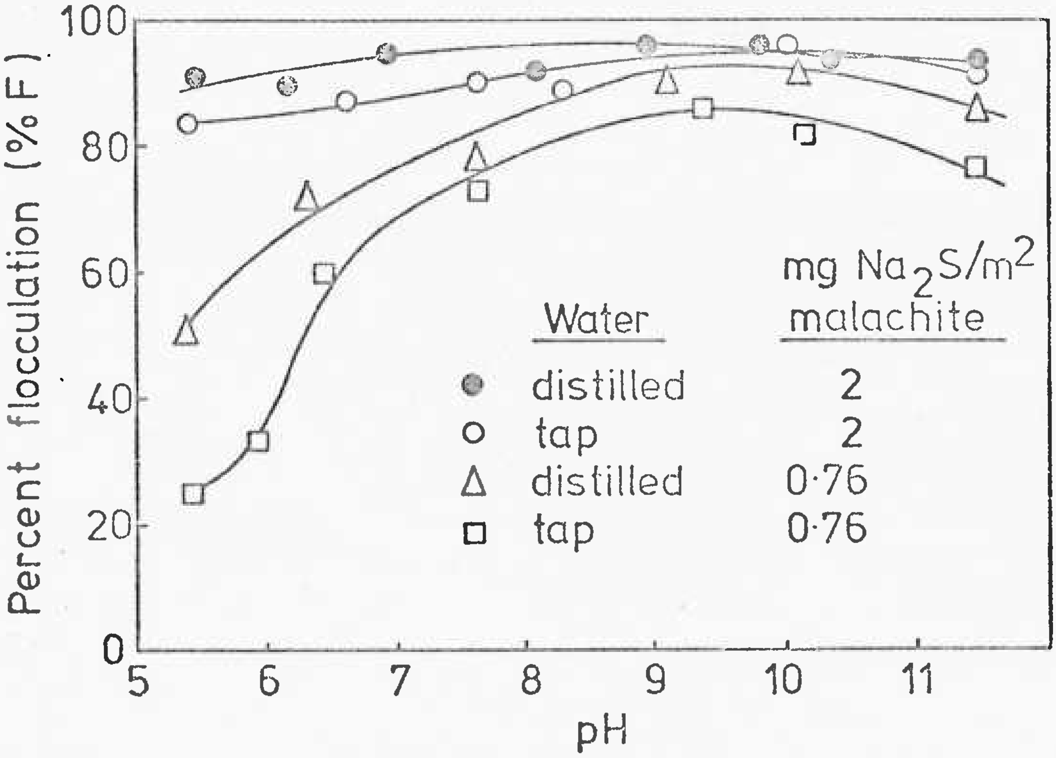

Figure 20

Effect of pH and tap water on the flocculation of sulphidized malachite suspensions (0.2% w/w) by PEO (3 ppm); 25 ppm Calgon to what extent the flocculation of sulphidized malachite by PEO is dependent on the concentration and the type of electrolyte. These effects were considered with conditions where complete flocculation was obtained. Results are presented in Table 9 .

Table 9

Effect of added salts on the flocculation (% F) of sulphidized malachite by PEO

0.76 mg Na_2S/m^2 malachite; 1 mg calgon/m^2 malachite; here, the addition of electrolyte was previous to the addition of Na_2S.

pH	Electrolyte	Concentration (moles/L)				
		5×10^{-3}	10^{-2}	2.5×10^{-2}	5×10^{-2}	2×10^{-1}
9.5	$NaC\ell$	90(18)	89(19)	89(21)	89(23)	87
9.5	$MgC\ell_2$	85	82	-	79	77
9.5	$CaC\ell_2$	91(19)	-	90(19)	90(19)	89
11.5	Na_2CO_3	92	93	80	34	-
11.5	$CaC\ell_2 + Na_2CO_3$ †	90	67	36	-	-

† % F values for concentration each salt. Values in brackets are results for untreated (no sulphidized) malachite.

From Table 9 it follows that

1) no flocculation of malachite by PEO takes place in the presence of common electrolytes (i.e., classical sensitization does not occur);
2) flocculation of malachite by PEO in the presence of Na_2S was decreased by addition of high levels of Na_2CO_3 or by the addition of $CaC\ell_2 + Na_2CO_3$ mixtures of concentrations greater than 5×10^{-3} M each ($CaCO_3$ formed " in situ") .

However, the following table shows that flocculation was always almost complete when the Na_2S was added before the electrolyte.

Table 10

Flocculation (% F) of sulphidized malachite in the presence of electrolytes

0.76 mg Na_2S/m^2 malachite; the Na_2S was added before the rest of the salts; 1 mg Calgon/m^2 malachite.

pH	Electrolyte	Concentration (moles/L)	
		2.5×10^{-2}	5×10^{-2}
11.5	Na_2CO_3	85	88
11.5	$CaCl_2 + Na_2CO_3$	87	85

It follows, therefore, that whatever the mechanism of flocculation depression, the addition of high dosages of Na_2CO_3 or "$CaCO_3$" (in situ), seems to have altered the process of sulphidization. This is certainly so because sulphidization prior to the addition of the depressing salts did not influence much the flocculation extent which was obtained in the absence of these salts.

7.3. Discussion

In order to make the discussion more comprehensive the different results are examined and presented here under separate headings.

1. The hydrophobic effect of collectors. It is remarkable that most collectors proposed or used in actual froth flotation practice are effective because of formation of complexes with the mineral surfaces. A distinction is sometimes made between " ordinary" collectors and chelating reagents, thus obscuring the general concept. For example, most of the thio-compounds (including potassium amyl xantahte) collectors are actually chelating agents for certain cations in solution and therefore, they may also be used, for example, in liquid-liquid extraction processes. The metal cation is bound into an essentially covalent complex. Chelating agents form complexes (in solution and at the solid/liquid interface) with

inorganic cations mainly by means of ordinary valence bonds (electron exchange) or through the action of the electric field thus created. Two main properties of these chelate compounds make the chelating reagents attractive for practical applications in the field of mineral processing:

a) the selective character of chelate forming organic compounds; a great number of processes are based upon natural specificity of these chemical reagents.

b) the hydrophobic character of some of the metal-organic compounds; many complexes are soluble in non-polar solvents and therefore, can be used, for example, in processes such as oil flotation or solvent extraction.

In a dispersed system, such as a mineral suspension, the formation of a surface chelate compound whose character is definitely " organic" in nature brings about destabilisation of the dispersed material by favouring particle/particle adhesion caused by the attraction between the hydrophobic coating and the reduction in the area (mineral/water interface). As a rule, the more hydrophobic the particles are, the more effective the aggregation phenomenon is. Selective aggregation based on this principle might certainly be possible in view of the specificity of the chelating agent. Yet Read and Hollick (194) have demonstrated that promising separations of lead and zinc could be obtained from a siliceous ore by selective aggregation of the mineral values with potassium amyl xanthate. The addition of a polymer (or with a simple organic fluid) with affinity for hydrophobic surfaces will form larger units (flocs) from these aggregates which will rapidly settle and separate from the dispersed phase. A good example of this phenomenon has been reported by Wright and Kitchener (145) in the system Laponite (a synthetic clay) - CTAB (cationic surfactant) and PEO. Addition of PEO improved the filtration characteristics (therefore, the floc size) of the clay suspensions. Accordingly, the findings of this study are in agreement with this principle - collector reagents (chelating or not) aggregate malachite or chrysocolla particles at certain dosages before flocculation by PEO. The addition of very low dosages of PEO were sufficient to enhance the size of the initial aggregate units, leaving a clear supernatant within seconds. It is noteworthy that with these complexing agents which do not form insoluble compounds (or hydrophobic inner complexes) with copper ions in solution, (for example, ethylene diamine and citric acid) neither aggregation nor flocculation by PEO was observed.

However, coagulation of the particles before flocculation is not a sufficient condition for inducing flocculation. For example coagulation of malachite or chrysocolla suspensions by inorganic (uni- or divalent) salts was not followed by subsequent flocculation with PEO. Moreover, high dosages of salts substantially decreased the flocculation of sulphidized malachite by PEO, possibly by affecting the sulphidization process itself (see below). It follows, therefore, that flocculation of malachite and chrysocolla aggregates is effective only if the aggregates are hydrophobic in character.

Alkyl xanthates are the most widely used collectors in froth flotation of sulphide minerals, however, the flotation of non-sulphide copper minerals by these reagents is usually ineffective. Whatever the explanations that may be postulated (e.g., detachment of the collector coating by capillary forces), xanthate molecules are adsorbed on these surfaces and give the particles some hydrophobicity (173) which is sufficient to destabilise their aqueous suspensions, making them susceptible to flocculation by PEO. Unlike flotation, flocculation by polymers requires, in most cases, the existence of only a few " active" sites for a flocculant molecule to be adsorbed and bridge the particles together.

2. The sulphidization phenomenon. The sulphidization process by sodium sulphide is alleged to be of paramount importance in the field of oxide flotation for two reasons:

a) Sulphidization of the oxide surface confers hydrophobicity. Rehbinder (211) showed that treatment of malachite with sodium sulphide led to major changes in the surface properties, in particular, the wettability by water droplets in air. The experiments showed that Na_2S adsorbs on the surface of malachite and sharply decreases its wettability. Thus, with a concentration of Na_2S of 1.3×10^{-5} M (that is very close to the concentration used in flotation of ores) the surface of malachite becomes hydrophobic. Accordingly, sulphidized malachite is favourably wetted by organic fluids and therefore it is assumed to be more hydrophobic than the oxide (210). Consequently, sulphidized carbonates, sulphates and silicates of heavy metals possess surfaces analogous to those corresponding metal sulphides and interact actively with xanthate type collectors.

b) Sulphidization of the oxide " stabilises" the surface. When it is desired to use thiol-type collectors to float non-sulphide mineral particles, leaching of the surface by these reagents usually occurs. Malachite, for instance, can be completely leached by potassium amyl xanthate under strong agitation. However, treatment of malachite with sodium sulphide protects the mineral from leaching by the chelating collector - obviously because of the thermodynamic stability of CuS.

In spite of the old use of the sulphidization process, its effect on many properties of oxides is still under investigation. Aggregation of sulphidized copper oxides has previously been observed on tenorite after treatment with sodium sulphide (212). The coagulation concentration range was found to be very narrow and redispersion was also found at higher dosages. Similarly, in this work, coagulation of sulphidized malachite suspensions was found only in a narrow concentration range and in the absence of a dispersing agent. However, flocculation by PEO was independent of the concentration of sodium sulphide after reaching a minimum surface coverage and, surprisingly, no depression of the flocculation at high dosages was observed. Finally, the fact that decreases in the extent of flocculation observed at low dosages of Na_2S by the addition of high levels of salts was overcome by sulphidizing the copper mineral before the addition of salts, indicated that sulphidization is significantly affected by an excess of carbonate ions. In the case of flocculation depression by calcite (formed "in situ") addition of high dosages of Calgon was found to overcome the problem, revealing that good dispersion of calcite is essential for sulphidization and flocculation to take place.

3. The activating role of polyphenols. Like tannic acid, quebracho, (a condensed tannin) is known to interact strongly with PEO in solution (see Appendix 1). This interaction is believed to occur via association between the phenolic OH group of the tannin structure and the ether oxygen of the polymer. These compounds have considerable potential for adsorption on to inorganic surfaces,

the phenolic OH groups presumably being involved (213). Such adsorption, whatever mechanism is involved, certainly changes the surface characteristics of the inorganic substrate, altering its reaction to collectors; for example, quebracho is well known for its flotation depressant characteristics of calcite (213).

In the same manner, quebracho (also tannic acid) adsorbs at the malachite (or chrysocolla)/water interface and also reacts in solution with PEO. This anchor effect causes the flocculation of the dispersed mineral particles.

4. The adsorption mechanism involved in the activation process. The present general results demonstrate that differences in the response of malachite and chrysocolla towards flocculation by PEO arose mainly from differences in the strength of adsorption of the polymer onto these surfaces. The differences arise from the various pretreatments to which the copper minerals were subjected before flocculation by PEO. A general feature, however, was the dependence on the hydrodynamics of the system. High collision energies were essential for effecting the flocculation of the particles. The fact that the extent of flocculation increases with increases in the stirring speed of the system for equal adsorption densities (see Table 7 and Figure 17) suggested that a minimum average energy of collisions between sulphidized malachite particles having polymer molecules adsorbed should be reached before flocculation could take place.

