Kirk-Othmer Encyclopedia of Chemical Technology.

POWDERS, HANDLING, DISPERSION OF POWDERS IN LIQUIDS

Suspensions (dispersions or slurries) of powders in liquids (vehicles) are involved in many commercial processes and products, eg, inks, paints, asphalt, and pharmaceuticals (qv). Surface forces control the flow and sedimentation characteristics of particles whose diameters are 0.02–200 μm. The preparation of a dispersion is not a trivial matter; special equipment and chemicals have been developed to facilitate the steps of dispersion, ie, wetting the external surface of the particles, breaking up clumps, and preventing reagglomeration. A surfactant (surface-active agent) is a chemical that concentrates in the interfacial region between the solid and the liquid. A surfactant that creates an interparticle repulsion large enough to overcome normal interparticle attractions may be called a dispersant for that particular solid–liquid pair.

Several factors have combined to improve the capabilities of dispersion science. Improved methods for polymer synthesis have led to a proliferation of highly effective dispersants; larger and faster computers have facilitated modeling details of interactions between particles, dispersants, and the liquid; and highly sophisticated instruments are available to measure particle–particle and particle–dispersant interactions. This article describes the technical bases and practical aspects of the three stages of dispersing a powder in a liquid: (*1*) wetting the powder into the liquid, (*2*) deagglomerating the wetted clumps, and (*3*) preventing reagglomeration (flocculation). Modification of the surface and use of additives (dispersants) to prevent reagglomeration are also described (1–7) (see Colloids; Dispersants; EMulsions; Surfactants).

1. Wetting Powders into Liquids

The atoms and molecules at the interface between a liquid (or solid) and a vacuum are attracted more strongly toward the interior than toward the vacuum. The material parameter used to characterize this imbalance is the interfacial energy density γ, usually called surface tension. It is highest for metals ($\leq$1 J/m^2) (1 J/m^2 = N/m), moderate for metal oxides ($\leq$0.1 J/m^2), and lowest for hydrocarbons and fluorocarbons (0.02 J/m^2 minimum) (4). The International Standards Organization describes well-established methods for determining surface tension, eg, ISO 304 for liquids containing surfactants and ISO 6889 for two-liquid systems containing surfactants.

1.1. Fundamentals

1.1.1. Contact Angle

When a drop of liquid is placed on a flat, horizontal, solid surface it spreads out until it attains an equilibrium shape with a fixed angle from the solid surface to the gas surface (through the liquid). This is the contact angle. Figure 1 shows how the contact angle is related to the balance of surface tension forces at the drop perimeter where the three phases meet the shoreline. In cases where neither gas nor solid dissolves in the liquid and there are no surface-active solutes present, the contact angle is related to the interfacial energy densities at

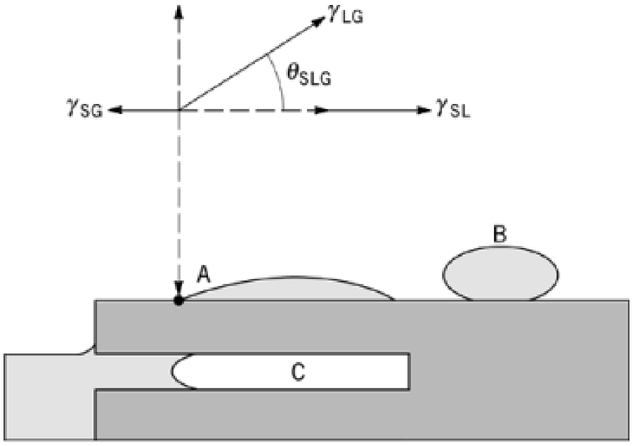

Fig. 1. Contact angles. The shapes of drops that are A, wetting and B, nonwetting with respect to the solid (■), and C, penetration of a wetting liquid into a pore to compress the gas (□) inside. The vector diagram shows the balance of forces at the perimeter of the liquid drop on the solid plate.

the solid–gas (SG), solid–liquid (SL), and liquid–gas (LG) interfaces by the Young-DuPre equation (8):

$$\gamma_{LG}\cos\theta_{SLG} + \gamma_{SL} = \gamma_{SG} + \Pi \qquad (1)$$

The surface film or spreading pressure, Π, is used to account for the change in gas–solid interaction caused by adsorption of vapor evaporated from the liquid. A liquid is called wetting if the contact angle from solid to liquid through gas, θ_{SLG}, $<90^\circ$ and nonwetting if $\theta_{SLG} > 90^\circ$. Because it is easier to measure the contact angle than to measure γ_{SL}, the Young-DuPre equation is usually used to determine γ_{SL} from a knowledge of the other parameters. This expression was derived for pure liquid and solid phases, so more complex expressions must be used if the solid is even slightly soluble in the liquid, if the solid has soluble impurities, or if the liquid contains surfactants or other solutes.

1.1.2. Wetting Single Particles

When a particle is submerged in a liquid, the work of wetting a surface, w, is the change in interfacial energy density times area, a, as the solid–gas and liquid–gas interfaces are replaced by a solid–liquid interface.

$$w = a\,[\gamma_{SL} - \gamma_{SG} - \gamma_{LG}] \qquad (2)$$

A buoyant spherical particle of diameter D floating in a liquid which has no tendency to wet, ie, pull the shoreline up, or to reject, ie, push the shoreline down, the solid submerges to a depth d at which the downward force of gravity on the sphere equals the upward buoyancy force of the displaced liquid. This occurs when

$$\rho_S V_{SPH} = \rho_L V_{SUBM} \qquad (3)$$

where the volume, V, of the sphere is $V_{\mathrm{SPH}} = (\pi/6)D^3$. For $d < D/2$, the volume of the submerged portion is as follows:

$$V_{\mathrm{SUBM}} = \frac{\pi d}{6D}\left[D^3 - (D-2d)^3\right] \qquad (4)$$

For $d > D/2$ the volume of the submerged portion is as follows:

$$V_{\mathrm{SUBM}} = V_{\mathrm{SPH}} - \frac{\pi}{3}\left(1 - \frac{d}{D}\right)\left[D^3 - (2d-D)^3\right] \qquad (5)$$

If the liquid wets the solid, surface tension pulls the solid down farther into the liquid. Centrifugal force does not affect the depth of submergence because it increases the buoyancy force as much as it increases the settling force. A nonbuoyant particle submerges fully unless the liquid is sufficiently nonwetting, eg, 0.2-mm polytetrafluoroethene [9002-84-0] particles in water. Here centrifugal force can be used to overcome the rejection and force submergence. The force of surface tension along the microdepressions in a rough surface causes wicking of a drop of wetting liquid so that it spreads farther than it would on a smooth horizontal surface. Rejection of a nonwetting liquid from the microdepressions keeps it from spreading as far as it would on a smooth surface (9).

