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# 14 Colloid Systems and Interfaces Stability of Dispersions Through Polymer and Surfactant Adsorption

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## CONTENTS



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## 14.1 INTRODUCTION

Dispersions in both aqueous and nonaqueous media are used in many products including paints, dyestuffs, pigments, printing inks, papers, adhesives, cosmetics, detergents, ceramics, and pharmaceutical and pesticidal formulations. The use of coagulants to clarify drinking water was practiced in ancient China and Egypt. Mineral and environmental engineers have applied the concepts of colloid science to help them utilize and preserve enormous resources which otherwise were waste material.[1] Nowadays, ceramic products ranging from building bricks to expensive china to rocket parts are made from clay/water sols by applying principles of colloid science.[2] The wide use of colloid science in the areas of cosmetics and detergents has added many products to the daily life of everybody.[3] Storing the knowledge of human life, either written on paper or stored on film or disk, has depended upon the application of colloidal science to paper-making and the development of new magnetic and electronic materials. High quality ceramics are also very important as substrates for electronic devices and are used in the preparation of capacitors, ferrites, and piezoelectrics.[4] The initial excitement over the discovery of the high-temperature superconducting oxide phases has been considerably dampened by the subsequent inability to process them into mechanically strong and durable products. The main reason for the structural failure of ceramic materials is the presence of flaws in the material which facilitate the initiation and propagation of cracks. These flaws are introduced into the material during the powder-processing stage, and hence the future of ceramics, to a great extent, will depend on the control of the state of dispersion of the powder prior to firing.[5] Agglomerates and inhomogeneities in the dispersion result in poor packing, grain-growth porosity, and other defects. Good initial dispersion of ceramic powders in liquids is essential for production of high-quality ceramics. The similarity between some biological systems and colloid dispersions, such as blood and proteins and polyelectrolytes,[6] has made colloid science more attractive to the scientific community. Successful applications of colloidal concepts in biological systems include encapsulation, controlled drug release, and prevention or promotion of cell adhesion.[7]

A colloidal system is composed of one or more dispersed phases and a continuous medium. Colloids are present as dispersed systems characterized by slow diffusion and slow (often negligible) sedimentation under normal gravity, which sets the size of the colloidal particles in the range of 1 nm to 1 μm. Systems in which a significant fraction of particles is in a range that is larger than the colloidal range are termed suspensions.

**TABLE 1**
**Summary of Forces Between Two Identical Particles in Aqueous Medium**

| Force | Nature | Source |
|---|---|---|
| Electrical double layer | Repulsive | Structure of surfaces and adsorption of ions |
| van der Waals | Usually attractive | Universal presence |
| Steric interaction | Repulsive | Induced by adsorbed species |
| Hydration/solvation interaction | Attractive/repulsive | Hydration or solvation of adsorbent and adsorbate |
| Polymeric bridging | Attractive | Induced by adsorbed long-chain polymer |
| Hydrophobic interaction | Attractive | Intrinsic or induced by adsorption |

Some colloidal systems, such as polymer and surfactant solutions, containing micelles are rmodynamically stable and form spontaneously. This type of colloid is called lyophilic; however, ost systems encountered contain lyophobic colloids (particles insoluble in the solvent). In the paration of such lyophobic colloidal dispersions, the presence of a stabilizing substance is ential. Since van der Waals forces usually tend to lead to agglomeration (flocculation) of the rticles, stability of such colloids requires that the particles repel one another, either by carrying iet electrostatic charge or by being coated with an adsorbed layer of large molecules compatible th the solvent.

In this chapter, theories as well as experimental justification for the mechanism of stabilization d destabilization of colloidal dispersions are outlined. Interacting forces between colloidal par-les are analyzed, and an overview of experimental methods for assessing the dispersion and levant properties is given. The stabilization and flocculation of dispersions in the presence of rfactants and polymers is discussed in the last two sections.

## 4.2 COLLOIDAL FORCES

olloidal systems are composed of one or more dispersed phases and a continuous medium. In the rocessing of dispersions, aggregates or agglomerates in the dry state are broken into smaller articles in the dispersion medium. The total energy of the system increases due to the increase in rface energy resulting from the increase in surface area and possible changes in the structure and mposition of the surface. The nature and the magnitude of the surface energy are determined by ie physico-chemical properties of the particles and the solvent, as the particles will have a tendency undergo aggregation to reduce the surface energy. A colloidal dispersion is not a thermodynam-ally stable system.

**Colloidal particles in a dispersion medium are always subjected to Brownian motion with requent collisions between them. Stability and other characteristics of dispersion are thus letermined by the nature of the interactions between the particles during such collisions. When ttractive forces dominate, the particles will aggregate and the dispersion may destabilize. When epulsive forces dominate, the system will remain in a dispersed state. Generally, there are six mportant types of particle-particle interaction forces that can exist in a dispersion as summarized n Table 1.**

### 14.2.1 VAN DER WAALS FORCE

London explained the van der Waals forces (the universal attractive forces) acting between all atoms, molecules, ions, etc. on the basis of wave mechanics. These short-range forces result from the interaction between temporary dipoles on some molecules and induced dipoles on the neighboring molecules, as well as a quantum mechanical effect leading to attraction between nonpolar molecules. Most of the interpretations of London-van der Waals forces in the past have been based on the Hamaker approach,[8] which involves the pairwise addition of the microscopic forces acting

between two bodies. The attractive energy between two atoms varies inversely as the sixth power of the distance separating them and is given by:

$$V_A = -\frac{\beta}{l^6} \tag{1}$$

where β is the London constant, which depends upon the properties of the specific atoms.

In the case of dispersion, these forces are due to spontaneous electric and magnetic polarizations giving rise to a fluctuating electromagnetic field within the dispersed solid and the medium separating the particles. The interaction energy between two identical spheres of radius $R$ at distance $H$ between their centers remains the same for a constant ratio of $R$ to $H$. Replacing $H/R$ with $S$, the interaction energy is given as:

$$V_A = \frac{-A}{6}\left[\frac{2}{S^2-4} + \frac{2}{S^2} + \ln\frac{S^2-4}{S^2}\right] \tag{2}$$

For the simplest case, the net attractive force between two particles at a small separation distance after neglecting the retardation correction is given as:

$$V = \frac{-AR}{12l} \tag{3}$$

where $l = H - 2R$, and $A$ is the combined Hamaker constant. The Hamaker constant can be estimated theoretically by calculating certain molecular constants from optical data. For a system of a solid (1) dispersed in a medium (2), the combined Hamaker constant can be expressed as:

$$A = A_{11} + A_{22} - 2A_{12} \tag{4}$$

As an approximation, $A_{12} = (A_{11}A_{22})^{1/2}$, so that

$$A = \left[A_{11}^{1/2} - A_{22}^{1/2}\right] \tag{5}$$

### 14.2.2 Hydrophobic Force

Hydrophobic interactions may exist naturally or be induced by the adsorbed hydrophobic species. Polar solvent molecules squeezed between two hydrophobic surfaces have reduced freedom to form structures in certain directions, since contact with the particle surfaces is essentially avoided. The hydrophobic surfaces, therefore, have a preference to associate with each other. It is found that hydrophobic interactions extend over a much longer range than the van der Waals force.[9] Graphite and coal are a few of the solids possessing natural hydrophobicity, and their aggregation is observed in polar solvents. More often, surface hydrophobicity of the solid particles can be induced by the adsorption of surfactants.

Hydrophobic forces were first measured experimentally by Israelachvili and Pashley[10] with mica surfaces in equilibrium with cetyltrimethylammonium bromide solution. The hydrophobic force was found to decay exponentially in the range of 0 to 10 nm. van Oss[11] described the rate of decay with distance in terms of interaction energy as:

$$\Delta G_l = \pi R \lambda \Delta G_{l_0} \exp\left[(l_0 - l)/\lambda\right] \tag{6}$$

where $\lambda$ is the correlation length of the molecules of the liquid medium, and $\Delta G$ is the interaction energy at the distance of $l_0$, the minimum equilibrium distance. In aqueous solutions, $\lambda \approx 0.6$, three times the water molecule dimension, which may be attributed to the fact that the water molecules tend to occur in clusters of three or more molecules resulting from hydrogen bonding with each other.

Though the real origin of the hydrophobic force still remains a mystery, its effect on the dispersion stability has long been recognized. Somasundaran et al.[12] reported a clear relationship between the stability and the surfactant adsorption density, as well as the chain length of the adsorbed surfactants.

### 14.2.3 Steric and Bridging Forces

Steric forces arise from the overlap of the adsorbed layers and can be repulsive or attractive in nature, depending on whether or not the outermost layers on the particles prefer to be in contact with the solvent. If the solvent power of the medium for the exposed portions of the exterior layer (for example, those of an adsorbed polymer layer) is satisfactory, they will be compatible with the medium, and the suspension will remain stable.[13,14] On the other hand, if the solvent power for the adsorbed layer is minimal, there will be a tendency for the exposed portions of the adsorbed layer on one particle to interpenetrate into those of a layer on another particle and thereby promote aggregation.

Interpenetration and aggregation is possible only if the net change in Gibbs free energy due to the interpenetration of the polymer chains is negative. The Gibbs free energy change is considered in such cases to be determined essentially by the change in entropy due to the release of solvent molecules and the decrease in randomness of the polymer chain and by the enthalpy of desolvation of the polymer chains. For flocculation to occur according to this mechanism, the increase in entropy due to the release of solvent molecules should outweigh the loss of entropy due to the interpenetration of polymer chains and increase in enthalpy of desolvation. It is clear that the desolvation characteristics of the adsorbed polymer species and the dependence of it on solution properties such as temperature and ionic strength will be important in determining aggregation by this mechanism. Ottewill and Walker derived an equation for the energy change due to an overlap of the adsorbed layers by using Flory's liquid lattice model for polymer solutions:[13,55]

$$V_{steric}(a) = \frac{4\pi kTC_v^2}{3v_1^2\rho_2^2}\left(\psi_1 - \kappa_1\right)(\delta - a)^2(3R + 2\delta + a/2) \tag{7}$$

where

$C_v$ = concentration of material in the adsorbed layer
$v_1$ = molecular volume of solvent molecules
$\rho_2$ = density of the adsorbate
$\Psi_1, K_1$ = entropy and enthalpy parameters of mixing proposed by Flory
$\delta$ = adsorbed layer thickness
$R$ = particle radius
$a$ = distance separating the surfaces of two approaching particles

Steric repulsion can be explained in the following manner. When two particles with adsorbed long-chain molecules approach each other, the entropy per adsorbed molecule decreases, causing desorption and a concomitant increase in the interfacial energy. This means that additional work has to be input to bring the particles together, and this manifests itself as a repulsive force.

A long-chain adsorbate with several active sites on it can induce aggregation by attaching itself to two or more particles. Polymers can provide such bridging between particles particularly under conditions where particles are not totally coated by the polymeric species. If particles are already

fully covered with polymers, bridging can take place only if there is either detachment of some portion of the polymer already on a particle to provide sites for attachment of polymer fractions adsorbed on other particles or polymer-polymer bonding itself. It has been suggested that maximum flocculation occurs when the fraction of particle surface covered by polymer molecules is close to 0.5. It is to be noted that this hypothesis has not, however, been proven experimentally. As indicated earlier, bridging should be possible even when particles are fully covered if some detachment and reattachment of the adsorbed polymer is possible. Adsorption of polymers is, in general, found to be irreversible, except in the occasional case of polymers with functional groups that form covalent bonds with the surface species, due only to the cumulative effect of adsorption of a single polymer molecule on several sites. Detachment and reattachment of portions of such a polymer should, however, be possible, and such a process should facilitate bridging. This has been shown to be so by allowing polymers to be displaced from the surface by adding competing agents into the system. Thus polyacrylamide can be desorbed from clay by adding phosphates into the solution. The absence of bridging might be interpreted to suggest the presence of strong repulsive steric interactions between dangling portions of the adsorbed polymer chains.

For steric stabilization and bridging flocculation by adsorbed polymers, there is still no satisfactory quantitative theory. This is because any theory for those processes must be couched in terms of one or the other of the theories of polymer solution thermodynamics which are at best semi-quantitative. Also, in order to calculate the distance dependence of the steric interaction, it is necessary to predict the conformation of close-packed polymer molecules. In fact, except in $\theta$ solvents, it is very difficult to predict the polymer conformation in solution.[13] Despite these difficulties, some progress has been made in developing pragmatic models capable of predicting the distance dependence of the steric and bridging interactions.

### 14.2.4 Hydration and Solvation Forces

Recent work on the measurement of forces acting between surfaces on liquids has revealed the existence of some powerful short-range forces which have their origin in the packing ordering of molecules at the interface.[15,16] These include hydration and solvation interactions and also effects due to phase changes in the interlayer between two surfaces in close proximity. The Derjaguin, Landau, Verway, Overbeek (DLVO) theory is based on the continuum theory — both the interacting bodies and the medium are characterized by their dielectric properties which does not change with surface separation; however, this is not valid for small separation distances where, due to molecular ordering, the properties are quite different than in the bulk. At these small separation distances, forces due to phase separation or phase transitions in the liquid film between the surfaces — including capillary condensation and cavitation and forces due to surface-induced solvent structures — come into play and can contribute significantly to the stability of dispersions. The repulsion between the particles is due to the necessity for ions to lose their bound water to allow the approach to continue, and this is thermodynamically unfavorable; however, the hydration effect can result in significantly enhanced attraction between two hydrophobic particles.

The presence of an isolated surface induces ordering (layering) of the adjacent molecules of the fluid in contact with it, and this gives rise to a density profile with an oscillatory nature. The magnitude of the oscillation decays with distance from the surface, and for the two surfaces at a sufficiently large separation the density profile from either surface has decayed to the bulk value at the midplane. As the surfaces are brought close together, there is an overlap of the density profiles. The enhancement of ordering at separation distances close to an integral number of layers or molecular diameters is energetically favorable. At intermediate distances, the density profiles overlap destructively and will cause a free energy maximum. The result is a free energy curve that oscillates between repulsive maxima and attractive minima as the surface separation is varied. Surface roughness smears out the ordering and removes this oscillatory force. Similarly, solvent penetration into an adsorbed layer removes these short-range forces. In force measurements of a mica surface immersed in organic solvents, it was found that the adsorption of small quantities of

water on the surfaces removed the oscillatory forces, probably by disturbing the molecular ordering of the solvent. The important aspect about these repulsive structural forces is that at distances below 30 Å they can exceed van der Waals forces and electrical double layer forces.

#### 14.2.4.1 Capillary Condensation Forces[17]

Phase changes can occur at the interface of solids and liquid mixtures. As mentioned earlier, a surface excess of a second species will cause disruption of the molecular ordering and a reduction of the free energy maxima and minima arising from packing constraints. In the case of water on the surface of mica in a nonpolar solvent, it will form an annulus around the contact area of two such surfaces due to the low contact angle of water on mica. This is analogous to capillary condensation from the vapor phase. The thermodynamically stable state for two surfaces in close proximity in a nonpolar liquid containing water is with a bridge of water connecting the two surfaces. The water bridge should be stable when the surface separation is less than or equal to twice the Kelvin radius. The net effect of this spontaneous capillary condensation occurring at separation distances lower than about 10 Å is to provide a very strong attractive force as well as large adhesion between the surfaces. The adhesion at contact reflects the interfacial tension of the water-nonpolar liquid interface and is an order of magnitude larger than expected from either van der Waals or solvation forces.

### 14.2.5 Interacting Double Layers

Most substances acquire surface electrical charges when brought in contact with a polar medium, resulting from one or more of the following:

1. Preferential dissolution and solvation of surface species followed by dissociation of some of these species
2. Lattice imperfection on solid surfaces
3. Adsorption of ions or impurities at the solid-liquid interface

The surface charge influences the spatial distribution of ions or molecules in the surrounding solution, attracting ions of opposite charge but repelling ions of similar charge from the surface. Along with the thermal motion, this leads to the formation of the diffused electrical double layer which consists of the charged surface, neutralizing counterion, and, farther from the surface, coions distributed in a diffuse manner (Figure 1).[18]

In the absence of any significant ionization in low dielectric constant media, the other three mechanisms are highly improbable. In the absence of any adsorbable surfactants, the dissociation of surface groups appears to be the most general mechanism, and the ion responsible for the charge transfer between the solvent and particle is the proton. The direction of protonic transfer depends on the relative basicity or acidity of solvent and particle. If the solid surface is represented by PH and the solution by SH, the sign of the surface charge due to proton acceptance or donation is governed by the relative proton donating/proton accepting capacity of the surface and the solution:

$$PH_2^+ + S^- = PH + SH = P^- + SH_2^+$$

In case the particle charge is the result of adsorption of ionic surfactants, its sign depends on the absorbability of the surfactant cation and anion. The most probable mechanism, as elucidated by Fowkes,[20] is the adsorption of the surfactant as an ion pair (neutral molecule) followed by a proton exchange reaction, the direction of which depends on the relative acidity/basicity of the surfactant and the surface. The final step in the charge generation process is the dissociation of the desorption of the protonated/deprotonated surfactant species, leaving a net charge at the interface. Figure 2 depicts this process schematically.

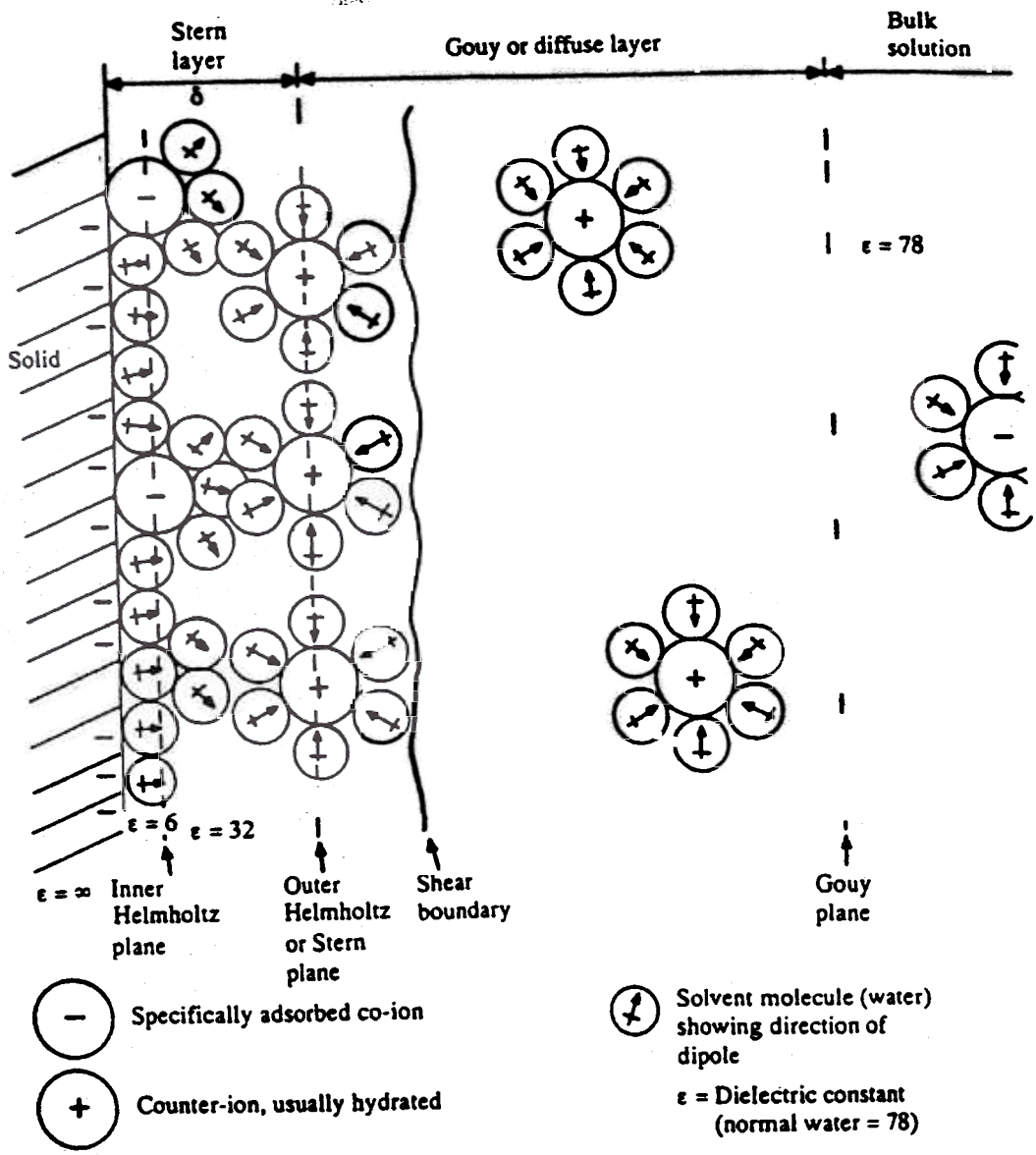



**FIGURE 1** Schematic representation of the electrical double layer in the vicinity of the solid-liquid interface.

Despite the difficulties in quantitative treatment, there exist theoretical models based on the classical treatment initiated by Gouy, Chapman, Debye, and Huckel and later modified by Stern and Grahame. As shown in Figure 3, a reasonable representation of the potential distribution by the Poisson-Boltzmann equation can be given as:

$$\frac{d^2\Psi}{dl^2} = -\frac{e}{\varepsilon}\sum_i z_i n_{i_0} \exp\left(\frac{z_i e \Psi}{kT}\right) \tag{8}$$

where $\psi$ is the potential at a distance, $l$, from the surface; $\varepsilon$ is the permittivity of the medium ($\varepsilon = \varepsilon_o\varepsilon_r$); $n_{i_0}$ is the bulk concentration of ions of charge $z_i$; $e$ is the electronic unit charge; $k$ is the Boltzmann's constant; and $T$ is the absolute temperature.