The interaction of polymer reagents with mineral surfaces is certainly more complex than at the air/water interface. However, it seems worth attempting to analyse the interactions between the polymer molecules with the surface of the non-sulphide copper minerals, on the basis of the nature of the forces arising during this interaction. Attempts were made in Part I to understand the several contributions that lead to adsorption of a molecule to PEO at various surfaces, but no quantitative analysis could be achieved. Nevertheless, the following mechanisms by means of which PEO can be attached to the surface of malachite or chrysocolla may certainly be operating:

a) The hydrogen bond effect. As discussed in Part I, PEO molecules may be adsorbed at the solid/liquid interface by means of hydrogen bond mechanism if the solid surface provides H-bond donors sites. In addition, the adsorption of PEO was found to be enhanced on to silica surfaces carrying " hydrophobic" groups in between hydrogen donor adsorption sites. Similarly, a proper sulphidized copper silicate or carbonate should carry sufficient - SH sites together with unionized CuS hydrophobic sites. Hence, this surface structure would definitely favour the adsorption of PEO by H-bonding, the hydrophobic section of the surface possibly matching the spacing of the hydrophobic groups, present in the PEO moiety.

b) Physical hydrophobic interactions should certainly be present in most cases. Accordingly, the activation of the adsorption (and hence, the flocculation) of a hydrophilic copper mineral, such as malachite or chrysocolla, should imply modification in terms of reduction on this hydrophobic character. The use of typical collectors like xanthates, fatty acids, etc., produced a hydrophilic--hydrophobic transition sufficient to allow interactions between PEO with the surface by means of physical hydrophobic interactions. On the same basis, methylated or sulphidized chrysocolla, copper sulphides, sulphidized tenorite or cuprite are readily flocculable by PEO.

c) Chemical mechanisms. The activation mechanism of the flocculation of copper minerals by PEO with the use of tannic acid or quebracho appears to be different from that of " hydrophobic activators" in that the adsorption forces involved may be the results of two subsequent interactions.

i) adsorption of quebracho (or tannic acid) at the copper substrate/water interface (actually, quebracho disperses malachite in water and therefore, malachite continues to be hydrophilic),

and ii) chemical interaction between quebracho (and tannic acid) and PEO in solution.

Similarly, it was found that other association complex-forming compounds with PEO in solution, namely, polyvinyl alcohol and polyacrylic acid can also be used for flocculating those substrates where PEO alone is weakly held, but not the associated polymer.

7.4. Conclusions

The flocculation of suspensions of malachite and chrysocolla, as examples of non-sulphide copper minerals, by PEO has been considered. Essentially, flocculation was not possible unless modifications of the copper mineral surfaces were introduced. The activation process consisted of treating the copper minerals with two different types of surface modifiers by means of which adsorption and subsequently flocculation were made possible. The flocculation of such modified particles did not require addition of common soluble salts (i.e., sensitization). The different surface modifiers can be classified as follows:

1. Hydrophobic activators; these produced a hydrophilic-hydrophobic transition of non-sulphide copper compounds allowing (physical) hydrophobic interactions with PEO. Examples of " hydrophobic activators" are potassium amyl xanthate and sodium sulphide. A general feature in the flocculation of such modified copper compounds was the dependence on the hydrodynamics of the system. Thus, a certain minimum speed (or fluid flow velocity gradient) was always required for almost complete flocculation to occur.

2. Chemical activators; these interact chemically with both the surface and PEO. Examples are tannic acid, quebracho, polyvinyl alcohol and polyacrylic acid.

CHAPTER 8

THE SELECTIVE FLOCCULATION OF NON-SULPHIDE COPPER MINERALS

The selective flocculation of non-sulphide copper minerals, namely malachite and chrysocolla, from their synthetic mixtures with siliceous or calcitic and dolomitic gangues, are to be considered following the studies on flocculation of separate minerals described in Chapter 7. After tests on synthetic mineral mixtures a selective flocculation scheme consisting of gangue dispersion, with either sulphidization or xanthation, followed by treatment with PEO was tested on an actual non-sulphide copper ore.

8.1. Separation of Non-Sulphide Copper Ores by Selective Flocculation

Experimental

1) Ores

Synthetic ores were prepared using chrysocolla and malachite (the same samples as described in Chapter 7) as examples of non-sulphide copper-bearing materials. The gangue consisted of pure calcite from France, a white, very pure, dolomite and a fine (- 10 μm) pure Brazilian quartz which was initially in the form of clear rock crystal lumps (dry-ground in the vibratory agate mill).

A natural ore for the selective flocculation tests was obtained from Shaba province of Zaire. This orebody assayed 8.5% total Cu and a mineralogical study showed that the copper was present in the form of malachite. The major gangue component was quartz but some chlorite and illite were identified (214). The following table shows the chemical and mineralogical composition of this ore. The chemical analyses were performed by X-ray fluorescence and by atomic absorption. The mineralogical composition was calculated utilising the element percentages from the head assay and the minerals identified by X-ray diffraction analysis and by electron probe examination (214).

(a) Concentration of various components in the feed (%)

Cu	8.5 ± 0.1	$A\ell$	1.5 ± 0.1
Acid-soluble Cu	8.42	Mg	2.4 ± 0.1
Co	0.329 ± 0.005	Mn	0.04 ± 0.01
Acid-soluble Co	0.328	K	0.31 ± 0.05
Fe	1.75 ± 0.02	P	0.06 ± 0.01
Acid-soluble Fe	0.39	SiO_2	61.4 ± 0.1

(b) Mineralogical composition of the feed

Mineral	Formula	Percentage
Malachite	$CuCO_3(OH)_2$	14.4
Pseudomalachite	$Cu_5(PO_4)_2(OH)_4.H_2O$	0.4
Heterogenite	$(CoO)_2(Co_2O_3)_6(H_2O)$	0.5
Quartz	SiO_2	61.5
Chlorite	$(Mg,Fe)A\ell SiO_3n.H_2O$	9.8
Illite	$K_2O(Mg,Fe).(A\ell,Fe)_2O_3.-(SiO_2)_{24}.12H_2O$	7.2
Goethite	FeOOH	0.6
Dolomite	$Mg,Ca(CO_3)$	0.2
Miscellaneous		5.4

A -60 mesh fraction was dry ground in the Tema mill for periods of 30, 45, 60 and 90 min. The first fraction (ground for 30 min) was used for selective flocculation tests because further treatment showed signs of changing the nature of the mineral components. The copper constituent became dark-brown in colour revealing a chemical change to other copper compounds (presumably, cupric oxide). This phenomenon has not been investigated here; however, it is thought that changes may have been caused by temperature effects [215]. The sample was analyzed for size distribution in the Cyclosizer (sub-siever sizer) (Warman Int. Ltd.)

Size range (μm)	>38	38-29	29-20	20-13	13-9	<9
% wt.	9	8	11	7	5	60

Other work (214)on liberation analysis by dense liquids has shown that about 90% of the copper mineral of this fraction should be liberated from the gangue. Before selective flocculation experiments, the dispensibility (% D) of this fraction in water was measured as a function of dispersant (sodium silicate) concentration, all tests containing approx. 10 g/l of dispersed solid. The results are given below.

Concentration				
sodium silicate (p.p.m.)	500	750	1000	1250
% D (t_x = 3 min)	54	68	76	78

In subsequent tests (unless otherwise stated) 1000 p.p.m. of sodium silicate was always used.

2) Procedure. Treatment of mixed synthetic suspensions

All the materials, dry-ground to less than 37 μm, were dispersed (in their respective proportions and in the presence of a dispersing reagent) by ultrasonic treatment for 3 minutes at high intensity with a Sonoprobe (Dawe, type 7530A, Dawe Instruments Ltd.). Highly dispersed suspensions were introduced to the cylindrical glass tube and stirring was maintained at 1900 r.p.m. for 5 minutes. This treatment was followed by addition of either sodium sulphide, quebracho or K-amyl xanthate and conditioned for 1.5 minutes at 960 r.p.m.. Finally, the flocculant was slowly added from a 1 ml pipette and then the normal procedure for flocculation described in Chapter 7 was followed. The supernatants were taken 1 minute after agitation was stopped. They were analyzed for malachite using the atomic absorption method for copper. The quartz or calcite (or dolomite) content was calculated from the malachite or chrysocolla and total solids content values by difference. At the end of the sedimentation time, t_x, the sediment was separated from the supernatant by removal via the bottom outlet. In multiple stage operations the supernatant was replaced by an equal volume of water containing half the initial concentration of dispersant. The floc-sediment was placed back in the tube and submitted to high shear to promote rupture of the flocs to release any entrapped particles from inside. Reflocculation was achieved by adding the half the initial concentration of PEO flocculant.

Treatment of the Ore The selective flocculation experiments followed the procedure described for synthetic mixtures with a slight but fundamental difference for the experiments done with the natural ore, in the method of dosing the system with the flocculant. It was found best to add the flocculant in stages and allow the denser particles of the copper mineral to settle after every partial polymer dosage. The procedure was repeated several times until the " green" floc units were formed and settled selectively from the " starved" supernatant.

The process of washing up the flocs in an elutriator column has been used, as well as the common procedure in the cylindrical tube system which has previously been described. The elutriator separator (203) consisted of an elutriator column in which the flocs were washed free from occluded particles by a constant rising water flow. The column was 1 m long and was divided in two sections of equal length. The upper section was 5 cm in diameter and the lower 2 cm. The feed material entered the upper part of the column through a tangential inlet (a funnel was used), and the wash water was fed from a manifold at the bottom of the lower section. The aggregates fell into the narrow section, where they were subjected to a tumbling, washing, action induced by the elutriation water. The cleaned flocs fell through the water manifold and were removed from the base of the column. The removal rate was adjusted to maintain a constant height of flocs in the lower section of the column and varied with the total weight of each feed sample.

3) Results. Synthetic mixtures

Before the selective flocculation experiments, the flocculation of separate calcite, dolomite and quartz suspensions by PEO in the presence of Na_2S and K-amyl xanthate was studied. No flocculation at all was observed (see Table 11) with these gangue minerals within a wide range of concentrations of flocculant and in the presence of Na_2S or K-amyl xanthate.

Selective flocculation tests of malachite and chrysocolla from their mixtures with either quartz, calcite or dolomite, were performed, following sulphidization (treatment with Na_2S) or xanthation (treatment with K-amyl xanthate) of the copper mineral

Table 11

Flocculation (% F) of Calcite, Quartz or Dolomite by PEO in the Presence of Na_2S and K-amyl Xanthate

pH 10.1, 1000 p.p.m. sodium silicate; h_x = 9 cm, t_x = 3 min, 1% w/w solids content; Na_2S between 50 and 200 p.p.m. and K-amyl xanthate between 50-300 p.p.m.

PEO concn. (p.p.m.) / Mineral	1	5	10	20
Quartz	No flocculation observed			
Dolomite	No flocculation observed			
Calcite	No flocculation observed			

before addition of PEO. The achievement of effective results required mainly a strict control of the gangue dispersion characteristics. Many attempts were made before obtaining the results presented here. Reasonable reproducibility of the experiments was generally obtained; four identical experiments (separation of chrysocolla from quartz) were reproducible to within 3% in both grades and recoveries (5% error for separations of malachite from quartz and calcite).

The separation parameters (concentrate grade of recovery) were studied as a function of feed grade and solids content; for simplicity, both variables were studied at the same time by keeping the copper mineral concentration constant and varying the concentration of the gangue. Data are presented as typical metallurgical balances, i.e., by analysing the different products (supernatants and sediments) for copper and measuring the dry-weights of each fraction. The values of copper content and dry-weights obtained from the 3 or 4 supernatants are summed up and presented here at " tails" . Also, the enrichment ratio (e_r) and the selectivity ratio (s_r) defined according to Attia (216) as:

$$e_r = \frac{\%\ \text{Cu in concentrate}}{\%\ \text{Cu in feed}}$$

and

$$s_r = \frac{\%\ \text{Cu in concentrate}}{\%\ \text{Cu in tailing}}$$

are given in each separation test.

Table 12 shows the influence of changing feed grade and solids content on the separation parameters obtained from the chrysocolla/-quartz system. The procedure followed was a multistage treatment with three dispersion and reflocculation stages.

Table 12

Selective Flocculation of Chrysocolla from Quartz

3 p.p.m. PEO flocculant, 27 kg Na_2S/tonne chrysocolla; pH 10.9 - 11.2; t_x = 4 min and 1000 p.p.m. sodium silicate. † is for 60 kg K-amyl xanthate/tonne chrysocolla instead of sodium sulphide; 34.5% Cu implies a 100% grade in chrysocolla.

Solids Content[1] (% w/w)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
1.15	conc.	12.00	30.79	88	7	51
	tails	88.00	0.60	12		
	calc. heads	100.00	(4.31)	100		
2.65	conc.	5.5	29.18	85	15	97
	tails	94.5	0.30	15		
	calc. heads	100.00	(1.88)	100		
5.15	conc.	2.9	27.7	84	29	193
	tails	97.1	0.16	16		
	calc. heads	100.00	(0.95)	100		
5.15†	conc.	2.9	27.86	86	30	199
	tails	97.1	0.14	14		
	calc. heads	100.00	(0.94)	100		

Table 12 [continued]

Solids Content[1] (% w/w)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
10.15	conc.	1.6	23.72	79	50	237
	tails	98.4	0.10	21		
	calc. heads	100.00	(0.47)	100		
10.15†	conc.	1.6	24.0	80	51	240
	tails	98.4	0.10	20		
	calc. heads	100.00	(0.47)	100		
20.15	conc.	0.70	17.58	59	76	195
	tails	99.30	0.09	41		
	calc. heads	100.00	(0.23)	100		

[1] The solids contents given here are indeed initial (feed) weighed values. The losses in weight during the whole procedure were always less than 0.6% of the initial figure.

