COLLOIDS

1. Introduction

Matter of colloidal size, just above atomic dimensions, exhibits physicochemical properties that differ from those of the constituent atoms or molecules yet are also different from macroscopic material. The atoms and molecules of classical chemistry are extremely small, usually having molar masses <1000 g/mol and measurable by freezing point depression. Macroscopic particles fall into the realm of classical physics and can be understood in terms of physical mechanics. Residing between these extremes is the colloidal size range of particles whose small sizes and high surface area-to-volume ratios make the properties of their surfaces very important and lead to some unique physical properties. Their solutions may have undetectable freezing point depressions, and their dispersions, even if very dilute, may sediment out very slowly, and not be well described by Stokes' law. Whereas the particles of classical chemistry may have one or a few electrical charges, colloidal particles may carry thousands of charges. With such strong electrical forces, complete dissociation is the rule rather than the exception. In addition, the electric fields can strongly influence the actions of neighbouring particles. In industrial practice it is very common to encounter problems associated with colloidal sized particles, droplets, or bubbles.

The field began to acquire its own identity when Graham coined the term colloid in 1861 (1–3). Since that time the language of colloid science has evolved considerably (4–6) and makes two principal distinctions: lyophobic (thermodynamically unstable) and lyophilic (thermodynamically stable) colloidal dispersions. Examples of lyophobic and lyophilic colloidal dispersions are suspensions of gold particles and surfactant micelles in solution, respectively. Colloidal particles (or droplets or bubbles) are defined as those having at least one dimension between $\sim$1 nm and 1 μm. In dealing with practical applications, the upper size limit is frequently extended to tens or even hundreds of micrometres. For example, the principles of colloid science can be usefully applied to emulsions whose droplets

Table 1. **Types of Colloidal Dispersion**

Dispersed phase	Dispersion medium	Name	Examples
liquid	gas	liquid aerosol	fog, mist
solid	gas	solid aerosol	smoke, dust
gas	liquid	foam	soap suds
liquid	liquid	emulsion	milk, mayonnaise
solid	liquid	sol, suspension	ink, paint, gel
gas	solid	solid foam	polystyrene foam, pumice stone
liquid	solid	solid emulsion	opal, pearl
solid	solid	solid suspension	alloy, ruby-stained glass

exceed the 1 μm size limit by several orders of magnitude (ie, in cases for which the surface properties of the dispersed phase dominate). Simple colloidal dispersions are two-phase systems, comprising a dispersed phase of small particles, droplets, or bubbles, and a dispersion medium (or dispersing phase) surrounding them. In modern practice, the terms lyophilic and lyophobic (especially hydrophilic and hydrophobic) are often used to characterize surfaces in addition to colloidal dispersions. This sometimes leads to confusing usage. For example, a clay dispersion in water could be classified as a lyophobic colloid with hydrophilic surfaces.

A variety of types of colloidal dispersions occur, as illustrated in Table 1. In practice, many colloidal dispersions are more complex and are characterized by the nature of the continuous phase and a primary dispersed phase, according to the designations in Table 1.

One reason for the importance of colloidal systems is that they appear in a wide variety of practical disciplines, products, and processes. The colloidal involvement in a process may be desirable, as in the stabilizing of emulsions in mayonnaise preparation, or undesirable, as in the tendency of very finely divided and highly charged particles to resist settling and filtration in water treatment plants. Examples of the variety of practical problems in colloid chemistry include control of filtration operations, breaking of emulsions, regulating foams, preparing catalysts, managing fluid flow, and cleaning surfaces (see Table 2).

The variety of systems represented or suggested by Tables 1 and 2 underscores the fact that the problems associated with colloids are usually interdisciplinary in nature and that a broad scientific base is required to understand them completely. A wealth of literature exists on the topic of colloidal dispersions, including a range of basic reference texts (7–11), dictionaries (4–6,12), and treatises on the myriad of applied aspects, of which only a few are cited here (13–24).

2. Preparation and Stability of Dispersions

2.1. Preparation. Colloidal dispersions can be formed either by nucleation with subsequent growth or by subdivision processes (7,8,11,25,26). The nucleation process requires a phase change, such as condensation of vapor to

Table 2. **Some Occurrences of Colloids**

Field	Liquid aerosol	Solid aerosol	Foam	Emulsion	Suspension	Solid foam	Solid emulsion	Solid suspension
environment and meteorology	fog, mist, cloud, smog	volcanic smoke, dust, smog	polluted river foams	water/sewage treatment emulsions, oil spill emulsions	river water, glacial runoff			
foods			champagne, soda and beer heads, whipped cream, meringue	milk, butter, mayonnaise, cheese, cream liqueurs	jellies	leavened breads		
geology, agriculture, and soil science	crop sprays		foam fumigant, insecticide and herbicide blankets	insecticides and herbicides	quicksand, clay soil suspensions	pumice stone, zeolites	opal, pearl	pearl
manufacturing and materials science	paint sprays	sand blasting	foam fractionation, pulping black liquor foam	polishes	ink, gel, paints, fiber suspensions	polystyrene foam, polyurethane foam	high impact plastics, alkaline battery fill	stained glass, ceramics, cement, plastics, catalysts, alloys, composites
biology and medicine	nasal sprays	airborne pollen, inhalant drugs	vacuoles, insect excretions, contraceptive foam	soluble vitamin and hormone products, biological membranes, blood	liniment suspensions, proteins, viruses	loofah plant		wood, bone

Table 2 (*Continued*)

Field	Liquid aerosol	Solid aerosol	Foam	Emulsion	Suspension	Solid foam	Solid emulsion	Solid suspension
petroleum production and mineral processing			refinery foams, flotation froths, fire extinguishing foams, explosion suppressant foam	oilfield emulsions, asphalt emulsion	drilling fluids, drill cuttings, mineral slurries, process tailings		oil reservoir	
home and personal care products	hair spray		shampoo suds, shaving cream, contraceptive foams, bubble bath foam	hair and skin creams and lotions		sponges, carpet underlay, cellular foam insulation		bakelite products

Table 3. **Industrially Produced Colloidal Materials and Related Processes**

Mechanism	Examples[a]
vapor→liquid→solid ↓→→→↑	oxides, carbides via high intensity arc; metallic powders via vaccum or catalytic reactions
vapor + vapor →solid	chemical vapor deposition, radio frequency-induced plasma, laser-induced precipitation
liquid→solid	ferrites, titanates, aluminates, zirconates, molybdates via precipitation
solid→solid	oxides, carbides via thermal decomposition

[a] Ref. 27,28.

yield liquid or solid, or precipitation from solution. Some mechanisms of such colloid formation are listed in Table 3. The subdivision process refers to the comminution of particles, droplets, or bubbles into smaller sizes by applying high shearing forces, using devices such as a propeller-style mixer, colloid mill or ultrasound generator. A complex technology has developed to conduct and to control comminution and size-fractionation processes. Mathematical models are available to describe changes in particle size distribution during comminution, but these are generally restricted to specific processes. Comprehensive reviews of the developments in preparing colloidal solids by subdivision should be consulted for further details (27,28) (see POWDERS, HANDLING, DISPERSION OF POWDERS IN LIQUIDS). A wide range of techniques is now available including, eg, atomizers and nebulizers of various designs used to produce colloidal liquid or solid aerosols, and emulsions having relatively narrow size distributions. Monosized powders and monodispersed colloidal sols are frequently used in many products, eg, pigments, coatings, and pharmaceuticals.

Colloidal suspensions of uniform chemical and phase composition, particle size, and shape are now available for many elements (including sulfur, gold, selenium, and silver, carbon, cobalt, and nickel), many inorganic compounds (including halide salts, sulfates, oxides, hydroxides, and sulfides), and many organic compounds [including, poly(vinyl acetate), polystyrene, poly(vinyl chloride), styrene-butadiene rubber, poly(acrylic acid), polyurea, poly(styrene)- poly(acrylate), and poly(methacrylate)-poly(acrylate)].

2.2. Stability. A complete characterization of colloid stability requires consideration of the different processes through which dispersed species can encounter each other: sedimentation (creaming), aggregation and coalescence. Sedimentation results from a density difference between the dispersed and continuous phases and produces two separate layers of dispersion that have different dispersed phase concentrations. One of the layers will contain an enhanced concentration of dispersed phase, which may promote aggregation. Aggregation is when two or more dispersed species clump together under the influence of Brownian motion, sedimentation, or stirring, possibly touching at some points, and with virtually no change in total surface area. Aggregation is sometimes referred to as flocculation or coagulation (although in specific situations these latter terms can have slightly different meanings). In aggregation, the species retain their identity but lose their kinetic independence since the aggregate moves as a single unit. Aggregation of droplets may lead to coalescence and the formation of larger droplets until the phases become separated. In coalescence thin film drainage occurs, leading to rupture of the separating film, and two or more particles, droplets or bubbles fuse together to form a single larger unit, reducing the total surface area. In this case the original species lose their identity and become part of a new species. In emulsions, inversion can take place, in which the emulsion suddenly changes form, from oil-in-water (O/W) to water-in-oil (W/O), or vice versa. For example, butter results from the creaming, breaking, and inversion of emulsified fat droplets in milk. Kinetic stability can thus have different meanings. A colloidal dispersion can be kinetically stable with respect to coalescence but unstable with respect to aggregation. Or, a system could be kinetically stable with respect to aggregation but unstable with respect to sedimentation. In summary, lyophobic colloids are thermodynamically unstable, but may be relatively stable in a kinetic sense, and it is crucial that stability be understood in terms of a clearly defined process.

3. Dispersed Species Characterization and Sedimentation

The characterization of colloids depends on the purposes for which the information is sought because the total description would be an enormous task. Among the properties to be considered are the nature and/or distributions of purity, crystallinity, defects, size, shape, surface area, pores, adsorbed surface films, internal and surface stresses, stability, and state of agglomeration (27,28).

3.1. Surface Area, Porosity, and Permeability. Some very interesting and important phenomena involve small particles and their surfaces. For example, SO_2 produced from mining and smelting operations that extract metals such as Cu and Pb from heavy metal sulfide ores can be oxidized to SO_3 in the atmosphere, thus contributing to acid rain problems. The reaction rate depends not only on the concentration of the SO_2 but also on the surface area of any catalyst available, such as airborne dust particles. The efficiency of a catalyst depends on its specific surface area, defined as the ratio of surface area to mass (17). The specific surface area depends on both the size and shape and is distinctively high for colloidal sized species. This is important in the catalytic processes used in many industries for which the rates of reactions occurring at the catalyst surface depend not only on the concentrations of the feed stream reactants but also on the surface area of catalyst available. Since practical catalysts are frequently supported catalysts, some of the surface area is more important than the rest. Since the supporting phase is usually porous the size and shapes of the pores may influence the reaction rates as well. The final rate expressions for a catalytic process may contain all of these factors: surface area, porosity and permeability.