For low charge density, $z_i e\psi/kT < 1$, an explicit solution of the above equation can be written in the form

$$\Psi(l) = \Psi_\delta \exp(-\kappa l) \tag{9}$$

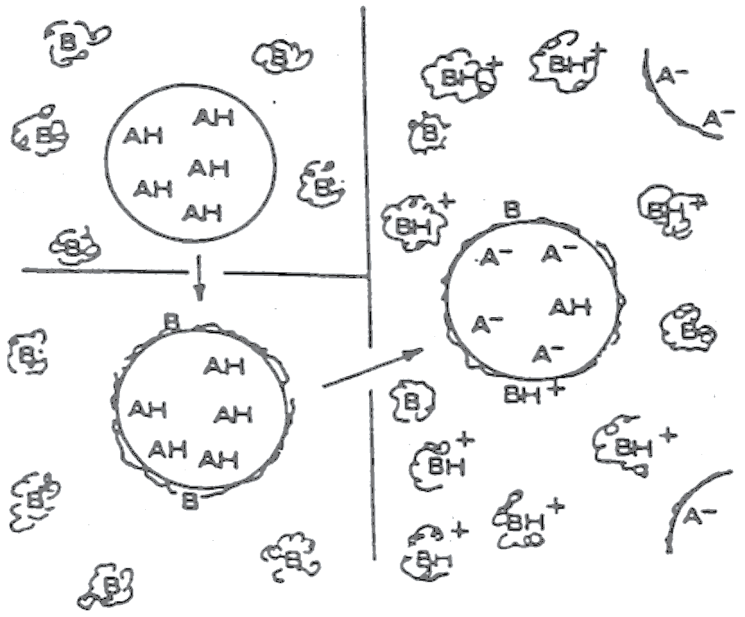



**FIGURE 2** Schematic representation of the origin of surface charge in nonaqueous media.

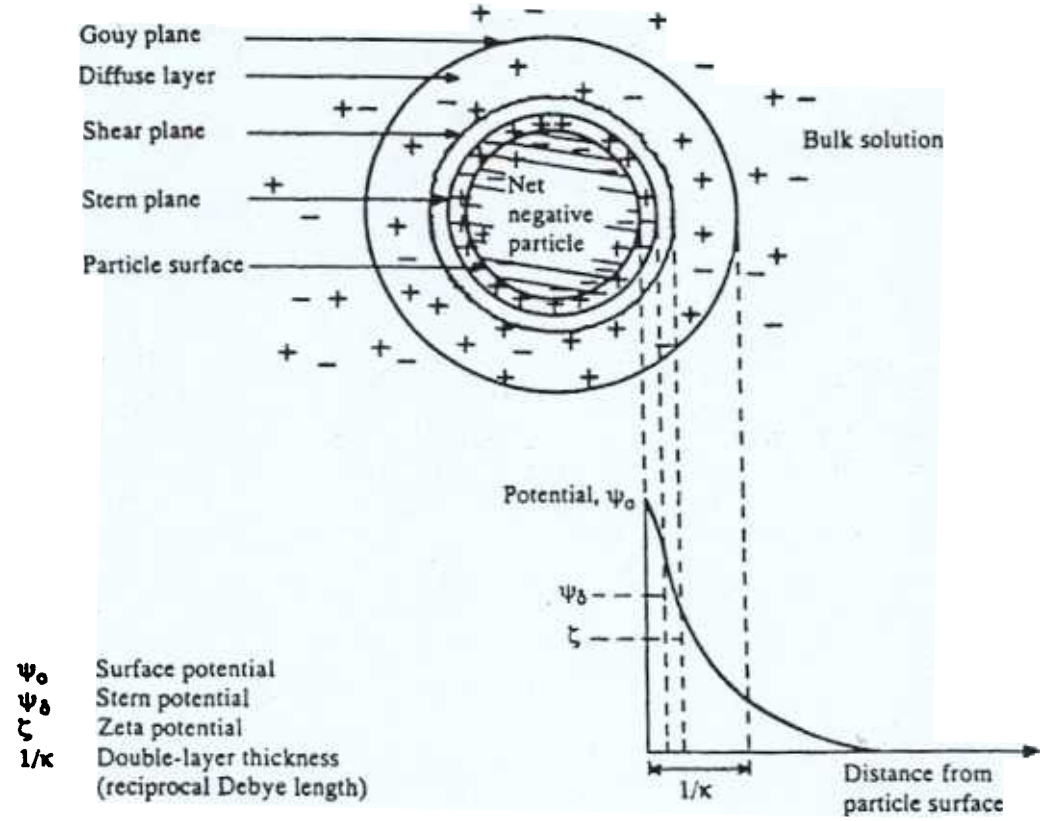



**FIGURE 3** Distribution of electrical potential in the double layer region surrounding a charged particle showing the position of zeta potential and the reciprocal Debye length.

where $\kappa$ is known as the reciprocal Debye length, with $1/\kappa$ often referred to as the double layer thickness which can be calculated from:

$$\kappa = \left( \frac{1000 e^2 N_A}{\varepsilon kT} \sum z_i^2 M_i \right)^{1/2}$$

where $N_A$ is Avogadro's constant and $Z_i$ and $M_i$ are the valency and molar concentration of the ion, respectively.

The nature and thickness of the electrical double layer are important because the interaction between charged particles is governed by the overlap of their diffuse layers. Unfortunately, it is impossible to directly measure the Stern potential $\psi_\delta$. Instead, the zeta potential, $\zeta$, which is the potential at the shear plane close to the Stern plane, can be experimentally measured and is often used as a measure of the surface potential.

For most simple situations, the repulsive interaction energy between two identical charged particles of equal radius, $R$, and zeta potential, $\zeta$, at a distance of separation, $l$, can be given by:

$$V_e = 0.5 \pi \varepsilon R \zeta^2 \ln[1 + \exp(-\kappa l)]$$

Though derived based on the low surface charge density, Equation 11 has been found to be valid for the situation where zeta potential is as high as 50 mV.

### 14.2.6 Summation of Various Forces

The DLVO theory which has been used with success to explain stabilization mainly in aqueous systems states that the overall interaction energy is the sum of the electrostatic and van der Waals forces; however, this has been extended now to include the steric forces, also. The total interaction energy can be expressed as:

$$V_T = V_{elec} + V_A + V_{steric}$$

Figure 4 shows the total interaction energy as a function of particle separation and displays a maximum, called the energy barrier.[19] For suspensions to be destabilized, the particles must have enough energy to surmount this barrier during collisions. In the absence of electrostatic interactions, the particles can get trapped in the secondary minimum and form loose aggregates which can usually be redispersed easily. The electrostatic forces, however, cause the disappearance of the secondary minimum and increase the barrier to the primary minimum, thereby decreasing the probability of aggregation. Thus, a combination of electrostatic and steric forces is necessary for effective stabilization.[20] In systems stabilized solely by electrostatic forces, an energy barrier of about 30 kT is desirable with a Debye length, $1/\kappa$, of not more than 1000 Å.

For systems stabilized solely by electrostatic repulsion, a decrease in the energy barrier will lead to rapid coagulation. The energy barrier can be decreased by the addition of counterions that can specifically adsorb and alter the surface charge or cause double-layer compression. The critical coagulation concentration for different ions depends on the valency of the ions as formulated by Schultze and Hardy. Typically, $c_c$, the critical coagulation concentration, is proportional to $z^2$, where $z$ is the valency of the ion.

Adsorbed layers of surfactants and polymers can affect stability in the following manner. If they are charged, they can produce, increase, or decrease the electrostatic repulsion. In the case of polymer or long-chain molecules, steric repulsion occurs when the adsorbed layers start to penetrate. The adsorbed layer has a Hamaker constant different from that of the particle, hence the van der Waals interactions are altered.

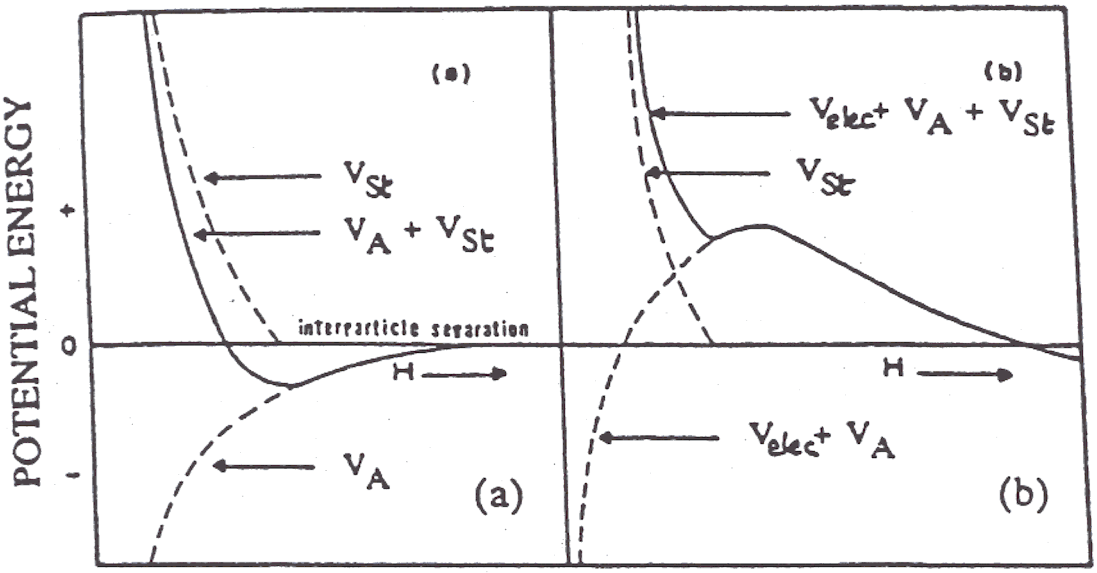



**FIGURE 4** Diagram representing the variation of total interaction energy between particles with separation distance.

### 14.2.7 Kinetics of Aggregation

The rate of aggregation will depend essentially on the probability of collision between particles, probability of attachment during such collisions, and probability of their subsequent detachment from the aggregates. While the probability of collision will depend on the Brownian motion determined essentially by the temperature of the system and on fluid flow motions determined by the viscosity of the fluid medium and external stirring, probabilities of adhesion and detachment are dependent on the type of physico-chemical interactions between the particles and, to some extent, on velocity gradients in the medium.

Both Brownian and velocity gradient aggregations are described by the Smoluchowski treatment, which relates the rate of aggregation to the radius of the particle and the total number of particles in the system in the following manner. Aggregation due to Brownian motion, known as perikinetic aggregation, leads to a decrease of particle number governed by the following second-order equation if every collision is successful in creating an adhesion:

$$\frac{dN_t}{dt} = -8\pi D r N_t^2$$

where $N_t$ is the total number of particle at time $t$, $D$ is the diffusion coefficient for the particle, and $r$ is the radius of the particle. The integrated form of Equation 1 is

$$N_t = \frac{N_0}{1 + 8\pi D r N_0 t}$$

This derivation takes into account the formation of only doublets. In reality, primary particles can also aggregate with multiplets. Solution for all particle aggregates containing $i$ particles is given as:

$$\sum_{i=1}^{\infty} N_i = \frac{N_0}{1 + 4\pi D r N_0 t}$$

Slow stirring can indeed promote aggregation. Such aggregation under the influence of the velocity gradient is known as orthokinetic aggregation. The rate of orthokinetic aggregation is given by:

$$-\frac{dN_t}{dt} = \frac{16Gr^3}{3}\sum_{k=1}^{p} N_k^2 k$$

where $G$ is the velocity gradient, $N_k$ is the number of $k$ particles per unit volume, $k$ is particles formed by the aggregation of two particles, and $p$ is a particle of limiting size in shear gradient $G$. As mentioned earlier, the above formulations assume that every collision is fruitful. In reality, only a fraction of the collisions might be effective, and as a result the aggregation might be slow. The magnitude of this fraction is dependent upon the nature of interactions between particles and, to some extent, viscous properties of the liquid film between the particles. If $V$ is the total energy of interaction between particles of radii $r_i$ and $r_j$ when they are separated by a distance, $d$, the fraction of effective collisions, $\alpha$, according to Fuchs is given by the following expression:

$$\frac{1}{\alpha} = 2\int_{2}^{\infty} \exp\left(\frac{V}{kT}\right)\frac{dS}{S^2}$$

where $k$ is the Boltzmann constant, and $S$ is equal to $2d/(r_i + r_j)$. As an example, for maximum $V$ equal to 5, 15, and 25 $kT$, $\alpha$ is $2.5 \times 10^{-2}$, $10^{-5}$, and $10^{-9}$, respectively.

The interactions between particles that are important in determining $\alpha$ are made up of London-van der Waals attractive forces ($V_a$); electrical double layer forces ($V_e$), which can be attractive or repulsive in nature; bridging forces ($V_b$), which are always attractive, and steric forces ($V_s$), which arise from the overlap of adsorbed layers. Steric forces can be repulsive or attractive depending on the solubility properties of the adsorbed layer.

## 14.3 EXPERIMENTAL ASSESSMENT OF DISPERSION STABILITY

Stability in colloidal dispersions is defined as resistance to molecular or chemical disturbance, and the distance that the system is removed from a reference condition may be used as a measure of stability. The stability can be analyzed from both energetic and kinetic standpoints. The kinetic approach uses the stability ratio, $W$, as a measure of the stability. $W$ is defined as the ratio of the rate of flocculation in the absence of any energy barrier to that when there is an energy barrier due to adsorbed surfactant or polymer. These processes are referred to as rapid and slow flocculation with rate constants $k_T$ and $k_S$, respectively, such that $W = k_T/k_S$. The stability of colloidal suspensions can be evaluated using various techniques. In practice, two methods are primarily used: sedimentation and rheology measurements.

### 14.3.1 Sedimentation Method

This is a relatively simple method using a series of tubes containing the dispersion in a homogeneous state. The settling rate is estimated by monitoring the rate of descent of the upper interface with time and provides information on the stability of the dispersion. A high value of settling rate corresponds to an unstable dispersion and vice versa, since flocculated particles settle more rapidly than deflocculated ones, except in concentrated systems where hindered settling occurs. Sedimentation volumes typically can be measured after a settling rate determination after allowing the samples to settle for a considerably long time. Sediment volumes provide valuable information on the nature of the flocs. For example, flocculated particles form soft and loosely packed sediments and have large sediment volumes that are easily redispersed in most cases; however, stable suspensions

will form compact sediments of smaller volume that are not easy to redisperse. Techniques such as visual observation, light scattering, and absorbance measurements with a spectrophotometer are generally used to study sedimentation rates. Two other useful parameters can be measured from these tests, which yield further qualitative information on the nature of the dispersion/flocculation. Percent weight settled is estimated by removing a fixed volume of the dispersion after a fixed amount of time and calculating the amount of solids settled in that time. In many applications, particularly when the liquid must be recycled, clarity of the supernatant is an important factor; therefore, the turbidity or light transmittance of supernatant after flocculation is also monitored, sometimes as a criterion for suspension stability. This parameter is dependent on the particle size distribution (the same is valid for settling rate determination).This is very useful especially in the case of polymers and reflects the efficiency of fine particle capture by the flocculating agent. Advanced imaging techniques such as computerized axial tomography (CAT) scans can also be used to gain information about the structure of suspensions and flocs.[21]

### Rheological Methods

These methods are widely used to assess dispersion stability and can give very useful information on the particle-particle interactions with the dispersion medium. These measurements, however, give indirect information on the stability of dispersions and must be used in conjunction with sedimentation tests for maximum benefit.

Additional tests to determine wettability of the surfaces include flotation and two-phase separation. In flotation, the particles (after treatment with the surface modifier) are introduced into a stream of bubbles, and the amount of solids floated out during a fixed period of time is taken as a measure of the hydrophobicity of the particles. A modification of the flotation technique is the bubble pickup, in which single bubbles are generated in a controlled manner and contacted with the dispersed particles. The weight of particles thus removed by a fixed number of bubbles is taken as a measure of the hydrophobicity.

In the two-phase separation test, a known amount of the dispersion is introduced into a separatory funnel consisting of two immiscible phases (one aqueous and the other organic). The particles are shaken thoroughly and then allowed to separate into the two phases. The two phases are then separated and the amounts of solids in each are then determined, providing a partition coefficient reflective of the wettability of the particle surface.