As may be seen in Table 12, separations were normally successful; but a deleterious effect resulting in about 29% loss in recovery (conc.-Cu-distribution %) with 13% loss in grade (Cu %) was found when the solids content increased about 20 times up to 20% w/w and the feed grade reduced 19 times to a value of 0.23% Cu. However, the enrichment ratio (e_r) and the selectivity ratio (s_r) values steeply increased to a value as high as almost 80 times in concentration (e_r) and about 200 times greater in selectivity for the copper mineral (s_r). The replacement of sodium sulphide by K-amyl xanthate as flocculation activator resulted in a slight enhancement in both grade and recovery of the chrysocolla under similar conditions.

Table 13 shows examples of selective flocculation separations of malachite from either quartz or calcite (also calcite and dolomite) with the use of either Na_2S or K-amyl xanthate as activators of the flocculation of the copper mineral by PEO.

Table 13

Selective Flocculation of Malachite from Quartz and from Calcite (or Calcite and Dolomite)

1) Malachite/quartz system; pH 9.1; t_x = 5 min; 1.5 mg calgon/g quartz and 50 kg Na_2S/tonne malachite (Na_2S as activator). pH 10.9; t_x = 5 min; 10 kg sodium silicate/-tonne quartz and 150 kg K-amyl xanthate/tonne malachite when the activator is the xanthate; 56.11% Cu implies a 100% grade in malachite.

Solids Content (% w/w)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
1.15 (Na_2S)	conc. tails calc. heads	13.8 86.2 100.00	50.77 0.34 (7.3)	96 4 100	7	150
2.65 (Na_2S)	conc. tails calc. heads	6.0 94.0 100.00	49.9 0.17 (3.20)	95 5 100	16	293
5.15 (Na_2S)	conc. tails calc. heads	3.1 96.9 100.00	47.4 0.11 (1.60)	93 7 100	30	431
5.15 (K-amyl xanthate)	conc. tails calc. heads	3.3 96.7 100.00	46.76 0.12 (1.64)	93 7 100	28	390
10.15 (Na_2S)	conc. tails calc. heads	1.6 98.4 100.00	45.8 0.07 (0.83)	91 9 100	55	654
10.15 (K-amyl xanthate)	conc. tails calc. heads	1.7 98.3 100.00	43.0 0.08 (0.81)	91 9 100	53	537
20.15 (Na_2S)	conc. tails calc. heads	0.8 99.2 100.00	42.71 0.05 (0.41)	87 13 100	104	854

Table 13 [continued]

2) Malachite/calcite system; pH 10.2; t_x = 5 min; 60 kg Calgon/tonne calcite and 100 kg Na_2S/tonne malachite or 150 kg K-amyl xanthate/tonne malachite.

Solids Content (% w/w)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
1.25 (Na_2S)	conc. tails calc. heads	20.9 79.1 100.00	48.32 1.14 (11.0)	92 8 100	4	42
2.25 (Na_2S)	conc. tails calc. heads	11.7 88.3 100.00	45.42 0.98 (6.18)	86 14 100	7	46
2.65 (Na_2S)	conc. tails calc. heads	5.8 94.2 100.00	45.21 0.99 (5.64)	84 17 100	8	46
5.15 (Na_2S)	conc. tails calc. heads	3.1 96.9 100.00	43.56 0.31 (1.64)	82 18 100	27	140
5.15 (K-amyl xanthate)	conc. tails calc. heads	3.0 97.0 100.00	45.86 0.28 (1.64)	83 17	28	164

3) Malachite/calcite + dolomite system; pH 10.2; t_x = 5 min; 60 kg Calgon/tonne calcite + dolomite and 100 kg Na_2S/tonne malachite or 150 kg K-amyl xanthate/tonne malachite, 2 kg " cataflot" P40† /tonne calcite + dolomite where stated; calcite/dolomite = 4 : 1; † a very low molecular weight acrylate polymer dispersant.

Solids Content (% w/w)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
5.15 (Na_2S + Calgon)	conc. tails calc. heads	3.0 97.0 100.00	43.56 0.32 (1.63)	81 19 100	27	136

Table 13 [continued]

Solids Content (% w/w)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
5.15 (K-amyl xanthate + Calgon)	conc. tails calc. heads	2.9 97.1 100.00	44.77 0.34 (1.64)	80 20 100	27	132
5.15 (K-amyl xanthate + Cataflot P40)	conc. tails calc. heads	2.8 97.2 100.00	48.09 0.31 (1.65)	82 18 100	29	155

The main features revealed by table 13 can be summarized as follows:

1) Quartz + malachite proved to be a particularly favourable system in which to flocculate selectively the latter by PEO and Na_2S or K-amyl xanthate. Very efficient separation was obtained, even at low feed grade and high solids content. The results obtained also indicate that malachite responded almost identically to flocculation with Na_2S or K-amyl xanthate as activators.

2) The efficiency is reduced when the gangue is of calcitic (216) nature; nevertheless, an enrichment ratio of about 28 was found for a 5.15% w/w solids content with a feed grade of 1.64% Cu. However, the latter required at least a 60 times greater consumption of polyphosphate type dispersant and twice the amount of Na_2S; the amount of K-amyl xanthate, however, was found to be the same. Separation of malachite from calcite and dolomite was also possible provided that a fairly high concentration of Calgon was added. The use of Cataflot P40, a low molecular weight acrylate polymer, as dispersing agent instead of Calgon, resulted in an enhancement of both grade and recovery.

3) The main characteristics of the nature of the flocs are the strength and the large size of these aggregate units. This permits a very rapid sedimentation and separation from the dispersed phase

to be carried out. However, some foreign material is entrapped within and around them. Breaking up these flocs into smaller sizes is possible under vigorous agitation for a prolonged period of time. This process allows release and dispersion of the entrapped material. Reflocculation is then readily achieved by addition of a supplementary amount of flocculant.

4) Multistage treatment. An improvement in grade with minimal loss in recovery has resulted from multistage treatments. The removal of the flocculated material from the supernatant, as described before, and its replacement by dispersant-flocculant solution simulates an elutriator. However, it is noteworthy that in all batch experiments nearly 80% of the gangue material remained dispersed and could be readily separated off from the flocculated material. This led to upgradings of the order of 5 times in most cases.

Natural ore Many attempts were made to flocculate the natural copper ore selectively, using schemes obtained from studies with separate minerals (Chapter 7) and synthetic mineral mixtures (this chapter). It was observed that, when these suspensions were treated in the manner described previously, much of the ore was unselectively flocculated by PEO. However, successful separations were performed when the " starvation" method of addition of flocculant was employed. The suspension was treated with 0.5 p.p.m. PEO added dropwise while stirring for 2 min at high shear rate (to disperse the flocculant), and then for 3 min at low shear; finally, the slurry was allowed to stand for 3 min. This flocculation procedure was repeated 3 times (1.5 p.p.m. PEO bulk concentration) and was used wherever there was an addition of flocculant. The flocculated material was recovered in the cylindrical tube already mentioned and then washed (redispersed) in 200 ml tap water containing half the initial amount of dispersant. Reflocculation by addition of 0.5 p.p.m. PEO was repeated and the products of this cleaning stage were recovered.

The tailings of the first flocculation stage (1st. supernatant) were treated with another 1.5 p.p.m. PEO and the flocculated fraction was similarly cleaned in 200 ml tap water, which also contained half the initial amount of dispersant reagent, to produce a second concentrate and tailing. When the elutriator was employed for cleaning the flocs, the suspensions were treated with 3 p.p.m. PEO added in 6 stages following the treatment given above.

Before considering the effect of various factors on the selective flocculation of the copper component, analytical determinations of copper in the sediment and supernatant fractions were performed without addition of PEO (blank).

Table 14

Distribution of copper in the dispersed and sedimented fractions

t_x = 3 min; h_x = 9 cm; 1000 p.p.m. sodium silicate;
1.5% w/w solids content.

Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
conc.	30	15.67	56	1.9	3
tails	70	5.25	44		
calc. heads	100	(8.37)	100		

Effect of solids content on separation parameters was investigated with the use of Na_2S or K-amyl xanthate as flocculation activators.

The results given in Table 14 show the following features.

1) The supernatant suspensions always contained mostly gangue mineral; but an increasing proportion of gangue was carried down with the flocs (possibly by " entrapment") as the total solids content of the original suspension was increased.
2) Neither the elutriator separator nor the redispersion-flocculation processes for washing up the flocs was effective enough to up-grade the copper content to reach the levels obtained with synthetic mixtures of the same initial composition.
3) Both recovery and grade were less than those obtained with synthetic mixtures, recoveries by 10% and grades by about 40%;

Table 15

Selective flocculation trials on a non-sulphide copper ore

a) The elutriator column was used here for the floc-washing and separation from the gangue; pH 11.2; t_x = 5 min; 7 kg sodium silicate/tonne ore, 2-4 kg Na_2S/tonne ore and 3 p.p.m. PEO.

Pulp density, (% w/w)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
3	conc.	22	21.91	58	2.6	4.8
	tails	78	4.6	42		
	head[†]	100	(8.5)	100		
5	conc.	23	23.24	63	2.7	5.7
	tails	77	4.08	37		
	head	100	(8.5)	100		
10	conc.	21	25.10	62	3.0	6.1
	tails	79	4.09	38		
	head	100	(8.5)	100		
15	conc.	27	20.67	67	2.4	5.3
	tails	73	3.87	33		
	head	100	(8.5)	100		

[†] Here the head is calculated from the differences in weight between the weighed sample and the weighed sediment; i.e., no dry weight was measured nor analysis performed in the elutriator liquor.

b) Same as (a) but the washing-up process was done by redispersion-flocculation as stated previously; t_x = 1 min (all stages)

Pulp density, (% w/w)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
3	conc.	25	23.1	67	2.7	6.2
	tails	75	3.72	33		
	calc. heads	100	(8.51)	100		

Table 15 [continued]

Pulp density, (% w/w)	Products	wt %	Cu %	Cu-distribution %	e_r	s_r
5	conc.	23	22.5	69.5	3.0	7.4
	tails	77	3.04	30.5		
	calc heads	100	(7.6)	100.0		
10	conc.	25	24.2	75	3.0	9.0
	tails	75	2.73	25		
	calc heads	100	(8.1)	100		
15	conc.	29	21.1	77	2.7	8.0
	tails	71	2.56	23		
	calc heads	100	(7.9)	100		
2^{α}	conc.	28	24.0	82.6	3.0	12.0
	tails	72	1.96	17.4		
	calc heads	100	(8.2)	100		
2^{β}	conc.	24	24.9	73.5	3.1	9.0
	tails	76	2.78	26.5		
	calc heads	100	(8.0)	100		
10^{β}	conc.	25	24.4	79	3.1	11.0
	tails	75	2.19	21		
	calc heads	100	(7.8)	100		
15^{β}	conc.	30	22.3	81.5	2.7	10.0
	tails	70	2.20	18.5		
	calc heads	100	(8.3)	100		

[α] With 1 kg Na_2S/tonne ore + 0.5 kg K-amyl xanthate/-tonne ore.

[β] With 1.5 kg K-amyl xanthate/tonne ore instead Na_2S as activator.

but with respect to the blank (Table 14) selective flocculation concentrated the copper component by 25% in recovery and grades by about 16%.

4) Lower recoveries but similar concentrate grades were obtained

by using the elutriator separator for the floc-cleaning process as compared with the usual procedure of redispersion--flocculation in the cylindrical glass tube.

5) The replacement of sodium sulphide by K-amyl xanthate resulted in increases in both recovery and grade.

The effect of feed grade on the separation extent was studied by diluting the sample with the same quartz described in 7.1. Results are shown in Table 16.

Table 16

Effect of feed grade on separation parameters

10% w/w solids content; K-amyl xanthate as stated; t_x = 1 min; 1000 p.p.m. sodium silicate.

kg Xanthate/-tonne	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
1.5	conc.	25	24.4	79	3.1	11
	tails	75	2.19	21		
	calc. heads	100	(7.8)	100		
1.5	conc.	19	24.5	73.5	3.9	12
	tails	81	2.05	26.5		
	calc. heads	100	(6.28)	100		
1.0	conc.	13	24.69	73	5.7	18
	tails	87	1.34	23		
	calc. heads	100	(4.33)	100		
0.5	conc.	2	26.92	71	34	112
	tails	98	0.24	29		
	calc. heads	100	(0.80)	100		

Table 16 shows that a substantial decrease in the proportion of the copper component in the feed resulted in a slight decrease in the recovery (by about 8%) and in a slightly higher concentrate grade (almost 3%); however, increased values of e_r and s_r were obtained.

The effect produced by the presence of calcite and dolomite (in proportions which are usually found associated with copper ores) on separation parameters was studied. The results obtained are shown in Table 17 .

Table 17

The effect of the addition of calcite and dolomite on separation parameters

10% w/w solids content; 1 kg K-amyl xanthate/ tonne ore; t_x = 1 min.