The total surface area can be estimated by measuring the amount of gas needed to form an adsorbed monolayer by physical adsorption (29,30), in which case the number of molecules adsorbed divided by the area per molecule yields the surface area. The classic models for physical adsorption are those of Langmuir (monomolecular adsorption and constant ΔH_{ads}, independent of the extent of surface coverage) and Brunauer, Emmett, and Teller (BET, multilayer adsorption and several ΔH_{ads} components); while many other models are available as well (8,10,17). These models require a knowledge of the area each molecule occupies on the surface. Chemisorption can be studied in the same fashion as described for nitrogen adsorption but using a gas that is chemisorbed, ie, that bonds chemically. This yields a specific chemisorption surface area. In evaluating supported catalyst samples, both kinds of surface area may need to be measured since particle size changes would be reflected in the specific surface area while site deactivation might change only the specific chemisorption area.

The Langmuir and BET equations work well with nonporous solids, but not as well for porous solids because the pores influence the local numbers of adsorption layers formed. By using adsorption gases of different molecular size or by varying the temperature, pores of different size will be accessible to the adsorbing molecule. Coupling this with the appropriate mathematical interpretation allows for the determination of solid porosity using BET analysis. The porosity of a solid (pore volume divided by bulk volume) is most easily determined by the imbibition method, frequently used in the petroleum industry. A sample of solid is dried and weighed, then saturated with a wetting liquid (often water or heptane) under vacuum. The pore volume accessible is calculated by a material balance. In prepared catalysts, the pore sizes may be quite uniform. However, in most naturally occurring materials there is a wide range of pore sizes. The actual pore size distribution can be obtained from methods such as porosimetry, in which a nonwetting liquid (usually mercury) is pumped into a solid sample (7,8,10,17,29,31). According to the Laplace equation each increment of applied pressure will cause only pores down to a certain size to be filled, and employing a series of pressure increments allows the pore size distribution to be obtained.

The ease with which a fluid can flow through a porous medium, permeability, can be determined through the measurement of pressure drop (Δp) across the porous medium under steady flow. The intrinsic permeability (k) is defined by Darcy's law and is given by $k = (Q/A)(\eta L/\Delta p)$, where Q is the discharge flow rate, A is the cross-sectional area normal to the main flow direction, η is the flowing fluid viscosity, L is the length of the flow path (sample), and Δp is the pressure gradient along the medium (15). Mercury porosimetry can also be used to assess permeability (17,29).

3.2. Size and Size Distribution.

If the sizes of particles, droplets, bubbles, or their aggregates in a colloidal dispersion are large enough, then optical microscopy can be used to determine the shape, size, and size distribution, but if they are smaller then ~0.5 μm they will not be resolved in a typical optical microscope. Confocal scanning laser microscopes can extend this resolution down to ~0.1 μm. For dispersions of such smaller-size species, the most direct methods include scanning and transmission electron microscopy. Adaptations, such as cryogenic-stage scanning electron microscopy can be used for emulsions and foams (32,33).

Small, dispersed particles or droplets cause the “cloudy” or “milky” appearance of such diverse colloids as dust clouds, rain clouds, suspended sediment in a river, and milk. This appearance is due to light scattering. When a beam of light enters a colloidal dispersion some light is absorbed, some is scattered, and some is transmitted. The intensity of the scattered light depends largely on the size and shape of the colloidal species, and on the difference in refractive index between the phases. Light scattering analysis is very powerful because it can yield the complete dispersed-phase size distribution. This is important in emulsions that are commonly, but generally incorrectly, characterized in terms of a specified droplet size whereas there is inevitably a size distribution. The theory underlying the determination of size distribution for a colloidal dispersion is quite involved (8,34). Rayleigh theory predicts that larger particles scatter more light than do smaller ones. Since the scattering intensity is proportional to $1/\lambda^4$ then blue light ($\lambda = 450$ nm) is scattered much more than red light ($\lambda = 650$ nm). With incident white light a scattering material will, therefore, tend to appear blue when viewed at right-angles to the incident light beam, and red when viewed end-on. Thus the sky can appear blue overhead while the sun appears yellowish-red when viewed across the horizon as it is rising or setting. When a test tube containing a dilute suspension of particles so small that they would be invisible under the light microscope is held up to the light it may appear to have a blue colour due to Rayleigh scattering. This phenomenon provides a way to indirectly observe particles that would otherwise be invisible. In the darkfield microscope, or ultramicroscope, the light scattered by small particles is viewed against a dark background. This method is applied in observing the electrophoretic motions of colloidal particles (35).

Other indirect techniques for determining colloidal species' size or size distribution include sedimentation–centrifugation, conductometric techniques, X-ray diffraction, gas and solute adsorption, ultrafiltration, diffusiometric, and ultrasonic methods (7,8,31,36). Care must be taken in selecting an indirect method since these require assumptions about either the real size distribution, the shape, or the process on which the analysis is based. For example, conductometric "sensing zone" equipment relies on the assumption of sphericity, which is reasonable for emulsion droplets but may not hold for particles in a suspension. Similarly, light-scattering techniques are reliable only if the particle shape and refractive index is known or assumed, and adsorption analyses rely on model adsorption isotherms, the uniformity of particle size and porosity, and the orientation of adsorbed species. In all cases, one must be careful that sample preparation techniques do not change the size distribution (32). Typically, more than one method is needed to characterize size and/or size distribution properly (see SIZE MEASUREMENT OF PARTICLES).

Nearly all colloidal systems undergo some aggregation leading to a distribution of aggregate sizes. Ultramicroscopy is the preferred method for measuring the rate and/or extent of aggregation because it is direct. The indirect methods listed above can also be used when tailored to suit the specific colloidal system in hand. More than one technique is required to assess the state of aggregation when a wide range of colloidal dimensions exists. If aggregates larger than approximately 5 μm are present, the aggregate-size distribution can be evaluated using classical techniques such as sieving (27,28,37), as long as such methods do not themselves induce or break aggregates.

3.3. Sedimentation. Whereas the use of light scattering to determine a complete size range distribution is quite involved, if the particles or droplets are not too small, a simpler approach can be used that yields an approximate average size. This is done by measuring settling velocities. Consider the small particles in a dust cloud, or suspended sediment in a river. It is principally the small size that keeps these particles from rapidly settling out. If a particle or droplet is placed in a fluid it will fall, or sediment out, if its density is greater than that of the fluid. The driving force is that of gravity. In the Stokes model, the terminal settling velocity is proportional to gravity and the square of particle size and inversely proportional to the fluid viscosity (7,8,31). This assumes that the species is uncharged and spherical, the situation being more complicated for charged and/or asymmetric particles. Further, if the particle concentration is high then the particles don't sediment independently but are influenced by the motions of surrounding particles producing slower, hindered, settling. Sedimentation under gravity is only practical down to $\sim$1 μm diameter, but the centrifuge or ultracentrifuge can be used to study sedimentation of colloidal systems since the added centrifugal forces can be employed to overcome the mixing tendencies of diffusion and convection. Centrifugal force, like gravitational force, is proportional to the mass but the coefficient is not the acceleration due to gravity (g) but rather the square of the angular velocity (ω) times the distance of the particle from the axis of rotation (x). Since ω^2x is substituted for g in the governing equation, one speaks of multiples of g in a centrifuge. For example, using a conventional laboratory bench-top centrifuge capable of applying thousands of "gs" one can reduce the time needed to sediment out 0.2 μm particles, from an aqueous suspension, to $\sim$20 min compared with the 16 days that would be needed to achieve the same sedimentation from a standing column. In an ultracentrifuge, even greater centrifugal forces ($\sim$40,000 g) can be employed.

4. Rheology

For calculations involving pumping and mass transfer, industrial process streams can sometimes be treated as simple, "single phase" fluids that obey Newton's law of viscosity, $\tau = \eta\dot{\gamma}$, in which the shear stress, τ, is given as a linear function of the shear rate, $\dot{\gamma}$, with the proportionality constant being the viscosity, η. In fact many industrial process streams occur as colloidal dispersions, introducing the complication that in many cases viscosity is not expressed by a single number at constant temperature and pressure, but also depends on whether the material is flowing, and even its recent history (see RHEOLOGICAL MEASUREMENTS). Due to polydispersity, high dispersed phase content, mutual orienting and/or structure formation of the dispersed species under flow a non-Newtonian dispersion exhibits a viscosity that is not constant, but is itself a function of the shear rate, [ie, $\tau = \eta\ (\dot{\gamma})\ \dot{\gamma}$]. The function itself can take many forms (38–43). Many different terms are used to express specific kinds of viscosities, including absolute, apparent, differential, intrinsic, reduced, relative, and inherent viscosity. These are defined elsewhere, as is an entire lexicon of terms used to describe the different rheological classifications of colloidal dispersions (4–6,39,42). Typical rheological classifications are listed in Table 4. Some descriptions appropriate to different yield stresses and some approximate values of shear rate appropriate to various industrial processes are given in reference (44).

A colloidal system can exhibit several of these characteristics at once. For example, paint must be plastic and thixotropic so that it will flow when brushed on and (only) immediately after brushing (for a smooth finish); a further benefit

Table 4. **Typical Rheological Classifications**

Rheological classification	Description	Examples
pseudoplastic (shear-thinning)	as shear rate increases viscosity decreases.	in paint, a suspension of pigment particles in a liquid, irregular particles can align to match the induced flow, lowering the viscosity.
dilatant (shear-thickening)	as shear rate increases viscosity increases	in the "drying" of wet beach sand when walked on, a dense packing of particles occurs. Under low shear the particles can move past each other, whereas under high shear the particles wedge together such that the fluid can't fill the increased void volume.
pseudoplastic with yield stress (plastic)	pseudoplastic or Newtonian flow begins only after a threshold shear stress, the yield stress, is exceeded.	in an oil well drilling mud the interparticle network offers resistance to any positional changes. Flow only occurs when these forces are overcome.
thixotropic	time-dependent pseudoplastic flow. At constant applied shear rate viscosity decreases. In a flow curve hysteresis occurs.	in bentonite clay "gels" which "liquefy" on shaking and "solidify" on standing there is a time-dependent aligning to match the induced flow. After the shear rate is reduced it takes some time for the original alignments to be restored.
rheopectic	time-dependent dilatant flow. At constant applied shear rate viscosity increases. In a flow curve hysteresis occurs.	a suspension that sets slowly on standing but quickly when gently agitated due to time-dependent particle interference under flow.
rheomalaxic	time-dependent behavior in which shear rate changes cause irreversible changes in viscosity.	an emulsion that when sheared inverts to a higher (or lower) viscosity emulsion, and does not reinvert when the shear is removed.

is that vigorous mixing readily disperses the pigments which then stay dispersed for some time when standing (high yield stress). Finally, shortly after brushing-on the paint should cease to flow so that it doesn't "run".

