1
General Introduction

The dispersion of powders into liquids is a process that occurs in many industries of which we mention paints, dyestuffs, paper coatings, printing inks, agrochemicals, pharmaceuticals, cosmetics, food products, detergents, and ceramics. The powder can be hydrophobic such as organic pigments, agrochemicals, and ceramics or hydrophilic such as silica, titania, and clays. The liquid can be aqueous or nonaqueous.

The dispersion of a powder in a liquid is a process whereby aggregates and agglomerates of powders are dispersed into "individual" units, usually followed by a wet milling process (to subdivide the particles into smaller units) and stabilization of the resulting dispersion against aggregation and sedimentation [1–3]. This is illustrated in Figure 1.1.

The powder is considered hydrophobic if there is no affinity between its surface and water, for example, carbon black, many organic pigments, and some ceramic powders such as silicon carbide or silicon nitride. In contrast a hydrophilic solid has strong affinity between its surface and water, for example, silica, alumina, and sodium montmorillonite clay.

1.1
Fundamental Knowledge Required for Successful Dispersion of Powders into Liquids

Several fundamental processes must be considered for the dispersion process and these are summarized below.

1.1.1
Wetting of Powder into Liquid

This is determined by surface forces whereby the solid/air interface characterized by an interfacial tension (surface energy) γ_{SA} is replaced by the solid/liquid interface characterized by an interfacial tension (surface energy) γ_{SL} [1]. Polar (hydrophilic) surfaces such as silica or alumina have high surface energy and hence they can be easily wetted in a polar liquid such as water. In contrast nonpolar
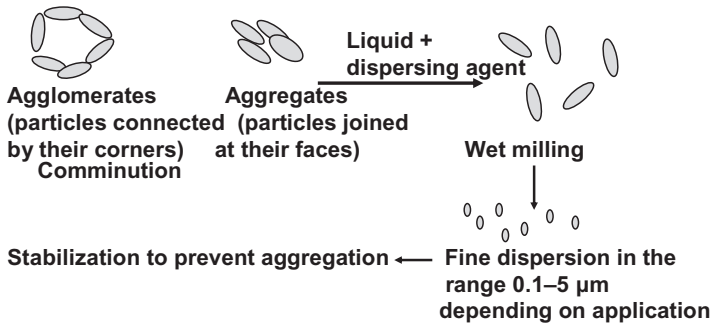
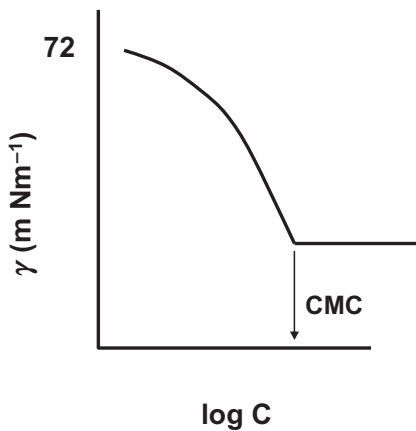**Figure 1.1** Schematic representation of the dispersion process.

Figure 1.2 Surface tension–log *C* curve.

(hydrophobic) surfaces such as carbon black and many organic pigments have low surface energy and hence they require a surface active agent (surfactant) in the aqueous phase to aid wetting. The surfactant lowers the surface tension γ of water from ~72 to ~ 30–40 mN m^{-1} depending on surfactant nature and concentration. This is illustrated in Figure 1.2, which shows the γ–log *C* (where *C* is the surfactant concentration) relationship of surfactant solutions. It can be seen that γ decreases gradually with the increase in surfactant concentration, and above a certain concentration it shows a linear decrease with the increase in log *C*. Above a critical surfactant concentration γ remains constant. This critical concentration is that above which any added surfactant molecules aggregate to form micelles that are in equilibrium with the surfactant monomers. This critical concentration is referred to as the critical micelle concentration (CMC).

There are generally two approaches for treating surfactant adsorption at the A/L interface. The first approach, adopted by Gibbs, treats adsorption as an equilib-

rium phenomenon whereby the second law of thermodynamics may be applied using surface quantities. The second approach, referred to as the equation-of-state approach, treats the surfactant film as a two-dimensional layer with a surface pressure π that may be related to the surface excess Γ (amount of surfactant adsorbed per unit area). Below, the Gibbs treatment that is commonly used to describe adsorption at the A/L interface is summarized.