1.1.3. Wetting Clumps

The density of a clump, ρ_{CLUMP}, is related to the fraction of void space within the perimeter of the clump (porosity), ϵ_{PORE}, by

$$\rho_{\mathrm{CLUMP}} = (1 - \epsilon_{\mathrm{PORE}})\,\rho_{\mathrm{S}} + \epsilon_{\mathrm{PORE}}\rho_{\mathrm{G}} \qquad (6)$$

If the liquid is nonwetting it does not enter the pores to displace the gas unless the hydrostatic pressure, P_{HYDRO}, at the bottom of the submerged clump, $P_{\mathrm{HYDRO}} = g\rho_{\mathrm{L}}d$, exceeds the pressure required to drive it into the pores, which for a cylindrical pore is as follows:

$$P_{\mathrm{ANTI}} = \frac{-4}{D_{\mathrm{PORE}}}\gamma_{\mathrm{LG}}\cos\theta_{\mathrm{SLG}} \qquad (7)$$

Gravity, g, or centrifugation rarely provide enough hydrostatic pressure to force liquid into nonwetting pores. If the liquid wets the solid the clump density increases as gas is displaced from the interior. It is best if submersion does not occur until the liquid has completely displaced gas from the pores (Fig. 2). For wetting liquids and pores with average diameter, D_{PORE}, and tortuosity, f_{TORT}, the length, L_{WET}, to which liquid is pulled into a bed of powder by capillary action depends on the viscous drag exerted by the increasing length of pore through which it is flowing as time, t, in seconds increases (10):

$$L_{\mathrm{WET}} = \frac{1}{f_{\mathrm{TORT}}}\left(\frac{D_{\mathrm{PORE}}t\gamma_{\mathrm{LG}}\cos\theta_{\mathrm{SLG}}}{8\eta}\right)^{1/2} \qquad (8)$$

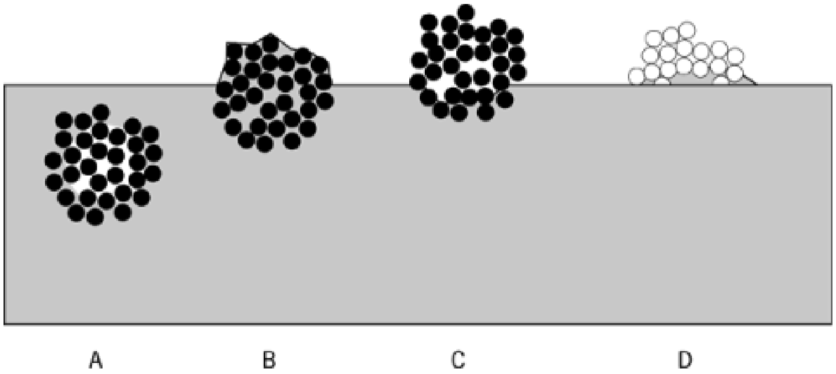

Fig. 2. Problems in wetting: A, liquids that wet the exterior before displacing gas from pores leave gas trapped in the submerged clump; B, fully wetted clumps of buoyant particles do not sink; C, nonwetting liquids do not penetrate and displace gas from pores, so clump remains buoyant and cannot submerge; and D, foam produced from air is drawn under the surface, sheared into small bubbles, and stabilized by the wetting agent.

D_{PORE} is related to ϵ_{PORE}, which is in turn related to the closeness of packing of the powder. The number of particles adjacent to a given particle is represented by n_{ADJ}. The maximum packing density for monosize spheres occurs at hexagonal close packing, where $n_{\text{ADJ}} = 12$ and $\epsilon_{\text{PORE}} = 0.2595$; for cubic packing of monosize spheres, $n_{\text{ADJ}} = 6$ and $\epsilon_{\text{PORE}} = 0.4764$. In a loose network n_{ADJ} approaches 2 and ϵ_{PORE} approaches unity (11). Packing densities higher than hexagonally close-packed spheres (ϵ_{PORE} approaching unity) can be achieved by using spheres that are not monosize or by using nonspherical particles.

If the clump submerges in a wetting liquid before all the gas has escaped, the liquid continues to advance into the pores, compressing the trapped gas, until the gas pressure balances the force pulling the liquid into the pores:

$$P_{\text{TRAP}} = \frac{4}{D_{\text{PORE}}}\gamma_{\text{LG}}\cos\theta_{\text{SLG}} \qquad (9)$$

Complete wetting cannot occur until either the clump is broken up to let the gas escape or the trapped gas dissolves in the liquid. A sudden decrease in hydrostatic pressure can help remove gas trapped in a submerged clump by expanding the bubble volume to break up the clump or extend the bubble past the clump's exterior so that it may escape.

If a wetting agent is present in the liquid, rather than as a pretreatment on the solid, it acts by adsorbing on the solid surface. As the liquid advances through a pore it becomes depleted in wetting agent so that the rate of advance of the meniscus depends on diffusion of fresh wetting agent from the bulk liquid outside the pore. A low molar mass, M, for the wetting agent (WA) gives the highest diffusion coefficient and hence the fastest rate of wet-in, as shown by the diffusion constant, F, for a spherical molecule where N_{AVO} represents the Avogadro constant, k, and T is the Boltzmann constant, absolute temperature in K.

$$F_{\text{WA}} = \frac{kT}{6\pi\eta_{\text{L}}}\left(\frac{4\pi N_{\text{AVO}}}{3M_{\text{WA}}}\right)^{1/3} \qquad (10)$$

1.1.4. Flushing a Dispersion into a Second Liquid

If a dispersion in one liquid is mixed with a second liquid which is immiscible with the first but which preferentially wets the powder, the powder transfers into and becomes dispersed in the second liquid. This process, called flushing, is sometimes used to prepare an oil-based suspension directly from a water-based dispersion. A dispersant may be needed to promote preferential wetting in the second phase. For example, stearic acid [57-11-4] dissolved in dodecane [112-40-3] transfers across a dodecane– water interface to adsorb on the surface of iron(III) oxide [1309-37-1] in the aqueous phase. Adsorption occurs with the acid group anchored on the particle and the alkane chain extending outward, making the coated particle hydrophobic and making its transfer into the dodecane phase energetically favorable (12).

1.2. Practical Matters and Process Equipment

The rate of wet-in may be enhanced by adding a wetting agent to the liquid or by exposing the powder, treated or not, to water or some other vapor. Some powders sold commercially have already been given surface treatments so they readily wet into the liquid used in a particular market application. Selection of a wetting agent can be difficult, because although many surfactants may be effective wetting agents in the laboratory for a given solid–liquid pair, few or none may be acceptable in a commercial formulation for that pair. The wetting agent may interfere with end use behavior, perhaps by altering the surface tension of a film during application or drying.

Gas that is drawn beneath the liquid surface, through a vortex or plunging jet, and enters a high shear region is dispersed into small bubbles which may be stabilized by a surfactant and rise to the surface to form a foam which is hard to dissipate. This is a particular problem when excessive wetting agent is present. Foam can be avoided even in the presence of a foaming agent by preventing air from being drawn beneath the liquid surface during the wet-in process (see Foams).

Figure 3 shows typical design features of commercial equipment to wet powders into liquids. These exploit the factors that lead to rapid wet-in: low gas pressure, high centrifugal force, distribution of powder in a thin and deagglomerated layer on the liquid, and liquid surface refreshing to expose a large area for powder addition. Provision for clear liquid flow down the walls helps prevent scale and encrustation. Scale forms above the liquid level when airborne dust sticks to a wall wetted either by vapor condensation or liquid drawn up the wall by capillary action through previously deposited scale. Encrustation may form near the shoreline in a tank as it alternately wets and recedes due to hydraulic pulses during agitation, then dries near that level.

2. Deagglomerating Wetted Clumps

2.1. Fundamentals

Individual particles in a dry powder are held together in clumps by polarizability attraction of adjoining particles, surface tension at wetted contacts, or moderately strong sintering or precipitation (particle or soluble salt) bonds. These bonds are formed at the contact points during drying or because of exposure to humidity or temperature cycles. Breaking these bonds to fully disperse the submerged and wetted clumps into individual particles may require high shear stress or mechanical impact (12–14). In contrast to milling, deagglomeration generates only a small amount of new surface area and thus uses only moderate energy per unit mass of material. The surface area newly created by deagglomeration may have higher adsorptivity and reactivity than the conditioned surface of the clump. ISO 8780 (parts 1–6) describes methods of deagglomeration for pigments (qv) and extenders.

High shear can be achieved in high viscosity systems, eg, molten plastic, using slowly turning mixing paddles. For intermediate viscosity systems, eg, highly loaded inks, the suspension may be passed through the gap between two mill rolls rotating with different surface velocities. For low viscosity systems, eg, mineral ore in water, suspensions may be circulated through the small gaps between a slotted stator and a close-fitting slotted rotor moving at a high rpm or forced at high pressure through a very small clearance in a spring-loaded valve.