A range of methods are available for making rheological measurements (39–42) (see RHEOLOGICAL MEASUREMENTS). A frequently encountered problem involves knowing the particle–droplet–bubble size and concentration in a dispersion and the need to predict the suspension, emulsion or foam viscosity. Many equations have been advanced for this purpose. In the simplest case, a colloidal system can be considered Einsteinian. Here, the viscosity of the colloidal system depends on that of the continuous phase, η_0, and the volume fraction of colloid, ϕ, according to the Einstein equation, which was derived for a dilute suspension of noninteracting spheres:

$$\eta = \eta_0\ (1 + 2.5\ \phi)$$

This relationship forms the basis for the use of volume fraction as the theoretically favored concentration unit in rheology. In practice once ϕ reaches between 0.1 and 0.5 dispersion viscosity increases and can also become non-Newtonian (due to particle/droplet/bubble "crowding," or structural viscosity). The maximum volume fraction possible for an internal phase made up of uniform, incompressible spheres is 0.74, although emulsions and foams with an internal volume fraction of >0.99 can exist as a consequence of droplet–bubble distortion.

Many empirical and theoretical modifications have been made to Einstein's equations. A useful extension to dilute suspensions of anisotropic particles, such as clays, is given by the Simha Equation, which is approximately

$$\eta = \eta_0 \ (1 + a\phi/1.47b)$$

where a is the major particle dimension and b the minor particle dimension. Many of the other viscosity equations are empirical extensions of Einstein's equation for a dilute suspension of spheres, including virial expansions such as

$$\eta = \eta_0 \ (1 + \alpha_0\phi + \alpha_1\phi^2 + \alpha_2\phi^3 + \cdots)$$

These equations usually apply if the particles or droplets are not too large, and if there are no strong electrostatic interactions. Additional equations are tabulated elsewhere (6,45).

Size distribution also has an important influence on viscosity. For electrostatically or sterically interacting drops, emulsion viscosity will be higher when droplets are smaller. The viscosity will also be higher when the droplet sizes are relatively homogeneous, ie, when the drop size distribution is narrow rather than wide. The rheological properties also depend on any specific interactions among the colloidal species, the dispersing medium, and the solute additives, ie, salts, surfactants, and polymers.

There are many important influences of rheology in industrial practice. From Stokes' law the terminal settling velocity is inversely proportional to the viscosity of a colloidal dispersion (see SEDIMENTATION), which has a direct impact on sedimentation in, eg, treatment of waste water (see WATER, MUNICIPAL WATER TREATMENT) and on mineral fractionation and/or flotation (47,48). Another major application area is transport behavior, involving the pumping of fluid systems containing colloids, such as in extrusion in the polymer industry, the processing of gelatinous foods and cosmetic items, the fabrication of high performance materials in the ceramic and metallurgical industries, transportation in the petroleum industry, and the preparation and handling of pigment slurries in the paint industry. The prediction and control of suspension, emulsion, and foam rheology, especially the thixotropic and dilatant tendencies, is primarily important for these and other uses.

5. Interfacial Energetics

In colloidal dispersions, a thin intermediate region or boundary, known as the interface, lies between the dispersed and dispersing phases. Each interface has a certain free energy per unit area that has a great influence on the stability and structure of the colloidal dispersion, and that has a great influence in practical areas such as mineral flotation, detergency and waterproofing.

5.1. Surface and Interfacial Tensions. For a liquid exposed to a gas the attractive van der Waals forces between molecules are felt equally by all molecules except those in the interfacial region. This makes the latter molecules tend to move to the interior and causes the interface to contract spontaneously. This is the reason droplets of liquid and bubbles of gas tend to adopt a spherical shape. For two immiscible liquids a similar situation applies, except it may not be so immediately obvious how the interface will tend to curve but there will still be an imbalance of intermolecular forces and a configuration that minimizes the interfacial free energy, or interfacial tension. Surface tension can be thought of as either the contracting force around the perimeter of a surface, or as the surface free energy associated with area change. Emulsions and foams represent colloidal systems in which interfacial properties are very important because emulsified droplets and dispersed gas bubbles have large interfacial areas, so that even a modest interfacial energy per unit area can become a considerable total interfacial energy. There are many methods available for the measurement of surface and interfacial tensions (46,49–51).

5.2. Pressure and Curved Surfaces. Interfacial tension causes a pressure difference to exist across a curved surface such that the pressure inside a bubble or drop exceeds that outside. The pressure difference is given, in terms of the principal radii of curvature and surface or interfacial tension, by the Young-Laplace equation (8,10). For spherical droplets of liquid in a gas, $\Delta p = 2\gamma/R$, ie, the pressure difference, Δp, varies inversely with the radius, R. Thus the vapor pressure of a drop should become higher as the drop becomes smaller. This is shown by the Kelvin equation (8,31), which gives the pressure, at equilibrium, above a spherical surface of given radius, r, and surface tension, γ, as $RT \ln (p/p_0) = 2V_L\gamma/r$, where p_0 is the normal vapor pressure and V_L is the molar volume of the liquid. By replacing pressure with activity of dissolved solute and relating activity, in turn, to molar solubility the Kelvin equation can be used to describe a number of supersaturation phenomena including supercooled vapors and supersaturated solutions.

5.3. Contact Angle and Wettability. When a drop of liquid is placed on a solid surface the liquid may form a bead on the surface, or it may spread to form a film. A liquid having a strong affinity for the solid will seek to maximize its contact (interfacial area) and form a film. A liquid with much weaker affinity may form into a bead. This affinity is termed the wettability (10,25,26). To account for the degree of spreading, the contact angle, θ, is defined as the angle, measured through the liquid, that is formed at the junction of three phases, eg, at the S-L-G junction. Whereas interfacial tension is defined for the boundary between two phases, contact angle is defined for a three-phase junction. If the interfacial forces acting along the perimeter of the drop are represented by the interfacial tensions, then an equilibrium force balance is given by Young's equation as, $\gamma_{L/G} \cos \theta = \gamma_{S/G} - \gamma_{S/L}$. The solid is completely wetted if $\theta = 0$ and only partially wetted otherwise. Although in theory complete nonwetting would be $\theta = 180^\circ$ this is not seen in practice and values of $\theta > 90^\circ$ are considered to represent "nonwetting" whereas values of $\theta < 90^\circ$ are often considered to represent "wetting". This rather arbitrary assignment is based on correlation with the visual appearance of drops on surfaces.

An example is provided in enhanced oil recovery. In an oil-bearing reservoir the relative oil and water saturations depend on the distribution of pore sizes in the rock, the pressure in a pore, the interfacial tension and contact angle according to the Young-Laplace and Young equations. The same relationships determine how water or other fluids can be injected to change pressure, interfacial tension, and/or contact angle and thereby change the liquid saturations and increase oil recovery (13,52).

Some compounds, like short-chain fatty acids, can be soluble in both water and oil because one part of the molecule has an affinity for oil (the nonpolar hydrocarbon chain) and one part has an affinity for water (the polar group). The energetically most favorable orientation for these molecules is at an interface so that each part of the molecule can reside in the solvent medium for which it has the greatest affinity. These molecules that form oriented monolayers at interfaces show surface activity and are termed surfactants (see SURFACTANTS). Some consequences of surfactant adsorption at a surface are that it causes a reduction in surface tension and an alteration in the wettability of the surface. Surfactant molar masses range from a few hundreds up to several thousands of g/mol.

Surfactants can be used to selectively alter wettability. For example, in mineral flotation surfactant can be added to adsorb on metal ore particles increasing the contact angle, so they attach to gas bubbles. The surfactant is chosen so that it will not adsorb much on silicates, so the latter do not attach to gas bubbles. The surfactant may also stabilize a foam containing the desired particles, thereby facilitating their recovery as a particle-rich froth that can be skimmed. Flotation processes thus involve careful modification of surface tension and wettability.

Another problem in colloids is detergency, which involves the action of surfactants (originally soaps were used) to alter interfacial properties so as to promote dirt or oil removal from solid surfaces. The detergent's role is to alter interfacial tensions in order to reduce the amount of mechanical energy required to dislodge the dirt. If the dirt is solid then it is a simple matter of wettability alteration.

Surfactants play an important role in the formation and stability of emulsions and foams. Surfactant adsorption at fluid interfaces can, eg, lower interfacial tension, increase surface elasticity, increase electric double-layer repulsion (ionic surfactants), lower the effective Hamaker constant, and sometimes increase surface viscosity. For emulsions, the nature of the surfactant can also determine the arrangement of the phases (ie, which phase will form the dispersed versus continuous phase). Several empirical rules and scales have been developed for categorizing emulsifying agents, including the oriented wedge and Bancroft theories, the hydrophile–lipophile balance, HLB, and the phase inversion temperature, PIT (13,26,45). Although there are exceptions to each of these rules, they remain useful for making initial predictions.

5.4. Lyophilic Colloids. Another key feature of surfactants is that above a certain solution concentration they form organized aggregates called micelles (19,26) in which the lipophilic parts of the surfactants associate in the interior of the aggregate, leaving hydrophilic parts to face the aqueous medium. A solution of micelles is a good example of a thermodynamically stable lyophilic colloidal dispersion. The concentration at which micelle formation becomes significant is called the critical micelle concentration (CMC). The CMC is a property of the surfactant and several other factors, since micellization is opposed by thermal and electrostatic forces. A low CMC is favoured by increasing the lipophilic part of the molecule, lowering the temperature, and adding electrolyte. Compilations of CMC values are given in references (19,53).

The ability of biological amphiphilic molecules to aggregate into spherical and nonspherical clusters, ie, vesicles, may have been important for the development of early living cells (54). Cellular biological membranes in plants and animals share features with these colloidal systems, although the molecular and hierarchical membrane structures, their hydration, and their dynamic properties are complex (54–56). The macroscopic nature of concentrated gels, such as lubricating greases formed by dispersing short-chain surfactants, eg, lithium 12-hydroxystearate, in mineral oil (57), is akin to the behavior of biological amphiphiles, being also dependent on self-assembly mechanisms. The associations between fibrous clusters, the length of threadlike surfactant strands, and the density of their contact points (cross-links) govern the grease's shear-resistance (57).

Microemulsions, like micelles, are considered to be lyophilic, stable, colloidal dispersions. In some systems, the addition of a fourth component, a cosurfactant, to an oil–water–surfactant system can cause the interfacial tension to drop to near-zero values, easily on the order of $10^{-3} - 10^{-4}$ mN/m, allowing spontaneous or nearly spontaneous emulsification to very small drop sizes, ~10 nm or smaller. The droplets can be so small that they scatter little light, the emulsions appear to be transparent and do not break on standing or centrifuging. Unlike coarse emulsions, microemulsions are thought to be thermodynamically stable. The thermodynamic stability is frequently attributed to transient negative interfacial tensions, but this, and the question of whether microemulsions are really lyophilic or lyophobic dispersions are areas of some discussion in the literature. As a practical matter, microemulsions can be formed, have some special qualities, and can have important applications in areas such as enhanced oil recovery, soil and aquifer remediation, foods, pharmaceuticals, cosmetics, herbicides and pesticides (13,16,45,58–60).

6. Electrokinetics

6.1. Charged Interfaces.

Most substances acquire a surface electric charge when brought into contact with a polar medium such as water. The origin of the charge can be ionization, as when carboxyl and/or amino functionalities ionize when proteins are put into water; ion adsorption, as when surfactant ions adsorb onto a solid surface; ion dissolution, as when Ag^+ and I^- dissolve unequally when AgI is placed in water; or ion diffusion, as when a clay particle is placed in water and the counterions diffuse out to form an electric double layer. In the AgI example, the ions Ag^+ and I^- will be potential determining because either may adsorb at the interface and change the surface potential. Conversely, indifferent ions, such as Na^+ and NO_3^-, will not change the surface potential.