Dispersant concentration	ore:-calcite:-dolomite	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
1000 p.p.m.	36 : 3 : 1	conc.	20	19.60	59.5	3.0	7.0
Sodium silicate		tails	80	3.33	49.5		
		calc. heads	100	(6.58)	100		
1500 p.p.m.	16 : 3 : 1	conc.	18	15.37	43.6	2.4	3.5
Sodium silicate		tails	20	4.37	56.4		
		calc. heads	100	(6.35)	100		
1000 p.p.m.	16 : 3 : 1	conc.	20	24.49	75.7	3.8	12.4
Sodium silicate + 0.2 kg Cataflot/-tonne ore + 4 kg Calgon/tonne ore		tails	80	1.97	24.3		
		calc. heads	100	(6.47)	100		

The results show that the presence of Calcite and dolomite caused a deleterious effect on both recovery and concentrate grade. However, good separations were obtained after addition of Calgon and Cataflot

P40 in concentrations similar to those used in the selective flocculation of synthetic mixtures of malachite from calcite and dolomite.

8.2. Studies to Improve Grade and Recovery

In the previous experiments, copper concentrates of copper grades over 24% (up to 26) had been achieved, while the recovery in most cases was about 70-80%. To improve the recovery, it was first thought that the flocculation time of 1 min. should be increased further. Thus, longer separation times and higher concentrations of dispersant were studied.

Table 18

Selective flocculation separations as a function of time

10% w/w solids content; 1.5 kg K-amyl xanthate/tonne ore. 1500 p.p.m. sodium silicate.

Standing time, min (all stages)	Products	wt. %	Cu %	Cu-distribution, %	e_r	s_r
1	conc.	24	24.92	78	3.3	11.4
	tails	76	2.19	22		
	calc. heads	100	(7.65)	100		
3	conc.	31	22.85	86.5	2.8	14
	tails	69	1.60	13.5		
	calc. heads	100	(8.19)	100		
5	conc.	36	19.57	88	2.4	13
	tails	64	1.51	12		
	calc. heads	100	(8.01)	100		

The results compared with previous tests show very high recoveries of copper in the concentrate. Also, the enrichment ratio slightly increased and the copper loss in tailings was very low but the enrichment ratio decreased as well as the concentrate grade.

In an attempt to understand the grade versus recovery dilemma, the following viewpoint was adopted.

a) If the copper components are surrounding the gangue minerals, a great proportion of the ore would behave as copper minerals, thus resulting in low-grade concentrate.

b) If the gangue minerals are surrounding the copper component (slime coating or embedding in a matrix) then copper particles would behave as gangue minerals, thus resulting in low recovery (if the gangue is not flocculable by PEO) and in low-grade concentrate if the gangue is flocculable by PEO.

c) If the constituents of the gangue are flocculable by PEO (to any extent), the selectivity ratio is reduced, thus resulting in low-grade concentrate.

The phenomenon of slime coating can be overcome by good dispersion whereas embedding in matrix (middlings) requires further grinding to liberation sizes. The problem of "self activation" of the gangue (especially quartz as the major component) towards flocculation was studied by direct and indirect methods. In addition, the depression of the gangue towards flocculation by means of a selective depressant was considered.

In all the previous experiments, ultrasound was used for dispersing the ore and sodium silicate was used as the main dispersing agent. It was decided to increase considerably the amount and quality of the dispersing agent and keep the ultrasound treatment constant.

These results (shown in Table 19) did not show a marked improvement in the performance of the process by increasing the sodium silicate and the addition of Calgon. A slight improvement in the concentrate grade was observed after the addition of Calgon.

Next, it was decided to study the factor b (in the text) by grinding a sample to a very fine sized material to ensure good liberation of the copper component. Accordingly, a 50 g sample was "wet-ground" (to avoid mineral decomposition) in a laboratory agate mortar for 2 hrs. at intervals of 30 min.

Table 19

The effect of dispersing agents on separation parameters

10% w/w solids content; 1.5 kg K-amyl xanthate/ tonne ore; t_x = 1 min.

Dispersant Concentration (per tonne ore)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
10 kg Na-silicate	conc.	24	24.92	78	3.3	11.4
	tails	76	2.19	22		
	calc. heads	100	(7.65)	100		
15 kg Na-silicate	conc.	24	24.65	76	3.1	10
	tails	76	2.45	24		
	calc. heads	100	(7.78)	100		
15 kg Na-silicate + 2 kg Calgon	conc.	23	26.51	74.8	3.2	10
	tails	77	2.66	25.2		
	calc. heads	100	(8.15)	100		

Table 20

The effect of wet grinding on separation parameters

Solids content as stated, 1.5 kg K-amyl xanthate t_x = 1 min, 10 kg Na-silicate/tonne ore.

Solids Content (% w/w)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
7.5	conc.	19	27.66	73	3.8	11.5
	tails	81	2.4	27		
	calc. heads	100	(7.20)	100		
10	conc.	20	27.30	74	3.7	11.4
	tails	80	2.40	26		
	calc. heads	100	(7.38)	100		

The results in Table 20 seem to confirm the previous conclusion, that there was not complete liberation of the copper minerals in the ore sample studied before, thus resulting in lower concentrate grades. The overall performance of these experiments was much better than previous tests with regard to up-grading but the recovery was rather low. Still, this factor did not prove to be responsible for the differences in separation extent found between the ore and the synthetic mixtures.

Therefore, the results should be discussed in terms of the differences between synthetic and real mineral mixtures, the differences possibly altering the relative adsorbability coefficient of the polymer on each substrate. Activation of siliceous gangue minerals by metallic ions is known to be necessary for their flotation with anionic collectors of the fatty acid type and may well also be a condition for their flocculation by PEO. This factor (C, in the text) was considered and tested by two different experiments.

1) Activation of the quartz for flocculation by PEO and flocculation of the ore gangue by PEO.
2) Depression of the ore gangue by a chelating compound.

Pure quartz was treated with minor quantities of $FeCl_3$, $Al_2(SO_4)_3$ (value roughly comparable with the ore composition) before addition of PEO. Weak (imperfect) flocculation was obtained; without addition of such electrolytes, quartz is not flocculable at all.

Natural sand (ground) was also dispersed in 1000 p.p.m. sodium silicate and treated for flocculation by PEO. Weak flocculation was obtained from 3 p.p.m. PEO for a solids content of 4% w/w.

The gangue material was separated from the copper compounds by multiple sedimentation, then dispersed in 1000 p.p.m. sodium silicate and treated for flocculation by PEO. Very weak flocculation was observed at low polymer concentration (up to 3 p.p.m.) but strong flocculation occurred with concentrations greater than 6 p.p.m. PEO for a 4% w/w solids content. Addition of 60 kg Calgon/tonne or 3 kg Cataflot P40/tonne did not protect the suspension from flocculation. These observations are certainly considered sufficient to show some affinity of the gangue for the flocculant. The flocculation extent of the gangue (resulting from this affinity) would, therefore, significantly influence the final concentrate grade to be obtained.

On the basis of these assumptions, attempts were made to depress the gangue by the addition of ethylene diamine tetra-acetic acid (EDTA). EDTA has proved to be an efficient flotation depressant of siliceous " activated" materials (217) by forming a hydrophilic or soluble inner complex through its combinations with metallic ions (either at the surface or in solution), thus removing them as factors in the process. Actually, the use of reagents forming soluble chelate compounds as depressants for gangue minerals is not new but their use has been limited for economic reasons.

Table 21

The gangue depressing action of EDTA in selective flocculation

Solids content as stated; 2 hrs wet ground sample; 1.5 kg amyl xanthate, t_x = 3 min; 15 kg Na-silicate/tonne ore. The ore was conditioned with 1 ml 0.02% solution EDTA before addition of the xanthate and PEO (3 p.p.m.).

Solids Content (% w/w)	Products	wt. %	Cu %	Cu-distribution %	e_r	s_r
5	conc.	24	28.08	79	3.3	12
	tails	76	2.35	21		
	calc. heads	100	(8.53)	100		
10	conc.	26	27.95	86	3.3	18
	tails	74	1.56	14		
	calc. heads	100	(8.42)	100		

While the "normal" selective flocculation procedure gave a concentrate with only 22.85% Cu (Table 18), flocculation with a chelating depressor produced a concentrate with 27.95% Cu (but with similar recovery, 86%) for the separations with 10% solids content. For a 5% w/w solids content (Table 21) the Cu % in the concentrate was even higher.

8.3. Discussion

The results obtained give strong support for the principle followed here to achieve the selectivity required. High recoveries and grades were obtained on synthetic mixtures. Selectivity for the flocculation of copper compounds compared to quartz or calcite or dolomite was found to be as great as expected from the use of K-amyl xanthate or sodium sulphide and from the low affinity of PEO for the gangue material.

However, contrary to optimistic expectations, there was a significant loss in selectivity when the same scheme was applied to a natural siliceous copper ore. Reasonably good results, much higher than others reported in the literature, were eventually obtained, but only with great care in the method of addition, dosage of flocculant and gangue control. Low-grade concentrates as compared with those obtained in synthetic mixtures were found to be the main problem to overcome. Some of the siliceous components were flocculated together with the copper minerals.

According to the results obtained it is believed that loss in selectivity, which resulted mainly in losses in concentrate grade, may be due to the " self activation" of the gangue material, especially the siliceous component which is probably covered (in the matrix) normally by iron, aluminium, lead, etc. This phenomenon makes the quartz flocculable. Therefore, despite the fact that " xanthated" or " sulphidized" copper malachite can be more reactive with the polymer, or " preferentially" adsorbed, there will always be the possibility of quartz being " co-flocculated" , which would reduce the concentrate grade. In other words, the relative adsorbability coefficient, K_{rel}ads., which is a function of the total free energy of adsorption, ΔG_{ads}, in the system, has been reduced by the same amount as a result of an increase in adsorption affinity of the polymer for the siliceous material.

Further improvements with a given ore could almost certainly be achieved by devoting further attention to gangue depression by means of selective depressants.

8.4. Economic Assessment of the Selective Flocculation Process Applied to a Non-sulphide Copper Ore

New separation processes must be not only technically feasible but also economical as compared with alternative classical procedures. Fine sized non-sulphide copper ores are likely to be treated by selective flocculation and a brief economic evaluation is to be made here.

Non-sulphide copper ores are usually treated by acid leaching, followed by electrowining. In addition, a pre-concentration by solvent extraction before the electrowining it is becoming common practice. The present ore has, indeed, been treated by direct leaching with sulphuric acid and this appears to be technically and economically a feasible process (214) However, the processing of the very finely divided material by leaching may not be always economical and rejection of the slimes is usually a normal procedure. The selective flocculation of these fines may well be used as an ancillary treatment to the leaching process.

The experiment described in Table was chosen for the economic evaluation of the selective flocculation process. The process employs hard water, 15% solids content and a feed grade equal to 8.3% Cu:

Products	wt. %	Cu %	Cu-distribution %
conc.	30	22.3	81.5
tails	70	2.20	18.5
calc. heads	100	(8.3)	100.0

According to the values given above, in order to produce one tonne of dry concentrate containing 22.3% Cu and with 81.5% recovery from an ore containing 8.3% Cu, approximately ($\frac{22.3}{8.3} \times \frac{100.0}{81.5}$), 3.3 tonnes of ore would have to be treated.

1. Cost of chemical reagents in selective flocculation.
   a) cost of K-amyl xanthate = $0.85/kg. The consumption of K-amyl xanthate in this process is 1.5 kg/tonne.

∴ cost of K-amyl xanthate per tonne ore = \$1.28.

b) cost of sodium silicate = \$0.07/kg. The consumption of silicate was 12/kg/tonne.

∴ cost of sodium silicate per tonne ore = \$0.84

c) cost of PEO (poly(ethylene oxide)) = \$1.10/kg. The consumption was 0.03 kg/tonne.

∴ cost of PEO per tonne ore = \$0.033.

Total cost of reagents per tonne of ore treated

= 1.28 + 0.84 + 0.033 = \$2.15

∴ Total cost of reagents per 3.3 tonnes of ore treated by selective flocculation = \$7.10

2. Mining cost: at an average of \$4.4 per tonne.

∴ cost of mining 33 tones of ore = \$14.52

3. Cost of crushing, grinding, thickening and drying: Cost of average \$4.80/tonne ore.

∴ cost of 3.3 tones or ore = \$15.84

The total processing costs to produce one dry tonne concentrate of 22.3% Cu is therefore:

= 15.84 + 14.52 + 7.10 = \$37.5, say \$40

4. Smelting costs. The price of the copper at the beginning of 1977 is \$1321/tonne Cu (\$1.32/kg Cu). The smelting costs include the following items:

a) cost of freight = \$16/tonne dry concentrate.

b) smelter deduction = 10 kg Cu for each tonne concentrate

∴ smelter deduction = 10 x 1.32 = \$13.2

∴ the total copper in one tonne of concentrate after smelter deduction = 223 - 10 = 213 kg.

c) Smelter charges = \$36/tonne concentrate.

d) Refining charges = \$0.13/kg copper metal

$\therefore$ cost of refining = 213 x 0.13 = \$27.7

e) Smelter participation = 6% x \$1321 = \$78.3

Total smelting cost =

16 + 13.2 + 36 + 27.7 + 78.3 = \$170.2

$\therefore$ Total value of copper from one tonne of concentrate =

213 x 1.32 = \$281

$\therefore$ Revenue from the smelter =

281 - 170 = \$111

$\therefore$ Net profit (after treatments costs) =

\$111 - 40 = \$71

$$\therefore \text{ Profit ratio } = \frac{\text{net profit x 100}}{\text{total treatment cost}}$$

$$= \frac{71 \times 100}{40} = 177\%$$

Despite the low price of the copper and high costs of the processing, the profit ratio obtained is quite reasonable. The relative cost of the reagents used in the selective flocculation is less than 4% of the total cost of producing copper metal and the total processing costs are about 20% of this amount. No evaluation of the capital cost of a selective flocculation plant will be made here. However, as no specially sophisticated machinery is required, it may be concluded that the selective flocculation of fine sized (slimes) of non-sulphide copper ores is technically and economically a feasible process.