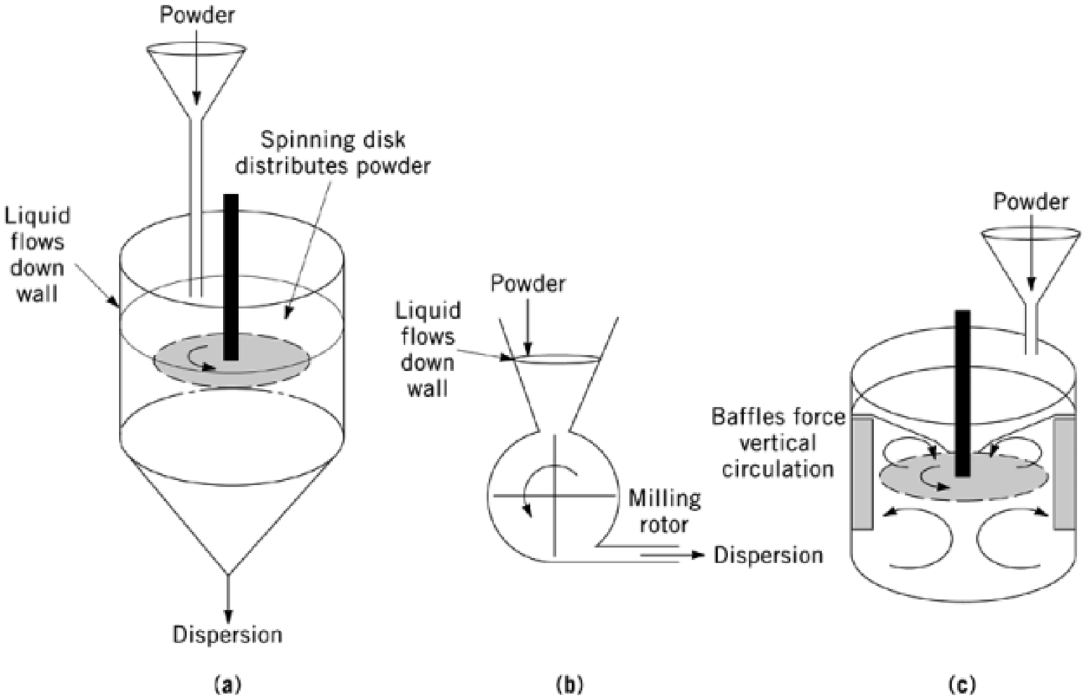

Fig. 3. Typical design elements for wet-in: (**a**)a spinning disk deagglomerates powder just prior to wet-in; (**b**) a rotor breaks clumps as they wet-in, andcentrifugal force helps submerge nonbuoyant powders; and (**c**) a disk impeller provides a rapidly refreshedliquid surface. In (**a**) and (**c**), the system may be under vacuum to speed porepenetration.

Impact can be achieved using grinding media beads set in motion by stirring with bars or disks, by vibration, or by cascading within a cylindrical container rotating on a horizontal axle. The cascading force can be enhanced by mounting several such rotating containers on a centrifuge with the axles parallel to the axis of centrifugation. Standard practice calls for using media approximately 20 times the diameter of the ultimate particle size; however, with high energy input size reduction can produce particles of submicrometer size. In autogenous milling, particles are ground by directing one high velocity jet of suspension against another or by vigorously stirring a highly loaded suspension (>40 vol% solids). Because it is difficult to achieve high energy impacts in a viscous medium, impact methods are restricted to low viscosity systems.

Ultrasonic probes, which create alternating pulses of vacuum (that pull the liquid apart to form evacuated cavities) and pressure (that cause the cavities to collapse) at up to millions of cycles per second, are commonly used to prepare laboratory dispersions. The cavities tend to form next to surfaces, so they are well placed to shatter bonds holding clumps together. Although large ultrasonic generators are available, industrial applications are limited. Cavitation occurs only in the volume near the surface of the probe and it is difficult to pass all the suspension through this zone and have sufficient residence time to achieve full dispersion without overheating the suspension, which diminishes the intensity of cavity collapse.

2.2. Practical Matters and Process Equipment

The strength of bonds holding clumps together may increase with storage time because of surface migration of material into the high energy contact region. Migration results from solubilization and mobilization caused

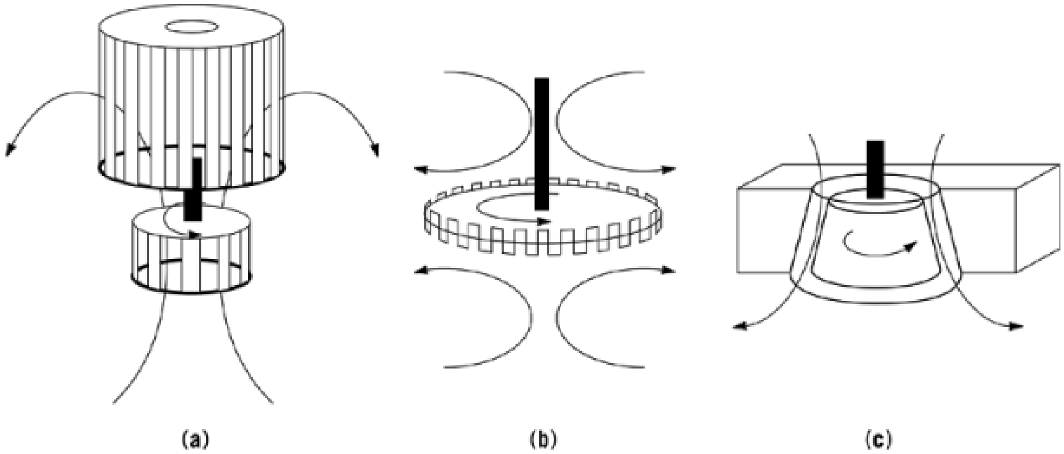

Fig. 4. Typical design elements for wet deagglomeration in low viscosity systems: (**a**) a high rpm rotor (shown below its normal position within stator) produces turbulence and cavitation as blades pass each other; (**b**) a rotating disk creates a deep vortex to rapidly refresh the surface, and up- and downturned teeth at the edge cause impact, turbulence, and sometimes cavitation; and (**c**) the clearance of a high rpm rotor can be reduced as the batch becomes more deagglomerated.

by adsorbed vapors or surface-treatment chemicals. Some powders sold commercially have been coated with a solid or liquid to decrease the likelihood of such changes and to keep the clumps soft or easy to deagglomerate.

Figure 4 shows several typical commercial devices used to deagglomerate clumps in low viscosity suspensions. These use slotted rotors, multiple teeth, and clearances that decrease as the suspension is pumped by centrifugal force through the annular gap. High shear stress is produced in systems with high viscosity, which can be achieved through high solids loading, close clearances between the shearing elements, and high rotational speed of the moving element. The heat generated by the shear may limit throughput.