Surface charge influences the distribution of nearby ions in a polar medium: ions of opposite charge (counterions) are attracted to the surface while those of like charge (coions) are repelled. Together with mixing caused by thermal motion a diffuse electric double layer is formed. The electric double layer (EDL) can be viewed as being composed of two layers: an inner layer that may include adsorbed ions and a diffuse layer where ions are distributed according to the influence of electrical forces and thermal motion. Gouy and Chapman proposed a simple quantitative model for the diffuse double layer assuming an infinite, flat, uniformly charged surface, and ions that can be regarded as point charges (also that solvent effects arise only through a uniform dielectric constant, and that the electrolyte is symmetrical [z-z]). The surface potential is designated as ψ° and the potential at a distance x as ψ. The Poisson-Boltzmann equation comes from a combination of the Boltzmann distribution of concentrations of ions (in terms of potential), the charge density at each potential (in terms of the concentration of ions), and the Poisson equation (describing the variation in potential with distance). Given the physical boundary conditions, assuming low surface potentials, and using the Debye-Hückel approximation yields,

$$d^2\Psi/dx^2 = [e^2\Psi/(\in kT)]\Sigma_i c_i z_i^2$$

If we now define the cluster of constants as $\kappa^2 = (e^2/\epsilon kT)\Sigma_i c_i z_i^2$ (having units of distance^{-2}) then this can be simplified to

$$d^2\Psi/dx^2 = \kappa^2\Psi \qquad \text{or} \qquad \Psi = \Psi^\circ \exp(-\kappa x)$$

This is the Debye-Hückel expression for the potential at a distance from a charged surface. The parameter $1/\kappa$ is called the double layer thickness and is given for water at 25°C by $\kappa = 3.288\ \surd I$ (nm^{-1}), where $I = (1/2)\Sigma_i c_i z_i^2$. For 1-1 electrolyte $1/\kappa$ is 1 nm for $I = 10^{-1}\ M$, and 10 nm for $I = 10^{-3}\ M$.

There remain some problems. In order to handle higher (more practical) potentials, the Gouy-Chapman theory can be applied, but with a more complicated result. One such result is

$$\Upsilon = \Upsilon^\circ \exp(-\kappa x)$$

where Υ is a complex ratio involving Ψ given by

$$\Upsilon = \frac{\exp[ze\Psi/2kT] - 1}{\exp[ze\Psi/2kT] + 1}$$

At low surface potentials this equation reduces to the Debye-Hückel expression above. Second, an inner layer exists because ions are not really point charges and an ion can only approach a surface to the extent allowed by its hydration sphere. The Stern model incorporates a layer of specifically adsorbed ions bounded by a plane—the Stern plane. In this case, the potential changes from ψ° at the surface, to $\psi(\delta)$ at the Stern plane, to $\psi = 0$ in bulk solution.

6.2. Electrokinetic Phenomena. Electrokinetic motion occurs when the mobile part of the electric double layer is sheared away from the inner layer (charged surface). There are several types of electrokinetic measurements, electrophoresis, electroosmosis, streaming potential, sedimentation potential, and two electroacoustical methods. The first four methods are described in references (35,61). Of these the first finds the most use in industrial practice. The electroacoustical methods involve detection of the sound waves generated when dispersed species are made to move by an imposed alternating electric field, or vice versa (62). In all of the electrokinetic measurements either liquid is made to move across a solid surface or vice versa. Thus the results can only be interpreted in terms of charge density (σ) or potential (zeta potential, ζ) at the plane of shear. The location of the shear plane is generally not exactly known and is usually taken to be approximately equal to the potential at the Stern plane, $\zeta \approx \psi(\delta)$. Several methods can be used to calculate zeta potentials (11,35,61).

7. Colloid Stability

A consequence of the small size and large surface area in colloids is that quite stable dispersions of these species can be made. That is, suspended particles may not settle out rapidly and droplets in an emulsion or bubbles in a foam may not coalesce quickly. Charged species, when sedimenting, present a challenge to Stokes' law because the smaller counterions sediment at a slower rate than do the larger colloidal particles. This creates an electrical potential that tends to speed up the counterions and slow down the particles. At high enough electrolyte concentrations the electric potentials are quickly dissipated and this effect vanishes.

Although some lyophobic colloidal dispersions can be stable enough to persist for days, months, or even years, they are not thermodynamically stable. Rather, they possess some degree of kinetic stability, and one must consider the degree of change and the timescale in the definition of stability. Having distinguished coalescence and aggregation as processes in which particles, droplets, or bubbles are brought together with and without large changes in surface area respectively, it is clear that there can be different kinds of kinetic stability. Finally, stability depends upon how the particles interact when this happens, since encounters between particles in a dispersion can occur frequently due to diffusion (as in Brownian motion), sedimentation, or stirring.

7.1. Electrostatic and Dispersion Forces. Several repulsive and attractive forces operate between colloidal species and determine their stability (7,8,10,25,31,54). In the simplest example of colloid stability, particles would be stabilized entirely by the repulsive forces created when two charged surfaces approach each other and their electric double layers overlap. The overlap causes a Coulombic repulsive force acting against each surface, and that will act in opposition to any attempt to decrease the separation distance. One can thus express the Coulombic repulsive force between plates as a potential energy of repulsion. There is another important repulsive force causing a strong repulsion at very small separation distances where the atomic electron clouds overlap, called the Born repulsion.

There also exist dispersion, or London-van der Waals forces that molecules exert towards each other. These forces are usually attractive in nature and result from the orientation of dipoles, whether dipole–dipole (Keesom dispersion forces), dipole–induced dipole (Debye dispersion forces), or induced dipole–induced dipole (London dispersion forces). Except for quite polar materials the London dispersion forces are the more significant of the three. For molecules, the force varies inversely with the sixth power of the intermolecular distance, whereas for particles, etc, the force varies approximately inversely with interparticle distance.

7.2. DLVO Theory. Derjaguin and Landau (63), and Verwey and Overbeek (64) developed a quantitative theory for the stability of lyophobic colloids referred to as DLVO theory. It was known from experiment that classical colloids (AgI, Au) coagulated quickly at high electrolyte concentrations and slowly at low concentrations with a very narrow electrolyte concentration range over which the transition from kinetically stable to kinetically unstable occurred. Thus a critical coagulation concentration (CCC) could be defined. Using DLVO theory one can calculate the energy changes that take place when two particles approach each other by estimating the potential energies of attraction (London-van der Waals dispersion, V_A) and repulsion (electrostatic including Born, V_R) versus interparticle distance. These are then added together to yield the total interaction energy, V_T. The theory has been developed for two special cases, the interaction between parallel plates of infinite area and thickness, and the interaction between two spheres. The original calculations of dispersion forces employed a model due to Hamaker although more precise treatments now exist (54).

The parameter V_R decreases exponentially with separation distance having a range about equal to κ^{-1} while V_A decreases inversely with separation distance. Figure 1 shows how van der Waals forces can predominate at small and large interparticle distances. Repulsive forces can predominate at extremely small (Born) and intermediate (electric double layer) separation distances. If the colloidal species are charged and have an interfacial potential of ~25–50 mV, the DLVO model predicts for binary particle interactions that a substantial repulsive potential energy barrier will inhibit the close approach of the particles, thereby stabilizing them against aggregation (V_{max} in Fig. 1). The primary maximum usually ensures stability, if its magnitude (V_{max}) exceeds the range 10–15 kT; smaller barriers lead to irreversible aggregation in the primary minimum (7,8,11,31,35,63,64). The secondary minimum (V_{min}) can promote a loose, easily reversible aggregation of particles, if its magnitude is on the order of 10 kT or more (54). In clay colloids, this is part of the explanation for flocculation as distinguished from coagulation. The overall energy barrier to coagulation in the primary minimum is given by $V_{barrier} = V_{max} - V_{min}$, where the primary minimum represents the potential energy at contact. Stability ensues if the magnitude of $V_{barrier}$ exceeds 10–15 kT and is therefore large compared to the thermal energy of the particles. Note that the primary minimum is a finite number because of the contributions that come into play for very small particle separations, ie, the Born repulsion (54).

The classic DLVO models are for flat planes and spheres, but more complex shapes arise in practice. For example, there will be some distortion of originally spherical emulsion droplets as they approach each other and begin to seriously

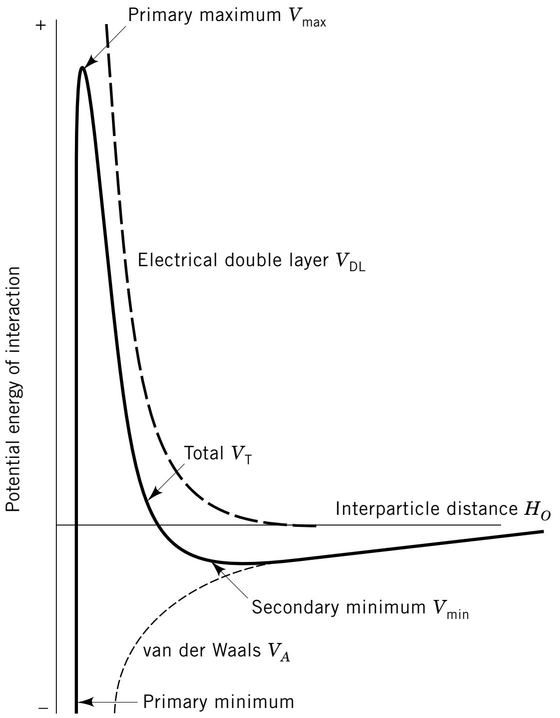

Fig. 1. Potential energies of interaction between two colloidal particles as a function of their distance of separation, for electrical double layers due to surface charge (V_{DL}), London-van der Waals dispersion forces (V_A), and the total interaction (V_T).

interact, causing a flattening. The model has been extended to systems with particles that differ in size, shape, and chemical composition (63), and to those with particles that have an adsorbed layer of ions (7,8,10,11,31,35,63,64), as depicted in Figure 2.

The role of electrostatic repulsion in the stability of suspensions of particles in nonaqueous media is not entirely clear. In attempting to apply DLVO theory it can be difficult to judge the electrical potential at the surface, the appropriate Hamaker constant, and the ionic strength to be used for the nonaqueous medium. The ionic strength will be low so the electric double layer will be thick, the electric potential will vary slowly with separation distance, and so will the net electric potential as the double layers overlap. As a result the repulsion between particles can be expected to be weak (70).