## DISPERSION IN THE ABSENCE OF DISPERSING AGENTS

Figure 5 shows the settling behavior of bare alumina particles in solvents of varying polarity.[22] It can be observed with an increase in solvent polarity that the dispersion stability displays a maximum which corresponds to a minimum in the normalized settling rate; the normalization is done to account for differences in the density and the viscosity of the solvents. The normalized settling rate equals the observed settling rate times the solvent viscosity/(particle density-solvent density). The maximum stability in this case is observed in moderately polar solvents ($20 < \varepsilon < 45$). Bare particles suspended in a liquid medium are in constant Brownian motion and can flocculate rapidly on collision if the $V_a$ term is larger than about 15 kT. Stabilization usually can be achieved by decreasing the van der Waals attractive forces. The potential energy due to the van der Waals interaction can be calculated approximately for two spherical particles suspended in a liquid medium using the following equation:

$$V_a = -A_{SLS}\left(a/12\,H_0\right) \text{for } H_0 << a \tag{18}$$

where $A_{SLS}$ is the combined Hamaker constant for the solid in the liquid and can be estimated from the equation:

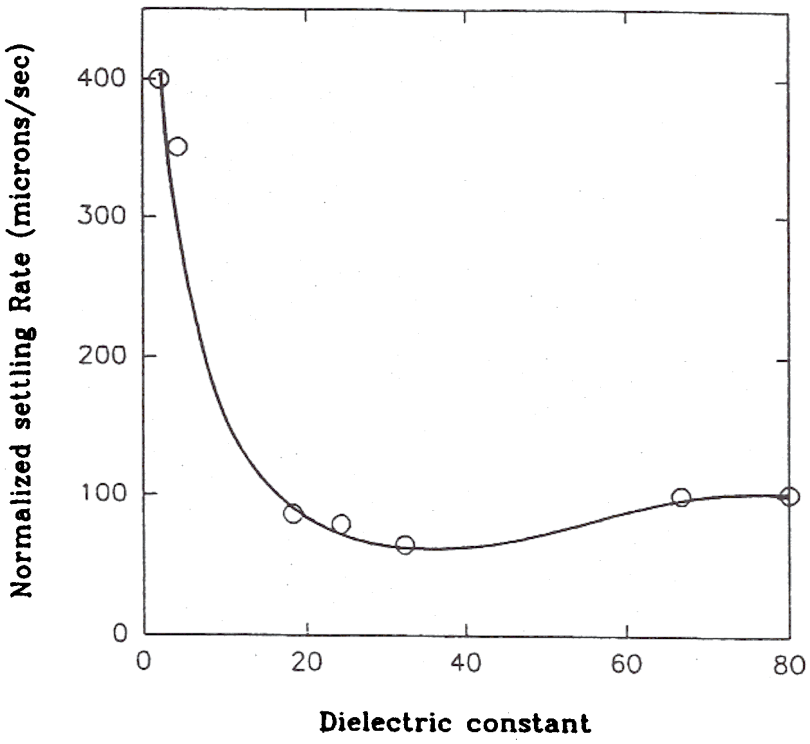



**FIGURE 5** Stability of bare alumina particles as a function of solvent polarity.

$$A_{SLS} = A_S + A_L - 2\left(A_S A_L\right)^{1/2}$$

where $A_S$ and $A_L$ are the Hamaker constants of the respective solids and liquids in vacuum:

$$A_S(kT) = 113.7\frac{(\epsilon - 1)^2}{(\epsilon + 1)^{3/2}(\epsilon + 2)^{1/2}}$$

The $A$ values for ceramic substrates and liquids can also be estimated from the following equation where $\epsilon$ is the static dielectric constant of the material being considered. A value of $\epsilon_s = 9.3$ is assumed for alumina based on reported measurements,[23] and $A_{al}$ is estimated to be 70.5 kT from Equation 20. Similar calculations have been performed for the different liquids considered here, and the results are shown in Table 2. For a given set of particles, the $A_{SLS}$ value is directly proportional to the van der Waals attractive energy. It can be seen from the values shown in Table 2 that the dispersion behavior as predicted by changes in the van der Waals interaction are similar to the observed behavior. This suggests that the primary cause for the observed changes in stability with solvent polarity is the change in the attractive interaction. Figure 6 depicts the variation of the attractive potential (Equation 20) with interparticle distance for these bare alumina particles in different liquids. It can be seen that at low interparticle separations the attractive energy is maximum for cyclohexane ($A_{SLS}$ = 25.5 kT) and minimum for isopropanol ($A_{SLS}$ = 1.1 kT). However, one should be aware that in polar liquids alumina is also capable of developing a significant amount of surface charge which can enhance the dispersion stability by contributing to the electrostatic repulsion term.

## 14.5 ADSORPTION AND ITS EFFECT ON DISPERSION

Adsorption of molecules on solids from solution is important in controlling a variety of interfacial processes such as mineral flotation and other solid-liquid separation processes, flocculation/dispersion,

TABLE 2
Hamaker Constant and Dispersion Stability for Alumina in Different Solvents

| Solvent | Dielectric constant | $A_{\iota}$ (kT) | $A_{SLS}$ (kT) | Observed behavior |
|---|---|---|---|---|
| Cyclohexane | 2.02 | 11.2 | 25.5 | Poor |
| Chloroform | 4.3 | 40.4 | 4.3 | Poor–okay |
| 2-Butanol | 10.8 | 85.7 | 0.8 | Good |
| Isopropanol | 18.3 | 89 | 1.1 | Good |
| Ethanol | 24.3 | 94.6 | 1.9 | Good |
| Methanol | 32.4 | 99 | 2.5 | Good–poor |
| Methanol/water (40%) | 66.7 | 106.3 | 3.8 | Good–poor |
| Water | 80 | 107.5 | 3.9 | Good–poor |

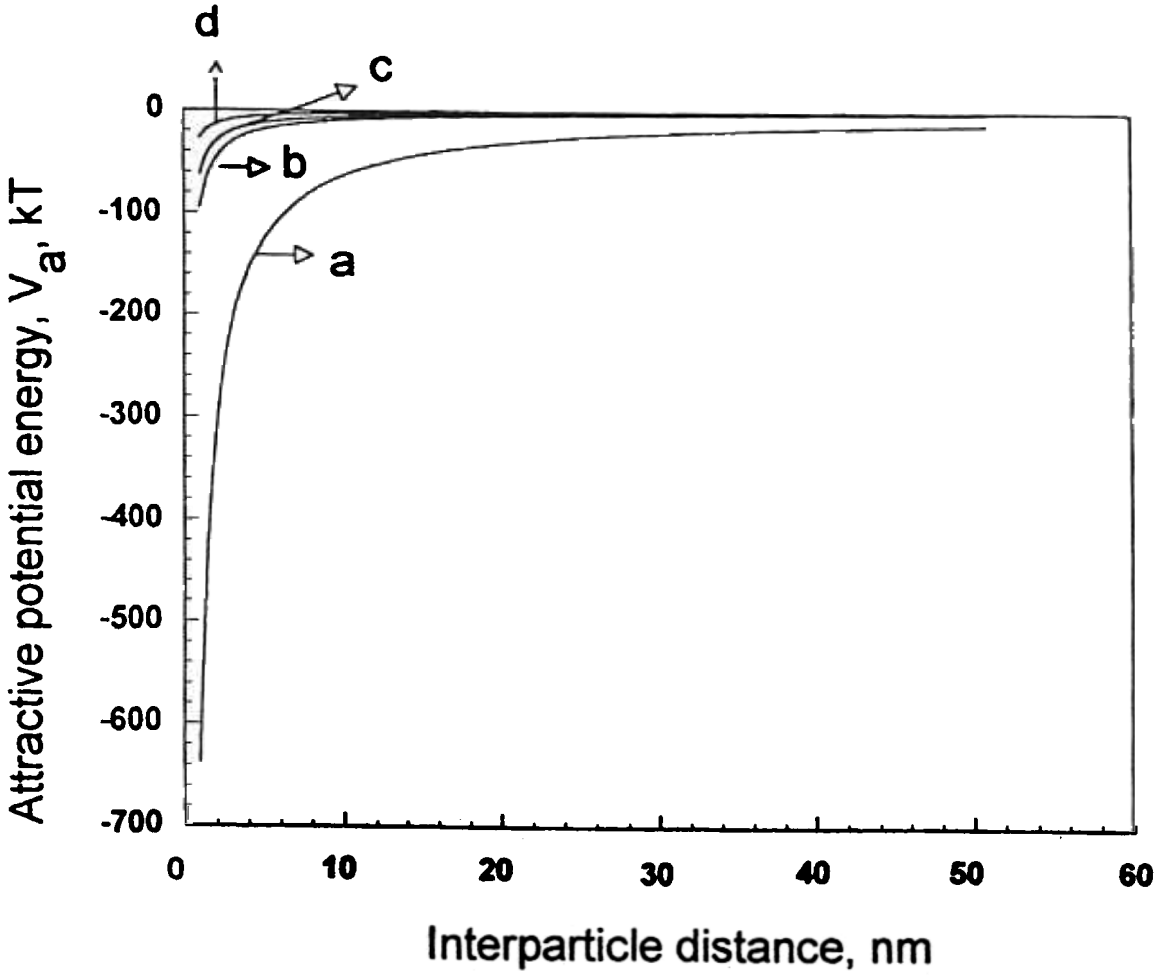



**FIGURE 6** Variation of attractive potential between particles as a function of separation distance for (a) cyclohexane, (b) water, (c) ethanol, and (d) isopropanol.

blood clotting, and micellar flooding of oil wells. Adsorption results from energetically favorable interactions between the solid adsorbate and the solute species. Adsorption of surfactants on minerals from aqueous or organic solutions is often a complex process since it can be influenced

by all solid, solvent, and solute components of the system. Several interactions such as electrostatic attraction, covalent bonding, hydrogen bonding, or nonpolar interactions between the adsorbate and the adsorbent species and lateral interaction between the adsorbed species, as well as their desolvation, can contribute to the adsorption process.

Adsorption can be considered to be a process of selective partitioning of the adsorbent species to the interface in preference to the bulk and is the result of interactions of such species with the surface species on the solid. The interactions responsible for adsorption can be either physical or chemical in nature. Adsorption can be broadly classified into two categories, physical adsorption and chemical adsorption, depending on the nature of the forces involved.[24] Physical adsorption is usually weak and reversible and involves small energy changes. The van der Waals forces and electrostatic forces are primarily responsible for physical adsorption that is also characterized by a high rate of adsorption and formation of multilayers.[25] Chemical adsorption occurs through covalent bonding between the adsorbate and the surface species on the solid. Chemical adsorption normally involves an activation stage and is characterized by relatively higher energy changes and a low rate of adsorption. The adsorption is usually strong and irreversible and is limited to a monolayer. A distinction between physical and chemical adsorption can usually be made from the temperature dependence of the adsorption process. In the case of physical adsorption, the adsorption generally decreases with temperature, while in the case of chemisorption it increases with temperature. However, it must be noted that the distinction between physical and chemical adsorption is an arbitrary one, and in many cases an intermediate or combined character of adsorption is encountered. In some cases, such as the adsorption of gases on metal surfaces, physisorption may take place initially and may be followed by adsorbent-adsorbate reactions resulting in chemisorption.[26]

The adsorption density, which is the amount of adsorbate removed from the solution to the interface, can be mathematically expressed as:[27]

$$\Gamma_i = 2rC\exp\left(\frac{-\Delta G^o_{ads}}{RT}\right)$$

**where $\Gamma_i$ is the adsorption density in the plane, δ, which is at the distance of closest approach of counterions to the surface; $r$ is the effective radius of the adsorbed ions; $C$ is the bulk concentration of the adsorbate in mol/ml; $R$ is the gas constant; $T$ is the absolute temperature; and $\Delta G^o_{ads}$ is the standard free energy of adsorption. In practice, however, the adsorption density is measured as the depletion of adsorbate from the solution as shown in the following equation:**

$$\Gamma = \left(C_f - C_i\right)\frac{V}{W}$$

where $\Gamma$ is the adsorption density in mol/g; $C_f$ and $C_i$ are the final and initial concentration, respectively, of the adsorbate in mol/l; $V$ is the volume of solution in a liter; and $W$ is the weight of the adsorbent in grams.

The net driving force for adsorption, $\Delta G^o$, can be considered to be the sum of a number of contributing forces:

$$\Delta G^o_{ads} = \Delta G^o_{elec} + \Delta G^o_{chem} + \Delta G^o_{c-c} + \Delta G^o_{c-s} + \Delta G^o_{H} + \Delta G^o_{H_2O} +$$

where $\Delta G^o_{elec}$ is the electrostatic interaction term, $\Delta G^o_{chem}$ is the chemical term due to covalent bonding, $\Delta G^o_{c\text{-}c}$ is the lateral interaction term owing to the cohesive chain-chain interaction among adsorbed long chain surfactant species, $\Delta G^o_{c\text{-}s}$ is due to the interaction between hydrocarbon chains

and hydrophobic sites on the solid, $\Delta G^{o}_{H}$ is the hydrogen bonding term, and $\Delta G^{o}_{H_2O}$ is the solvation or desolvation term owing to hydration of the adsorbate or any other species from the interface during adsorption. For each surfactant-solid-solvent system, several of the above terms can be significant depending on the mineral and the surfactant type, surfactant concentration, background electrolyte, and solvent temperature. For nonmetallic minerals, electrostatic attraction and lateral interaction effects are considered to be the major factors determining adsorption, while for salt-type minerals (e.g., calcite) and sulfides (e.g., galena), the chemical term often becomes significant. In organic liquids, the electrostatic forces are minimal, and adsorption depends on the hydrophobic and hydrophilic interactions among the constituents.

### 14.5.1 Factors Affecting Adsorption

There are several factors controlling adsorption which also influence the mechanisms governing the adsorption process. These have been reviewed by Parfitt and Rochester[25] and are briefly discussed here.

1. *Nature of the surface:* The physical characteristics of the solid (surface area, porosity, etc.) determine the area available for adsorption, while the chemical nature of the surface determines the reactivity of the surface towards a given solute. The heterogeneity and the presence of adsorbed impurities can also affect the adsorption process.
2. *Chemical structure of the solute and its interactions with the solvent:* The structure (hydrocarbon chain length, branching, nature, and location of polar functional groups) of the solute and its interactions with the solvent (solubility, micellization) have a marked effect on its adsorption. For example, it is well known from Traube's rule that for aqueous solutions the surface activity and hence the adsorption at the liquid/air interface increases with an increase in the chain length of the solute molecule. The solutes of interest, surfactants, are also capable of forming association structures in solution (micelles or reverse micelles, depending on the solvent), which is a measure of their solvophobicity.
3. *Nature of the solvent:* The solvent can influence the adsorption by interacting with the surface and/or the solute, thereby weakening the interaction between the solute and the surface. The chemical nature of the solvent and its polarity are important properties in question.
4. *Nature of the interactions between the surface and the adsorbed solute:* The structure and orientation of the adsorbed layer depend upon the relative strength of the interaction between the surfactant and the surface and the surfactant association behavior in the bulk solution. An example of such an interaction in aqueous systems is the electrostatic interaction between the charged surface sites and the charged surfactant molecules.
5. *Temperature:* Temperature can affect adsorption by altering the properties of the solute, surface, and solvent, as well as their mutual interactions. Usually physical adsorption, which is weak, decreases with an increase in temperature, probably due to the increased solubility of the solute. The effect of temperature on chemisorption depends on the nature of the chemical reaction taking place at the surface. Chemisorption usually increases within a certain temperature range, above which it decreases.

### 14.5.2 Surfactant Adsorption and Its Effect on Dispersion Properties

#### 14.5.2.1 In Aqueous Media

Dispersion properties can be modified by adsorption of surfactants at the solid-liquid interface. Surfactant adsorption can alter the dispersion properties by changing the van der Waals attraction, electrostatic repulsion, and steric forces between the particles, as discussed earlier. The extent of the modification depends on the adsorption density (surface coverage), packing, and orientation of

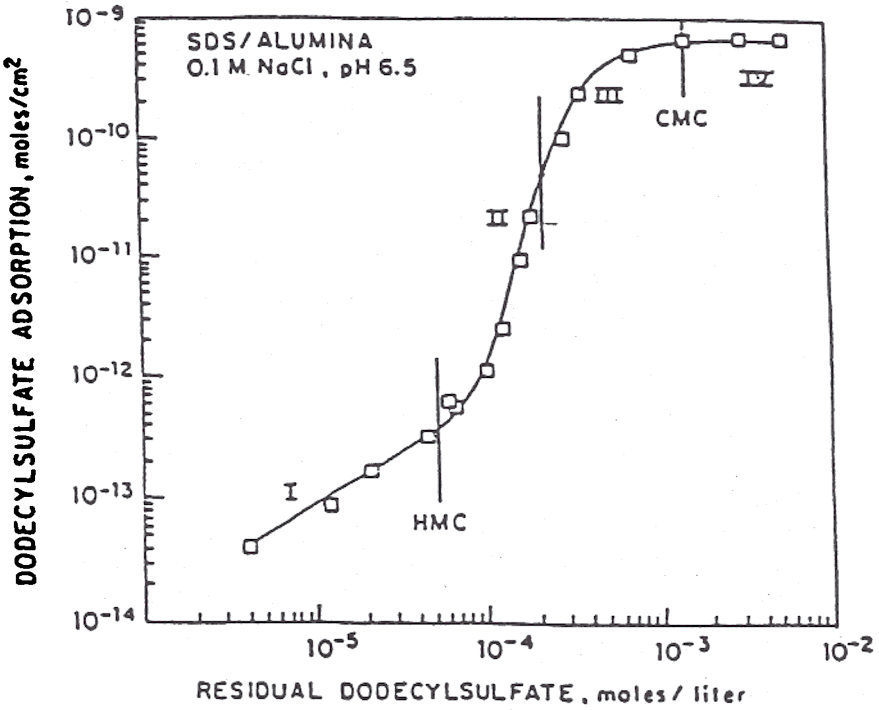



**FIGURE 7** Adsoprtion isotherm of sodium dodecyl sulfate on alumina at pH 6.5.

molecules at the interface and on the nature of charges on the molecule. Therefore, it is important to discuss first the adsorption process itself in terms of the dominant mechanisms and possible orientations.

#### *14.5.2.1.1 Ionic surfactants*

A typical adsorption isotherm of charged surfactants on oppositely charged surfaces is shown in Figure 7,[28] where the adsorption of negatively charged sodium dodecylsulfate (SDS) on positively charged alumina is shown. This isotherm is characterized by four regions, attributed to four different dominant mechanisms being operative in each region. Mechanisms involved in these regions may be viewed as follows:

- Region I has a slope of unity under constant ionic strength conditions and is characterized by the existence of electrostatic interactions between the ionic surfactant and the oppositely charged solid surface.
- Region II is marked by a conspicuous increase in adsorption which is attributed to the onset of surfactant aggregation at the surface through lateral interaction between hydrocarbon chains. This phenomenon is referred to as a hemimicelle formation.[23,29] Such colloidal aggregates formed on the surface are referred to as solloids (surface colloids). In the case of simple ionic surfactants, such aggregates are called hemimicelles, admicelles, and surfactant self-assemblies.[30]
- Region III shows a marked decrease in the slope of the isotherm ascribed to the increasing electrostatic hindrance to the surfactant adsorption following interfacial charge reversal caused by the adsorption of the charged species in Region III and beyond; both the adsorbent species and the adsorbate are similarly charged.
- Region IV and the plateau in it correspond to the maximum surface coverage as determined by micelle formation in the bulk or monolayer coverage, whichever is attained at the lowest surfactant concentration; further increase in surfactant concentration does not alter the adsorption density. A schematic representation of adsorption by lateral interactions is given in Figure 8.

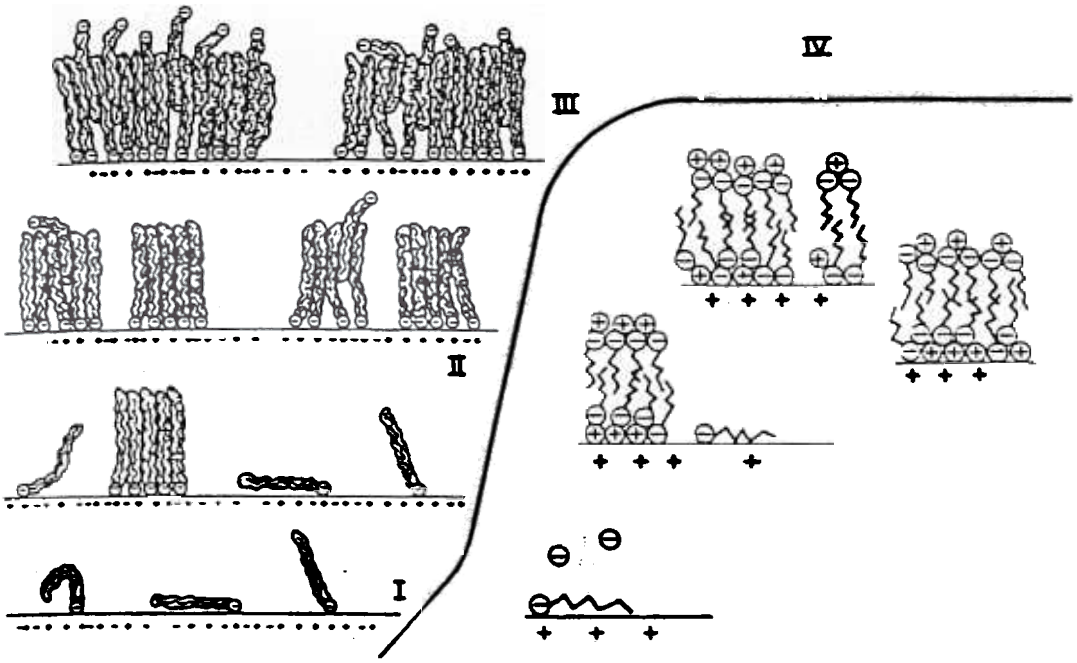



**FIGURE 8** Schematic representation of the correlation of surface charge and the growth of aggregates.

Figure 9 shows the variation in electrophoretic mobility of alumina as a function of the dodecyl sulfonate concentration. It can be seen that the electrophoretic mobility changes sign and then increases with surfactant concentration. This suggests that the dispersions should be electrostatically stabilized at high surfactant concentrations; however, measurements of particle hydrophobicity by bubble pickup showed an initial increase in particle hydrophobicity followed by a decrease at higher surfactant loadings.[31] This can be explained by examining Figure 8, where the surface is shown to be rendered hydrophilic at higher surfactant concentrations by adsorption of a second layer of surfactant with reverse orientation. Also, the particles continue to aggregate even after the system has undergone charge reversal which is attributed to the fact that it may be possible for the partially covered surfaces to be bridged by the adsorbed surfactant species.