3. Preventing Reagglomeration

3.1. Factors Affecting Dispersion Stability

3.1.1. Polarizability Attraction

All matter is composed of electrical charges which move in response to (become electrically polarized in) an external field. This field can be created by the distribution and motion of charges in nearby matter. The Hamaker constant for interaction energy, A, is a measure of this polarizability. As a first approximation it may be computed from the dielectric permittivity, ϵ, and the refractive index, n, of the material (15), where ν_{e} is the frequency of the principal electronic absorption

$$A = \frac{3}{4}kT\left[\frac{\epsilon - 1}{\epsilon + 1}\right]^2 + \frac{3h\nu_e\left(n^2 - 1\right)^2}{16\sqrt{2}\left(n^2 + 1\right)^{1.5}} \qquad (11)$$

band and h is Planck's constant. For two identical spheres of diameter, D, whose surfaces are separated in a liquid by a distance $s < D$ the attractive energy, u, due to polarizability is $u_{\mathrm{POLAR}} = -D/12s((A_{\mathrm{S}} - A_{\mathrm{L}})^{1/2})^2$, which becomes infinite at $s = 0$. A strongly adsorbed ($u_{\mathrm{ADS}} > kT$) layer of liquid (vicinal fluid) or other solute limits the minimum separation to s_{MIN}, and the maximum attractive energy to u_{PMAX}; s_{MIN} may be set equal to twice the molecular diameter of the liquid (16).

$$s_{\mathrm{MIN}} = 2\left[\frac{M_{\mathrm{L}}}{N_{\mathrm{AVO}}\rho_{\mathrm{L}}}\right]^{1/3} \qquad (12)$$

For example, water has $A_{\mathrm{L}} = 3.7 \times 10^{-20}$ J, $M = 0.018$ kg/mol, $\rho = 1000$ kg/m^3, and $s_{\mathrm{MIN}} = 0.62$ nm. Two silica [7631-86-9] particles with $A_{\mathrm{S}} = 6.6 \times 10^{-20}$ J and $D = 50$ nm have $u_{\mathrm{PMAX}} = -2.8 \times 10^{-20}$ J (17).

3.1.2. Thermal Jostling

The thermally driven random motion of molecules jostles particles to provide a one-dimensional translational energy which averages $kT/2$ over several seconds. However, it is conventional to use $u_{\mathrm{THERMAL}} = kT$ as a measure of thermal energy. At 298 K, $u_{\mathrm{THERMAL}} = 4.11 \times 10^{-21}$ J. At any instant many particles have less energy than this, and some have several times as much. If $u_{\mathrm{PMAX}} < u_{\mathrm{THERMAL}}$, thermal jostling disrupts the agglomerates sufficiently often to keep the particles dispersed. In water, 4-nm silica particles have a maximum attractive energy only 55% of u_{THERMAL}.

3.1.3. Sedimentation

Gravity makes all particles that are more dense than the suspending liquid move downward, and also causes beds of particles to compress toward the state of minimum-included liquid. The sedimentation force, f_{SED}, for a single spherical particle (not part of a bed) submerged in a liquid is as follows:

$$f_{\mathrm{SED}} = \frac{\pi}{6} g\,(\rho_{\mathrm{S}} - \rho_{\mathrm{L}})\,D^3 \qquad (13)$$

A larger sedimentation force can be developed by centrifuging the suspension. At an angular velocity of ω radians per second the centrifugal acceleration, a_{CENT}, at a distance R from the axis is as follows:

$$a_{\mathrm{CENT}} = \omega^2 R \qquad (14)$$

$$\omega = 2\pi\,\frac{\mathrm{rpm}}{60}$$

If the principal force is centrifugal rather than gravitational, a_{CENT} can be substituted for g in the above equations. If $u_{\mathrm{THERMAL}} > f_{\mathrm{SED}}H$, where H is the height of a container, then thermal jostling keeps the particles well distributed throughout the container and prevents them from settling into a dense bed at the bottom (or top) of the container.

3.1.4. Viscous Drag

The velocity, v, with which a particle can move through a liquid in response to an external force is limited by the viscosity, η, of the liquid. At low velocity or creeping flow ($N_{Re} < 1$), the viscous drag force is $f_{\mathrm{DRAG}} = 3\pi\eta_{\mathrm{L}}Dv$. The Reynolds number (*Re*) is determined from $N_{Re} = \rho_{\mathrm{L}}Dv/\eta_{\mathrm{L}}$. The balance between the forces due to gravity and viscous drag determines the terminal sedimentation velocity, which is upward for particles less dense than the liquid.

$$v_{\mathrm{SED}} = \frac{g}{18\eta}\,(\rho_{\mathrm{S}} - \rho_{\mathrm{L}})\,D^2 \qquad (15)$$

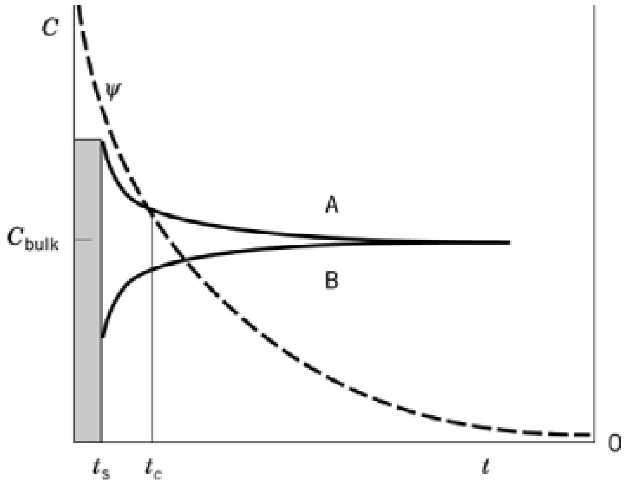

Fig. 5. Variation of ion concentrations, C (—), and effective surface potential, ψ (_), with distance from a positively charged surface. The layer of strongly bound anions, A, is the Stern layer, and beyond this anions are attracted into, whereas cations, B, are driven out of, the region near the surface (■); t=distance from the surface, m; t_c=the counterion atmosphere decay distance; and t_s=thickness of the Stern layer.

3.1.5. Electrostatic Interaction

Similarly charged particles repel one another. The charges on a particle surface may be due to hydrolysis of surface groups or adsorption of ions from solution. The surface charge density can be converted to an effective surface potential, ψ, when the potential is <30 mV, using the following equation, where N_{Far} represents the Faraday constant and N_{gas}, the gas law constant.

$$\psi_0 = \frac{\sigma}{N_{\mathrm{Far}}}\left(\frac{N_{\mathrm{gas}}T}{2\epsilon_0\epsilon_{\mathrm{L}}}\right)^{1/2} \qquad (16)$$

The layer of solution immediately adjacent to the surface that contains counterions not part of the solid structure, but bound so tightly to the surface that they never exchange with the solution, is the Stern layer. The plane separating this layer from the next is the Stern plane. The potential at the Stern plane is smaller than that at the surface.

Figure 5 shows the enhanced concentration of oppositely charged ions near the charged surface, and the depleted concentration of similarly charged ions near the charged surface due to electrostatic attractions and repulsions. Both factors reduce the effective potential, ψ, as the distance from the surface, x, increases. The distance at which ψ drops to $1/e$ (37%) of its value at the Stern plane is called the counterion atmosphere decay distance, t_c:

$$t_c = \frac{\epsilon_0\epsilon_{\mathrm{L}}N_{\mathrm{gas}}T}{4\pi N_{\mathrm{Far}}^2 I} \qquad (17)$$

where the ionic strength, I, depends on both the charge, z_j, and the concentration, C_j, of the ions, $I = 1/2\Sigma z_j^2 C_j$.