CHAPTER 9

CONCLUSIONS

The main conclusions reached as a result of the investigation carried out in Part II can be briefly summarized as follows.

1. Non-sulphide copper minerals are amenable to flocculation by PEO only after treatment with a surface modifier which acts as an anchor between the surface and the polymer. These flocculation activators are all adsorbed at the copper mineral/water interface and interact with the polymer either by a chemical mechanism (e.g., with tannic acid) or by hydrophobic interaction (K-amyl xanthate).
2. The efficiency of the processes of flocculation and adsorption was found to be a function of the energy of collisions between the treated particles having polymer molecules adsorbed. Thus a minimum average energy should be reached before further adsorption and subsequently flocculation can take place.
3. A novel principle for achieving the selective adsorption of a polymer on to a copper compound has been demonstrated and tested successfully for synthetic and natural oxidized copper minerals. The principle consists of activating the adsorption of PEO flocculant on to copper-bearing substrates by treating the suspensions with either sodium sulphide or potassium amyl xanthate before the addition of the polymer. The loss in concentrate grade obtained with natural ores, as compared with synthetic ores, was found to be due to co-flocculation of the siliceous material, despite the high selective affinity for the treated minerals.
4. The selective flocculation of the copper compounds in the siliceous ore has proved to be both a technically feasible and economic unit process. Further improvements may be developed by additional attention to liberation, depression and dispersion of the gangue.
5. The presence of calcite and dolomite reduced the effectiveness of the separation process; but the problem can be overcome by addition of high dosages of sodium hexametaphosphate or polyacrylate type polymers, which disperse these minerals and eliminate them as factors in the chemistry of the system.
6. The principle developed should also be applicable to all mineral

systems which are likely to be separated by froth flotation. In addition, the principle should be relevant to the flocculation of flotation concentrates.

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APPENDIX 1

DETERMINATION OF VERY LOW CONCENTRATIONS OF POLYACRYLAMIDE AND POLYETHYLENEOXIDE FLOCCULANTS BY NEPHELOMETRY

Br. Polym. J. 1975, 7, 135–138

Determination of Very Low Concentrations of Polyacrylamide and Polyethyleneoxide Flocculants by Nephelometry

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A method is described for the analytical determination of low concentrations of polyacrylamide or polyethyleneoxide flocculants in water, in the range 0–10 parts/10^6. It depends on measuring the turbidity produced by mixing the polymer solution with a dilute solution of tannic acid in the presence of 1 M NaCl. With a sensitive nephelometer, as little as 0.1 parts/10^6 of flocculant can be detected.

1. Introduction

Understanding of adsorption of polymers at solid–liquid interfaces is important in many fields and, in particular, in the flocculation of fine particles. Optimum bridging and hence flocculation is clearly affected by the extent and strength of polymer adsorption.[1] The average surface concentration of polymer molecules for a given optimum flocculant dose and surface coverage can be obtained from adsorption isotherms. Unfortunately the usefulness of adsorption isotherms has been limited due to the inaccuracy of experimental measurements, especially at very low polymer concentrations and low surface coverage.[2,3] Slater *et al.*[1] pointed out that there was no satisfactory method for the determination of non-ionic polyacrylamide flocculants at low concentrations, whereas anionic polymers (e.g. partially hydrolysed polyacrylamide (PAM)) could be determined by nephelometry, depending on the turbidity produced with "Hyamine 1622" (cf. Crummett and Hummel[5]). This method cannot be used directly with non-ionic polyacrylamide—for this case, prehydrolysis is needed (Griot and Kitchener[6]). Similarly, there was no simple and reliable method for the determination of polyethyleneoxide (PEO) in very dilute solutions, although many techniques (including precipitation with simple phenols) have been reported for PEO hydrophobic derivatives[7] of lower molecular weight.

In this work, a nephelometric method has been developed for the direct determination of high molecular weight flocculants such as polyacrylamide and polyethyleneoxide in dilute solutions. The polymers were precipitated by tannic acid and the method was made more sensitive at very low concentrations (i.e. between 0–1 parts/

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10^6) with the aid of sodium chloride. This followed a chance discovery of the precipitation of polyacrylamide by tannic acid.

The nephelometric method described here is simple and does not require elaborate equipment. Measurements made with this technique were found to be accurate and reproducible in the polymer concentration range studied, i.e. 0–10 parts 10^6 (which is the order of magnitude of flocculant dosages usually needed for flocculation). The calibration curves, in Figures 1 and 2, are typical for light scattering of very dilute colloids, being linear for 0–2 parts/10^6 and gently curved above 2 parts/10^6. The calibration curves for PAM and PEO, which were constructed as below, could be used for determining the polymer concentration of unknown samples. Concentrations as low as 0.1 parts/10^6 could be determined. The reproducibility was ± 1%.

2. Experimental

2.1. Materials and equipment

A nephelometer head in conjunction with a galvanometer (Unigalvo type 20/DR, Evans Electroselenium Ltd) were used. Standard solutions of the reagents used in the measurements were prepared to the following strengths: polyethyleneoxide ("Polyox" coagulant, molecular weight 5 million), and pure polyacrylamide (N100S, molecular weight 1 million), 100 mg litre^{-1}; tannic acid, 1000 mg litre^{-1} (or 0.1% solution); sodium chloride, 0.1 M, 0.5 M and 1 M. All reagents were supplied by BDH chemicals (Poole, England), except polyacrylamide N100S which was from BTI chemicals (Bradford, England).

2.2. Procedure

A series of sample solutions of known polymer concentrations in the range 0–10 parts/10^6 were treated with tannic acid and sodium chloride in separate 50 ml volumetric flasks; the required volumes of PEO or PAM standard solutions were added to each flask already containing 5 ml of tannic acid and 40 ml of sodium chloride (0.1 M or 0.5 M for PEO and 1 M for PAM). The solutions were adjusted to 50 ml volumes with distilled water to make up the final concentrations. The flasks were shaken for about one minute by inverting end over end, and were then allowed to stand for a period of time (15 min for PEO suspensions, and about one hour for PAMs) before measuring the turbidity with the nephelometer. In the measurements, the samples of highest polymer content were used as standards and the galvanometer reading was adjusted to 100 on the linear scale, while blank solutions (i.e. zero polymer content) were used to adjust the galvanometer reading to zero. These adjustments were repeated until stability of the galvanometer was achieved. The galvanometer reading was noted for each sample, which represented the turbidity of the sample in relation to the standard. Typical measurements were plotted against polymer concentrations to produce the calibration curves for PEO and PAM in Figures 1 and 2.

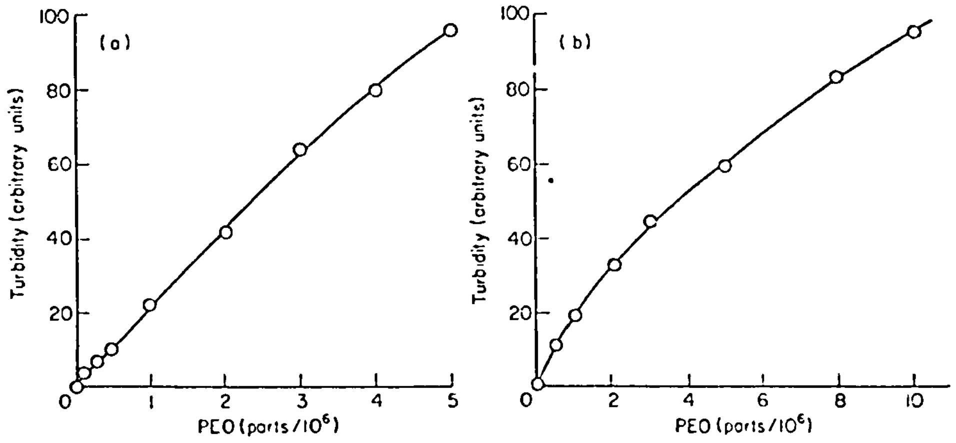

Figure 1. Calibration curves for PEO-tannic acid nephelometric analysis. (a) 0.5 M NaCl; (b) 0.1 M NaCl.

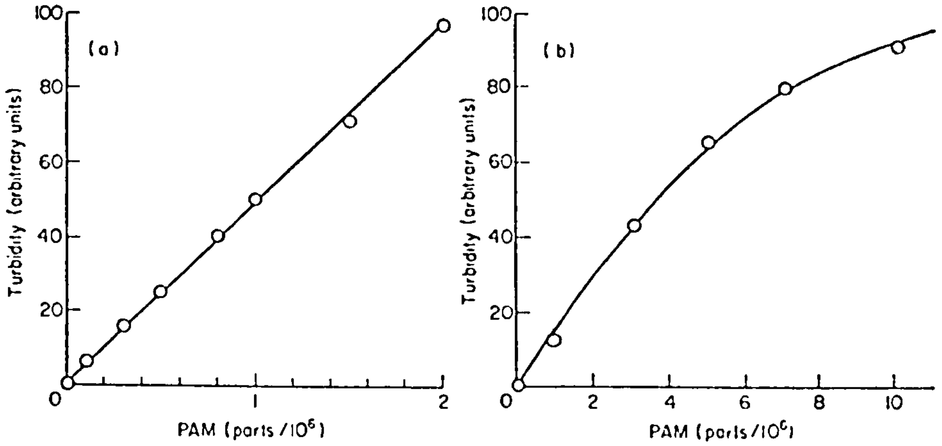

Figure 2. Calibration curves for PAM-tannic acid nephelometric analysis. 1 M NaCl; (a) and (b) show different ranges and different sensitivity scales.

The effect of pH on turbidity measurements was studied experimentally in the pH range 2.5–10; no significant change was detected. However, at pH $\geq$ 10 the colour of tannic acid changes to yellow, indicating a change in its molecular structure and it is therefore desirable to maintain the pH below 10.

It was found that the turbidity slowly increased with time; but if the measurements were made within 30 min of one other, after the initial waiting period, the galvanometer readings would fit the calibration curve.

Simple electrolytes are not expected to interfere at low concentrations (i.e. below 0.1 M). On the other hand, other polymers could interfere with the determination of a higher molecular weight polymer; for example, the presence of polyethylene glycol gave erroneous readings for the PEO.

It has also been found that certain commercial flocculants of the polyacrylamide type can equally well be determined by the present method. Figure 3 shows the calibration graphs for N-100 (a non-ionic polyacrylamide) and C-100 (a cationic polyacrylamide). On the other hand, a strongly anionic polyacrylamide (A-140) gave no turbidity with tannic acid; but such flocculants can be determined by the Hyamine method, as mentioned previously.[5] (The above flocculants were kindly supplied by BTI (Chemicals) Ltd, Bradford.)

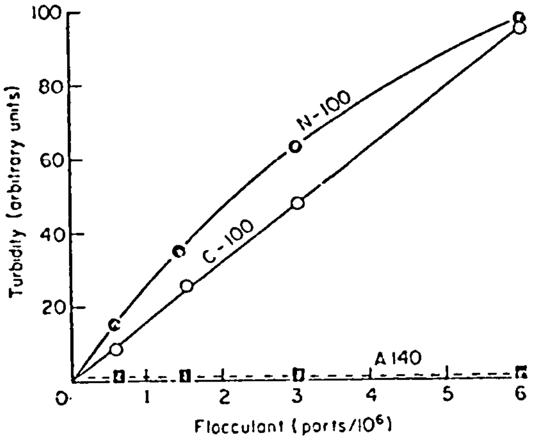

Figure 3. Calibration curves for three commercial polyacrylamide flocculants. 1 M NaCl.

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APPENDIX 2

THE MECHANISM OF ADSORPTION OF POLY(ETHYLENE OXIDE) FLOCCULANT ON SILICA.