#### *14.5.2.1.2 Nonionic surfactants*

The adsorption of ethoxylated alcohol on silica[32] displays an isotherm similar to that for SDS on alumina (Figure 10); however, the absence of electrostatic repulsion between the adsorbed nonionic species results in an exceedingly high slope for the hemimicellar region. Adsorption of these surfactants was found to depend on the degree of ethoxylation as well as the alkyl chain length (Figures 11 and 12).[33] At constant chain length, the extent of adsorption at low concentration was found to be greater for surfactants with a higher degree of ethoxylation; however, the plateau adsorption is higher for the surfactants with a lower degree of ethoxylation. A linear relationship is obtained when the parking area at plateau adsorption is plotted against the ethoxylation number. This yields a parking area per $-OCH_2CH_2$ segment of 9.2 Å$^2$, suggesting direct adsorption of the ethylene oxide (EO) chains on the silica surface. On the other hand, the alkyl chain length only affects the onset of plateau adsorption, which is in line with the decrease in critical micelle concentration (CMC) that accompanies an increase in hydrocarbon chain length. Based on these observations, hydrogen bonding is proposed to be the initial driving force for the adsorption, and the higher uptake of surfactants with higher EO numbers, at low concentrations, is clearly due to the cumulative hydrogen bonding interactions of the EO chains with the hydroxylated silica surface. However, at higher concentrations, hydrophobic chain-chain interactions become more significant as evidenced by the progressive increase in slope of the adsorption isotherm with a decrease in EO number (the smaller the EO number, the lesser the steric hindrance due to the ethoxyl groups which promotes the chain-chain interaction).

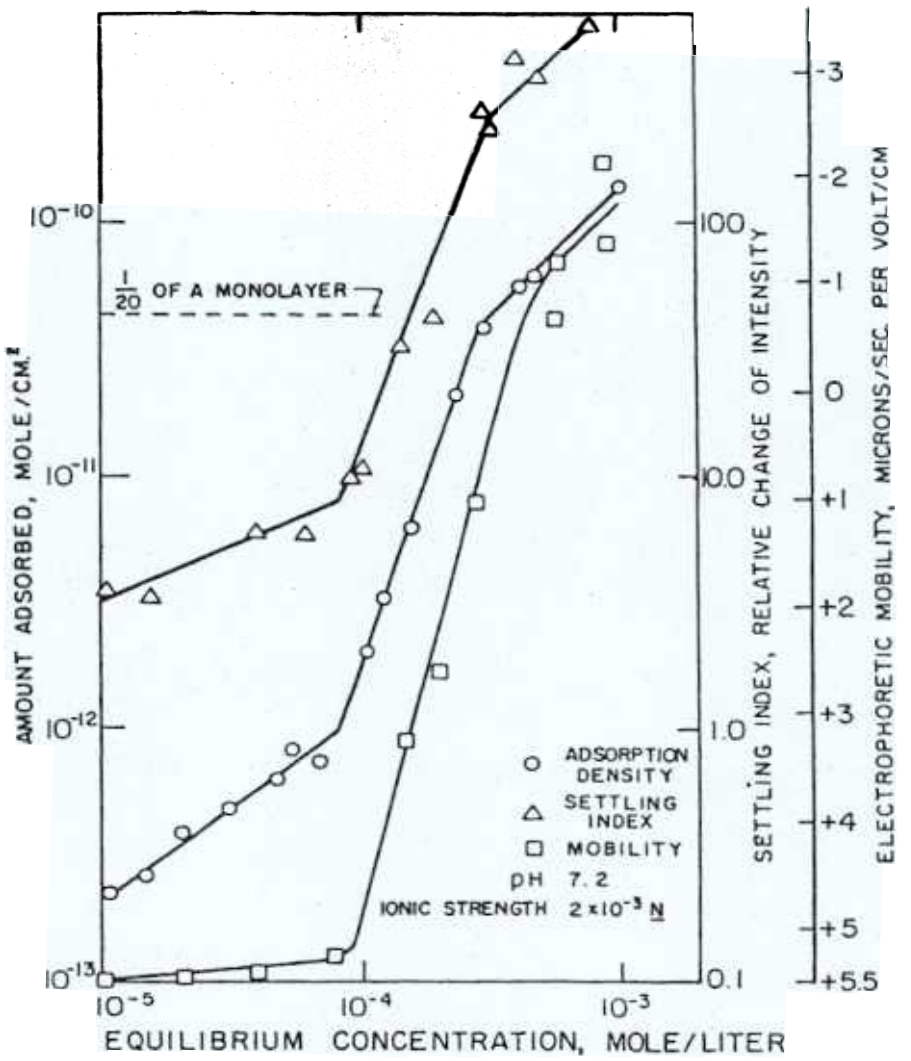



**FIGURE 9** Variation in the electrophoretic mobility of alumina particles with SDS concentration.

The effects of adsorption density and surfactant structure on the hydrophobicity of silica are shown in Figure 13.[33] In the absence of any adsorbed surfactant, silica is hydrophilic and its hydrophobicity increases with an increase in the adsorption of $C_8EO_{10}$. In the case of the higher ethoxyl chain length, $C_8EO_{40}$, the hydrophobicity decreases at higher surface coverages, and the original surface coverage is restored when plateau adsorption is reached. The observed changes in hydrophobicity are explained in terms of conformational changes of the hydrocarbon chains of the adsorbed surfactant molecules at the silica-liquid interface. At low absorption densities, the hydrocarbon chains are most likely lying flat on the surface, providing maximum coverage with hydrocarbon chains and thereby rendering the surface hydrophobic. As adsorption density increases, however, the flatly adsorbed hydrocarbon chains will be pushed out by the adsorbing ethylene oxide chains and hence the surface coverage by the hydrocarbon chains is reduced. This explains the decrease in hydrophobicity at higher adsorption for $C_8EO_{40}$; at plateau adsorption, the surface is covered least by hydrocarbon chains, hence the hydrophilicity of silica is restored. The possibility of bilayer adsorption being responsible for the restoration of hydrophilicity is precluded by the fact that in this case no surface aggregation occurs due to steric hindrance; however, for $C_8EO_{10}$ the higher adsorption density and the higher aggregation at the interface (which causes hydrophobic patches on the surface) will offset the effect of any conformational changes in the hydrocarbon chains and lead to maximum hydrophobicity at plateau adsorption. In the case of surfactant mixtures, for example, both SDS and $C_{12}EO_8$ adsorb on kaolinite by themselves. Adsorption of $C_{12}EO_8$ on

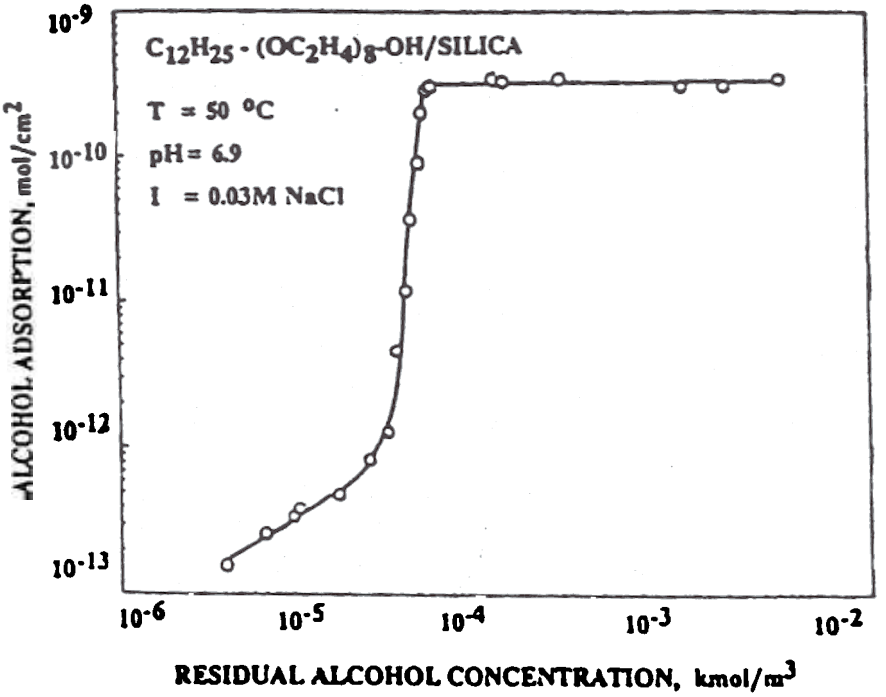



FIGURE 10 Adsoprtion of alkylaryl ethoxylated alcohol ($C_{12}EO_8$) on silica.

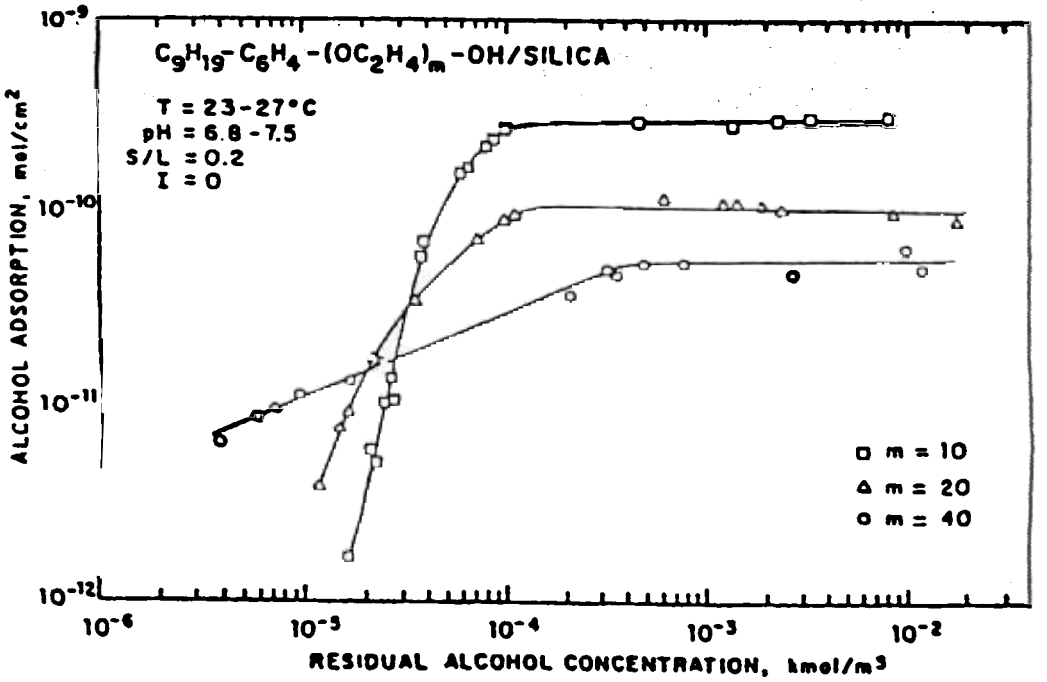



FIGURE 11 Adsoprtion density of nonylphenoxyethoxylated alcohols on silica.

kaolinite is influenced by the presence of anionic sodium dodecyl sulfate. The plateau adsorption in all cases is higher from its mixtures with SDS than in its absence.[34] These higher plateau adsorption values are due to additional adsorption of $C_{12}EO_8$ with reverse orientation. At low concentrations, the chain-chain interactions between the adjacently adsorbed sodium dodecyl sulfate and $C_{12}EO_8$ molecules will provide additional energy gain for the adsorption process. These hydrophobic interactions at the interface will result in the formation of the hydrophobic microdomains

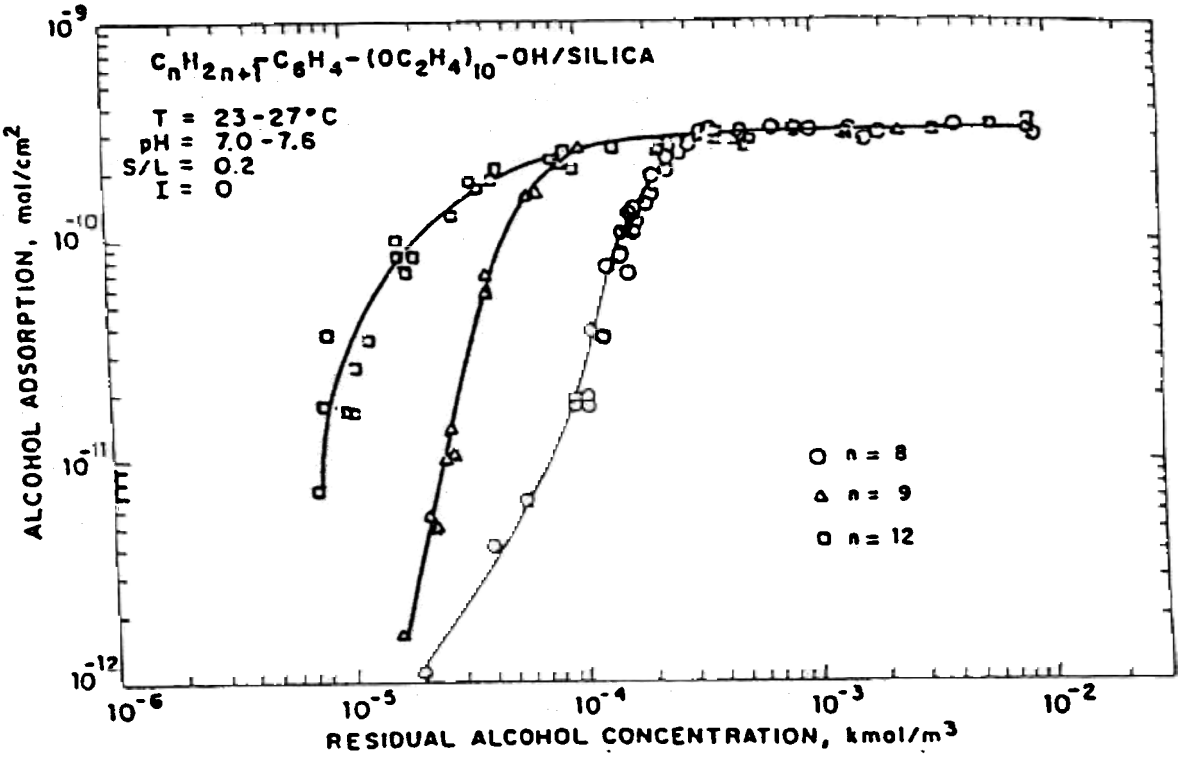



**FIGURE 12** Adsoprtion density of $EO_{10}$ alcohols of different chain lengths on silica.

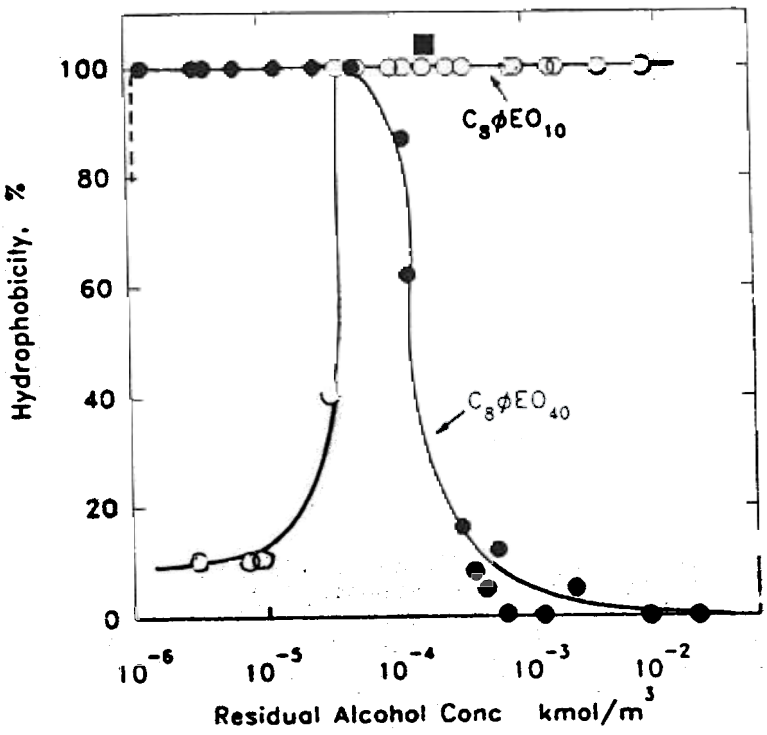
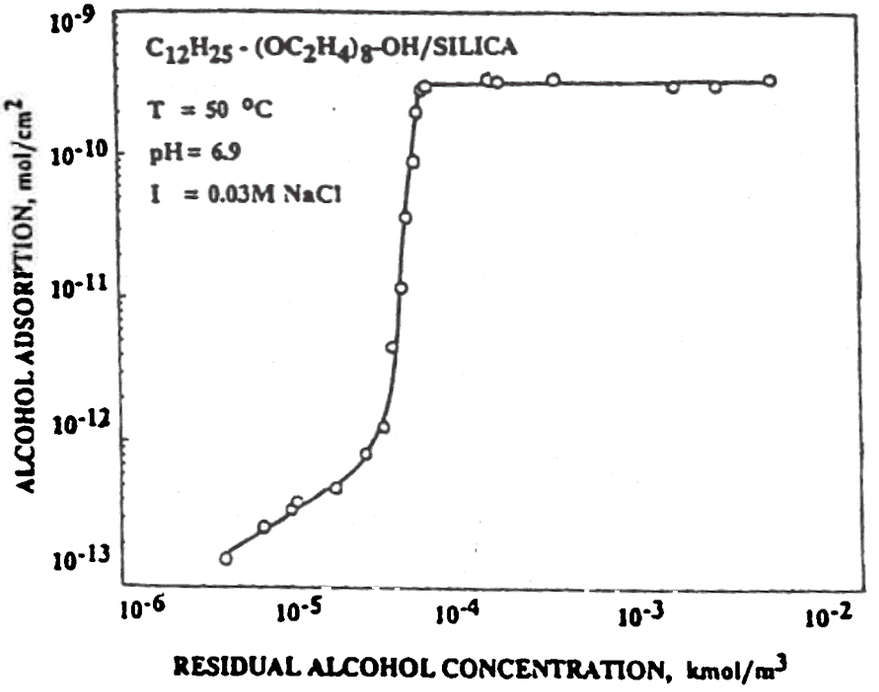



**FIGURE 13** Change in hydrophobicity of silica upon adsoprtion of nonionic surfactant.

into which the hydrocarbon chains of additional $C_{12}EO_8$ molecules can get incorporated as a second layer. This is schematically shown in Figure 14.[32] The evolution of such an adsorbed layer clearly changes the wetting behavior of the particle surface as indicated by the skin flotation tests. This