At the shear plane, fluid motion relative to the particle surface is zero. For particles with no adsorbed surfactant or ionic atmosphere, this plane is at the particle surface. Adsorbed surfactant or ions that are strongly attracted to the particle, with their accompanying solvent, prevent liquid motion close to the particle, thus moving the shear plane away from the particle surface. The effective potential at the shear plane is called the zeta potential, ζ. It is smaller than the potential at the surface, but because it is difficult to determine t_{SHEAR} or ψ_0, the usual assumption is that ψ_0 is effectively equal to ζ, which can be measured by observing the velocity, v, with which the charged particle moves in response to an electric (ELEC) field gradient, E:

$$v_{\mathrm{ELEC}} = \frac{2\epsilon_0\epsilon_{\mathrm{L}}}{3\eta_{\mathrm{L}}}E\zeta \qquad (18)$$

In an aqueous system with large particles well-separated by a distance, s, (D and $s > t_c$) the electrostatic repulsion energy between two identical charged spheres may be approximated (1):

$$u_{\mathrm{ELEC}} = \pi\epsilon_0\epsilon_{\mathrm{L}}D\zeta^2\ln\left[1 + \exp\left(-s/t_c\right)\right] \qquad (19)$$

If this repulsion exceeds the polarizability attraction at the distance of closest approach, determined by vicinal fluid, the particles can be prevented from agglomerating. For example, water with $\epsilon_{\mathrm{L}} = 81$, containing NaCl at $I = 10^{-7}$ mol/m^3, creates a counterion layer with $t_c = 0.15$ nm. The maximum repulsion in water between two silica particles with $D = 50$ nm and $\zeta = 50$ mV is $u_{\mathrm{EMAX}} = 2.86 \times 10^{-19}$ J. Because $u_{\mathrm{EMAX}} > u_{\mathrm{PMAX}}$, electrostatic repulsion prevents the surfaces from coming into contact unless the particles are in a bed of sediment and are being pressed together by the weight of it. Particles are more commonly characterized by surface potential than by surface charge density (18).

In a nonaqueous system with small closely spaced particles ($s < t_c$) the electrostatic repulsion energy between two identical charged spheres may be approximated (1):

$$u_{\mathrm{ELEC}} = \pi\epsilon_0\epsilon_{\mathrm{L}}\zeta^2\beta\frac{D^2}{s + D}\exp\left(\frac{-s}{t_c}\right) \qquad (20)$$

where β is a numerical factor between 0.6 and 1 and depends on the relative values of parameters in differential equations. Most surfactants have small solvation energies in organic liquids and consequently do not dissociate into ions in the clear liquid. However, when a particle with a strong tendency to donate protons is present, a surfactant with a strong tendency to accept protons can adsorb on the particle, accept transfer of a proton from the surface, and desorb, leaving a charged particle with the surfactant forming the counterion atmosphere.

3.1.6. Polymer Chain Interactions

If the surface of each particle is covered with links to polymer chains, whose segments are soluble in the surrounding liquid, then particles will be hindered from coming close together. The chains extend out a distance, δ. In this context the liquid is referred to as the solvent. There are two phenomena involved: (*1*) mixing energy, based on the enthalpy change due to increased segment–segment interaction and decreased segment–solvent interaction as the solvent is squeezed out of the region between the particles, and (*2*) elastic energy, based on the entropy change as the number of possible chain configurations becomes restricted when the particle surfaces come closer together (19). Unlike the polarizability and electrostatic interactions which extend out to large distances, the steric repulsive interactions act only when $s < 2\delta$. As a first approximation the joint effect of these two contributions to the interparticle potential is a single term:

$$u_{\mathrm{STERIC}} = kT\frac{\rho_{\mathrm{L}} N_{\mathrm{Avo}}}{M_{\mathrm{L}}}\phi^2 (0.5 - \chi)\pi D(2\delta - s)^2 \qquad (21)$$

where φ is the volume fraction of polymer in the adsorbed layer and χ is the Flory polymer–solvent interaction parameter. The value of χ is both solvent- and temperature-dependent; when the segment–segment interaction equals the segment–solvent interaction, $\chi = 0.5$ and the system is said to be at the theta point. Lower values of χ indicate a better solvent for the segments and cause a more extended configuration for the polymer chains; larger values lead to a more compact configuration.

3.1.7. Total Interaction Energy

Figure 6**a** shows the dependence of individual energy components of two-particle interaction on the separation between their surfaces; Figure 6**b** shows the shapes that arise when these are combined in typical situations. The suspension can be considered stabilized against reagglomeration if the maximum attractive (negative) energy is smaller than the thermal energy. Note from the component energy equations that whereas thermal energy is independent of particle diameter D, the polarizability attraction, electrostatic repulsion, and the steric repulsion energies increase with D.

3.2. Surface Modification

Reaction or adsorption at the solid surface can alter its properties and lead to a surface charge or steric stabilization (20, 21).

3.2.1. Hydrolysis

The surfaces of metal oxides and hydroxides can take up or release H^+ or OH^- ions and become charged. Potentials as high as ± 100 mV may be sustained in aqueous solutions. For aqueous solutions this is a function of the pH; the zeta potential for the particle is positive if the solution pH is below the particle's isoelectric pH ($\mathrm{pH_{iso}}$), and negative if the pH is above $\mathrm{pH_{iso}}$. Isoelectric points for metal oxides are presented in several publications (22, 23). Reactions of hydroxyl groups at a surface, Q, with acid and base may be written as follows:

$$\mathrm{Q{-\!\!-}AlOOH + H^+ \longrightarrow Q{-\!\!-}Al(OH)_2^+}$$

$$\mathrm{Q{-\!\!-}AlOOH + OH^- \longrightarrow Q{-\!\!-}AlOO^- + H_2O} \qquad (22)$$

For boehmite [1318-23-6], AlOOH, $\mathrm{p}K_{\mathrm{iso}} = 7.6$ (22). In the region where the potential varies rapidly with pH, the slope is -59 mV per pH. Figure 7 shows how the zeta potential varies with pH for a typical metal oxide. In many cases a zeta potential greater than 30 mV (positive or negative) is sufficient to keep the particles well dispersed. Lower values might be sufficient for particles with weak attractive forces (Hamaker constant close to the liquid), whereas higher values may be needed for particles with strong attractions, eg, magnetic particles.

3.2.2. Differential Dissolution/Complexation

For ionic salts, one of the ions making up the lattice may be complexed or hydrated more readily than the other resulting in an imbalance in particle charge. In the case of silver iodide [7783-96-2], dispersion in water leads

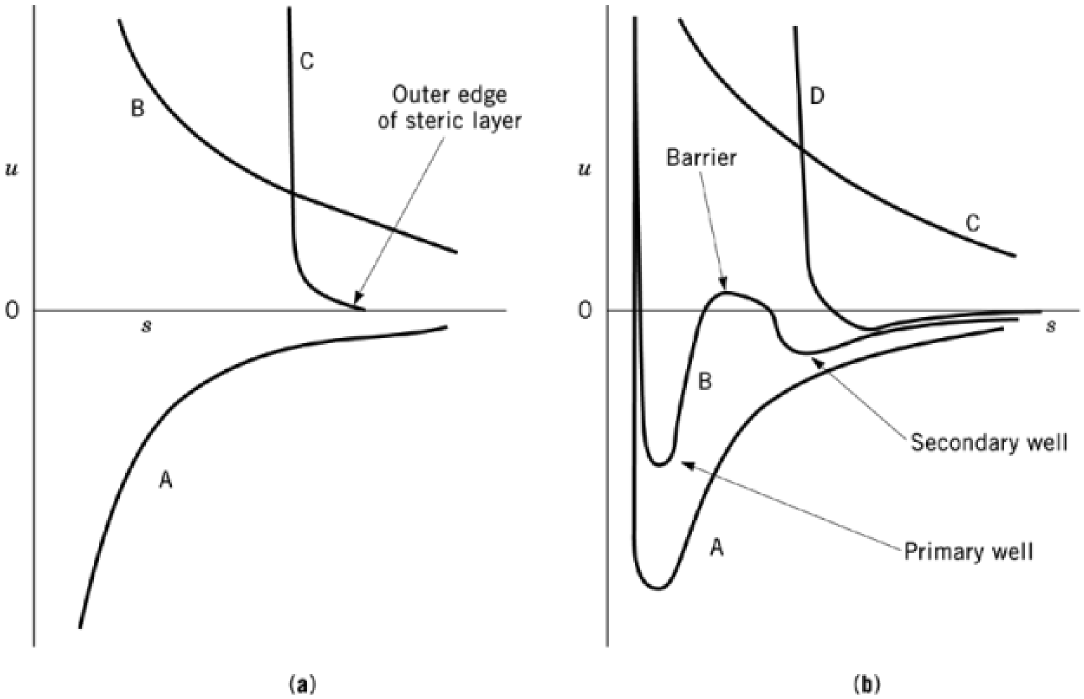

Fig. 6. (**a**) Components of potential energy and (**b**) typical total potential energies as a function of separation between two particles, where *s* is the separation of particle surfaces and *u* is the energy of interaction. In (**a**), A represents polarizability attraction; B, electrostatic repulsion, and C, steric exclusion. In (**b**), A, polarizability attraction dominates (vertical portion at small *s* is due to vicinal fluid); B, electrostatic repulsion nearly balances polarizability attraction providing a shallow secondary minimum that leads to weak flocs, an energy barrier that can prevent weak flocs from becoming strong if it is several times larger than kT, and a deep primary minimum that can bind particles into a strong floc; C, electrostatic repulsion dominates; and D, polarizability attraction is almost completely offset by steric exclusion.