Gibbs [4] derived a thermodynamic relationship between the surface or interfacial tension γ and the surface excess Γ (adsorption per unit area). The starting point of this equation is the Gibbs–Deuhem equation. At constant temperature, and in the presence of adsorption, the Gibbs–Deuhem equation is

$$d\gamma = -\sum \frac{n_i^{\sigma}}{A} \, d\mu_i = -\sum \Gamma_i \, d\mu_i \tag{1.1}$$

where $\Gamma_i = n_i^{\sigma}/A$ is the number of moles of component i and adsorbed per unit area.

Equation (1.1) is the general form for the Gibbs adsorption isotherm. The simplest case of this isotherm is a system of two components in which the solute (2) is the surface active component, that is, it is adsorbed at the surface of the solvent (1). For such a case, Eq. (1.1) may be written as

$$-d\gamma = \Gamma_1^{\sigma} \, d\mu_1 + \Gamma_2^{\sigma} \, d\mu_2 \tag{1.2}$$

and if the Gibbs dividing surface is used, $\Gamma_1 = 0$ and,

$$-d\gamma = \Gamma_{1,2}^{\sigma} \, d\mu_2 \tag{1.3}$$

where $\Gamma_{2,1}^{\sigma}$ is the relative adsorption of (2) with respect to (1). Since

$$\mu_2 = \mu_2^{o} + RT \ln a_2^{l} \tag{1.4}$$

or

$$d\mu_2 = RT \, d \ln a_2^{l} \tag{1.5}$$

then

$$-d\gamma = \Gamma_{2,1}^{\sigma} RT \, d \ln a_2^{l} \tag{1.6}$$

or

$$\Gamma_{2,1}^{\sigma} = -\frac{1}{RT} \left(\frac{d\gamma}{d \ln a_2^{l}} \right) \tag{1.7}$$

where a_2^{l} is the activity of the surfactant in bulk solution that is equal to $C_2 f_2$ or $x_2 f_2$, where C_2 is the concentration of the surfactant in mol dm^{-3} and x_2 is its mole fraction.

Equation (1.7) allows one to obtain the surface excess (abbreviated as Γ_2) from the variation of surface or interfacial tension with surfactant concentration. Note that $a_2 \sim C_2$ since in dilute solutions $f_2 \sim 1$. This approximation is valid since most surfactants have low c.m.c. (usually less than 10^{-3} mol dm^{-3}) but adsorption is complete at or just below the c.m.c.

The surface excess Γ_2 can be calculated from the linear portion of the γ–log C_2 curves before the c.m.c. Such a γ–log C curve is illustrated in Figure 1.2 for the air/water interface. As mentioned above, Γ_2 can be calculated from the slope of the linear position of the curves shown in Figure 1.2 just before the c.m.c. is reached. From Γ_2, the area per surfactant ion or molecule can be calculated since

$$\text{Area/molecule} = \frac{1}{\Gamma_2 N_{\text{av}}} \tag{1.8}$$

where N_{av} is Avogadro's constant. Determining the area per surfactant molecule is very useful since it gives information on surfactant orientation at the interface. For example, for ionic surfactants such as sodium dodecyl sulfate, the area per surfactant is determined by the area occupied by the alkyl chain and head group if these molecules lie flat at the interface, whereas for vertical orientation, the area per surfactant ion is determined by that occupied by the charged head group, which at low electrolyte concentration will be in the region of $0.40\,\text{nm}^2$. Such an area is larger than the geometrical area occupied by a sulfate group, as a result of the lateral repulsion between the head group. On addition of electrolytes, this lateral repulsion is reduced and the area/surfactant ion for vertical orientation will be lower than $0.4\,\text{nm}^2$ (reaching in some case $0.2\,\text{nm}^2$). On the other hand, if the molecules lie flat at the interface, the area per surfactant ion will be considerably higher than $0.4\,\text{nm}^2$.

Another important point can be made from the γ–log C curves. At concentration just before the break point, one has the condition of constant slope, which indicates that saturation adsorption has been reached. Just above the break point,

$$\left(\frac{\partial \gamma}{\partial \ln a_2}\right)_{p,T} = \text{constant} \tag{1.9}$$

$$\left(\frac{\partial \gamma}{\partial \ln a_2}\right)_{p,T} = 0 \tag{1.10}$$

indicating the constancy of γ with log C above the c.m.c. Integration of Eq. (1.10) gives

$$\gamma = \text{constant } x \ln a_2 \tag{1.11}$$

Since γ is constant in this region, then a_2 must remain constant. This means that the addition of surfactant molecules, above the c.m.c., must result in association with form units (micellar) with low activity.