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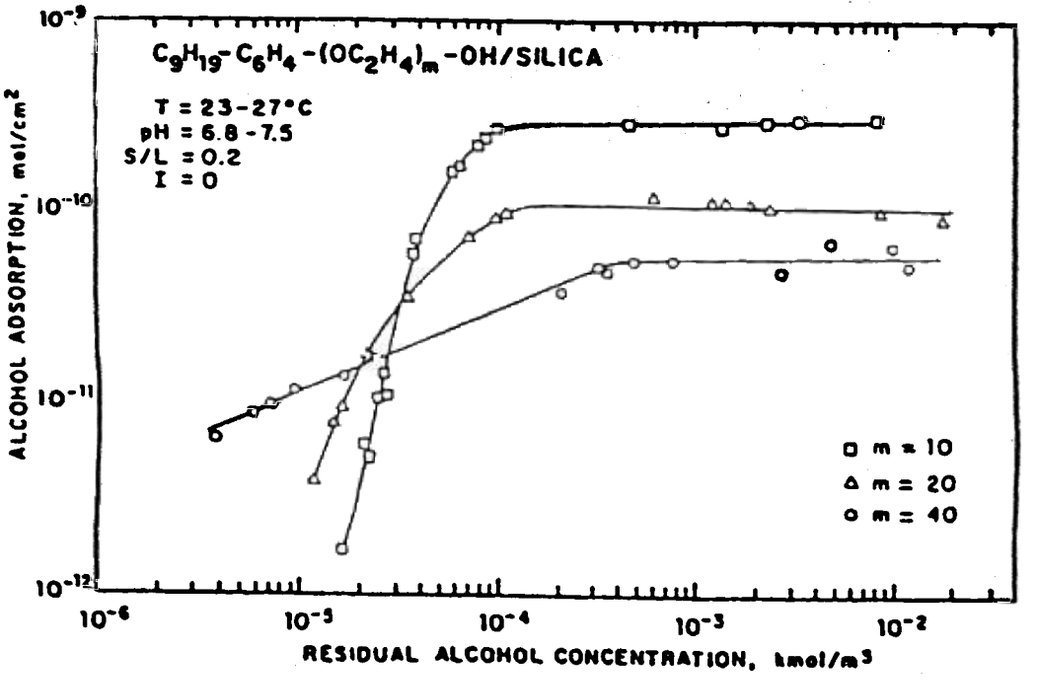


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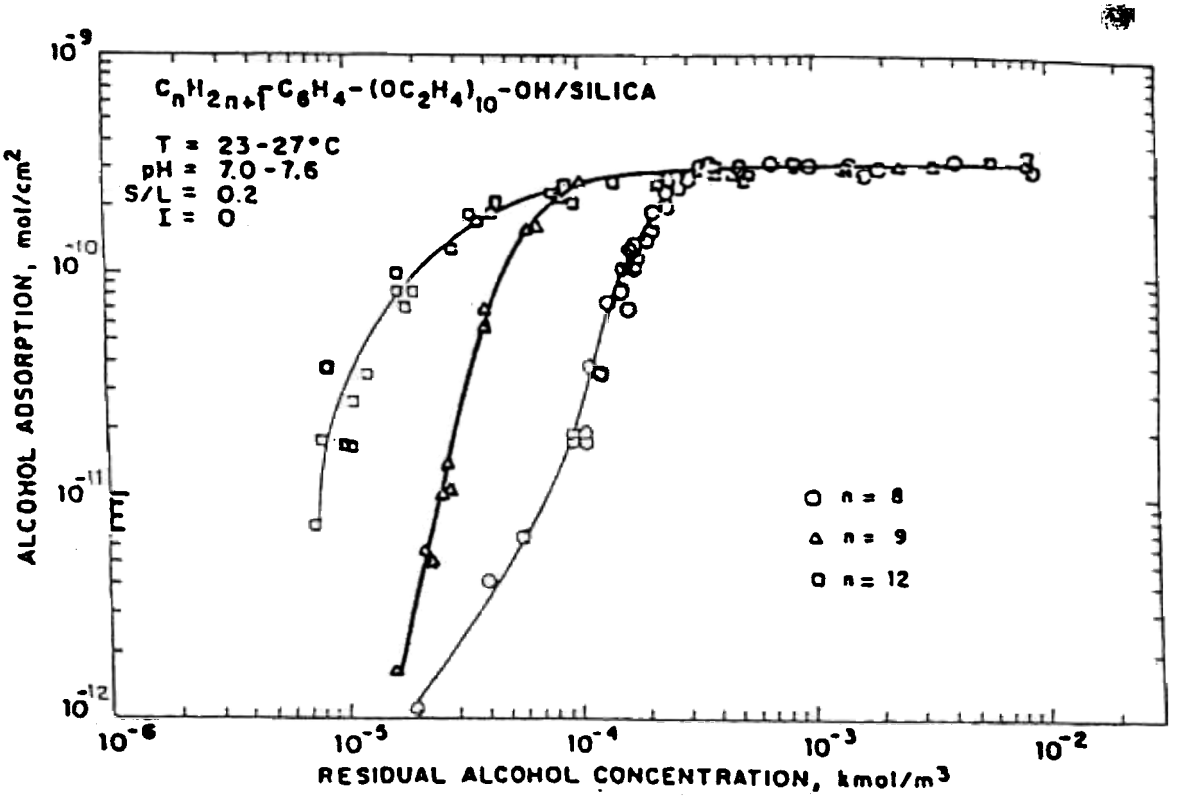


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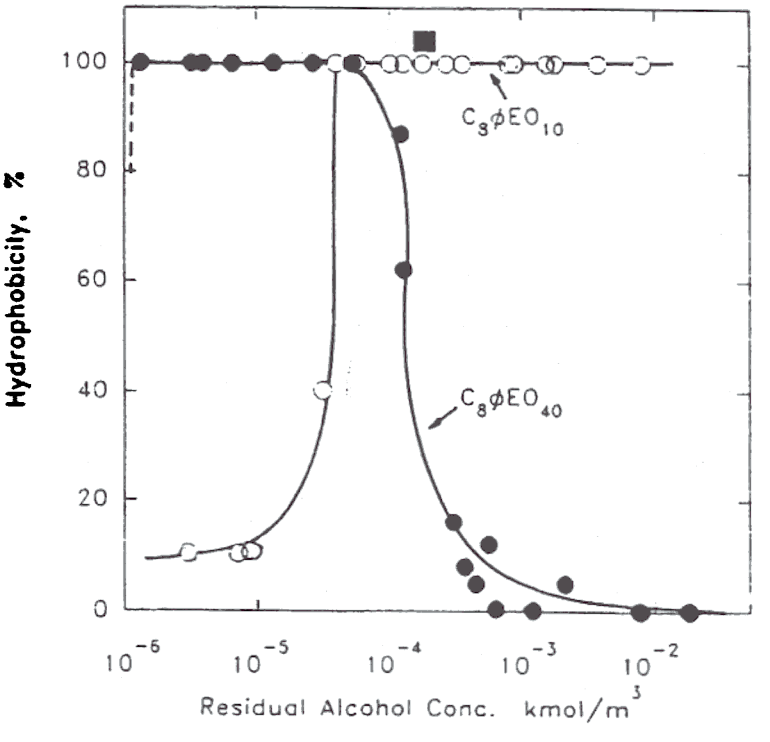


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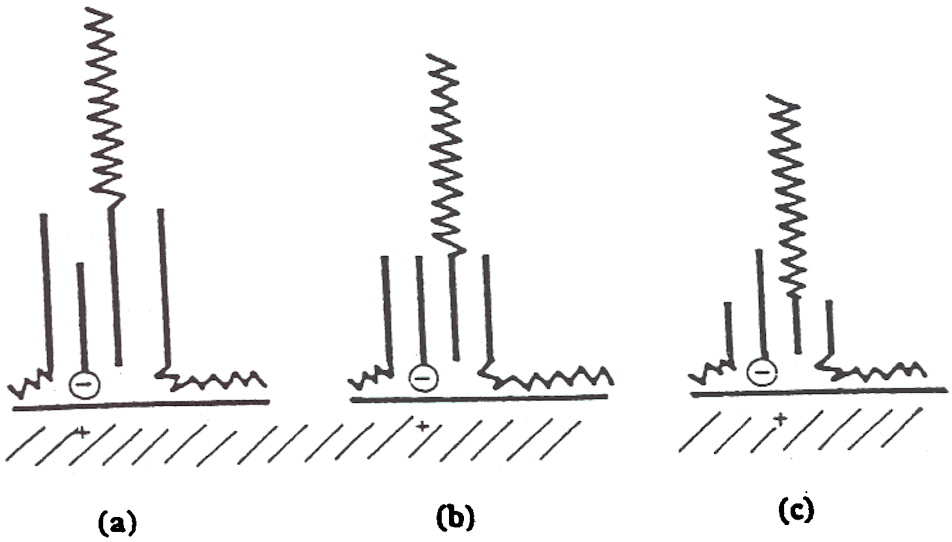


FIGURE 14 Schematic presentation of the adsorption mechanisms for SDS/$C_{12}EO_8$ mixtures on kaolinite.

shows a sharp decrease in the flotation of kaolinite with an increase in the adsorption of the nonionic surfactant. Mixed surfactant adsorption also causes stabilization in these dispersions. The settling rate is dramatically reduced in this case without significant alterations in zeta potential. The observed stability is attributed to the reversed adsorption layer, with the protruding ethylene oxide chains providing steric repulsion to the approaching particles.

### 14.5.2.2 In Organic Media

Adsorption of surfactants from nonaqueous media has been widely employed to disperse hydrophilic solids in organic liquids. The main goal of most of these applications is to achieve uniform and complete coverage of the surface with the surfactant. For a majority of systems involving adsorption in nonpolar media, a maximum monolayer coverage has been observed. Adsorption from organic solutions usually involves physical forces and can be described by the following exchange process:

$$B_{surf} + A_{sol} = A_{surf} + B_{sol}$$

where $A_{sol}$ and $B_{sol}$ are the adsorbate and solvent molecules, respectively, in solution, while $A_{surf}$ and $B_{surf}$ are the respective molecules on the surface. The adsorption process according to the above scheme can usually be described by the Langmuir adsorption isotherm:

$$\Gamma_A = \frac{K_{ads} X_{A,s}}{1 + K_{ads} X_{A,s}}$$

where $\Gamma_A$ is the surface concentration, $X_A$ is the mole fraction of the adsorbate in solution, and $K_{ads}$ is the equilibrium constant for the adsorption. Several other modified Langmuirian equations have been proposed for measuring adsorption data taking into account heterogeneities of the adsorbent.[35,36]

In nonpolar media, due to the low ionization of the solute species, electrostatic attractive or repulsive forces can be ruled out as major mechanisms for adsorption; however, polar interactions have to be considered, especially when polar surfaces such as oxides are involved. Recent work has shown acid-base interactions between the surface species and the solute molecules to be responsible for adsorption in nonaqueous media. Fowkes[37] has suggested that the interaction

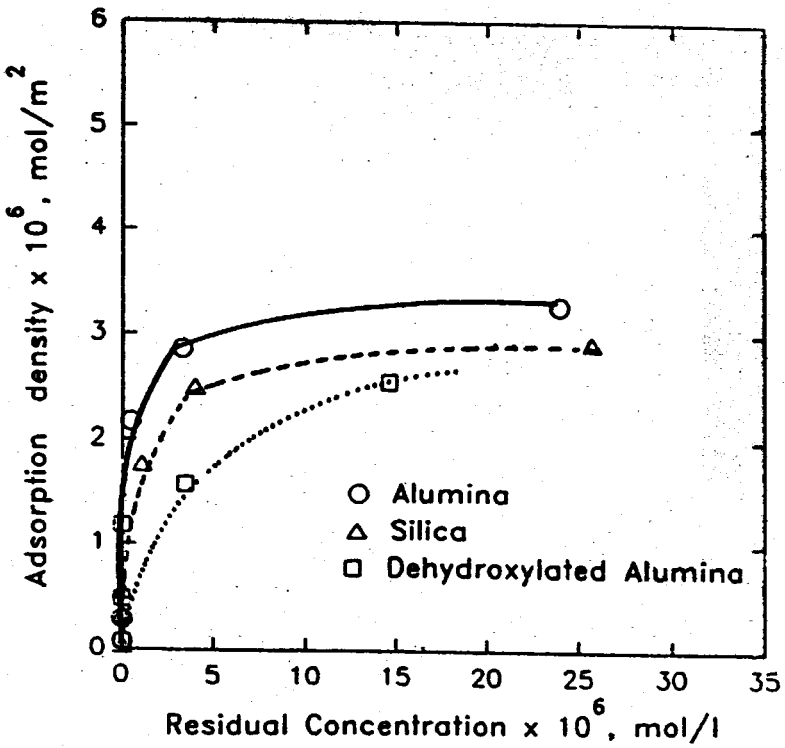


**FIGURE 15** Adsorption isotherm of AOT on different solids from cyclohexane.

between a solid surface and an uncharged adsorbate can be divided into two parts: dispersive and polar interactions. The dispersive interactions are due to the fluctuating dipole moments created by the movement of electrons in any atom or molecule and thus occur between all atoms and molecules. Polar interactions refer to specific interactions between hydrophilic surface groups and functional groups in the adsorbate molecules.

#### *14.5.2.2.1 Oxide surfaces*

Figure 15 shows the adsorption isotherms of aerosol OT (AOT) on alumina and silica from cyclohexane.[38] It can be seen that the anionic surfactant has a greater affinity for the basic oxide than for the acidic oxide. The situation is reversed in the case of the adsorption of the cationic surfactant dimethyl dodecylamine (DDA). DDA adsorbs more on acidic silica than on alumina (Figure 16). Calculations based on a plateau adsorption value of about $3 \times 10^{-6}$ mol/m$^2$ on alumina give a parking area of about 0.55 nm$^2$ for the AOT molecule. This is in good agreement with the published values for AOT parking areas at the water-xylene and water-isooctane[39] interfaces, suggesting that it adsorbs at the alumina-cyclohexane interface as a monolayer in an orientation perpendicular to the adsorbent with the hydrocarbon chain extending into the solution. Similar calculations based on the plateau adsorption for the cationic surfactant give a parking area of 1.6 nm$^2$ per molecule, which is much less than the area occupied by a flatly adsorbing DDA molecule (approx. 4 nm$^2$), suggesting that this also adsorbs perpendicular to the adsorbent. Figure 16 also shows the adsorption of AOT on dehydroxylated alumina. Dehydroxylation, in this case, is achieved by heating the alumina at 900°C for 48 hr and verified by observing the disappearance of the OH vibration bands at 3800 cm$^{-1}$ from the infrared spectrum of the alumina sample. Dehydroxylation increases the acidity of the surface and hence reduces the adsorption of the anionic AOT. It is clear from these results that AOT adsorbs through interactions with the hydroxyl groups on the oxide surface. These results also suggest that for a given surfactant the relative acidity of the oxide surface is one of the major factors that determine the extent of interaction. From the fact that both anionic and cationic surfactants adsorb on alumina and silica, we infer that electrostatic forces do not play a major role in this adsorption.

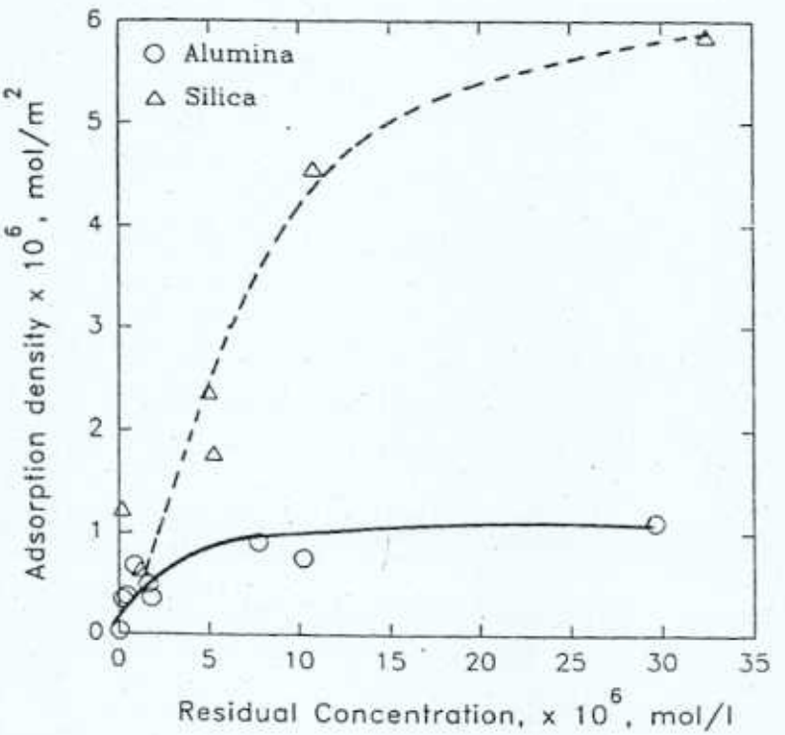


**FIGURE 16** Adsorption of cationic dimethyldocecyl amine (DDA) on different solids.

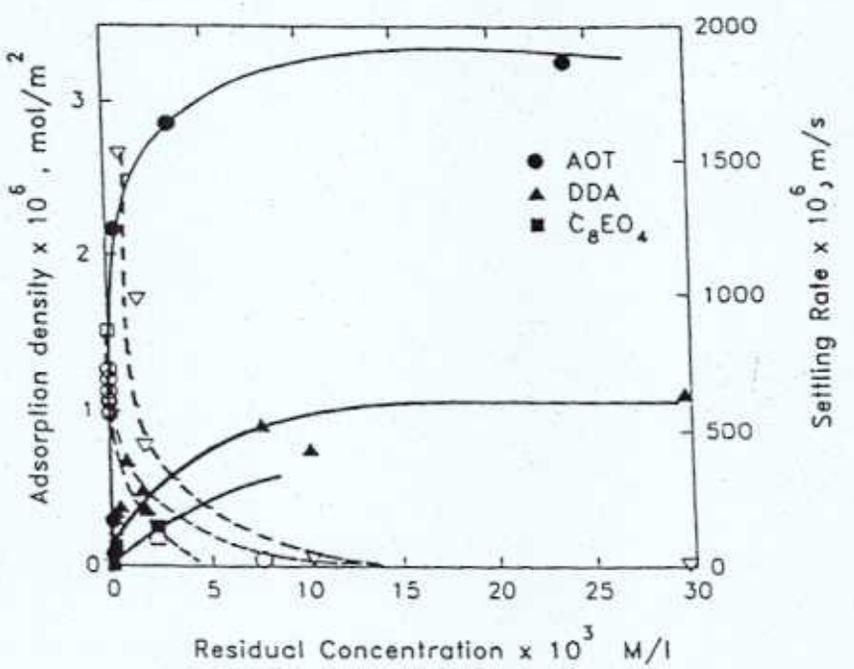


**FIGURE 17** Settling rate variation of alumina suspensions upon adsorption of different surfactants in organic media.

Figure 17 shows the settling rates of alumina suspensions as a function of surfactant adsorption. It can be observed that the suspensions are stabilized by the adsorption of the anionic, cationic, and nonionic surfactants (although to different extents), and the maximum stability corresponds to the onset of the plateau in the adsorption isotherm. The adsorption, as discussed earlier, takes place with the polar group of the surfactant interacting with the surface hydroxyls and the hydrocarbon

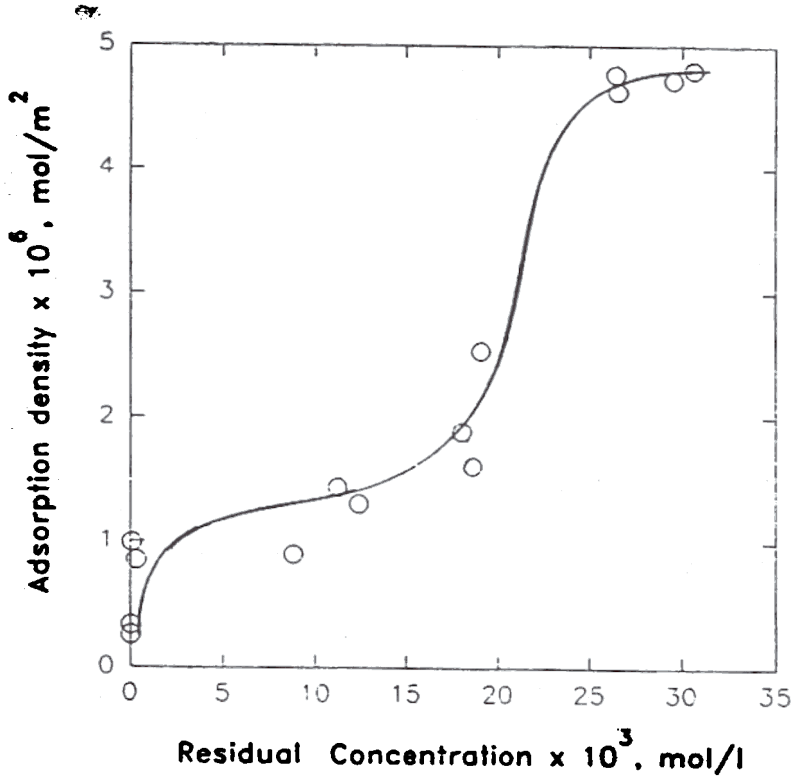


**FIGURE 18** Adsorption of AOT on graphite from cylcohexane.

tails of the amphipathic surfactant molecules sticking out into the solvent phase. Thus, the stability produced by surfactant adsorption can be attributed to a hydrophobic modification of the surface which disperses well in the nonpolar liquids.