to a net positive particle charge as the iodide ion is hydrated to a greater extent and thus goes into solution more readily than the silver ion (24). The surface charge of the particle may change with solution composition as the degree of complexation is affected by additives that adsorb on the surface, complex with the ion or the solvent, or affect the ionic strength and thus the distance over which the particle potential is effective.

3.2.3. Chemical Grafting

Polymer chains which are soluble in the suspending liquid may be grafted to the particle surface to provide steric stabilization. The most common technique is the reaction of an organic silyl chloride or an organic titanate with surface hydroxyl groups in a nonaqueous solvent. For typical interparticle potentials and a particle diameter of 10 μm, steric stabilization can be provided by a soluble polymer layer having a thickness of ~10 nm. This can be provided by a polymer tail with a molar mass of 10 kg/mol (25) (see Dispersants).

3.2.4. Surface Coating

A dense surface coating (encapsulation) that contains no occluded solvent decreases interparticle attraction provided that the coating has a Hamaker constant intermediate between the particle and the liquid. This is

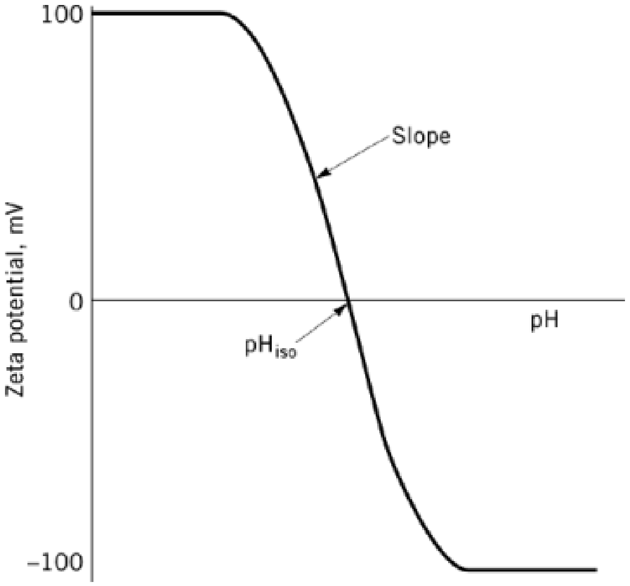

Fig. 7. Dependence of zeta potential on pH for a typical metal hydroxide particle in water. The isoelectric pH (pH$_{iso}$) is at low pH for acidic hydroxides and high pH for basic hydroxides. Maximum slope=$-59\ \mathrm{mV/pH}$.

called semisteric stabilization (ST). The energy of interaction between coated spheres is as follows (26):

$$u_{\mathrm{COATED}} = \frac{-1}{12}\left[A_{\mathrm{LT}}X_{\mathrm{T}} + A_{\mathrm{ST}}X_{\mathrm{S}} + 2X_{\mathrm{ST}}\left(A_{\mathrm{LT}}A_{\mathrm{ST}}\right)^{1/2}\right] \qquad (23)$$

where

$$A_{\mathrm{LT}} = \left[(A_{\mathrm{L}} - A_{\mathrm{T}})^{1/2}\right]^2 \qquad (24)$$

$$A_{\mathrm{ST}} = \left[(A_{\mathrm{S}} - A_{\mathrm{T}})^{1/2}\right]^2$$

and for each subscript T, S, or ST

$$X = \frac{y}{Y_{\mathrm{N}}} + \frac{y}{Y_{\mathrm{D}}} + 2\ln\left(\frac{Y_{\mathrm{N}}}{Y_{\mathrm{D}}}\right) \qquad (25)$$

$$Y_{\mathrm{N}} = x^2 + yx + x \quad Y_{\mathrm{D}} = Y_{\mathrm{N}} + y$$

For subscript T, $y = 1$, $x = s/(D + 2\delta)$; for subscript S, $y = 1$, $x = (s + 2\delta)/D$; and for subscript ST, $y = 1 + 2\delta/D$, $x = (s + 2\delta)/D$, where δ represents the thickness of the steric layer. For example, a 10-nm coating of polytetrafluoroethene $(A = 3.8 \times 10^{-20}\ \mathrm{J})$ reduces the attraction between 1-μm particles of silica $(A = 6.6 \times 10^{-20}\ \mathrm{J})$ in water $(A = 3.7 \times 10^{-20}\ \mathrm{J},\ s_{\mathrm{MIN}} = 0.62\ \mathrm{nm})$ from 53 to 1.6 times the thermal energy (17).

3.3. Additives Used To Stabilize Dispersions

A dispersant for a particular solid–liquid pair consists of molecules having one region that is soluble in the liquid and a second region that is not very soluble. The insolubility of the second region causes it to adsorb on the particles and, at concentrations above the critical micelle concentration (CMC), to force the dispersant molecules into multimolecular clusters with the soluble regions on the outside. The adsorbed dispersant may prevent agglomeration by keeping the particles from coming close enough to be strongly attracted (steric stabilization) or by creating a large enough charge to overwhelm interparticle attraction (electrostatic stabilization). Polarizability interactions attract dispersant molecules from solution onto the particle surface.

If an adsorbed chemical group (anchor) is more strongly bound to the surface than a solvent molecule would be at that site, an equilibrium expression may be written for the displacement of solvent by adsorbate. Adsorption is particularly strong if the chemical nature of the adsorbed group is similar to that of the particle surface; for example, in aqueous systems perfluoroalkane groups adsorb well on polytetrafluoroethene particles and aromatic polyethene oxides adsorb well on polystyrene.

In the simplest case, for which all adsorption sites are equivalent and do not interact with each other, the fraction of surface covered by adsorbate, f_{COVERED}, is related to the surfactant concentration, C_{SURF}, and the adsorption constant, K_{ADS}, in mol/m^3, by the Langmuir adsorption isotherm:

$$f_{\mathrm{COVERED}} = \frac{K_{\mathrm{ADS}}C_{\mathrm{SURF}}}{1 + K_{\mathrm{ADS}}C_{\mathrm{SURF}}} \qquad (26)$$

Near-monolayer coverage ($f_{\mathrm{COVERED}} > 0.95$) can be achieved only at $K_{\mathrm{ADS}}C_{\mathrm{SURF}} > 19$. This can pose problems for surfactants, since solution concentration can be no higher than the CMC (20, 27, 28).