Returning to aqueous systems, it will be apparent that the DLVO calculations can become quite involved, requiring considerable foreknowledge about the systems of interest. There are empirical “rules of thumb” that can be used to give a first estimate of the degree of colloidal stability a system is likely to have if the Zeta potential is known. For example, in the case of colloids dispersed in aqueous solutions, one such rule stems from observations that the colloidal particles are quite stable when the Zeta potential is ~30 mV (positive or negative) or more, and quite unstable due to aggregation when the Zeta potential is

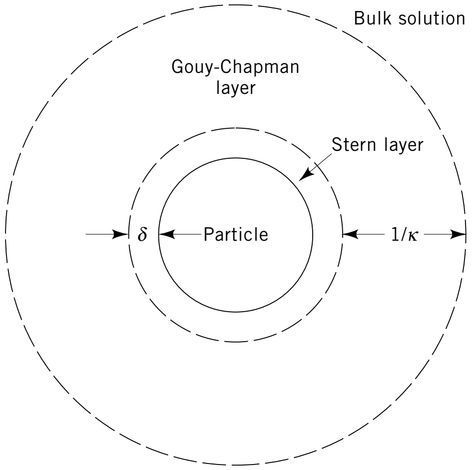

Fig. 2. Schematic diagram of a suspended colloidal particle, showing relative locations of the Stern layer (thickness, δ) that consists of adsorbed ions and the Gouy-Chapman layer (1/κ), which dissipates the excess charge, not screened by the Stern layer, to zero in the bulk solution (69). In the absence of a Stern layer, the Gouy-Chapman layer dissipates the surface charge.

between +5 and −5 mV. The transition from stable dispersion to aggregation usually occurs over a fairly small range of electrolyte concentration. This makes it possible to determine aggregation concentrations, often referred to as critical coagulation concentrations (CCC). The Schulze-Hardy rule summarizes the general tendency of the CCC to vary inversely with the sixth power of the counterion charge number (for indifferent electrolyte). The ability to predict CCCs was the first success of DLVO theory.

7.3. Steric and Hydrodynamic Effects. Additional influences on dispersion stability beyond those accounted for by the DLVO theory, like steric, surface hydration, and hydrodynamic effects have received considerable attention over the past several decades (54). More generally, the stability of a dispersion can be enhanced (protection) or reduced (sensitisation) by the addition of material that adsorbs onto particle surfaces. Protective agents can act in several ways. They can increase double layer repulsion if they have ionisable groups. The adsorbed layers can lower the effective Hamaker constant. An adsorbed film may necessitate desorption before particles can approach closely enough for van der Waals forces to cause attraction.

Long-chain surfactants and natural and synthetic high molecular weight polymers can be adsorbed at the surfaces of dispersed species such that a significant amount of adsorbate extends out from the surfaces. In this situation, an entropy decrease can accompany particle approach providing a short-range stabilization mechanism referred to as steric stabilization. Molecular structure and solvation, adsorption layer thickness and hydrodynamic volume, and temperature determine the effectiveness of steric stabilization (71–75). Finally, the adsorbed material may form such a rigid film that it poses a mechanical barrier to droplet coalescence. Sensitizing agents are the opposite of protective agents.

Again there are several possible mechanisms of action. If the additive is oppositely charged to the dispersed particles then decreased double layer repulsion will result. In some kinds of protecting adsorption a bilayer is formed with the outer layer having lyophilic groups exposed outward; the addition of enough additive to form only the single layer will have lyophobic groups oriented outward with a sensitising effect. If the additive is of long chain length, sometimes a bridging between particles occurs. Colloidal destabilization by electrolytes and bridging flocculation by polymers have been addressed both experimentally and theoretically. Comprehensive reviews on the relevant phenomena that derive from soluble and adsorbed polymers are available (71–75).

Oilfield W/O emulsions may be stabilized by the presence of a protective film around the water droplets. Such a film can be formed from the asphaltene and resin fractions of the crude oil. When drops approach each other during the process of aggregation, the rate of oil film drainage will be determined initially by the bulk oil viscosity, but within a certain distance of approach the interfacial viscosity becomes important. A high interfacial viscosity will significantly retard the final stage of film drainage and promote kinetic emulsion stability. If the films are viscoelastic, then a mechanical barrier to coalescence will be provided, yielding a high degree of emulsion stability (76,77).

Another example can be found in the field of water and wastewater treatment. Water treatment, whether for drinking water or for disposal of industrial wastes involves the removal of suspended solids usually silt, clay, and organic matter. The electric charge on the solids is often sufficiently negative to yield a stable dispersion that settles slowly and is difficult to filter. The solution to this problem is to reduce the Zeta potential to values that permit rapid coagulation increasing both sedimentation and filterability. A first step toward coagulating the suspension might be to add aluminum sulfate (alum), from which the trivalent aluminum ions will have a powerful effect on the Zeta potential (according to the Schulze-Hardy rule). Figure 3**a** shows an example of this effect. In practice,

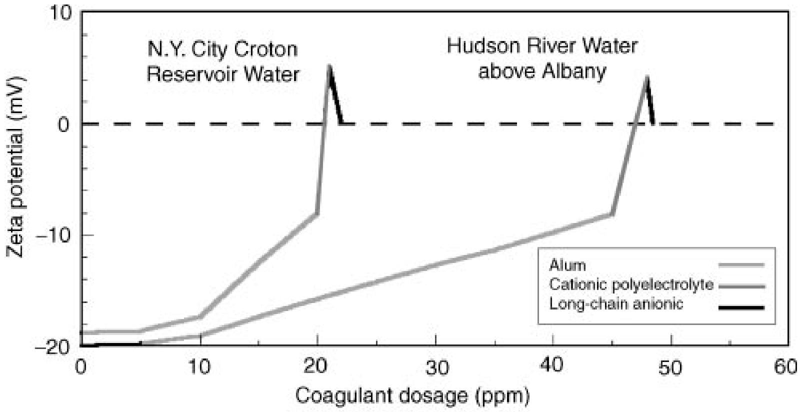

Fig. 3. Illustration of Zeta potentials and coagulation of solids in New York City water treatment through sequential additions of aluminum sulfate (alum), cationic polyelectrolyte, and anionic polymer. [Adapted from reference (78). Used with permission, L.A. Ravina, Zeta-Meter, Inc., Staunton, Va.]

however, the alum required to reduce the Zeta potential to below about -10 mV or so reduces the solution pH too much (unreacted alum becomes carried to other parts of the plant and forms undesirable precipitates). A second step can be introduced, in which a cationic polyelectrolyte is added to reduce the Zeta potential to about zero without changing the pH. As a final step a high molecular weight anionic polymer may be added (MW 500,000–1,000,000, or more) whose molecules can bridge between agglomerates yielding very large, rapid settling flocs. Figure 3**b** shows how two New York water samples were treated in this way.

8. Kinetic Properties

The best experimental technique for monitoring colloid stability is usually dictated by the nature of the specific colloidal material and the dispersing medium. In principle, any distinctive physical property of the colloidal system in question can be used, at least empirically, to monitor changes in the dispersed state. The more complex a system is (chemically or with respect to its particulate heterogeneity), the less likely it is that a single property uniquely and completely describes changes in the colloidal state. Aggregation and/or coalescence of colloidal material can be monitored by a wide variety of techniques including light scattering, neutron scattering, microscopy, rheology, conductivity, filtration, sedimentation, and electrokinetics.

Encounters between colloidal species can occur frequently due to any of Brownian motion, sedimentation, or stirring. If velocity or shear gradients are present and are sufficiently large, the frequency of collisions depends on the volume fraction of solids and the mean velocity gradient. Assuming that sedimentation is slow compared to other collision mechanisms, the overall aggregation rate, $-dN/dt$, is

$$-dN/dt = k_d N^2 + k_s N$$

where N is the number concentration of dispersed species, k_d and k_s are the respective rate constants corresponding to diffusion-controlled and shear-induced collision processes, and the minus sign denotes that the number concentration decreases with time, t. The constants, k_d and k_s, depend on particle–droplet–bubble properties such as: chemical composition of the bulk and surface phases, dielectric constant, dipole moment, size, size distribution, shape, surface charge, solid-phase distribution within particles, and particle anisotropy. Properties of the liquid-dispersing medium that contribute significantly to the values of these rate constants are dielectric constant, dipole moment, and the ability to dissolve electrolytes and polymers, in addition to those properties cited earlier. The k_d term usually dominates in quiescent systems containing submicrometre particles. The full expression for ($-dN/dt$) and its use are treated in more detail elsewhere (7,8,31,79).

Chemical reactions can also affect the k_d and k_s terms and thereby influence or control colloidal stability (80). Pertinent examples are dissolution, precipitation, hydrolysis, precipitation, and chemical complexing. The last reaction may involve either simple species, eg,

$$\mathrm{Al^{3+} + SO_4^{2-} \rightleftarrows AlSO_4^{+}}$$

Table 5. **Representative Solution and Surface Equilibria Influencing Colloidal Stability**

Solution	Surface analogue
Hydrolysis	
$CH_3(CO)OCH_3 + H_2O \rightleftharpoons CH_3(CO)OH + CH_3OH$	$M_2O + H_2O \rightleftharpoons 2\ MOH$
$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$	
$MOH + H_2O \rightleftharpoons MOH_2^+ + OH^-$	
Dissociation	
$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$	$MOH_2^+ \rightleftharpoons MO^- + 2\ H^+$
$C_6H_5(CO)OH \rightleftharpoons C_6H_5(CO)O^- + H^+$	$MOH \rightleftharpoons MO^- + H^+$
Dissolution	
$ZnC_2O_4\ (S) \rightleftharpoons Zn^{2+} + C_2O_4^{2-}$	
$Al(OH)_3(S) + OH^- \rightleftharpoons AlO_2^- + 2H_2O$	
Complexation	
$Cu^{2+} + 4OH^- \rightleftharpoons Cu(OH)_4^{2-}$	$MO^- + Na^+ \rightleftharpoons MO^-Na^+$
$n\text{-}C_{12}H_{25}N(CH_3)_2 + HCl \rightleftharpoons n\text{-}C_{12}H_{25}NH^+(CH_3)_2Cl^-$	$MOH + HCl \rightleftharpoons MOH_2^+Cl^-$

or complicated solutes such as $Al_8(OH)_{20}^{4+}$, chelated metals (77), synthetic and natural polymers (25,71–75), or a variety of surfactants and dispersants (19,81). Many of the possible bulk solution chemical reactions that influence colloidal stability, along with specific sample reactions and their general interfacial analogues, are listed in Table 5.

9. Applications

9.1. General Uses. Diffusion, Brownian motion, sedimentation, electrophoresis, osmosis, rheology, mechanics, interfacial energetics, and optical and electrical properties are among the general physical properties and phenomena that are primarily important in colloidal systems (7,8,27,28,31). Chemical reactivity and adsorption often play important, if not dominant, roles. Any physical and chemical feature may ultimately govern a specific industrial process and determine final product characteristics and colloids are deemed either desirable or undesirable based on their unique physiochemical properties.

Although colloids may be undesirable components in industrial systems, particularly as waste or by-products and, in nature, in the forms of fog and mist, they are desirable in many technologically important processes such as mineral beneficiation and the preparation of ceramics, polymers, composite materials, paper, foods, textiles, photographic materials, drugs, cosmetics, and detergents. The remainder of this section specifies some applications for colloidal solids, liquids, and gases and illustrates how colloids affect many technologically important systems in a positive manner.