#### *14.5.2.2.2 Hydrophobic surfaces (graphite)*

The adsorption isotherm of AOT on graphite from cyclohexane follows a very interesting pattern, as shown in Figure 18.[40] The adsorption increases sharply in the initial part, suggesting high affinity of the surfactant for the solid at low concentrations. The adsorption then appears to reach a plateau, and calculations based on apparent monolayer coverage at this level yield a parking area of approximately 1.03 $nm^2$ per AOT molecule. This molecular parking area corresponds to an AOT molecule adsorbing flatly at the solid-liquid interface. At higher AOT concentrations, above $10^{-2}$ $mol/dm^3$, there is a further sharp increase in the adsorbed amount, and this reaches to about five times the initial plateau value at about $3 \times 10^{-2}$ $mol/dm^3$. It is interesting to note that this sharp increase occurs above the CMC of AOT ($1 \times 10^{-3}$ $mol/dm^3$), although it does not coincide with the onset of micellization.

The settling behavior of these dispersions as a function of the adsorbed AOT amount is also very interesting (Figure 19). The settling rate rises sharply first and then decreases as sharply, suggesting restabilization. At low surface coverages, the polar head group of the flatly adsorbing AOT is exposed to the solvent with which it is not compatible. In such a case, the AOT molecules, as shown in Figure 20a, can form interparticle aggregates that would effectively create a polar microdomain to shield the head groups from the solvent. Such an interparticle aggregation can account for the increased settling rate. As the AOT concentration is increased, the adsorbed molecules are proposed to form aggregates at the interface, as shown in Figure 20b. This leads to the sharp increase in the adsorption density, as well as the decrease in settling rate due to the disappearance of the interparticle aggregation observed at low surface coverages. Formation of such reverse hemimicelle-like aggregates at the interface has been reported earlier for the adsorption of 1-decanol on graphitized carbon black from nonpolar solvents.[41]

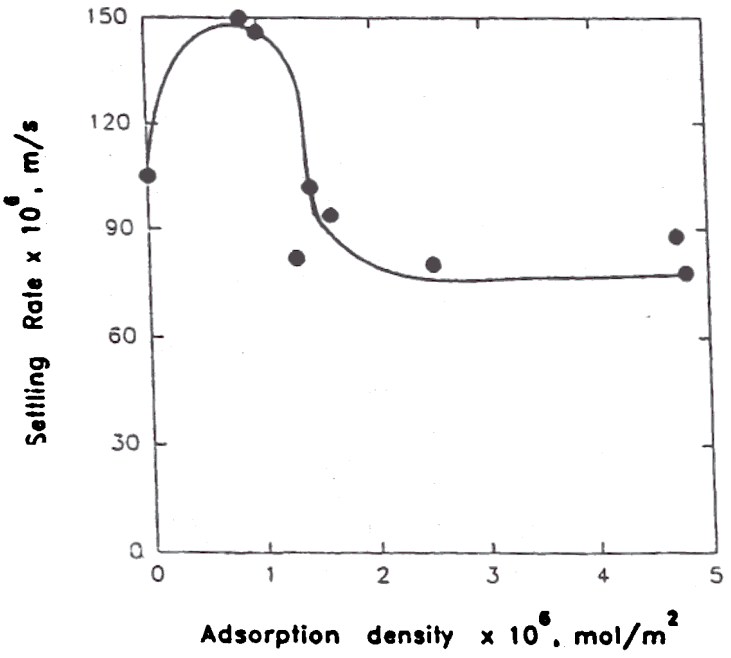


**FIGURE 19** Variation in settling rate of graphite suspensions in cyclohexane as a function of AOT adsorption density.

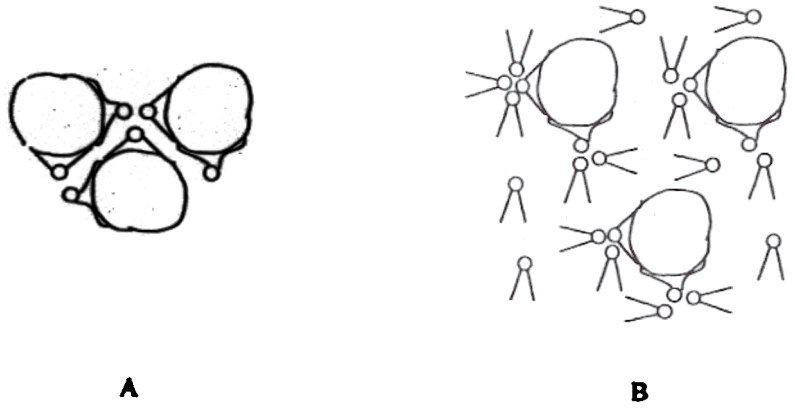


**FIGURE 20** Schematic representation of adsorption of AOT on graphite at (A) low concentrations and (B) high concentrations.

### *14.5.2.2.3 Effect of water on dispersion stability of alumina*

Figure 21 shows the effect of water on the stability of alumina suspensions which have been dispersed in cyclohexane by the adsorption of a monolayer of AOT. As the water content in the system increases, the suspension goes through a series of flocculated, stabilized, and flocculated stages. In an extremely dry state, the dispersions flocculate rapidly, and the addition of trace amounts of water stabilizes the suspensions quite significantly. Thereafter, the suspensions remain stable over a range of water concentration and then flocculate very rapidly at higher water concentrations. The concentration of water at which the suspension reflocculates correlates well with the solubility of water in the bulk solution. Surface charge measurements made using the electrokinetic sonic amplitude (ESA) system (Figure 22) clearly shows that the addition of trace amounts of water induces a significant amount of charge at the surface. This observation, along with that of the drastic increase of conductivity of the dispersions (also shown in Figure 22) upon small additions of water,

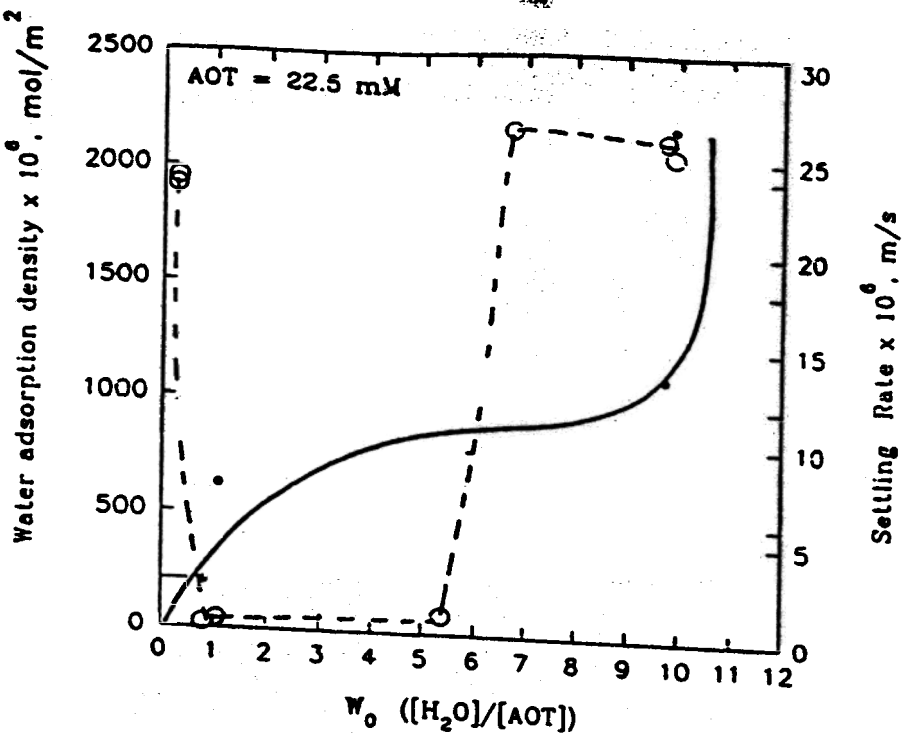


FIGURE 21 Effect of water on the alumina suspension stability and the corresponding adsorption of water.

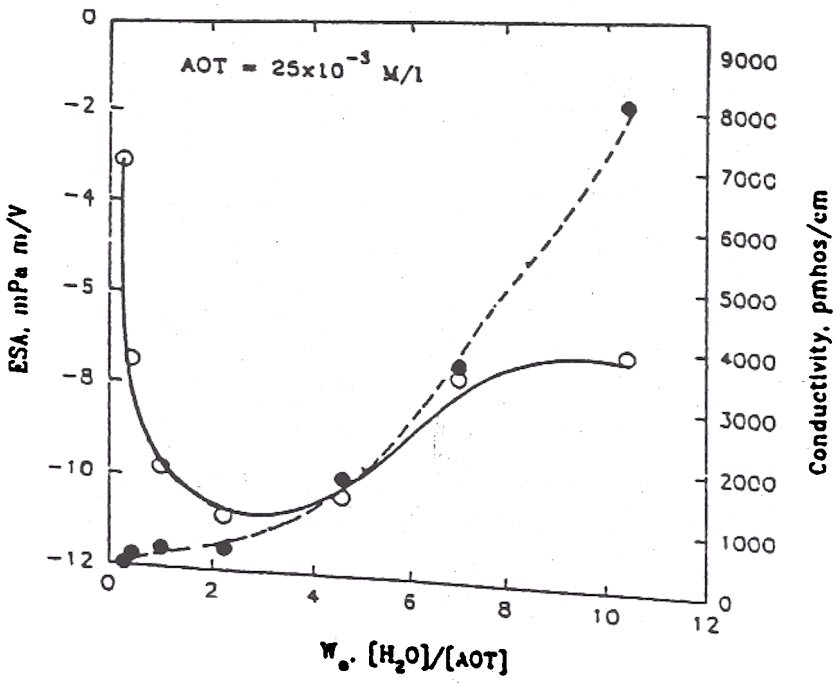


FIGURE 22 Electrokinetic sonic amplitude (ESA) and conductivity of alumina suspensions with adsorbed AOT as a function of water concentration.

leads to the conclusion that the stabilization in this case is due to the water-induced ionization of the adsorbed surfactant layer and resultant electrostatic repulsion among the particles. At higher water concentrations, there is a slight decrease in the surface charge as measured by the ESA. But, this decrease in surface charge cannot fully explain the massive flocculation observed in this case.

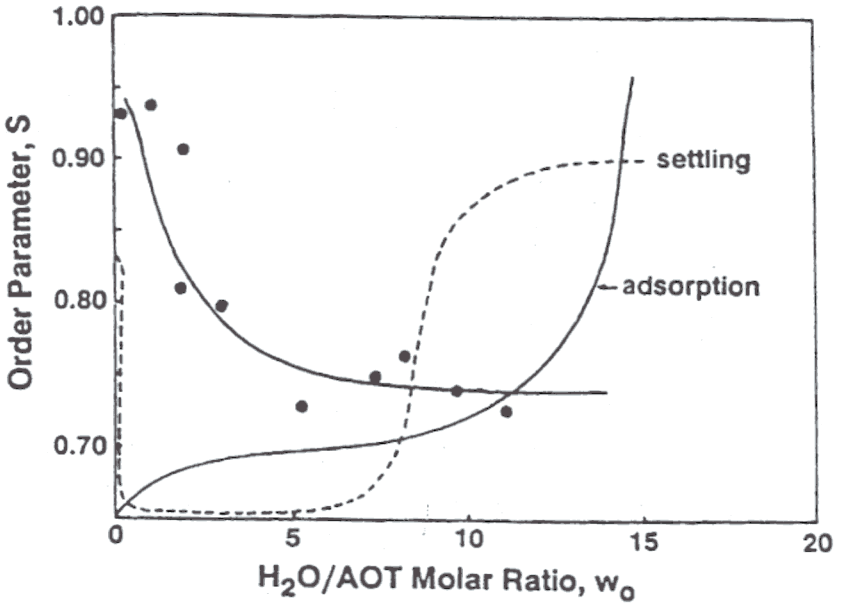


**FIGURE 23** Effect of water on the order parameter, *S*, calculated from the ESR spectra of 7-doxyl stearic acid co-adsorbed with AOT at the alumina/cyclohexane interface.

From the water adsorption isotherm shown in Figure 21, it can be seen that the water adsorption increases sharply close to the onset of the flocculation. We further investigated this behavior using electron spin resonance spectroscopy.

#### *14.5.2.2.4 Electron spin resonance studies on the water-induced flocculation*

In these studies, the spectral response of 7-doxyl stearic acid, which is co-adsorbed along with the surfactant, was monitored as a function of water adsorption. 7-doxyl stearic acid adsorbed on the alumina surface gives a characteristic anisotropic spectrum which can be quantified using the order parameter calculated from the spectral characteristics. The order parameter varies between S = 1 (highly ordered, restricted) and S = 0 (highly random and mobile) and reflects the state of the environment in which the probe resides. The order parameter calculated in this case decreases with an increase in water concentration and levels off at approximately the same water concentration corresponding to the onset of flocculation (Figure 23). These results indicate that there is a change in the structure of the adsorbed layer, with the surfactant layer becoming more fluid and mobile as water adsorbs at the interface. This opens up the possibility for the water layers on different particles to penetrate across the surfactant layers and bridge the particles together during collisions, thereby causing massive flocculation as observed.

### 14.5.3 Adsorption of Polymers and the Effect on Dispersion Properties

#### 14.5.3.1 Theoretical Considerations on Polymer Adsorption

In order to understand the behavior of polymers at interfaces, it is essential to get a clear picture of their behavior in solution first. Modern polymer solution studies were pioneered by Flory.[13,42] Since then, there has been considerable effort to elucidate the solution behavior of polymers, and many models have been proposed. The theoretical treatment of polymer adsorption characteristics and conformation characteristics received considerable attention, mainly because of the significant applications.

One parameter that is commonly used to specify the dimension of a linear polymer molecule is the root-mean-square (rms) end-to-end length. The simplest, and also the most primitive, model for a polymer molecule is the random flight chain, also termed the freely jointed chain. In this model, the bonds are represented by volumeless lines in space, and there are no restrictions on the

**TABLE 3**
**Some Scaling Law Predictions in the Semidilute Regime**

| | Scaling law | |
|---|---|---|
| **Property** | **Good solvent** | **θ solvent** |
| $c^* \sim$ | $N^{-4/5}$ | $N^{-1/2}$ |
| $R_g^2 \sim$ | $Nc^{-1/4}$ | $N$ |
| $\xi \sim$ | $c^{-3/4}$ | $c^{-1}$ |
| $(\Pi/T) \sim$ | $c^{9/4}$ | $c^3$ |

*Note:* $c$ = polymer concentration; $N$ = number of steps; $T$ = absolute temperature; $R_g$ = rms radius of gyration; $c^*$ = the polymer concentration at which the total volume of the chain just fills the available volume, whose value must be comparable to that in polymer coil; $\xi$ = the correlation length or average mesh size, representing the mean distance between intersections of the trajectories of the polymer chains; and $\Pi$ = osmotic pressure.

valency angles or on the rotations about bonds. The rms end-to-end length, $\langle h^2 \rangle_0^{1/2}$, can be represented as:

$$\langle h^2 \rangle_0^{1/2} = lN^{1/2}$$

where $l$ is the step length, and $N$ is the number of steps.

The random flight chain has the simplest mathematical properties but, unfortunately, also has the smallest degree of structural similarity to real polymers. A more complex model considering the fixed valency angle ($\tau$) and the restrictions of free rotation has been proposed as:

$$\langle h^2 \rangle^{1/2} = lN^{1/2} \left\{ \frac{1-\cos\tau}{1+\cos\tau} \right\}^{1/2} \delta_f$$

where $\delta_f$ is the steric factor, which clearly also is a measure of the flexibility of the polymer chain (usually $1.5 \leq \delta_f \leq 2.5$). For the most often used carbon backbone polymers, $\cos\tau = -1/3$ and $\delta_f \sim 2.0$; therefore, the $\langle h^2 \rangle / \langle h^2 \rangle_0$ is equal to 8.

Other parameters used as a measure for the dimension of a polymer molecule include rms radius of gyration ($R_g$), average span $\langle S_x \rangle$, the maximum extension averaged in all directions), and Hollingsworth radius $\langle R_{Holl} \rangle$, the radius of the smallest sphere which contains all the segments of a chain). Their relationships, for a random coiled polymer chain, can be summarized as:

$$R_g : \langle S_x \rangle : \langle h^2 \rangle^{1/2} : \langle R_{Holl} \rangle = \left( \frac{1}{6} \right)^{1/2} : 0.92 : 1.00 : 1.14$$

As discussed by de Gennes,[43] scaling law focuses attention on the exponents and refrains from the determination of any prefactory constants, which usually are much more difficult to determine. Some predictions of scaling law theory for polymers of high molecular weight in both good solvents and θ solvents in the semidilute regime are summarized in Table 3.

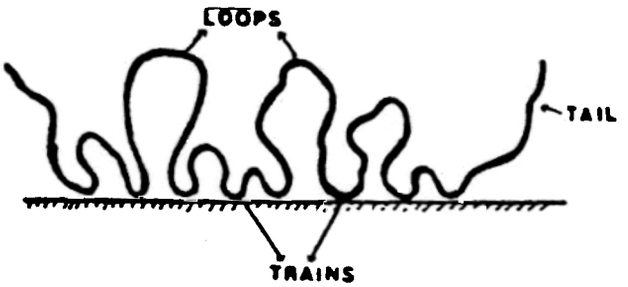


FIGURE 24 Schematic representation of an adsorbed polymer chain at the solid-liquid interface.