3.3.1. Inorganic Ions

Because of electrostatic attraction, positive ions are attracted to negatively charged surfaces and have a higher concentration near the surface than in the bulk. Negative ions are repelled from the negative surface and have a lower concentration near that surface. Ions which are very strongly bound ($\mu_{\mathrm{ADS}} > kT$) are in the Stern layer, whereas those that can move into and out of the ionic atmosphere ($u_{\mathrm{ADS}} \leq kT$) are in the Helmholtz layer. The effect of ionic attraction or repulsion from the surface is to enhance or reduce the nonionic adsorption coefficient:

$$K_{\mathrm{ION}} = K_{\mathrm{NONION}}\exp\left[\frac{zN_{\mathrm{Far}}\psi_0}{N_{\mathrm{gas}}T}\right] \qquad (27)$$

Multiply charged ions such as Ba^{2+} adsorb on an ionic surface more strongly than singly charged ions such as Cl^-. The addition of a solution of $BaCl_2$ to a suspension of AgI in water can provide sufficient charge to stabilize the dispersion at low ionic strength.

3.3.2. Short-Chain Organics

Adsorption of an organic dispersant can reduce polarizability attraction between particles, ie, provide semisteric stabilization, if $A_{\mathrm{L}} < A_{\mathrm{T}} < A_{\mathrm{s}}$ or $A_{\mathrm{s}} < A_{\mathrm{T}} < A_{\mathrm{L}}$ (T = dispersant) and the adsorption layer is thick. Adsorption in aqueous systems generally does not follow the simple Langmuir profile because the organic tails on adsorbed molecules at adjacent sites attract each other strongly.

Ionizable organic dispersants can lose or gain protons (H^+) in aqueous solution if the pH is in the right region for that particular dispersant. Organic acids (anionic surfactants) lose a H^+ ion at pH > pK_a to attain a negative charge; organic amines (cationic surfactants) add a H^+ ion at pH < pK_b to attain a positive charge. Amino acids (zwitterionic surfactants) become positively charged at pH < pK_b, are neutral at pK_b < pH < pK_a,

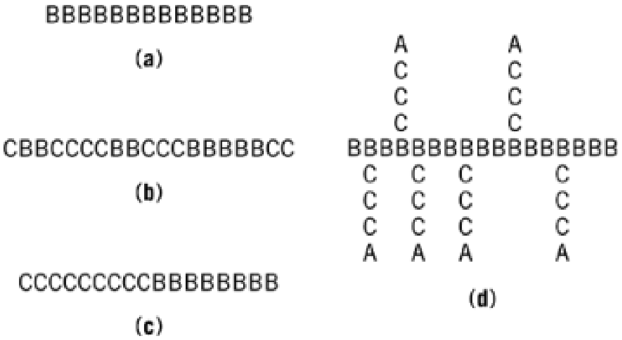

Fig. 8. General structures of polymeric dispersants: (**a**) homopolymer, (**b**) random copolymer, (**c**) diblock copolymer, and (**d**) comb polymer, where A=anchor group, B=soluble repeat unit, and C=repeat unit with solubility different from B. The repeat units may occur in sequences hundreds of units long that fill space as random coils thrashing due to thermal jostling.

and become negatively charged at $\mathrm{pH} > \mathrm{p}K_a$. The ionic species may adsorb on an oppositely charged (typically inorganic) surface and provide semisteric stabilization or may adsorb on an uncharged (typically organic) surface to create a surface potential that can stabilize the suspension.

An ionizable organic dispersant can provide electrostatic stabilization for a typically inorganic particle in an organic liquid even though it does not ionize appreciably in the absence of such particles. The mechanism for ionization is adsorption of the nonionized dispersant molecule, followed by proton (H^+) transfer to or from the particle, or a film of water adsorbed on the particle, and desorption of the organic ion, creating a charged particle with the dispersant forming the counterion atmosphere (29, 30).

3.3.3. Polymeric Nonionics

Some polymeric units can be hydrated, such as polyethylene oxide, and thus are water soluble or adsorb strongly to highly polar materials. Other polymeric units, such as alkane or fluorinated alkane, are oil soluble and adsorb strongly on nonpolar materials. Langmuir adsorption theory is not applicable for polymeric adsorbates because adsorption at one site strongly influences the adsorption at a neighboring site. Figure 8 depicts the structures of several significant types of polymer. Homopolymers consist of a series of identical segments. If the segments adsorb strongly on the particle the polymer layer will have a compressed conformation (little occluded solvent) and provide only semisteric stabilization. Less strongly adsorbed homopolymers provide a coating whose off-surface sequences may be anchored to the surface at both ends (loops) or at only one end (tails) to provide a steric layer. Because the desorption and readsorption of an adsorbed polymer segment is severely restricted by the location of nearby adsorbed segments, attainment of conformational equilibrium for the adsorbed molecule may be so slow that the configuration will effectively remain what it was when the dissolved polymer first made contact with the surface.

Random copolymers consist of random length sequences of soluble segments interspersed with less soluble segments. The less soluble segments adsorb on the particle and the more soluble sequences form loops or tails extending into the liquid. The provision of separate anchor segments and soluble segments provides better control over adsorbed layer depth and desorption than can be achieved using a homopolymer. The movement of the loops and tails through the solution is driven by thermal energy and provides a steric barrier whose thickness in a good solvent is roughly one-third the fully extended length of the loop or tail. Steric stabilization can often be achieved with a steric barrier thickness of about 10 nm, which can be provided by tails having a molar mass of about 10 kg/mol (mol wt 10,000 g/mol) (31).

Diblock copolymers consist of one sequence of anchor segments and a second sequence of backbone segments. The relative lengths of the two sequences can be controlled to provide a wide variety of adsorption and barrier characteristics. Typical commercial dispersants may use alkane $-\!\left(\mathrm{CH_2}\right)\!-$, ester

$$-\!\left(\mathrm{C_5H_{10}}\text{—}(\mathrm{CO})\text{—}\mathrm{O}\right)\!-$$

, methyl methacrylate [80-62-6],

$$-\!\left(\mathrm{C(CH_3)(COOCH_3)}\text{—}\mathrm{CH_2}\right)\!-$$

propylene oxide

$$-\!\left(\mathrm{CH_2}\text{—}\mathrm{CH(CH_3)}\text{—}\mathrm{O}\right)\!-$$

, or ethylene oxide [75-21-8],

$$-\!\left(\mathrm{CH_2}\text{—}\mathrm{CH_2}\text{—}\mathrm{O}\right)\!-$$

, segments. Comb polymers have a soluble backbone with a number of side chains, each of which contains an anchor group (see Polymers).

3.3.4. Selecting a Dispersant

To select a dispersant for a system that includes a third component (such as a binder), the following steps may be used so that only a few candidates remain for the testing required at the final step (32, 33). (*1*) Evaluate the dispersant solubility in the liquid with the third component, but not the powder, present and eliminate from further consideration any dispersant not readily soluble. (*2*) Measure the zeta potential of the particles in the liquid with the third component present. If the zeta potential is positive, eliminate from further consideration all cationic dispersants; if negative, eliminate all anionic dispersants. (*3*) Measure the viscosity of a highly loaded ($>$40 vol% solids) suspension containing only the liquid and the powder. Eliminate from further consideration any dispersant that has poor flow characteristics (high viscosity). (*4*) Observe sedimentation behavior of a moderately loaded (5–10 vol % solids) suspension containing only the liquid and powder. For small powders use centrifugation to force settling in a reasonable time. Eliminate from further consideration any dispersant that gives a large sediment volume. (*5*) Check the quality of the complete formulation, ie, liquid, powder, dispersant, third component, and other components, in whatever end-use quality tests are important and eliminate any dispersants which are incompatible with other components or cause failure in the end-use tests.

Reference 4 and several standards provide guidelines for selecting dispersants: ASTM standard B821-92 for metal powders (and some carbides and sulfides) in water; British Standard (BS) 3466 (part 4) for oxides; and ISO TC24/SC4/WG11 (1997) for a wide range of powder–liquid combinations.