9.2. Colloidal Solids. Some uses of solid colloids include reinforcement aids in metals, ceramics, and plastics; as adhesion promoters in paints and thermoplastics; as nucleating agents in cloud seeding; as activated powder catalysts; as thickening agents in gels and slurries; and as abrasives in toothpastes (7,8,27,28,31,37,82–85). When used as reinforcement agents, the colloidal particles may be spherical, angular, fibrillar, or flake-shaped. Alumina and thoria are used to reinforce aluminum and nickel, respectively, by providing obstacles to the movement of dislocations in the metals, and zirconia and silicon carbide to reinforce a variety of ceramics (eg, alumina, silicon nitride, and glass, by inhibiting the propagation and opening of cracks in the matrix). (See COMPOSITE MATERIALS.) Stable but ordered suspensions can be regarded as precursory systems for ordered, prefired, ceramic components; outlets for such systems include various processing techniques such as slip, tape, freeze, pressure, centrifugal, and ultrasonic casting, as well as isostatic, and hot pressing (86,87). Asbestos, crystalline silicas, and organic solids are added to concrete to improve its strength by providing an interlocking particulate structure within the concrete matrix (83); asbestos, various oxides, and carbon black are added to reinforce polymers by inducing a stiffened or high yield matrix (27,28,80–83).

The magnitude of the strengthening often depends on particle shape. Fibrillar fillers are used as discontinuous fibers in metals and plastics, eg, in epoxy resin (80–82) and as whiskers in ceramics (88). Glass and aluminum oxide are common fillers that are occasionally pretreated with a polymeric or metallic coating; silica and various clays are also used. The mechanism by which ceramics and metals are reinforced often involves precipitation of colloidal material during thermal treatment of the matrix composition, eg, TiO_2 in borosilicate glasses designed for enamels (89). Strengthening mechanisms (27,28) include precipitation and dispersion when the reinforcing phase is metallic and the toughened materials are metals or ceramics. When inorganic, nonmetallic ceramics strengthen metals or polymers (45), the mechanism may be dispersion or reinforcement, for example, by cross-linking. Reinforcement implies a higher volume fraction than in dispersion hardening. Fillers can be added not only to improve mechanical properties such as impact strength, fracture toughness, and tensile strength of structural ceramics, but also to enhance optical properties, as is done for colored glasses containing colloidal gold or crystalline, chromium-based oxides.

Particle suspensions have long been of great practical interest because of their widespread occurrence in everyday life. Some important kinds of familiar suspensions include those occurring in foods (batters, puddings, sauces), pharmaceuticals (cough syrups, laxative suspensions), household products (inks, paints, "liquid" waxes) and the environment (suspended lake and river sediments, sewage). In the petroleum industry alone, suspensions may be encountered throughout each of the stages of petroleum recovery and processing, including migrating fine solid suspensions during secondary and enhanced oil recovery, dispersions of asphaltenes in crude oils, produced (well-head) solids in oil recovery, drilling muds, well stimulation and fracturing suspensions, well cementing slurries, and oilfield surface treatment facility sludges.

Other applications of colloidal solids include the preparation of rigid, elastic and thixotropic gels (80–82), aerogel-based thermal insulators (81), and surface coatings (25,27,28,81). Commercial uses of silica gel and sol–gel processing (90) often focus on rigid gels having 20–30 vol% SiO_2. The principal interparticulate forces in a rigid gel are chemical and irreversible, and the colloid improves the gel's mechanical strength. Elastic gels are commonly associated with cellophane, rubber, cellulosic fibers, leather, and certain soaps. Many thixotropic gels and surface coatings contain colloidal solids, eg, clays, alumina, ferric oxide, titania, silica, and zinc oxide. Consumer and industrial pastes belong to this category; putty, dough, lubricating grease, toothpaste, and paint are some examples.

9.3. Colloidal Liquids. These fluids are commonly used in the form of emulsions by many industries. Permanent and transient antifoams consisting of an organic material, eg, polyglycol, oils, fatty materials, or silicone oil dispersed in water, is one application (10,91,92) that is important to a variety of products and processes: foods, cosmetics, pharmaceuticals, pulp and paper, water treatment, and minerals beneficiation. Other emulsion products (see Table 2) include foods, insecticides and herbicides, polishes, drugs, biological systems, asphalt paving emulsions, personal care creams and lotions, paints, lacquers, varnishes, and electrically and thermally insulating materials.

Emulsions may be encountered throughout all stages of the process industries. For example, in the petroleum industry both desirable and undesirable emulsions permeate the entire production cycle, including emulsion drilling fluid, injected or *in situ* emulsions used in enhanced oil recovery processes, wellhead production emulsions, pipeline transportation emulsions, and refinery process emulsions (13). Such emulsions may contain not just oil and water, but also solid particles and even gas, as occur in the large Canadian oil sands mining and processing operations (13–15).

Some emulsions are made to reduce viscosity so that an oil can be made to flow. Emulsions of asphalt, a semisolid variety of bitumen dispersed in water, are formulated to be both less viscous than the original asphalt and stable so that they can be transported and handled. In application, the emulsion should shear thin and break to form a suitable water-repelling roadway coating material. Another example of emulsions that are formulated for lower viscosity with good stability are those made from heavy oils and intended for economic pipeline transportation over large distances. Here again the emulsions should be stable for transport but will need to be broken at the end of the pipeline.

Some special problems arise at sea, when crude oil is spilled on the ocean a slick is formed that spreads out from the source with a rate that depends on the oil viscosity. With sufficient energy an O/W emulsion may be formed, which helps disperse oil into the water column and away from sensitive shorelines. Otherwise, the oil may pick up water to form a W/O emulsion, or mousse ("chocolate mousse"). These mousse emulsions can have high water contents and have very high viscosities, and with weathering, they can become semisolid and considerably more difficult to handle. The presence of mechanically strong films makes it hard to get demulsifiers into these emulsions, so they are hard to break.

Deemulsification, ie, the breaking of emulsions, is an important process, with the oil industry being a common one in which the process is often critical. The stability of emulsions is often a problem. Demulsification involves two steps. First, there must be agglomeration or coagulation of droplets. Then, the agglomerated droplets must coalesce. Chemical and particulate agents that displace the surfactant and permit an unstabilized interface to form are used for this purpose.

Only after these two steps can complete phase separation occur. It should be realised that either step can be rate determining for the demulsification process. This is a large subject in its own right; see references (13,16,91–93).

Other common applications of colloidal liquids include liquid aerosols, such as those occurring in the areas of environment (fog, mist, cloud, smog), agriculture (crop sprays), manufacturing (paint sprays), medicine (nasal sprays) and personal care (hair spray).

9.4. Colloidal Gases. Fluid foams are commonplace in foods, shaving cream, fire-fighting foam, mineral flotation, and detergents (10,65,94–96). Thus, in view of the fact that the concentration of bubbles greatly affects the properties of foams, the production, dispersion, and maintenance of colloidal gas bubbles are basic to foams and related materials. Often, natural and synthetic soaps and surfactants are used to make fluid foams containing colloidal gas bubbles. These agents reduce the interfacial tension and, perhaps, increase the viscosity at the gas–liquid interface, making the foam stable. Also, some soluble proteins that denature upon adsorption or with agitation of the liquid phase can stabilize foams by forming insoluble, rigid layers at the gas–liquid interface (91).

A class of enhanced oil recovery processes involves injecting a gas in the form of a foam. Suitable foams can be formulated for injection with air–nitrogen, natural gas, carbon dioxide, or steam (14,16). In a thermal process, when a steam foam contacts residual crude oil, there is a tendency to condense and create W/O emulsions. On the other hand, in a nonthermal process, the foam may emulsify the oil itself (now as an O/W emulsion), which is then drawn up into the foam structure; the oil droplets eventually penetrate the lamella surfaces, destroying the foam (14).

Microfoams (also termed colloidal gas aphrons) comprise a dispersion of aggregates of very small foam bubbles in aqueous solution. They can be created by dispersing gas into surfactant solution under conditions of very high shear. The concept is that, under the right conditions of turbulent wave break-up, one can create a dispersion of very small gas bubbles, each surrounded by a bimolecular film of stabilizing surfactant molecules. Under ambient conditions the bubble diameters are typically in the range 50–300 μm. There is some evidence that such microfoams tend to be more stable than comparable foams that do not contain the bimolecular film structure (97–99). Some interesting potential applications have been reported: soil remediation (98,100–103) and reservoir oil recovery (95,104,105), but the literature for these applications is sometimes inconsistent; more work needs to be done in this area.

Some agents will act to reduce the foam stability of a system (termed foam breakers or defoamers) while others can prevent foam formation in the first place (foam preventatives, foam inhibitors). There are many such agents, Kerner (65) describes several hundred different formulations for foam inhibitors and foam breakers. In all cases, the cause of the reduced foam stability can be traced to changes in the nature of the interface, but the changes can be of various kinds. The addition to a foaming system of any soluble substance that can become incorporated into the interface may decrease dynamic foam stability if the substance acts in any combination of: increase surface tension, decrease surface elasticity, decrease surface viscosity or decrease surface potential. Such effects may be caused by a cosolubilization effect in the interface or by a partial or even complete replacement of the original surfactants in the interface. Some branched, reasonably high molecular mass alcohols can be used for this purpose. Not being very soluble in water they tend to be adsorbed at the gas–liquid interface, displacing foam promoting surfactant and breaking or inhibiting foam. Alternatively, a foam can be destroyed by adding a chemical that actually reacts with the foam-promoting agent(s). Foams may also be destroyed or inhibited by the addition of certain insoluble substances such as a second liquid phase or a solid phase. Antifoaming and defoaming represent a large subject on their own [see (106,107)].

Other common applications of colloidal gases include solid foams, such as those occurring in the areas of food (leavened breads), geology (pumice stone, zeolites), manufacturing (polystyrene foam, polyurethane foam), and personal care (synthetic sponges). Solid foams such as polyurethane foam contain dispersed gas bubbles that are often produced via viscoelastic polymer melts within which gas, eg, carbon dioxide, bubbles are nucleated (66).

10. Chemical and Surface Analysis

Any classical wet-chemical analyses or instrumental techniques that are routinely used to analyze the bulk composition of solids and liquids are, in principle, also suitable for colloids. The available instrumental methods range, eg, from spectrographic analysis for chemical composition, which is limited to crude estimates for impurities, to Raman spectroscopic identification of chemical functionalities, which can be very accurate (see SPECTROSCOPY, OPTICAL). These techniques can also be used to analyze adsorbed layers if they can be quantitatively desorbed and collected for study. Surface-chemical analyses that cannot be conducted using conventional methods designed for bulk materials are usually accomplished by optical, diffraction, and spectroscopic techniques; these are often applied under conditions of an ultrahigh vacuum. The spectroscopies measure the responses of solid surfaces to beams of electrons, ions, neutral species, and photons (see SURFACE AND INTERFACE ANALYSIS). Each spectroscopy has unique attributes (10), making it suitable for certain colloids but unsuitable for others. Although too numerous to list here, descriptions and tabulations of surface techniques and their synonyms and acronyms are given in references (6,10,67,68). A wide range of information can be obtained including surface and adsorbed layer compositions (including heterogeneity); surface morphology, atom packing, and structure; and surface reactions and their kinetics. Advances in these fields continue at a significant rate (see ANALYTICAL METHODS, TRENDS).