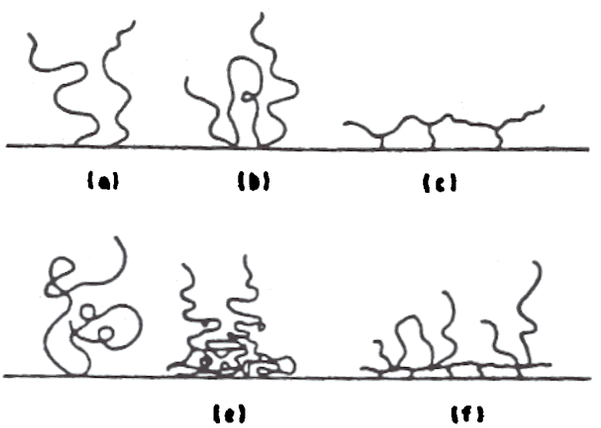


FIGURE 25 Conformation of adsorbed polymer: (a) single point attachment, (b) loop adsorption, (c) flat multiple site attachment, (d) random coil, (e) nonuniform segment distribution, and (f) multilayer.

The structure of adsorbed polymer layers on specific substrates from given solvents is less understood than the properties of polymer solution. It has, for many years, been derived by the self-consist theory where each chain has an average potential with a short-range part and a long-range repulsive part proportional to the concentration profile.[44-46] de Gennes[47] constructed from scaling laws a completely different scheme which provided a better insight into the polymer adsorbed layers, despite the fact that it does not predict the numerical parameters of any governing formula. The two techniques (self-consist field and scaling) complement each other and have provided considerable useful information for understanding the polymer behavior at interfaces.

Compared to most cases addressed by the above researchers, the behavior of polyelectrolytes are more complex. One of the most prominent differences is the occurrence of long-range electrostatic interactions, whereas in the case of uncharged polymers only nearest-neighbor interactions play a role. Due to the wide application of polyelectrolytes, some attempts have been made to describe the adsorption of polyelectrolytes. Most theories have been developed by incorporating the electrostatic free energy into the models for the uncharged polymers.[48]

### 14.5.3.2 Basic Concepts of Adsorbed Polymer Conformation

The process of polymer adsorption is quite different in many aspects from that of small molecules, the latter having been studied extensively in the past. These differences in their adsorption characteristics arise in turn from the obvious flexibility of the larger polymer molecules, so that in addition to the usual adsorption factors considered such as the adsorbate-adsorbent, adsorbate-solvent, and adsorbent-solvent interactions, a major aspect to be understood is the conformation of polymer molecules at the interface and its role in dispersion. Polymers have a large number of functional groups, each of which can potentially adsorb at the surface, whereas smaller molecules are mostly monofunctional.

The importance of adsorbed polymer conformation at interfaces was first recognized by Jenkel and Rumbach in 1951.[49] A model of adsorbed polymer conformation was proposed based on the observation that the amount of polymer adsorbed per unit area of the surface corresponds to a layer more than 10 molecules thick. In that model, not all the segments of a polymer are in contact with the surface. As schematically shown in Figure 24, those segments which are in direct contact with the surface are termed "trains"; those in between and extending into the solution are termed "loops"; the free ends of the polymer extending into solution are termed "tails". Sato and Ruch[50] classified the possible conformations for most situations into six types, as shown in Figure 25.

### 14.5.3.3 Mechanisms of Flocculation by Adsorbed Polymers

As mentioned earlier, polymers can exert a dramatic influence on colloidal stability; however, the description of particle interactions in the presence of polymers is complex and even a qualitative estimation of conditions for attraction or repulsion is yet to be developed. Three theories have been proposed to explain flocculation of charged particles by oppositely charged polyelectrolytes: bridging, simple charge neutralization, and charge patch neutralization.

#### *14.5.3.3.1 Bridging*

The original bridging mechanism was proposed by Ruehrwein and Ward[51] in 1952 and later advanced by La Mer and his co-workers.[52,53] Bridging is considered to be a consequence of the adsorption of the segments of individual polymer molecules on the surfaces of more than one particles. Such bridging links the particles together into loose aggregates. This mechanism has been validated by many works:[54]

1. Polymers produce larger, stronger, and better settling flocs than simple electrolytes.
2. The effectiveness of a polymer of a given type increases with molecular weight.
3. Linear polymers are more effective than branched polymers of comparable molecular weight and chemical structure.
4. At high concentrations, polymeric flocculants restabilize the particles.
5. Highly charged particles are flocculated by like-charged polymers only after their electrostatic potential has been sufficiently reduced by the addition of electrolyte.

When two particles with preadsorbed polymer approach each other, the free energy diminishes or rises depending upon the surface coverage ($\theta$) and the nature of the polymer.[55] Due to adsorption of additional segments, there can be a free energy contribution, $\Delta G_{ads}$, which is proportional to the additional segments adsorbed and related to the affinity between the polymer and solid surface, $\chi_s$. Adsorption occurs only if there are unoccupied sites on the particle surface so that additional adsorption is unlikely at high coverages, $\theta \sim 1$. In most cases, $\Delta G_{ads}$ is $< 0$, meaning an attractive contribution. It is also possible to have an entropic contribution, $\Delta G_{con}$, due to the restriction of the number of available conformations if adsorbed polymer layers overlap. This contribution is always repulsive. Another contribution may exist from the free energy of mixing, $\Delta G_{mix}$, due to the interaction between segments and solvents as determined by the Flory-Huggins parameter, $\chi$. Upon overlap, the number of those interactions increases. In good solvents ($\chi < 0$), $\Delta G_{mix} > 0$ and repulsion occurs between the segments, e.g., steric hindrance; in poor solvents, $\Delta G_{mix} < 0$ and segment attraction prevails, e.g., hydrophobic flocculation. The overall effect is determined by the sum of these contributions. Unfortunately, these effects are often interdependent, which makes their quantitative description extremely difficult.

Ottewill and Walker derived an equation for the energy change for the overlap of adsorbed layers by using the Flory's liquid lattice theory for polymer solutions:[56]

$$V_r = \frac{4\pi kTc}{3vp[\phi - K][\delta - H/2]^2[3r + 2\delta + H/2]} \tag{29}$$

where $c$ is the concentration of material in the adsorbed layer, $v$ is the molecular volume of the solvent, $p$ is the density of the adsorbate, $\phi$ and $K$ are the entropy and enthalpy of mixing, respectively (as proposed by Flory), $\delta$ is the adsorbed layer thickness, $H$ is the closest distance of approach, and $r$ is the particle radius.

LaMer[57,58] and others[59] have related the bridging efficiency factor to the fractional surface coverage of polymers ($\theta$). The original LaMer model and subsequent modified models can be generally described as:

$$E = f\theta(1-\theta)$$

where $E$ is the bridging efficiency factor, and $f$ is the constant ($1 < f < 2$). From Equation 30, it is clear that E will have a maximum when $\theta$ is 0.5, corresponding to 50% particle surface coverage with polymer; however, in practice, optimum polymer dosages are often found at much lower $\theta$ values.

Other than the classical bridging, for which a polymer chain must adsorb on more than two particles, Somasundaran et al.[12] postulated that bridging may occur between two particles by two separate adsorbed polymer molecules. Similar to the hydrophobic interaction, when surface-active polymers adsorb on particles via terminal-hydrophilic groups with hydrophobic groups extending into the bulk solution, bridging may occur through lateral interactions between the hydrophobic groups extending from particles in order to reduce the surface energy of hydrophobic groups.

#### *14.5.3.3.2 Simple charge neutralization and charge patch neutralization*

Oppositely charged polyelectrolytes reduce the particle surface charge density such that particles may approach each other sufficiently closely so that the attractive van der Waals force becomes effective. Flocculation caused by this mechanism should not be sensitive to the molecular weight of the polymer.

Gregory[60] proposed another flocculation mechanism: charge patch neutralization. There is no need for a one-to-one correspondence between charges on the surface and the adsorbed polymer. If the charge density of the polymer in its adsorbed state is higher than that of the surface, then patches of positively and negatively charged sites will appear on the particles. Thus, although the particles may have overall neutrality or even excess charge of the same sign, there exists the possibility of aggregation due to the attraction of oppositely charged patches on different particles. Charge neutralization (simple and/or patch) is often the mechanism for flocculation by low-molecular-weight polyelectrolytes.

### 14.5.3.4 Role of Polymer Conformation in Flocculation and Stabilization

Bridging can occur only if the extent of adsorbed polymer chain from the particle surface into the medium is greater than the minimum particle approach distance over which the interparticle repulsion acts. This distance is of the order of the sum of the thickness of the electrostatic double layers of the approaching particles. The spatial extension of polymer molecules depends not only on molecular weights of the polymer but also, significantly, on the conformation of the adsorbed polymer molecules. To meet the requirement of bridging, one can either reduce the thickness of electrostatic double layers or use polymers of high molecular weight and extended conformation. An increase in ionic strength reduces the thickness of the double layers; however, the extension of the polyelectrolyte is reduced at the same time because of potential screening effect.

Apparently, polymer conformation plays an important role in flocculation caused predominantly by bridging. This effect of polymer conformation on the dispersion properties has been confirmed by many observations where significantly different dispersion behavior is obtained with identical adsorption density and electrostatic property. There have been substantial efforts both theoretically and experimentally to develop relationships between the stability and the polymer conformation and guidelines for the optimum conformation to achieve desired dispersion properties. Despite these efforts, the progress is meager mainly because of the absence of reliable techniques and the

complexity of systems. Tjipangandjara and Somasundaran[61,62] showed the conformation of adsorbed polyacrylic acid to have a significant effect on the stability of alumina dispersions. An experiment involving manipulation of polymer conformation in solution and at interface by shifting pH up and down was designed with polymer conformation monitored with the pyrene fluorescence emission technique. They found that the conformation of adsorbed polymer can be altered by changing the solution conditions, and, depending upon the adsorption density and direction of pH shift, significant enhancement in flocculation or stabilization can be obtained.

Another important effect which is critical but often ignored is the time scale involved in flocculation processes. The kinetics of polymer diffusion to interface, adsorption, conformation and reconformation, and particle collision are quite different for different particle-polymer-solvent systems.[63] The polymer diffusion and collision rate can be controlled by the intensity and time of agitation applied. Unfortunately, there is very little information on the rate at which adsorbed polymer chains attain their equilibrium conformation. The only information available is that of polymer adsorption on a flat surface.[64] A two-step process was observed, in which the polymer first adsorbs and then undergoes a very slow reconformation, which may take hours. This information is not very useful for the flocculation of suspensions. Optimum flocculation is usually obtained at a much lower surface coverage instead of the saturation condition used in the above study. Nevertheless, of importance is the relative rate of the reconformation process compared to the particle collision, whether particles collide before or after an equilibrium conformation state of the adsorbed polymers is achieved. This effect is manifested in the case of concentrated suspensions in which there is a high particle collision rate. In most practical polymeric flocculations, it is very unlikely that an equilibrium conformation is achieved.

### 14.5.3.4 Stability of Dispersion in the Presence of Polymers

Besides the electrostatic forces, the suspension stability in the presence of polymers and surfactants is controlled by several other forces.[65] In the case of flocculation, a bridging theory by adsorbed polymers and surfactants is an accepted mechanism in addition to charge neutralization. On the other hand, in the case of suspension stabilization, steric interactions by adsorbed polymer and/or surfactant layer on particle surfaces become dominant.[66] In addition to adsorption density of the dispersant, conformation and orientation of the polymers and surfactants adsorbed on the particles will play a major role in controlling the suspension stability.[55] However, the conformation requirements for flocculation or dispersion are not known, mainly because of the complex nature of adsorption and the lack of reliable techniques to monitor conformation *in situ*. Techniques normally used to determine the polymer adsorbed-layer thickness (e.g., ellipsometry, viscometry, etc.) do not give sufficient information and, more importantly, cannot work *in situ*. In contrast, fluorescence and electron spin resonance spectroscopy techniques are powerful tools for probing *in situ* the microstructure orientation and conformation of adsorbed polymer and surfactant layers.[67] These techniques, used along with classical ones to determine suspension properties such as settling rate, supernatant turbidity, zeta potential, and adsorption density, can provide required information for developing predictive capabilities on the conformation criteria and schemes to manipulate the stability of suspensions.

#### *14.5.3.5.1 Fluorescence spectroscopy for polymer conformation and association measurement*

Pyrene has been used widely as a photophysical probe because of its long fluorescence lifetime and a great tendency for excimer formation. Emission characteristics of pyrene molecules depend upon the nature of the solvent. The ratio of relative intensities of the first (373 nm) and third (383 nm) peaks, $I_{III}/I_I$, in a pyrene emission spectrum decreases as the polarity of the solvent increases. This ratio has been used to estimate polarities of solvents, as well as surfactant micelles and aggregates in aqueous solutions.[68] Here, we will show the use of pyrene fluorescence spectroscopy for determination of the association of hydrophobically modified polymers in bulk solution, as well

as at the solid-liquid interface. This type of polymer has been developed recently to increase the viscosity and elasticity of solutions because they undergo interesting intra- and intermolecular associations.[69] We have found the use of hydrophobically modified polymers for controlling the stability of polar and nonpolar suspensions to be promising because of their unique structure, which can provide either flocculation by intermolecular aggregation or stabilization by steric hindrance, depending on the orientation at the solid-liquid interface, which is dependent on the nature of the particles and the extent of adsorption.[70]

Excimer fluorescence of pyrene attached to synthetic polymer chains can be used to study polymer conformation in solution and on the surface of particles. In this case, fluorescence spectroscopy involves measurement of the emission intensity of the monomer ($I_m$ observed at 375 nm) and excimer ($I_e$ at 480 nm). The ratio of $I_e$ to $I_m$ is related to the coiling/stretching behavior of a labeled polymer, and we have called it the coiling index.[71] In the absence of intramolecular interactions (the polymer concentration used is usually below this limit), a high value of $I_e/I_m$ can be considered to be the result of a coiled conformation, while a low value is associated with a stretched one.

Recent developments of some new high-performance composite materials, cosmetics, paints, and microelectronic components require a better understanding and manipulation of the colloidal interactions in nonpolar media;[5,72] however, unlike in the previous cases, pyrene cannot be used as a probe for studying aggregation in apolar media. Due to its own hydrophobicity, it will stay in the hydrophobic bulk environment. Therefore, a less hydrophobic fluorescence probe, 7-dimethyl amino 4-methylcoumarine (Coumarin 311) was chosen for the study of the alumina-toluene interface. It has been reported that the wavelength of the Coumarin 311 emission maximum shifts from 391 to 471 nm when the solvent is changed from hexane to water.[5] Polarity of an unknown environment can then be estimated by monitoring the position of the emission maximum.

#### *14.5.3.5.2 Electron spin resonance spectroscopy for the study of adsorbed polymer and surfactant layers*

Electron spin resonance spectroscopy (ESR), also known as electron paramagnetic resonance (EPR), is based on the property that an unpaired electron placed in a magnetic field shows a typical resonance energy absorption spectrum sensitive to its environment. Recently, this technique, which was primarily developed for biological studies of membrane properties, has been adapted for the study of adsorbed polymer/surfactant layers.[73] The mobility of the ESR probe (stable free radical incorporated into the polymer or surfactant molecule) depends on the orientation of the surfactant or polymer and the viscosity of the local environment around the probe.

#### *14.5.3.5.3 Effect of adsorbed polymer conformation on dispersion characteristics*

In a study of dispersion characteristics of an alumina suspension with polyacrylic acid ($M_w$ = 88,000) the polymer conformation at the alumina-water interface was determined as a function of pH using pyrene-labeled polymer along with settling rate and transmittance (Figure 26). It can be seen that the polymer is coiled (high $I_e/I_m$) at low pH and that the stretched polymer results in better flocculation in terms of increasing settling rate and larger floc size (observed by CAT scan) but poor flocculation in terms of the supernatant clarity. Apparently, the stretched polymer at a high pH provides better interparticle bridging, while the electrostatic attraction between oppositely charged polymer molecules and alumina particles causes better capture of fine particles yielding a clear supernatant at low pH values.

The above experiments were conducted under "fixed" pH conditions; the pH was preadjusted, and both polymer and alumina particles were conditioned at the same pH before mixing. In order to investigate the effect of polymer conformational changes of adsorbed polymer on flocculation performance, polyacrylic acid was adsorbed at pH 4, and the pH of the suspension was then shifted to 10 and vice versa. Enhanced flocculation was observed in terms of both the settling rate and the

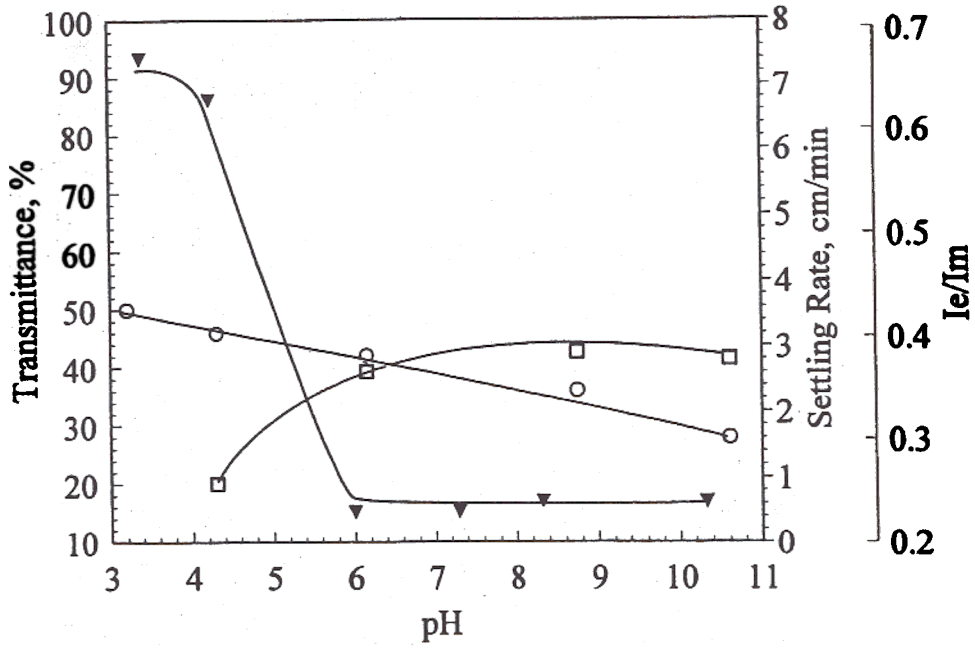


**FIGURE 26** Flocculation of alumina with 20 ppm polyacrylic acid. □ = settling rate; ○ = transmittance; ▽ = $I_e/I_m$.

supernatant clarity (Figure 27a), when pH was shifted up from 4. In contrast, when the pH was shifted down from 10, the settling rate was similar to that observed under the fixed pH conditions (Figure 27b). A maximum in the supernatant transmittance was observed at pH 7, the value which corresponds to the iso-electric point of alumina with adsorbed polymer. The direction of the pH shift (low to high or reverse) governs the polymer conformational changes: coiled polymer adsorbed on the alumina surface at low pH stretches out when pH is raised, but the initially stretched polymer does not coil when the pH is lowered.

Changes in polymer conformation at the alumina-water interface are shown schematically in Figure 28. When the polymer is initially adsorbed at low pH in coiled conformation, it stretches out because of increasing electrostatic repulsion caused by the ionization of the carboxyl groups and the charge reversal of alumina particles (Figure 28, a to c). In this case, some of the polymer chains are dangling into the solution and providing interparticle bridging. In the reverse case, when pH was shifted from 10 to 4 (Figure 28, d to f), the stretched polymer that initially adsorbs on the particle surface through hydrogen bonding retains the same conformation throughout the change in pH.

For significant improvement in supernatant clarity obtained in the scheme when the pH was shifted rather than fixed, the following two-step flocculation mechanism is proposed:

1. At low pH, the polymer chain captures all alumina particles into small flocs.
2. When the pH is shifted up, the stretched polymer bridges these small flocs to create much larger aggregates which settle rapidly but retain the smallest particles as well.