The Mechanism of Adsorption of Poly(Ethylene Oxide) Flocculant on Silica

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Adsorption of poly(ethylene oxide) (PEO) of high molecular weight from water on to various forms of silica has been investigated and correlated with the varying degrees of flocculation produced. Both effects are most marked with silicas which carry "isolated" silanol groups *and* hydrophobic groups (either methyl or siloxane). A combination of hydrogen bonding and hydrophobic association may be responsible. Silicas which have been fully dehydroxylated by heating above 1000°C do not adsorb PEO and are extremely slow to rehydrate in water. The marked influence of pH on the adsorption of this nonionic polymer (and of others such as polyvinyl alcohol and polyacrylamide) needs explanation. It is suggested that ionization of silica reduces its affinity for nonionic compounds by a general "salting-out" effect, since any factor which favors the presence of *water* on the surface (in preference to organic compounds) tends to weaken the, already fragile, attachment of the solute. The concept of competition between water and other units for surface sites provides a unified qualitative explanation of all the phenomena reported.

INTRODUCTION

The adsorption of polymers from aqueous solution is influenced by hydrogen-bonding and other factors, in addition to purely electrostatic forces. Non-Coulombic interactions are obviously particularly important with nonionic flocculants and protective colloids such as polyacrylamide, starch and gums, which are widely adsorbed by a variety of solids. But the detailed mechanism is not well understood and there is clearly a need for further investigations with a range of polymers and adsorbents.

Silica dispersions present an especially suitable substrate for study because it is known that small changes in the surface condition of the silica can greatly affect the adsorption. In addition, the surface chemistry of silica has been more thoroughly investigated than that of almost any other solid—and, clearly, a connection must be sought between the strength of adsorption and the chemical structure of the surface of the adsorbent.

The literature contains a number of significant observations for which, however, a coherent explanation is lacking. Griot and Kitchener (1) reported that high molecular weight polyacrylamide (PAM) is a good flocculant for fresh suspensions of "Aerosil" (a flame-hydrolyzed silica) but not for "aged" suspensions or for precipitated silica. It was shown that precipitated silica became sensitive to flocculation if it was first subjected to heat treatment (e.g., at 730°C) before the flocculation test. These results were correlated with changes in the adsorption of the polymer and with alterations in the infrared spectra of the silicas. A rather similar phenomenon was reported by Greenland (2) with polyvinyl alcohol (PVA) and silica, and this system was subsequently studied by Tadros (3), who recorded its dependence on pH. Parallel observations have now been made with

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TABLE II

Partition of Silicas between Ether, Water, and Interface

Test no.	Form of silica	Pretreatment	Particles present in		
			Water	Interface	Ether
1	Precipitated	Untreated (pH 6 or pH 2)	+	−	−
2		Heated 24 hr 450°C	+	+	+
3		500°	−	+	+
4		700°	−	+	+
5		880°	−	−	+
6	Flame	Untreated (pH 6)	+	++	+
7		Heated 24 hr 500°	−	+	+
8		700°	−	−	+
9		930°	−	−	+
10		No. 6 boiled in water 96 hr	+	−	−
11		No. 9 steamed for 96 hr	−	−	+
12	Hydrophobic	Untreated (pH 6)	−	−	+
13		(pH > 8)	+	−	−
14		No. 13 then acidified to pH ~ 2	−	+	+
15	Ground quartz	Untreated (pH 6)	−	++	+
16		Heated 24 hr 800°	−	+	++
17		900°	−	+	++

Adsorption sites. Numerous papers deal with the question of the functional groups on silica and a valuable review of the field was given by Snoeyink and Weber (17). The salient points for the present discussion are the following:

(a) Precipitated silica is a fully hydrated form in which the surface is densely covered with silanol groups, the majority of which are "adjacent" or "hydrogen-bonded" (Type B).

(b) Heating above 400°C begins to cause some irreversible dehydroxylation, eliminating first the Type B groups, which are virtually all removed at 500°C. Type A "isolated" or "single" silanol groups remain, to the extent of about 1.4 groups per 100 Å^2.

(c) Type A groups begin to be lost above 700°, but dehydroxylation is not complete until above 1000°C.

(d) After total dehydroxylation the surface is covered with siloxane groups.

(e) Flame silica corresponds broadly to precipitated silica that has been dehydrated to about 500°C.

(f) In hydrophobic silica, about 70% of the silanols of flame silica have been methylated, but some Type A remain, about 0.9 per 100 Å^2 [Thies (18)].

The present results show that adsorption of PEO is strongest on flame silica or on precipitated silica which has been heated to about 600°C. A plausible explanation is that *isolated silanol groups* provide the best adsorption sites, acting as proton donors in hydrogen bonding to ether oxygens

$$-\mathrm{SiOH}\cdots\mathrm{O(CH_2CH_2)_2}=$$

This hypothesis was previously suggested for the case of PAM (1) and for low mol wt PEO by Howard and McConnell (4) and by Fontana (14) for a copolymer of ethylene oxide and methyl methacrylate. Complete dehydroxylation leaves siloxane groups, which are hydrophobic and incapable of providing a proton; consequently, adsorption of PEO is nil (from dilute solutions).

It must then be assumed that the Type A silanols left on hydrophobic Aerosil R-972 are available for hydrogen-bonding, as this silica is only a little less sensitive to PEO than flame silica.

A scale molecular model of PEO shows that it is impossible to arrange the chains with all the –O– atoms in contact with a plane. Arranging alternate –O– atoms on opposite sides, it is possible to bring half of them close to a plane, with an O–O distance of about 7.5 Å. In this configuration, two of the CH_2 groups between the O-atoms are in contact with the plane. Thus, the hydrogen bond acceptors are separated by a significant hydrophobic section, possibly matching the spacing of the hydrophobic groups, either methyl or siloxane, present on the silica.

The main question now is why precipitated silica has a low affinity for PEO. The possible influence of basic impurities in the commercial material can be dismissed as a result of the following test. A sample of precipitated silica was boiled with dilute HCl and then washed and tested for adsorption of PEO; its affinity was unchanged by this treatment, which would certainly have eliminated any exposed cations such as Na^+, Ca^{2+}, Al^{3+}. Thus, the lower affinity of hydrated silica for PEO is a consequence of its silanol surface, not its impurities.

It must also be remembered that precipitated silica is *not* deficient in affinity *at pH 2* (Fig. 2).

These observations are concordant with other facts concerning the interaction of PEO and silica. For example, *colloidal* silica is almost quantitatively precipitated by PEO at low pH (~pH 2) but not from alkaline media (pH > 7). (PVA apparently behaves similarly with colloidal silica at high and low pH according to Iler (19) and Tadros (3).) Colloidal silica is also known to form complexes at pH 2 with nonpolymeric analogues of PEO, such as ethylene glycol diethyl ether, $CH_3CH_2OCH_2$-$CH_2OCH_2CH_3$ (20).

Therefore, the problem which particularly needs an explanation is the effect of pH on the adsorption of nonionic polymers, which is shown by all forms of silica, quartz [the flotation of which by PEO surfactants is also drastically cut by pH > 5.5 (11)] and even the surface-methylated hydrophobic silica (Table II, Nos. 12–14). Previous work has shown not only that some silanol groups are inaccessible to methylation but also that they continue to ionize, giving a zeta-potential close to that of nonmethylated silica (21).

Effects of pH. As the pH is raised above 2, silica begins to take up bases by cation exchange. Tadros (3) has suggested that loss of adsorption (e.g., of PVA) with rise of pH is due to reduction in the number of silanol groups available for hydrogen bonding. However, the number of groups ionized at, say, pH 6 in absence of salts is very small indeed compared with the total number present on hydrated silica (probably ≪1%). Therefore, *either* (a) there is a certain minority type of silanol group which is the important one for both hydrogen bonding and base-binding, *or* (b) the effect of surface ionization is through general electrical double-layer phenomena (rather than loss of sorption sites). At present either theory seems plausible and conceivably both effects might be operative. It is difficult to decide between them. Some of the evidence seems to point to (a) and some to (b), as follows:

(a) Several authors have concluded that the hydroxyl groups on silica have a range of (Bronsted) acid strengths (22, 23) in presence of water. Strazhesko and co-workers (24) have proposed an electronic valence theory to explain the acidity of silica gel in the pH range 3–6 (which they consider is not consistent with the accepted pK value of monosilicic acid.) Ethers are known to form oxonium salts and hydrogen-bonded complexes with strong acids. It therefore seems plausible to suggest that the most readily dissociable silanol groups will also be the important ones for adsorption of PEO.

(b) Reduction of adsorption of polyethers by ionization of the silica might be caused by non-specific "salting-out" due to the electrostatic field near an ionized surface. At pH 2, $\psi_0 = 0$, while at pH 6 $\zeta \approx -100$ mV and the poly(ethylene oxide) (PEO) and are reported in detail in the present paper.

The poly(ethylene oxide) chain, $-(CH_2CH_2O)_n-$, is usually considered as the hydrophilic, nonadsorbed, unit in conventional nonionic surfactants; clearly, the ether groups are responsible for the solubility of the PEO and presumably they operate as hydrogen-bond acceptors to water. However, these groups can also act as links to hydrophilic adsorbents, even in aqueous media. Direct adsorption measurements of "polyethylene glycols" (i.e., PEO of low mol wt) from water and other solvents on to Aerosil have been reported by Howard and McConnell (4), Rupprecht and Liebl (5), and Killman and Winter (6). In addition, PEO of high molecular weight is known to be a good flocculant for clays (7, 8) and for quartz (9). Similarly, the observation that conventional PEO surfactants can act as flotation "collectors" to minerals such as quartz and cassiterite (10, 11) shows that the ether groups provide sufficient adsorption affinity to attach the molecule by its PEO moiety.

On the other hand, the $-CH_2CH_2-$ groups in PEO are sufficiently hydrophobic to lead to physical adsorption at the air/water interface (12), the oil/water interface (13), and the mercury/water interface at the point of zero charge (9).

Unfortunately the mechanism of adsorption of nonionic flocculants cannot be studied directly by ir spectroscopy in the presence of water. Studies which have been made on dried samples or from nonaqueous solvents (4, 6, 14) agree in indicating hydrogen bonding between surface silanol groups and ether groups, i.e., $-SiOH\cdots O(CH_2CH_2)_2=$. In an aqueous medium, however, such bonding must be reduced by competition from water molecules. Greenland (2) suggested that the nonadsorption of PVA (presumably at pH ~7) by a hydrated silica (which, apparently, has plenty of silanol groups as potential sites for hydrogen bonding), could be due to the difficulty of displacing water from it. A full explanation must, clearly, take account of the *relative* adsorption affinity of sites for H_2O or $O(CH_2CH_2)_2=$ units.

TABLE I

Specific Surface Areas of Silicas and Influence of Heat Treatment (24 hr)

Form of silica	Temp. of heating (°C)	Surface area (m² g⁻¹)
A. Flame silica (Cabosil M5)	—	171
	500	167
	700	156
	880	115
	930	103
	1030	94
B. Hydrophobic silica (R-972)	—	98
C. Precipitated silica (BDH)	—	73.3
	350	72.4
	500	69.2
	700	61.1
	800	49.1
	940	9.6

If it is assumed that hydrogen bonding is the only means of attachment of PEO, problems remain in explaining the influence of pH, ionic strength, and heat treatment. The present work was undertaken to provide more information on these phenomena.

EXPERIMENTAL

Materials. The flocculant used was "Polyox," a polyethylene oxide stated by the manufacturers (Union Carbide Corp.) to have a mol wt > 5 million.

Three much-studied forms of silica were chosen for flocculation and adsorption experiments, namely,

A. "Flame silica" ("Cabosil M5" from Cabot Corp.).

B. "Hydrophobic silica" ("Aerosil R-972" from Degussa Co.; believed to be prepared from a flame silica similar to *A* by reaction with dimethyl dichlorosilane).

C. "Precipitated silica" (from B.D.H. Ltd.).

In addition, some experiments were made with a fractionated sample of high purity powdered quartz (<27 μm). In part of the

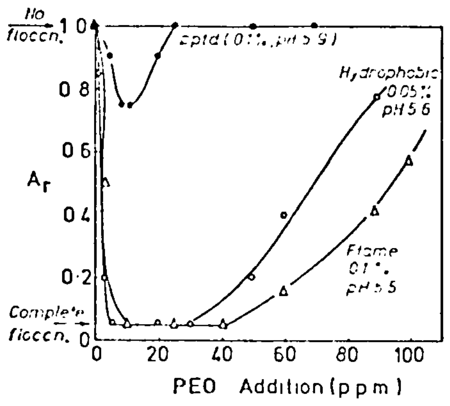

FIG. 1. Flocculation of suspensions of precipitated silica (B.D.H.), hydrophobic silica (Aerosil R-972), and flame silica (Cabosil M5) by polyethylene oxide (PEO) (A_r = relative optical absorbance of suspension after 1 hr).

work, the various silicas were pre-treated by heating or "ageing" in water, as detailed later.

Surface areas were determined by the dynamic one-point BET method, using a "Monosorb" surface area analyzer (Quantachrome Corp.). Values were reproducible to about 1% and differ from full N_2-BET values by less than 5%. The results are summarized in Table I.

Dispersions. Silica suspensions were generally of 0.1 wt% for A or C and 0.05% for B, and were prepared by shaking the weighed amount of silica in water. But the hydrophobic silica (B) was first wetted with a little ethanol (3 ml for 1 liter of dispersion), then stirred into water by hand and finally subjected to the action of an ultrasonic probe for 10 min. The resulting dispersions were stable for many hours.