3.4. Associative Thickeners

Although low viscosity is convenient for mixing and pumping operations during manufacture, high viscosity is desirable to deter the formation of a dense sediment bed and possible agglomeration during transportation and storage. Associative thickeners are polymers which have insoluble (with respect to the suspending liquid) end groups and a long soluble backbone (34). The insoluble end groups form weakly bonded clusters which are kept apart by the backbones. In some cases the end groups may adsorb on small particles in the system and incorporate these in the network. The three-dimensional network of linked micelles forms quickly in the absence of shear to prevent particles from settling when the suspension is quiescent, but breaks up readily when subjected to low shear forces. Short-term disruption of the network (and consequent small-scale sedimentation) may occur if the system is jolted or vibrated during transportation or storage.

3.5. Independent Floc Network

A space-filling structure similar to that created by an associative thickener can be provided by a loose network of weakly bonded particles. For example, at $pH < 7$ and low salt concentration, kaolinite [1318-74-7] clay platelets have positively charged faces and negatively charged edges which floc to form a weakly bonded space-filling house of cards structure (35). The addition of clay to a suspension of particles that are not stable to reagglomeration can prevent the particles from coming into contact with each other and forming large flocs.

3.6. Adsorption of Microparticles

Microparticles, having diameters less than one-tenth that of the particles to be dispersed, can be attached to the larger particles by sintering prior to wet-in, polarizability attraction if the Hamaker constant is midway between the liquid and larger particle, or electrostatic attraction if the microparticles have a charge opposite that of the larger particle. The attached microparticles prevent the surfaces of the larger particles from coming close together, thus reducing the maximum attractive energy in essentially the same way that encapsulation does.

4. Evaluating Dispersions

Several publications discuss in detail a variety of methods for evaluating dispersions (36) and the chemical character of the particle surface (37, 38). Numerous standards provide the details of well-established methods for evaluating dispersions, eg, ASTM D185-84 for measuring coarse particles in paint (qv), ASTM D869 for evaluating settling and ease of remixing in paints, ASTM D1210-79 for fineness of grind in coatings (qv), ASTM D1316-93 for measuring fineness of grind in inks (qv), ASTM D2066-91 for evaluating tinting strength in inks, ASTM D2067-92 for determining coarse particles in inks, ASTM D3015-72 for microscopic evaluation of the dispersion of pigments in plastics, ASTM E20-85 for particle size analysis by optical microscopy, ASTM F20-843 for color strength in ink, and ISO 8781 (parts 1–3) for evaluating tinting strength, fineness of grind, and gloss.

4.1. Degree of Deagglomeration

4.1.1. Viscosity

Because a clump of particles contains occluded liquid, the effective volume fraction of a suspension of clumps is larger than the volume fraction of the individual particles; that is, there is less free liquid available to facilitate the flow than if the clumps were deagglomerated. The viscosity of a suspension containing clumps decreases as the system becomes deagglomerated. This method is not very sensitive in the final stages of deagglomeration when there are only a few small clumps left.

4.1.2. Particle Size Distribution

Much of the progress of deagglomeration may be monitored using either sieving (particles $>20\ \mu m$) or instrumental particle size analysis (smaller particles). The instrumental analysis techniques cannot reliably detect part per million levels of large particles (grit) unless the larger particles are concentrated by removing smaller particles. This can be done by letting the smaller particles escape from the suspension through a screen, an array of parallel capillary tubes, or a filter with openings of well-defined diameter in a series of partial filtrations followed by dilutions with fresh liquid.

4.1.3. Tinting Strength

When a fixed mass of particles is well-dispersed, it blocks more light than when the mass is present as clumps. To follow the progress of deagglomeration of a suspension, a series of samples may be taken as deagglomeration proceeds. A fixed quantity of each sample is mixed with a fixed quantity of a well-dispersed contrasting color pigment and a thin film is painted on a flat sheet. A sensitive colorimeter can quantify changes in color as a function of improving deagglomeration. Ultraviolet or infrared light may be used for samples that are transparent in the visible. The method does not work if the contrasting pigment is agglomerated by the sample or if the sample and contrasting pigment settle out. The colorimeter can be eliminated if the samples can be placed side by side for direct visual comparison (12).

4.1.4. Grind Gauge

This gauge consists of a metal bar with a rectangular milled depression the depth of which gradually decreases from 25 μm to zero as a function of length from one end to the other. A sample of paste, more than enough to fill the depression, is placed in the depression and the excess is scraped off by drawing a straight-edged drawdown bar toward the shallow end in a single pass. Particles having a diameter nearly equal to or larger than the depth of the depression at any given point rise up through the surface or cause a streak in the surface as the bar passes by. Although this method makes evident the presence of a few large particles among millions of smaller ones, the results are subject to considerable variability (12).

4.2. Stability to Reagglomeration

4.2.1. Examination with a Microscope

Examination of a dilute ($<$1 mass% solids) suspension using an optical microscope at a magnification of 100–400 can be helpful for evaluating the dispersion stability of particles 1–10 μm in diameter. If the dispersion is stable, thermal jostling can be seen and particles avoid coming close to one another or separate soon after collision. If the dispersion is unstable, particles remain attached after collision. The motion of particles as small as 0.1 μm may be observed with an ultramicroscope which uses side lighting and a dark field. Even in suspensions having an average diameter larger than 10 μm there are usually some smaller particles that can indicate whether or not the suspension is stable.

4.2.2. Sediment Volume

If the dispersion is unstable, the sediment bed will be quite deep and sedimenting particles will stick together where they first strike the sediment bed, thus forming an open structure with considerable occluded liquid. If the dispersion is stable to reagglomeration, the particles will move freely past one another to avoid contact as long as possible. The result is a thin sediment bed with maximum solids packing and minimum occluded liquid (12). Since dispersed particles settle more slowly than flocs, centrifugation may be needed to force sedimentation of small particles within a reasonable analysis time.

4.2.3. Response to Electric and Acoustic Fields

If the stabilization of a suspension is primarily due to electrostatic repulsion, measurement of the zeta potential, ζ, can detect whether there is adequate electrostatic repulsion to overcome polarizability attraction. A common guideline is that the dispersion should be stable if $\zeta > 30$ mV. In electrophoresis the applied electric field is held constant and particle velocity is monitored using a microscope and video camera. In the electrosonic amplitude technique the electric field is pulsed, and the sudden motion of the charged particles relative to their counterion atmospheres generates an acoustic pulse which can be related to the charge on the particles and the concentration of ions in solution (18).

The attenuation of ultrasound (acoustic spectroscopy) or high frequency electrical current (dielectric spectroscopy) as it passes through a suspension is different for well-dispersed individual particles than for flocs of those particles because the flocs adsorb energy by breakup and reformation as pressure or electrical waves jostle them. The degree of attenuation varies with frequency in a manner related to floc breakup and reformation rate constants, which depend on the strength of the interparticle attraction, size, and density (inertia) of the particles, and viscosity of the liquid.

4.2.4. Spectroscopy

The spin-lattice coupling in nuclear magnetic resonance (nmr) is sensitive to the environment of the proton, so it can be used to determine whether the soluble parts of a polymeric dispersant are well solvated (desired situation for steric stabilization) or lying in a compact grouping near the particle surface (inadequate solvency) (39). Electron spin resonance (esr) or fluorescence spectroscopy can provide a more location-specific analysis, but these techniques require grafting special chemical probe groups onto the polymer chains. One negative factor is that the presence of the probe groups may alter the segment–solvent interaction parameters from the unsubstituted values (38).

4.2.5. Drift in Tinting Strength

Just as tinting strength can be used to follow deagglomeration, it may also be used to detect reagglomeration of fine powders. Sensitive colorimeters can follow changes in the color of a mixture of the sample suspension and a contrasting pigment. A drift in color indicates flocculation. The method does not work if the contrasting pigment is agglomerated by the sample or if the sample or contrast pigment settle out. The colorimeter can be eliminated if the agglomerates (flocs) can be broken up by passing a brush through part of the film so that a freshly deagglomerated region is adjacent to the agglomerated region (12).

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