11. Hazards of Colloidal Systems

The occurrence of some materials in the form of a colloidal dispersion can introduce or enhance safety hazards. Considering that the dispersion of a material down to colloidal size results in a high specific surface area and colloidal chemical reactivity may differ considerably from that of the identical macroscopic material with less surface area. This is particularly important if the colloidal surface is easily and rapidly oxidized. Dust explosions and spontaneous combustion are potential dangers whenever certain materials exist as finely divided dry matter exposed to oxidizing environments (69,116) (see POWDERS, HANDLING AND COATING PROCESSES, POWDER TECHNOLOGY). Dispersions of charged colloidal particles in nonaqueous media occur throughout the petroleum industry. The flow of petroleum fluids in tanks or pipelines, combined with the low conductivity of the petroleum fluids themselves, can allow the build-up of large potential gradients and a separation of charges. Sufficient charging for there to be an electrostatic discharge can cause an explosion (70).

Health problems can be caused by solids and liquids suspended in air or water. Specific potential hazards have been associated with a diverse spectrum of colloidal materials, including chemicals, coal, minerals, metals, pharmaceuticals, plastics, and wood pulp. Limits for human exposure for many particulate, hazardous materials are published (67,68). The effects of the colloidal solids and liquids that comprise smog are widespread and well known. Liquid droplets may also constitute a hazard; eg, smog can contain sulfuric acid aerosols. Elements such as lead, zinc, and vanadium, that are released into the atmosphere as vapors, can subsequently condense or be removed as solid particulates by rain (108,109). Similarly, exposure to airborne pollutants found indoors and in confined spaces, many of which are particulates or microbes of colloidal size, can lead to complex physiological responses. This hazard ranges from short-term allergic reactions (eg, pollen and household dust causing asthma and hay fever) to long term, possibly fatal effects (eg, silicosis, asbestosis, and black lung disease).

There is a need to understand the environmental properties and risks associated with any large volume chemicals. The mass of surfactants that could ultimately be released into the environment, for example, is significant. A 1995 estimate of the global use of linear alkylbenzenesulfonates, alcohol ethoxylates, alkylphenol ethoxylates, alcohol sulfates, and alcohol ether sulfates totaled 3 million tonnes (110). Surfactant usage in industry will probably increase as new applications are found. The toxicity and persistence of surfactants is now fairly predictable for a variety of environmental situations (108,111,112) and although surfactants are not generally viewed as a serious threat to the environment (108) they can exhibit considerable toxicity to aquatic organisms. In addition to products, many industries produce waste containing significant amounts of suspended matter for which treatment incurs significant technological challenges and costs (113–115). Trace metals that are commonly found as suspended matter in the chemical form of hydrous oxides and other insoluble matter are tabulated elsewhere (69,116). Large fractions of readily hydrolyzable metals exist as adsorbed species on suspended (colloidal) solids in fresh and marine water systems and can also be anticipated to exist in industrial wastewater. Continued research is needed to understand the health hazards linked to colloidal pollutants.

12. Emerging Areas in Colloid Science

Advances on the theoretical front continue to be aided by advances in bulk and surface analytical technology (composition) and in physical surface characterization technology (topology, structure, and forces). Applications of atomic force microscopy in particular continue to expand into diverse areas, including magnetic force microscopy (117).

Much is known about colloids, their formation, properties and applications, but considerably more surely remains unknown. In particular, the full potential to control colloids is not presently realized. There are several types of mixed colloids that are only poorly understood. For example, the properties of colloids in which more than one type of colloidal particle is dispersed may be dominated by the behavior of the minor dispersed phase component. The nature and properties of colloids within colloids, such as suspended solids in the dispersed phase of an emulsion, or emulsified oil within the aqueous lamellae of a foam, are only beginning to be understood (13–15).

Nanotechnology refers to the production of materials and structures in the 0.1–100 nm range by any of a variety of nanoscale physical and chemical methods (see NANOTECHNOLOGY). This is a rapidly growing area of materials science. As the size range indicates, there is an overlap between nanotechnology and colloid science since they share some similarity of scale, both dealing with matter having dimensions of tens and hundreds of nm. Although many areas of nanotechnology do not directly deal with colloidal dispersions, such as nanotubes, nanoelectronic devices, other areas do, eg, the use of colloidal ink dispersions in robocasting to build near-nanometer scale three-dimension structures. Examples of work at the interface between these fields is provided by current research aimed at controlling the solubility of nanotubes (118), and in the fabrication of nano-engineered films on colloidal particles (119).

Smart colloids are colloidal dispersions for which certain properties, such as size and structure, can be altered by changing an external influence, such as temperature. Example: cross-linked polymer gels of poly(*N*-isoproplyacrylamide). Such polymer systems can swell or shrink in response to temperature changes, and are also termed “thermo-shrinking polymers.” (See 120–122).

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BIBLIOGRAPHY

“Colloids” in *ECT* 3rd ed., Suppl. Vol., pp. 241–259, by Alan Bleier, Massachusetts Institute of Technology; in *ECT* 4th ed., Vol. 6, pp. 812–840, by Alan Bleier, Oak Ridge National Laboratory; “Colloids” in *ECT* (online), posting date: December 4, 2000, by Alan Bleier, Oak Ridge National Laboratory.

CITED PUBLICATIONS

1. M. Kerker, *J. Colloid Interface Sci* **116**(1), 296 (1987).
2. I. Asimov, *Words of Science and the History Behind Them*, Riverside Press: Cambridge, Mass., 1959.

3. H. Freundlich, *Colloid and Capillary Chemistry*, English translation of 3rd. ed., Methuen, London, 1926.
4. P. Becher, *Dictionary of Colloid and Surface Science*; Dekker, New York, 1990.
5. L. L. Schramm, *The Language of Colloid and Interface Science*, American Chemical Society, Washington, and Oxford University Press, New York, 1993.
6. L. L. Schramm, *Dictionary of Colloid and Interface Science*, John Wiley & Sons, Inc., New York, 2001.
7. D. J. Shaw, *Introduction to Colloid and Surface Chemistry*, 3rd ed., Butterworths, London, 1980.
8. P. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, 3rd. ed., Dekker, New York, 1997.
9. D. Myers, *Surfaces, Interfaces, and Colloids*; 2nd ed., Wiley-VCH, New York, 1999.
10. A. W. Adamson, *Physical Chemistry of Surfaces*; 5th ed., John Wiley & Sons, Inc., New York, 1990.
11. H. R. Kruyt, *Colloid Science, Volume I, Irreversible Systems*, Elsevier, Amsterdam, The Netherlands, 1952.
12. S. P. Parker, ed., *McGraw-Hill Dictionary of Scientific and Technical Terms*, 3rd ed., McGraw-Hill, New York, 1984.
13. L. L. Schramm, ed., *Emulsions: Fundamentals and Applications in the Petroleum Industry*, American Chemical Society, Washington and Oxford University Press, New York, 1992.
14. L. L. Schramm, ed., *Foams: Fundamentals and Applications in the Petroleum Industry*, American Chemical Society, Washington and Oxford University Press, New York, 1994.
15. L. L. Schramm, ed., *Suspensions: Fundamentals and Applications in the Petroleum Industry*, American Chemical Society, Washington, and Oxford University Press, New York, 1996.
16. L. L. Schramm, ed., *Surfactants: Fundamentals and Applications in the Petroleum Industry*, Cambridge University Press, Cambridge, U.K., 2000.
17. S. Lowell and J. E. Shields, *Powder Surface Area and Porosity*, Chapman and Hall, London, 1991.
18. D. Myers, *Surfactant Science and Technology,* VCH, New York, 1988.
19. M. J. Rosen, *Surfactants and Interfacial Phenomena*, 2nd ed., John Wiley & Sons, Inc., New York, 1989.
20. M. El-Nokaly and D. Cornell, eds., *Microemulsions and Emulsions in Foods*, American Chemical Society, Washington, D.C., 1991.
21. R. Beckett, ed., *Surface and Colloid Chemistry in Natural Waters and Water Treatment,* Plenum Press, New York, 1990.
22. H. van Olphen, *An Introduction to Clay Colloid Chemistry*, 2nd ed., Wiley-Interscience, New York, 1977.
23. M. M. Rieger and L. D. Rhein, eds., *Surfactants in Cosmetics*, 2nd ed., Dekker, New York, 1997.
24. E. Dickinson, *An Introduction to Food Colloids*, Oxford University Press, New York, 1992.
25. G. D. Parfitt, ed., *Dispersion of Powders in Liquids*, 3rd ed., Applied Science, London, 1981.
26. S. Ross and I. D. Morrison, *Colloidal Systems and Interfaces*, John Wiley & Sons, Inc., New York, 1988.
27. C. R. Veale, *Fine Powders*, John Wiley & Sons, Inc., New York, 1972.
28. J. K. Beddow, *Particulate Science and Technology*, Chemical Publishing, New York, 1980.