Flocculation tests were carried out by an arbitrary, but standardized, routine. The very dilute flocculant solution was run slowly into a well-stirred silica suspension which was then left to stand for 1 hr. The optical absorbance of a sample of the supernatant liquid was then determined and compared with that of a blank to which no flocculant was added. Results are reported as "relative absorbance" (A_r)

$$\equiv \frac{\text{absorbance of test sample}}{\text{absorbance of blank}}.$$

Thus a relative absorbance of 1.0 indicates that the added reagent did not affect the stability of the suspension, whereas strong flocculation is indicated by a low value of A_r, approaching zero, because flocs have formed and settled out [Fleer (15)].

Adsorption measurements were carried out, after equilibration for 4 hr and centrifuging at 900 g, by determination of the concentration of residual PEO by a nephelometric method based on tannic acid, as recently described by Attia and Rubio (16).

RESULTS

Flocculation. Figure 1 indicates that whereas flame silica and hydrophobic silica in distilled

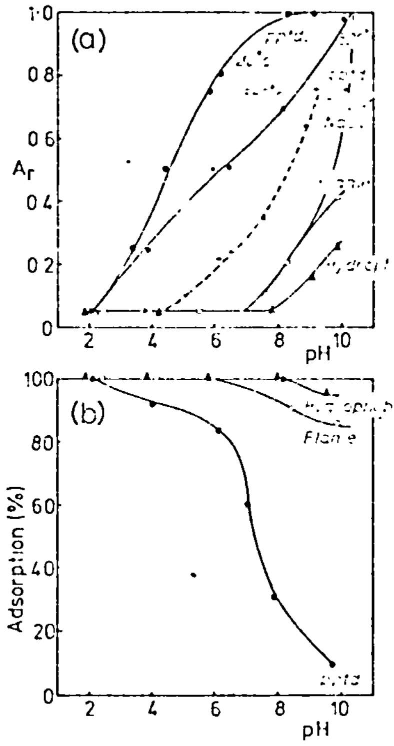

FIG. 2. Effect of pH on flocculation (a) and adsorption (b) of PEO.

water are strongly flocculated by PEO, precipitated silica is only weakly affected. All three silicas are restabilized by an excess of polymer.

In Fig. 2(a) flocculation results are given for a constant dosage of 11.4 ppm of PEO, over a range of pH values. All three silicas are strongly flocculated at pH 2 (which is the accepted pzc); but each has a critical pH above which it begins to lose sensitivity to the flocculant. Precipitated silica is seen to be virtually nonflocculable at pH > 8.

A sample of precipitated silica, which was flocculated at pH 2, deflocculated when the pH was raised to 6. Analysis confirmed that the PEO was simultaneously desorbed in approximately quantitative agreement with the direct adsorption isotherm. This provides some evidence for reversibility of the polymer adsorption.

The broken line in Fig. 2(a) shows that in presence of 0.02 *M* NaCl flocculation of precipitated silica is enhanced, but the general effect of pH remains. This proves that the pH effect is distinct from any ionic strength effect, and must be a true acid-base reaction of the silica surfaces.

Nevertheless, the flocculation is improved by increase of ionic strength, as shown by Fig. 3 for precipitated silica at pH 5.9, with 11.3 ppm of PEO. Under these conditions, complete flocculation of precipitated silica was obtained by adding 0.09 *M* NaCl (or more), 0.003 *M* $MgSO_4$ or 0.0009 *M* $LaCl_3$.

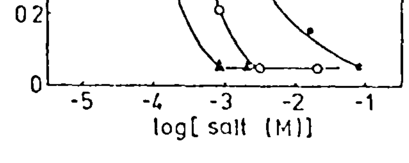

FIG. 3. Influence of electrolytes on flocculation of pptd. silica by PEO (11.3 ppm) at pH 5.9.

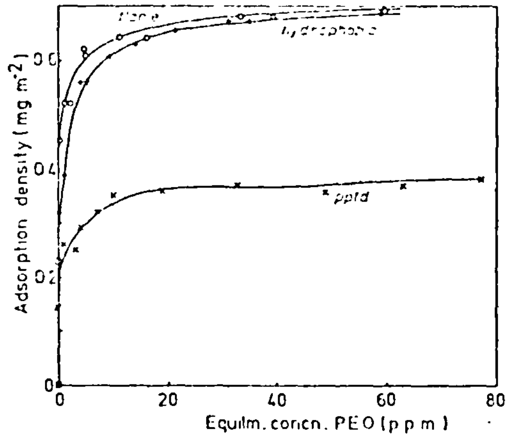

FIG. 4. Adsorption isotherms for PEO on different silicas at pH 5.7.

Adsorption. Figure 4 shows adsorption isotherms for conditions comparable with those used in the flocculation measurements of Fig. 1. The amount of PEO adsorbed per gm of silica has been divided by the BET surface area, although the surfaces of the three silicas are not necessarily of equal accessibility to the polymer (but see below). On this basis, it appears that the adsorption density lies in the order flame silica ≈ hydrophobic silica > precipitated silica, which corresponds to the order of sensitivity of the silicas to flocculation (Fig. 1.)

The correlation between adsorption and flocculation is also clearly seen in Fig. 2. Figure 2(b) shows the percentage of PEO adsorbed in the flocculation experiments of Fig. 2(a), as a function of pH. In every case, strong flocculation ($A_r \sim 0.05$) corresponds to practically *complete* removal of the polymer (>99% adsorbed) and, for each silica, gradations of flocculation correspond to gradations of strength of adsorption. Zero flocculation of precipitated silica corresponds to weak adsorption (<20%). Under these conditions, addition of 11.4 ppm of PEO already constitutes an "overdose" for precipitated silica at pH 8. Although it is the "optimum" dosage

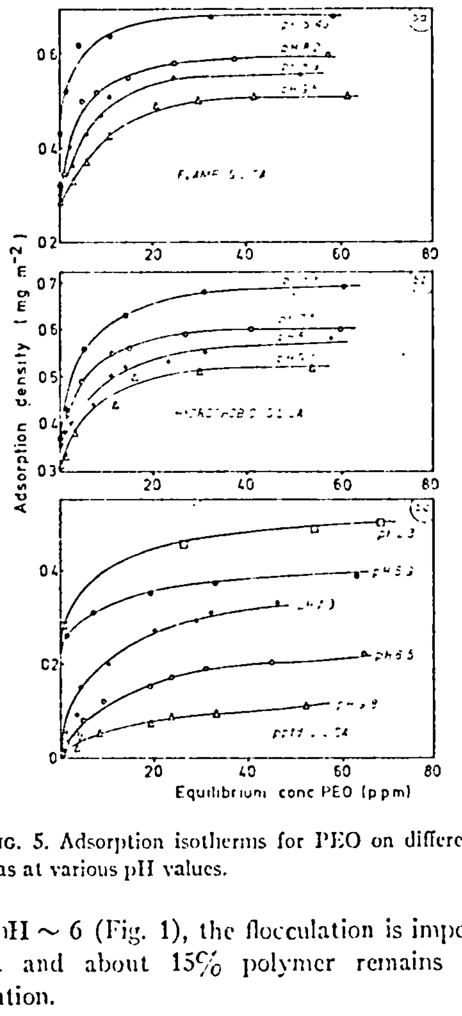

FIG. 5. Adsorption isotherms for PEO on different silicas at various pH values.

at pH ~ 6 (Fig. 1), the flocculation is imperfect and about 15% polymer remains in solution.

Figure 5 shows sets of complete isotherms for the three silicas, at a range of pH values. The striking feature of these results is that the isotherms are all of the same form, but are more expanded along the concentration axis as the affinity for the surface decreases. This appears in the height of the (apparent) intercept on the ordinate axis (note that (a) and (b) have a suppressed zero) and the level of the (apparent) "plateau."

The correlation between flocculation and adsorption is complete. In every case, perfect flocculation corresponds to virtually complete adsorption of the polymer; any measurable excess PEO left in solution corresponds to some degree of restabilization. The converse does not apply, of course, in the "underdose" region, where complete adsorption of polymer is insufficient to flocculate all the silica.

Optimum flocculation was generally obtained with a dosage (which was wholely adsorbed) corresponding to about 20-30% of the maximum adsorption capacity of the silica.

Heat treatment of silicas. Figure 6(a) shows that pretreatment of flame silica in a furnace (in air) for 24 hr, at any temperature up to 800°C, does not affect its flocculation or the adsorption of PEO (virtually complete). Above 800°C, however, adsorption and flocculation are progressively reduced and above 1000°C, both are zero.

Figure 6(b), on the contrary, shows the "activation" affect of moderate heating, mentioned earlier, with precipitated silica. Maximum sensitivity to the polymer is obtained by heating to about 600°C. At > 800°C, adsorption and flocculation fall off exactly as with the flame silica.

Figure 7 gives adsorption isotherms for the same heat-treated silicas. Heating of flame

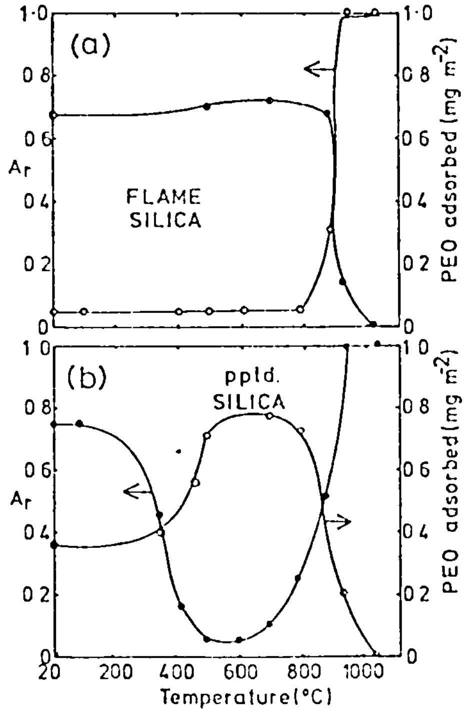

FIG. 6. Effect of heat treatment of silicas on flocculation by PEO (11.5 ppm), pH 5.9.

silica slightly increases the adsorption density from 20 up to 700°C, but higher temperatures then produce progressive reduction, until virtually zero adsorption results if the silica is heated above 1000°C. Similarly (Fig. 7b) heating of precipitated silica above 350°C causes a very marked increase of adsorption density, up to a maximum at 700°, followed by a fall to zero at the highest pretreatment temperature.

Figures 7 and 8 show that flame silica and precipitated silica become practically identical in adsorption properties towards PEO, provided both are pre-treated to 500°C or more. This is remarkable, remembering that the surface areas were determined with N_2, and suggests that the two silicas have similar accesibility to PEO (after heating to 500°).

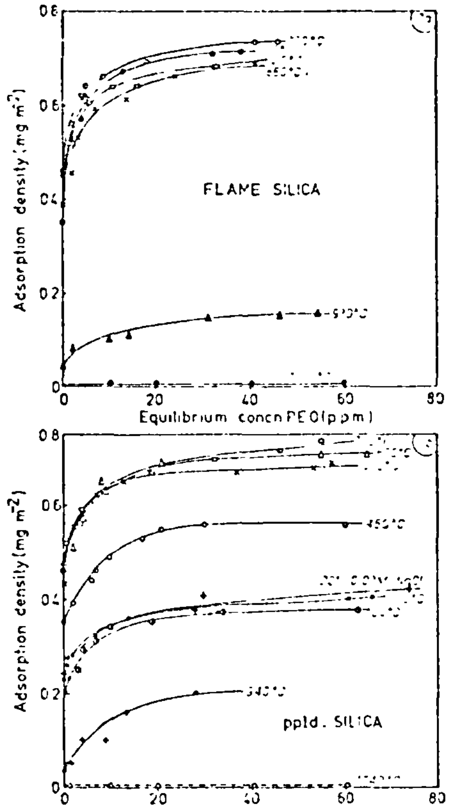

FIG. 7. Adsorption isotherms for PEO on silicas heat treated to various temperatures (pH 5.9).

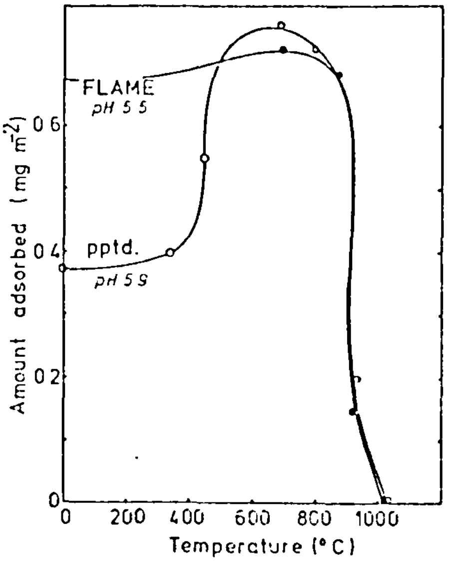

FIG. 8. Effect of heat treatment (24 hr) of silicas on the plateau adsorption of PEO.