#### *14.5.3.5.3 Dual polymer system for enhanced flocculation*

Combined use of two or more polymers in order to enhance a desired suspension property (flocculation or stabilization) is not an unknown procedure.[12,74] In some systems, it is possible to achieve the synergistic effect of two different polymers when one (usually of low molecular weight) can adsorb strongly onto a particle surface, while the other (of much higher molecular weight) can

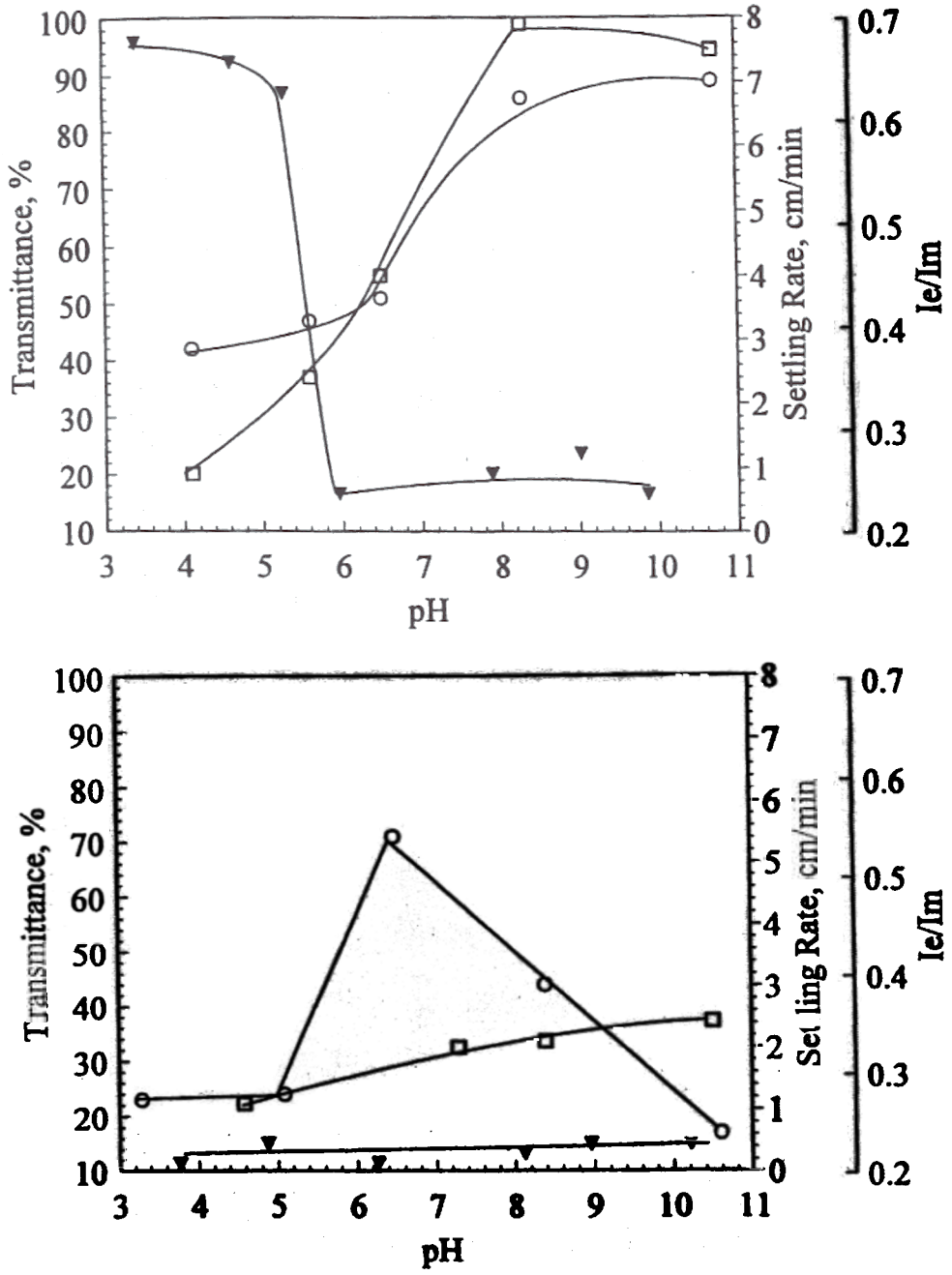


**FIGURE 27** Flocculation of alumina with PAA under changing pH conditions: (top) initial pH = 4; (bottom) initial pH = 10. □ = settling rate; ○ = transmittance; ▽ = $I_e/I_m$.

provide interparticle bridging. Some authors have reported such synergism for the combination of low-molecular-weight cationic and high-molecular-weight anionic polymers.[75,76] Most studies on double flocculants, however, have been empirical, and the mechanisms are not well developed.

Flocculation of alumina suspensions obtained by the sequential addition of polystyrene sulfonate ($M_w$ = 4600) and cationic polyacrylamide ($M_w$ = 4,000,000) at pH 4.5 is compared in Figure 29 with that obtained using single polymers. While the anionic polystyrene sulfonate had only a

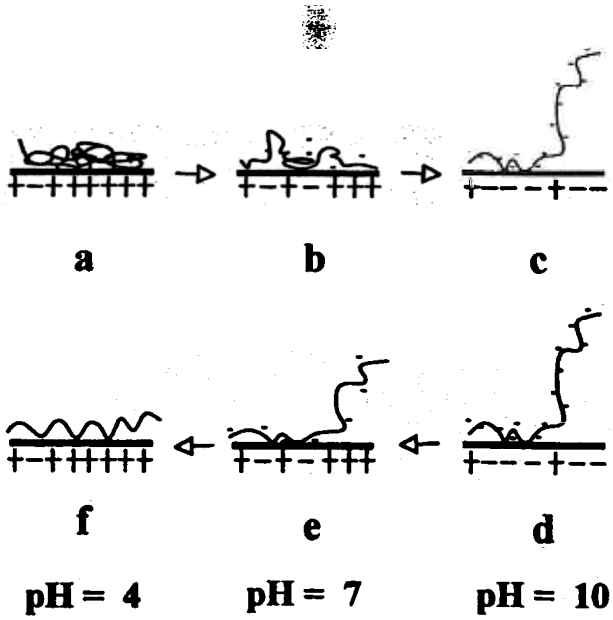


**FIGURE 28** Schematic representation of the variation of polymer conformation at the interface.

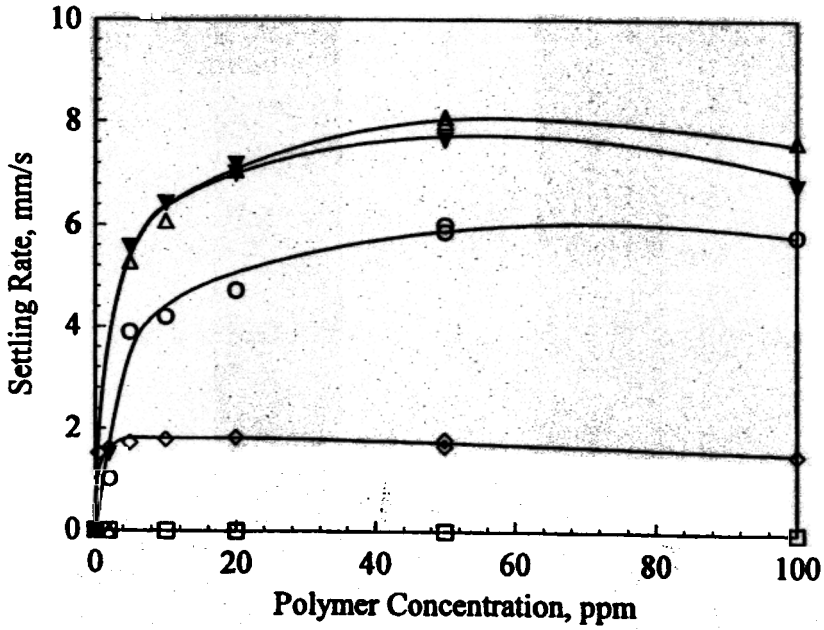


**FIGURE 29** Flocculation response of alumina suspension with dual polymer systems. □ = C-PAM alone; ◇ = PSS alone; ○ = PSS and C-PAM; △ = C-PAM after PSS; ▽ = PSS after C-PAM.

minor effect, cationic polyacrylamide did not produce any flocculation; however, when used together, both polymers adsorb completely. This co-adsorption is attributed to the interaction of complexes between cationic polyacrylamide and the polystyrene sulfonate at the solid-liquid interface.[77] The mechanism of the superior flocculation obtained with the dual polymer system is illustrated schematically in Figure 30. The anionic polystyrene sulfonate adsorbs on the alumina surface and acts as an anionic "anchor" for the adsorption of the long-chain cationic polymer, which ultimately provides interparticle bridging and excellent flocculation.

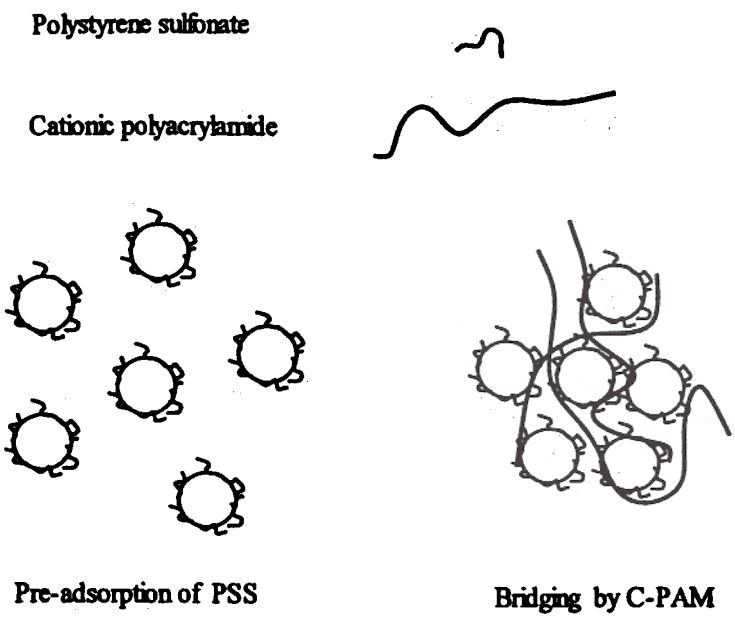


**FIGURE 30** Schematic model for flocculation with dual polymer system.

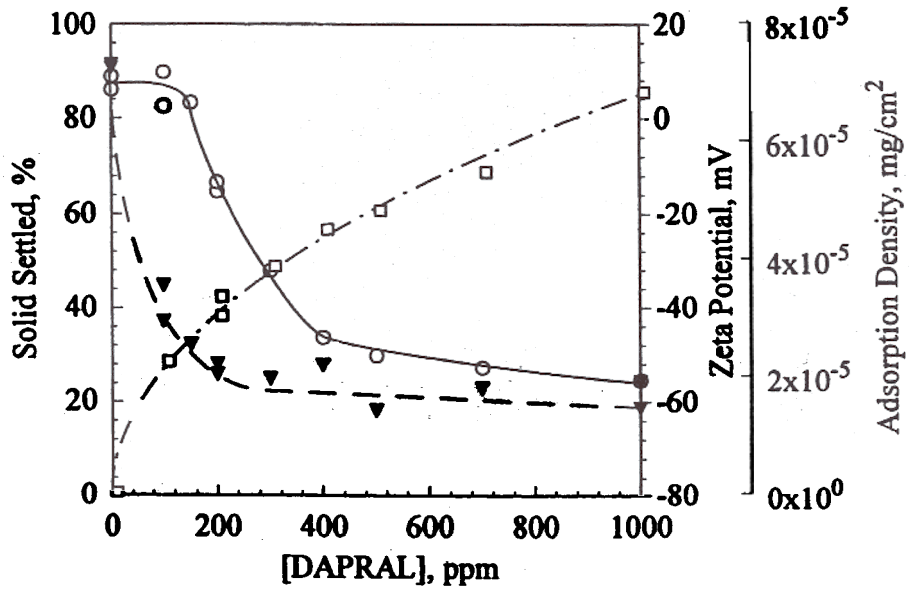


**FIGURE 31** Adsorption of DAPRAL on alumina and its effect on stability and zeta potential. pH = 8; S/L = 2.5%; ▽ = zeta potential; □ = adsoprtion; ○ = settling rate.

### *14.5.3.5.5 Stabilization of aqueous and nonaqueous suspensions with a hydrophobically modified polymer*

The interest in hydrophobically modified polymers (containing both hydrophilic and hydrophobic groups along a polymer backbone) has increased recently due to their possible use in many different applications, including stabilization of both aqueous and nonaqueous suspensions. A study using DAPRAL GE 202 (polymer with comb-like structure: hydrophobic and hydrophilic chains and

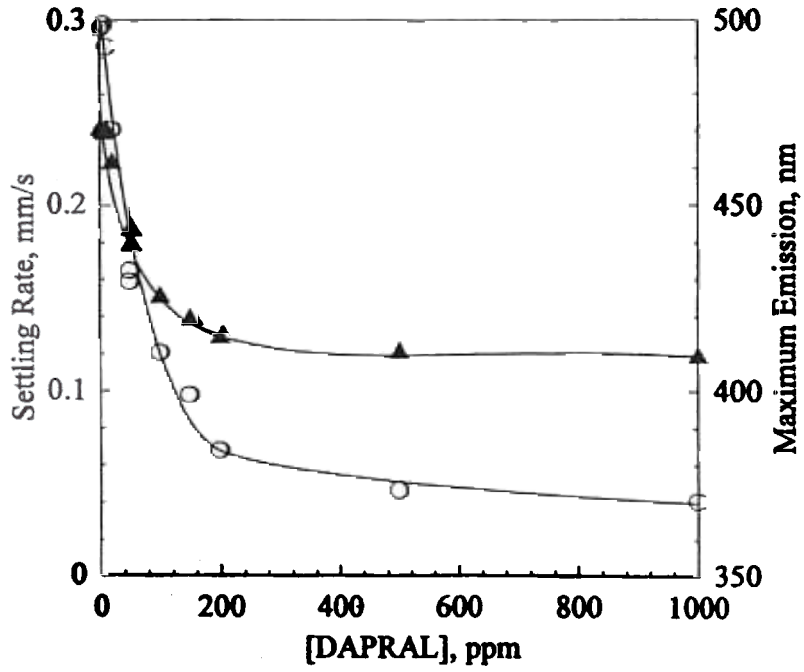


**FIGURE 32** Effect of DAPRAL on stability and hydrophobicity of alumina in toluene. Δ = emission wavelength; o = settling rate.

carboxyl groups along the backbone) has shown unusual performance.[78] The effect of DAPRAL on the stability of aqueous alumina suspensions is shown in Figure 31 along with the zeta potential change and adsorption isotherm. The drastic effect of the polymer addition on suspension stability cannot be attributed to electrostatic forces: suspension stability remains unchanged up to a polymer concentration of 150 ppm, while most of the zeta potential change takes place in that region. Subsequently, the stability of the suspension increases markedly with a further increase in the DAPRAL concentration, while there is only a minor change in the zeta potential.

The same polymer (DAPRAL) having both hydrophobic and hydrophilic groups can also be used for stabilizing nonaqueous suspensions. The results obtained for the settling rate of alumina in toluene as a function of DAPRAL concentration are given in Figure 32. The polymer adsorption is proposed to be primarily through the interaction between surface hydroxyl groups and the hydrophilic (ethylene oxide) polymer side chains, with the hydrophobic side chains exposed toward the bulk solution, causing suspension stabilization. This possibility was investigated by using 7-dimethyl amino 4-methylcoumarin as a fluorescence probe to detect the polymer orientation on the particles. Correlation of the observed shift of maximum wavelength (Figure 32) with suspension stability suggests an increase in the hydrophobicity of the alumina surface; this supports the mechanism proposed above for the observed stability of the alumina suspension.

## 4.6 SUMMARY

Colloidal particles are subjected to a number of attractive and repulsive forces, and the stability of dispersions depends on the interplay of these various forces. The van der Waals attractive forces between particles has their origin in the electron wave fluctuations and is usually effective at close ranges. Electrical double layer interactions stem from the presence of ionized species at the interface and are effective at distances proportional to the double layer thickness for the given system. In aqueous systems, this is usually of the order of 100 Å at ionic strength of about $10^{-3}$ mol/l. In nonaqueous systems, this is very large as the potential decays very slowly from the surface. Another

dominant force, steric force, depends on the nature and size of the adsorbed species but is typically short range. Other forces such as solvation, hydration, and capillary forces occur due to structural ordering at the interface and are active at separation distances of the order of about 4nm.

These forces and, hence, the stability of the dispersions can be altered or controlled by the adsorption of ions, surfactants, or polymers at the solid-liquid interface. Adsorption of surfactants and polymers at the solid-liquid interface depends on the nature of the surfactant or polymer, the solvent, and the substrate. Ionic surfactants adsorbing on oppositely charged surfaces exhibit a typical four-region isotherm. Such adsorption can alter the dispersion stability by mainly changing the double layer interaction, which depends on the extent of adsorption. Thus, it is seen that alumina suspensions are destabilized by adsorption of sodium dodecyl sulfate when the zeta potential is reduced to zero. At higher concentrations, bilayered surfactant adsorption can occur and changes in wettability and flocculation of the particles by altering the hydrophobic interactions.

Nonionic surfactants adsorb primarily through hydration or hydrogen bond interactions, which depends on the hydration characteristics of the substrate. Nonionic surfactants can also affect the double layer forces due to charge screening effects. Nonionic surfactants affect the dispersion stability mainly by altering the van der Waals interaction and the hydrophobic forces, which in turn depend on the nature and orientation of the surfactant adsorbed layer. The adsorption of nonionic surfactants can be greatly enhanced by the presence of ionic surfactants and vice versa. Experiments have shown that nonionic and ionic surfactants when used in mixtures can be forced to adsorb on substrates on which they do not show much adsorption by themselves. The synergistic effect of these mixtures on adsorption is hypothesized to be due to reduction in charge repulsion causing better packing of the ionic surfactants, while for the nonionic surfactants the increase in adsorption is due to their solubilization in the hydrophobic microdomains formed by the ionic surfactants. These mixed systems give rise to interesting adsorbed layer structures which can be manipulated for desired dispersion properties.

In organic media, adsorption of surfactants depends on the relative acid-base characteristics of the solute, solvent, and substrate. Adsorption of ionic surfactants on oxide surfaces proceeds to a monolayer, and there is no evidence of lateral interaction between the adsorbed molecules. Such uniform adsorption imparts stability to the dispersion mainly by reducing the van der Waals attractive forces; however, on hydrophobic surfaces, interactions are possible among the polar groups of the adsorbed molecules, leading to the formation of reverse solloids and a concomitant increase in adsorption density somewhat resembling solloid formation in aqueous media. This leads to a decrease in dispersion stability. The presence of water markedly affects the suspension stability in nonaqueous media. When present in trace amounts it induces ionization in the adsorbed layer and imparts electrostatic stability to the dispersion, while at high concentrations it promotes capillary condensation between the particles leading to flocculation.

Adsorption of polymeric dispersants and flocculants in aqueous media is controlled by the polymer charge, molecular weight, solvent, solution conditions (pH, ionic strength), and porosity of the substrate; however, the adsorbed layer structure is very different in the case of polymers compared to that of the surfactants. A polymer can have various configurations at the interface, and the adsorbed layer can be thought of as a fuzzy polymer layer with trains, loops, and tails. Polymer adsorption affects dispersion stability by altering the electrostatic forces (in case of polyelectrolytes) and mainly the steric forces, which, in this case, are significant since the adsorbed layer thickness is large for polymers. Flocculation by polymers is mainly by charge neutralization and bridging, which depend on the relative size of the polymer chain and the particle and, more importantly, on the conformational state of the adsorbed polymer. Also, it is clear that reorientation of the polymer molecules at the interface can take place in response to changes in the environmental conditions such as pH, in this can produce drastic alternations. Interactions between different polymers can also influence dispersion behavior. Thus, the use of two polymers in sequence is very effective, as it can control the kinetics of aggregation and the floc structure. It has been clearly established that the dispersion stability can be manipulated through control of the polymer structure and its conformation at the solid-liquid interface.

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