29. M. J. Jaycock and G. D. Parfitt, *Chemistry of Interfaces*, Ellis Horwood, Chichester, U.K., 1981.
30. G. D. Parfitt and K. S. W. Sing, eds., *Characterization of Powder Surfaces*, Academic Press, New York, 1976.
31. R. D. Vold and M. J. Vold, *Colloid and Interface Chemistry*, Addison-Wesley, Reading, Mass., 1983.
32. R. J. Mikula and V. A. Munoz, in L. L. Schramm, ed., *Surfactants: Fundamentals and Applications in the Petroleum Industry*, Cambridge University Press, Cambridge, U.K., 2000, pp. 51–77.
33. L. L. Schramm, S. M. Kutay, R. J. Mikula, and V. A. Munoz, *J. Petrol. Sci. Eng.* **23**, 117 (1999).
34. M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation*, Academic Press, New York, 1969.
35. R. J. Hunter, *Zeta Potential in Colloid Science*, Academic Press, New York, 1981.
36. A. J. Babchin, R. S. Chow, and R. P. Sawatzky, *Adv. Colloid Interface Sci.* **30**, 111 (1989).
37. C. Orr, *Particulate Technology*, Macmillan, New York, 1966.
38. Th. G. M. van de Ven, *Colloidal Hydrodynamics*, Academic Press, Inc., London, 1989.
39. R. W. Whorlow, *Rheological Techniques*, Ellis Horwood, Chichester, U.K., 1980.
40. J. R. Van Wazer, J. W. Lyons, K. Y. Kim, and R. E. Colwell, *Viscosity and Flow Measurement*, John Wiley & Sons, Inc., New York, 1963.
41. C. C. Mill, ed., *Rheology of Disperse Systems*, Pergamon Press, Inc., Elmsford, New York, 1959.
42. A. G. Fredrickson, *Principles and Applications of Rheology*, Prentice-Hall, Englewood Cliffs, N.J., 1964.
43. K. Walters, *Rheometry: Industrial Applications*, Research Studies Press, New York, 1980.
44. H. A. Barnes and S. A. Holbrook, In P. Ayazi Shamlou, ed., *Processing of Solid–Liquid Suspensions*, Butterworth Heinemann, Oxford, U.K., 1993, pp. 222–245.
45. L. E. Murr, *Interfacial Phenomena in Metals and Alloys*, Addison Wesley, London, 1975.
46. W. D. Harkins and A. E. Alexander, in A. Weissberger, ed., *Physical Methods of Organic Chemistry*, Interscience, New York, 1959, pp. 757–814.
47. J. Leja, *Surface Chemistry of Froth Flotation*, Plenum Press, New York, 1982.
48. L. L. Schramm, *J. Can. Petrol. Technol.* **28**, 73 (1989).
49. J. F. Padday, in E. Matijevic, ed., *Surface and Colloid Science*, Vol. 1, Wiley-Interscience, New York, 1969, pp. 101–149.
50. C. A. Miller and P. Neogi, *Interfacial Phenomena Equilibrium and Dynamic Effects*, Dekker, New York, 1985.
51. A. I. Rusanov and V. A. Prokhorov, *Interfacial Tensiometry*, Elsevier, Amsterdam, The Netherlands, 1996.
52. L. W. Lake, *Enhanced Oil Recovery*, Prentice Hall, Englewood Cliffs, N.J., 1989.
53. P. Mukerjee and K. J. Mysels, *Critical Micelle Concentrations of Aqueous Surfactant Systems*, NSRDS-NBS 36, National Bureau of Standards, Washington, D.C., 1971.
54. J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed., Academic Press, New York, 1992.
55. G. Cevc and D. Marsh, *Phospholipid Bilayers*, John Wiley & Sons, Inc., New York, 1987; D. Marsh, *Handbook of Lipid Bilayers*, CRC Press, Boca Raton, Fla., 1990.
56. R. Miller and G. Kretzschmar, *Adv. Colloid Interface Sci.* **37**, 97 (1991).
57. J. Prost and F. Rondelez, *Nature (London)* **350**, 11 (1991).

58. D. O. Shah, ed., *Macro-and Microemulsions: Theory and Applications*, American Chemical Society, Washington, D.C., 1985.
59. D. A. Sabatini, R. C. Knoz, and J. H. Harwell, eds., *Surfactant-Enhanced Subsurface Remediation Emerging Technologies*, American Chemical Society, Washington, D.C., 1995.
60. M. El-Nokaly and D. Cornell, eds., *Microemulsions and Emulsions in Foods*, American Chemical Society, Washington, D.C., 1991.
61. A. M. James, in R. J. Good and R. R. Stromberg, eds., *Surface and Colloid Science*, Vol. 11, Plenum, 1979, pp. 121–186.
62. A. J. Babchin, R. S. Chow, and R. P. Sawatzky, *Adv. Colloid Interface Sci.* **30**, 111 (1989).
63. B. V. Derjaguin and L. D. Landau, *Acta Physiochem. URSS* **14**, 633 (1941); B. V. Derjaguin, N. V. Churaev, and V. M. Miller, *Surface Forces*, Consultants Bureau, New York, 1987.
64. E. J. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, The Netherlands, 1948.
65. H. T. Kerner, *Foam Control Agents*, Noyes Data Corp., Park Ridge, New Jersey, 1976.
66. F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd ed., Wiley-Interscience, New York, 1971.
67. D. P. Woodruff and T. A. Delchar, *Modern Techniques of Surface Science*, Cambridge University Press, New York, 1986.
68. G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, Wiley-Interscience, New York, 1994.
69. S. Budavari, M. J. O'Neil, A. Smith, P. E. Heckelman, and J. f. Kinneary, *The Merck Index*, 11th ed., Merck, Rahway, New Jersey, 1989, p. MISC-53.
70. I. D. Morrison, *Colloids Surfaces* **71**, 1 (1993).
71. T. Sato and R. Ruch, *Stabilization of Colloidal Dispersions by Polymer Adsorption*, Marcel Dekker, New York, 1980.
72. Th. F. Tadros, ed., *The Effect of Polymers on Dispersion Properties*, Academic Press, London, 1982.
73. Y. S. Lipatov and L. M. Sergeeva, *Adsorption of Polymers*, Halsted, New York, 1974.
74. C. A. Finch, ed., *Chemistry and Technology of Water-Soluble Polymers*, Plenum Press, New York, 1983.
75. B. Vincent, in Th. F. Tadros, ed., *Solid/Liquid Dispersions*, Academic Press, Inc., 1987, pp. 147–162.
76. R. J. R. Cairns, D. M. Grist, and E. L. Neustadter, in A. L. Smith, ed., *Theory and Practice of Emulsion Technology*, Academic Press, New York, 1976, pp. 135–151.
77. T. J. Jones, E. L. Neustadter, and K. P. Whittingham, *J. Can. Petrol. Technol.* **17**, 100–108 (1978).
78. Zeta-Meter applications brochures, Zeta-Meter Inc., New York, 1982.
79. W. Stumm and J. J. Morgan, *Aquatic Chemistry*, 2nd ed., John Wiley & Sons, Inc., New York, 1981.
80. E. Matijević, in K. J. Mysels, C. M. Samour, and J. H. Hollister, eds., *Twenty Years of Colloid and Surface Chemistry*, American Chemical Society, Washington, D.C., 1973, p. 283.
81. *McCutcheon's Detergents and Emulsifiers*, MC Publ. Co., Glen Rock, N.J., 1980.
82. Z. D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 2nd ed., John Wiley & Sons, Inc., New York, 1977.
83. J. E. Gordon, *The New Science of Strong Materials*, 2nd ed., Princeton University Press, Princeton, N.J., 1976.

84. A. G. Guy, *Essentials of Materials Science*, McGraw-Hill Book Co., Inc., New York, 1976.
85. S. J. Lefond, ed., *Industrial Minerals and Rocks*, 4th ed., American Institute of Mineralogy and Metallurgy, Petroleum Engineering, Inc., New York, 1975.
86. F. Y. Wang, *Ceramic Fabrication Processes*, Academic Press, Inc., New York, 1976.
87. J. S. Reed, *Introduction to the Principles of Ceramic Processing*, Wiley-Interscience, New York, 1988.
88. A. Kelly and R. B. Nicholson, eds., *Strengthening Methods in Crystals*, Applied Science Publishing, London, 1971.
89. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2nd ed., Wiley-Interscience, New York, 1976.
90. C. J. Brinker, and G. W. Sherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*, Academic Press, San Diego, Calif., 1990.
91. C. G. Sumner, *Clayton's The Theory of Emulsions and Their Technical Treatment*, 5th ed., Blakiston, New York, 1954.
92. K. J. Lissant, *Demulsification. Industrial Applications*, Dekker, New York, 1983.
93. P. Becher, *Emulsions: Theory and Practice*, 3rd ed., American Chemical Society and Oxford University Press, New York, 2001.
94. D. H. Everett, *Basic Principles of Colloid Science*, Royal Society of Chemistry, London, 1988.
95. A. K. Mirzadjanzade, I. M. Ametov, A. A. Bokserman, and V. P. Filippov, in *Proceedings, 7th European IOR Symp.*, Moscow, Russia, 1993, pp. 27–29.
96. E. Dickinson, ed., *Food Emulsions and Foams*, Royal Society of Chemistry, London, 1987.
97. F. Sebba, *J. Colloid Interface Sci.* **35**, 643 (1971).
98. F. Sebba, *Foams and Biliquid Foams-Aphrons*, John Wiley & Sons, Inc., New York, 1987.
99. F. Sebba, *Chem. Ind.* **4**, 91 (1985).
100. D. Roy, K. T. Valsaraj, and A. Tamayo, *Sep. Sci. Technol.* **27**, 1555 (1992).
101. D. Roy, K. T. Valsaraj, W. D. Constant, and M. Darji, *J. Hazardous Mat.* **38**, 127 (1994).
102. D. Roy, R. R. Kommalapati, K. T. Valsaraj, and W. D. Constant, *Water Res.* **29**, 589 (1995).
103. D. Roy, S. Kongara, and K. T. Valsaraj, *J. Hazardous Mat.* **42**, 247 (1995).
104. M. V. Enzien, D. L. Michelsen, R. W. Peters, J. X. Bouillard, and J. R. Frank, in *Proceedings, 3rd Int. Symp. In-Situ and On-Site Reclamation*, San Diego, Calif., 1995, pp. 503–509.
105. A. K. Mirzadjanzade, I. M. Ametov, A. O. Bogopolsky, R. Kristensen, U. N. Anziryaev, S. V. Klyshnikov, A. M. Mamedzade, and T. S. Salatov, in *Proceedings, 7th European IOR Symp.*, Moscow, Russia, 1993, pp. 469–473.
106. J. J. Bikerman, *Foams*, Springer-Verlag, New York, 1973.
107. J. J. Bikerman, *Foams, Theory and Industrial Applications*, Reinhold, New York, 1953.
108. A. E. Martell, *Pure Appl. Chem.* **44**, 81 (1975).
109. F. T. Mackenzie and R. Wollast, in E. D. Goldberg, ed., *The Sea*, Vol. 6, Wiley-Interscience, New York, 1977, p. 739.
110. L. N. Britton, *J. Surf. Det.* **1**, 109–117 (1998).
111. L. N. Britton, in L. L. Schramm, ed., *Surfactants, Fundamentals and Applications in the Petroleum Industry*, Cambridge University Press, Cambridge, U.K., 2000, pp. 541–565.
112. C. M. Maddin, Preprint, *International Conference Health, Safety and Environment*, Society of Petroleum Engineers, Richardson, Tex., SPE paper 23354, 1991.

113. J. Wei, T. W. F. Russel, and M. W. Swartzlander, *The Structure of the Chemical Processing Industries*, McGraw-Hill, New York, 1979.
114. M. P. Freeman and J. A. Fitzpatrick, eds., *Physical Separations*, Engineering Foundation, New York, 1980.
115. A. J. Rubin, ed., *Chemistry of Wastewater Technology*, Ann Arbor Sci., Ann Arbor, Mich., 1978.
116. R. C. Weast and M. J. Astle, eds., *Handbook of Chemistry and Physics*, 62nd ed., Chemical Rubber Company, Boca Raton, Fla., 1981, p. D-101.
117. M. Rasa, B. W. M. Kuipers, and A. P. Philipse, *J. Colloid Interface Sci.* **250**, 303–315 (2002).
118. R. Dagani, *Chem. Eng. News* **80**(28), 38 (2002).
119. G. B. Sukhorukov, in D. Möbius and R. Miller, eds., *Novel Methods to Study Interfacial Layers*, Elsevier, New York, 2001, pp. 383–414.
120. E. S. Matsuo and T. Tanaka, *Nature (London)* **358**, 482 (1992).
121. M. Snowden, *Science Spectra.* **6**, 32 (1996).
122. M. Snowden, M. J. Murray, and B. Z. Chowdry, *Chem. Ind.*, 15 July, 531 (1996).

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