Heat treatment at above 350°C is well known to cause dehydroxylation of silica. It is obvious from the changes of colloidal properties that the treated silicas did not fully rehydrate when put into water for the flocculation and adsorption tests. That these effects were not due to loss of porosity was confirmed by similar experiments on a microcrystalline quartz powder; heat treatments lowered the adsorption isotherm in the same way as with flame silica. The influence of pH on heat-treated precipitated silica is also marked, as shown in Fig. 2a.

Rehydration after heat treatment. It is recognized that flame silicas such as Cabosil M-5 are not fully surface-hydrated. In water at room temperature and ordinary pH, the hydroxylation process is very slow (>72 hr, see Fig. 9). Treatment in a Soxhlet extractor in condensing steam for 96 hr produced a marked reduction of adsorption, and boiling in water for 96 hr was more effective (Fig. 9), the adsorption being about halved, and comparable with that of precipitated silica. It is assumed that the accessible surface area has not been reduced correspondingly. It should be recalled that flame silica "aged" in water also becomes nonflocculable by PAM (1).

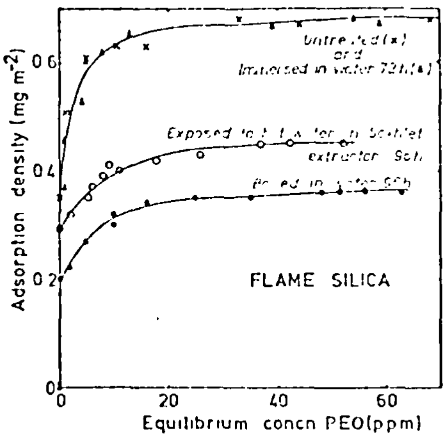

FIG. 9. Effect of hydration treatments on the adsorption isotherms of PEO on flame silica (pH 5.5).

Figure 10 gives isotherms for flame silica pre-heated to 880, 930, or 1030°C and then partially rehydrated. These results show that moderate rehydroxylation *increases* the adsorption affinity; but an optimum is reached and thereafter further rehydration *reduces* the adsorption of PEO. After the strongest heating, recovery of adsorption affinity was barely detectable after 96 hr in boiling water.

Hydrophilic/ether-philic character. Since adsorption of poly(ethylene oxide) involves a "competition" between H_2O and $-(CH_2CH_2OCH_2CH_2)-$ units for surface sites, some correlation is to be expected with the free energy of immersion of silica in water or in diethylether, $C_2H_5OC_2H_5$, (which could be regarded as the precursor of PEO). More simply, the relative affinities of silicas for water or ether should be shown by the 3-phase contact angle, and hence the partition behavior of finely divided silicas in a (mutually saturated) ether–water mixture.

When variously treated silica powders were shaken with equal volumes of water and ether, they were observed to either remain in the water or stick at the ether/water interface or (in the case of methylated silica) pass wholly into the ether. The qualitative observations are indicated by + in Table II for the location of the silica.

It is clear that fully hydrated silica "prefers" water to ether; but partial or complete dehydroxylation or methylation reduces the hydrophilicity and thereby favors the ether–silica interaction. The development of hydrophobicity on strong heating of silica is well established and White (25) has presented air/water/silica contact angle data. Furthermore, Howard and McConnell have suggested a greater affinity of heat-treated silicas for nonpolar solvents to explain the decrease of adsorption of polyethers on to heat-treated silicas from benzene and chloroform and an enhancement from methanol.

Although there is a broad correlation between wetting characteristics and adsorption of PEO, it is not universal. For example, Nos. 5 and 12 (Table II) passed into ether, but 12 showed strong adsorption of PEO whereas 5 showed weak adsorption.

DISCUSSION

The present results demonstrate that differences in response of various samples of silica to flocculation by PEO arise from differences in the strength of adsorption of the polymer and are related to the nature of the surface groups on the silica.

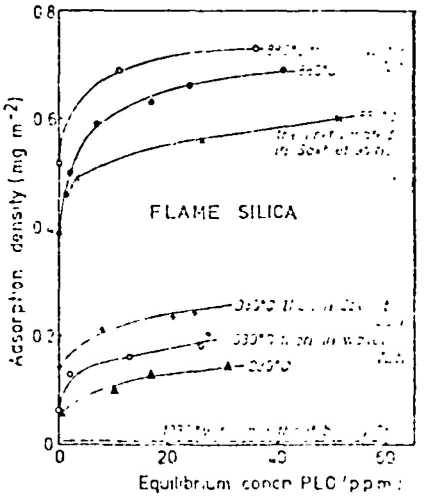

FIG. 10. Effect of rehydration treatments of heated flame silicas on adsorption of PEO. (pH 5.5).

TABLE II

Partition of Silicas between Ether, Water, and Interface

Test no.	Form of silica	Pretreatment	Particles present in		
			Water	Interface	Ether
1	Precipitated	Untreated (pH 6 or pH 2)	+	−	−
2		Heated 24 hr 450°C	+	+	+
3		500°	−	+	+
4		700°	−	+	+
5		880°	−	−	+
6	Flame	Untreated (pH 6)	+	++	+
7		Heated 24 hr 500°	−	+	+
8		700°	−	−	+
9		930°	−	−	+
10		No. 6 boiled in water 96 hr	+	−	−
11		No. 9 steamed for 96 hr	−	−	+
12	Hydrophobic	Untreated (pH 6)	−	−	+
13		(pH > 8)	+	−	−
14		No. 13 then acidified to pH ∼ 2	−	+	+
15	Ground quartz	Untreated (pH 6)	−	++	+
16		Heated 24 hr 800°	−	+	++
17		900°	−	+	++

Adsorption sites. Numerous papers deal with the question of the functional groups on silica and a valuable review of the field was given by Snoeyine and Weber (17). The salient points for the present discussion are the following:

(a) Precipitated silica is a fully hydrated form in which the surface is densely covered with silanol groups, the majority of which are "adjacent" or "hydrogen-bonded" (Type B).

(b) Heating above 400°C begins to cause some irreversible dehydroxylation, eliminating first the Type B groups, which are virtually all removed at 500°C. Type A "isolated" or "single" silanol groups remain, to the extent of about 1.4 groups per 100 Å².

(c) Type A groups begin to be lost above 700°, but dehydroxylation is not complete until above 1000°C.

(d) After total dehydroxylation the surface is covered with siloxane groups.

(e) Flame silica corresponds broadly to precipitated silica that has been dehydrated to about 500°C.

(f) In hydrophobic silica, about 70% of the silanols of flame silica have been methylated, but some Type A remain, about 0.9 per 100 Å² [Thies (18)].

The present results show that adsorption of PEO is strongest on flame silica or on precipitated silica which has been heated to about 600°C. A plausible explanation is that *isolated silanol groups* provide the best adsorption sites, acting as proton donors in hydrogen bonding to ether oxygens

$$-\mathrm{SiOH}\cdots\mathrm{O(CH_2CH_2)_2}{=}{=}$$

This hypothesis was previously suggested for the case of PAM (1) and for low mol wt PEO by Howard and McConnell (4) and by Fontana (14) for a copolymer of ethylene oxide and methyl methacrylate. Complete dehydroxylation leaves siloxane groups, which are hydrophobic and incapable of providing a proton; consequently, adsorption of PEO is nil (from dilute solutions).

It must then be assumed that the Type A silanols left on hydrophobic Aerosil R-972 are available for hydrogen-bonding, as this silica is only a little less sensitive to PEO than flame silica.

A scale molecular model of PEO shows that it is impossible to arrange the chains with all the –O– atoms in contact with a plane. Arranging alternate –O– atoms on opposite sides, it is possible to bring half of them close to a plane, with an O-O distance of about 7.5 Å. In this configuration, two of the CH_2 groups between the O-atoms are in contact with the plane. Thus, the hydrogen bond acceptors are separated by a significant hydrophobic section, possibly matching the spacing of the hydrophobic groups, either methyl or siloxane, present on the silica.

The main question now is why precipitated silica has a low affinity for PEO. The possible influence of basic impurities in the commercial material can be dismissed as a result of the following test. A sample of precipitated silica was boiled with dilute HCl and then washed and tested for adsorption of PEO; its affinity was unchanged by this treatment, which would certainly have eliminated any exposed cations such as Na^+, Ca^{2+}, Al^{3+}. Thus, the lower affinity of hydrated silica for PEO is a consequence of its silanol surface, not its impurities.

It must also be remembered that precipitated silica is *not* deficient in affinity *at pH 2* (Fig. 2).

These observations are concordant with other facts concerning the interaction of PEO and silica. For example, *colloidal* silica is almost quantitatively precipitated by PEO at low pH (~pH 2) but not from alkaline media (pH > 7). (PVA apparently behaves similarly with colloidal silica at high and low pH according to Iler (19) and Tadros (3).) Colloidal silica is also known to form complexes at pH 2 with nonpolymeric analogues of PEO, such as ethylene glycol diethyl ether, $CH_3CH_2OCH_2$-$CH_2OCH_2CH_3$ (20).

Therefore, the problem which particularly needs an explanation is the effect of pH on the adsorption of nonionic polymers, which is shown by all forms of silica, quartz [the flotation of which by PEO surfactants is also drastically cut by pH > 5.5 (11)] and even the surface-methylated hydrophobic silica (Table II, Nos. 12–14). Previous work has shown not only that some silanol groups are inaccessible to methylation but also that they continue to ionize, giving a zeta-potential close to that of nonmethylated silica (21).

Effects of pH. As the pH is raised above 2, silica begins to take up bases by cation exchange. Tadros (3) has suggested that loss of adsorption (e.g., of PVA) with rise of pH is due to reduction in the number of silanol groups available for hydrogen bonding. However, the number of groups ionized at, say, pH 6 in absence of salts is very small indeed compared with the total number present on hydrated silica (probably $\ll 1\%$). Therefore, *either* (a) there is a certain minority type of silanol group which is the important one for both hydrogen bonding and base-binding, *or* (b) the effect of surface ionization is through general electrical double-layer phenomena (rather than loss of sorption sites). At present either theory seems plausible and conceivably both effects might be operative. It is difficult to decide between them. Some of the evidence seems to point to (a) and some to (b), as follows:

(a) Several authors have concluded that the hydroxyl groups on silica have a range of (Bronsted) acid strengths (22, 23) in presence of water. Strazhesko and co-workers (24) have proposed an electronic valence theory to explain the acidity of silica gel in the pH range 3–6 (which they consider is not consistent with the accepted pK value of monosilicic acid.) Ethers are known to form oxonium salts and hydrogen-bonded complexes with strong acids. It therefore seems plausible to suggest that the most readily dissociable silanol groups will also be the important ones for adsorption of PEO.

(b) Reduction of adsorption of polyethers by ionization of the silica might be caused by non-specific "salting-out" due to the electrostatic field near an ionized surface. At pH 2, $\psi_0 = 0$, while at pH 6 $\zeta \approx -100$ mV and the

ψ_0-potential operative for adsorption must be even more strongly negative.

In support of this hypothesis is the observation that addition of neutral salts improves the flocculation (Fig. 3) and is also needed to permit interaction of hydrated silica with simple ethers (20). Since addition of salts, at constant pH, actually *increases* the degree of cation exchange, this effect is clearly electrostatic rather than a question of the number of undissociated silanol groups. In fact, the adsorption of PEO was slightly increased by adding 0.02 *M* NaCl (Fig. 7b).

A slightly different hypothesis has been kindly suggested by one of the referees to explain the pH effects with the different silicas—namely, that hydrated counterions, associated with ionized sites, prevent PEO from approaching the surface. Since methylated or partially dehydroxylated silicas carry a lower surface density of silanol groups than does precipitated silica, the former two would have to be carried to a higher pH to reach a given cation density. On this view, charge density is more important than surface potential in repelling the PEO. It is not possible to discriminate between these alternatives with the evidence available, but the fact that addition of neutral electrolytes slightly *increases* adsorption of PEO seems to favor the potential hypothesis.

Increase of ionic strength has a more marked effect on the flocculation (Fig. 3) than on the adsorption of PEO. Since the salt concentrations (e.g., 0.02 *M* NaCl) are not high enough to produce electrolytic coagulation of hydrated silica at pH 6, the ionic strength effect can be ascribed to reduction in the long-range double-layer repulsion between silica particles; the double-layer thickness, $1/\kappa \approx 22$ Å, is then small enough to allow PEO molecules to bridge the gap.

Whichever the mechanism, it is clear that rise of pH increases the hydrophilicity of any form of silica (even methylated, cf. Table II, Nos. 12–14), and a stronger silica–water interaction correlates with reduced adsorption of PEO from solution.

GENERAL CONCLUSIONS

The data presented in this paper can be rationalized with the following generalizations:

(a) "Isolated" silanol groups are probably the principal adsorption sites.

(b) Adsorption of PEO is favored if the regions between the sites are hydrophobic (siloxanes, or methylated).

(c) Adsorption of PEO is disfavored if the regions between the adsorption sites are hydrated, and particularly disfavored if the surface is appreciably ionized.

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