The hydrophilic head group may be unionized, for example, alcohols or poly(ethylene oxide) alkane or alkyl phenol compounds, weakly ionized such as carboxylic acids, or strongly ionized such as sulfates, sulfonates, and quaternary ammonium salts. The adsorption of these different surfactants at the air/water interface depends on the nature of the head group. With nonionic surfactants, repulsion between the head groups is small and these surfactants are usually strongly adsorbed at the surface of water from very dilute solutions. Nonionic surfactants have much lower c.m.c. values when compared with ionic surfactants

with the same alkyl chain length. Typically, the c.m.c. is in the region of 10^{-5}–10^{-4} mol dm^{-3}. Such nonionic surfactants form closely packed adsorbed layers at concentrations lower than their c.m.c. values. The activity coefficient of such surfactants is close to unity and is only slightly affected by the addition of moderate amounts of electrolytes (or change in the pH of the solution). Thus, nonionic surfactant adsorption is the simplest case since the solutions can be represented by a two-component system and the adsorption can be accurately calculated using Eq. (1.7).

With ionic surfactants, on the other hand, the adsorption process is relatively more complicated since one has to consider the repulsion between the head groups and the effect of the presence of any indifferent electrolyte. Moreover, the Gibbs adsorption equation has to be solved taking into account the surfactant ions, the counterion, and any indifferent electrolyte ions present. For a strong surfactant electrolyte such as Na$^+$R$^-$,

$$\Gamma_2 = \frac{1}{2RT}\frac{d\gamma}{d\ln a\pm} \tag{1.12}$$

The factor of 2 in Eq. (1.12) arises because both surfactant ion and counterion must be adsorbed to maintain neutrally, and $d\gamma/d\ln a\pm$ is twice as large as for an un-ionized surfactant.

If a nonadsorbed electrolyte, such as NaCl, is present in large excess, then any increase in the concentration of Na$^+$R$^-$ produces a negligible increase in the Na$^+$ ion concentration and therefore $d\mu_{Na}$ becomes negligible. Moreover, $d\mu_{Cl}$ is also negligible, so the Gibbs adsorption equation reduces to

$$\Gamma_2 = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial\ln C_{NaR}}\right) \tag{1.13}$$

that is, it becomes identical to that for a nonionic surfactant.

The above discussion clearly illustrates that for the calculation of Γ_2 from the γ–log C curve one has to consider the nature of the surfactant and the composition of the medium. For nonionic surfactants the Gibbs adsorption (Eq. (1.7)) can be directly used. For ionic surfactant, in the absence of electrolytes the right-hand side of Eq. (1.7) should be divided by 2 to account for surfactant dissociation. This factor disappears in the presence of the high concentration of an indifferent electrolyte.

Surfactants also adsorb on hydrophobic surfaces with the hydrophobic group pointing to the surface and the hydrophilic group pointing to water. Adsorption increases with the increase in surfactant concentration reaching a limiting value (the saturation adsorption) near the critical micelle concentration. This is illustrated in Figure 1.3. With many solid/surfactant systems the adsorption follows the Langmuir theory.

The adsorption of ionic surfactants on hydrophobic surfaces may be represented by the Stern–Langmuir isotherm [5]. Consider a substrate containing N_s sites (mol m^{-2}) on which Γ mol m^{-2} of surfactant ions are adsorbed. The surface coverage θ is (Γ/N_s) and the fraction of uncovered surface is $(1 - \theta)$.
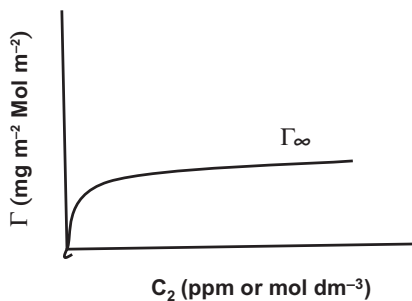
Figure 1.3 Langmuir-type adsorption isotherm.

The rate of adsorption is proportional to the surfactant concentration expressed in mole fraction, $(C/55.5)$, and the fraction of free surface $(1 - \theta)$, that is,

$$\text{Rate of adsorption} = k_{\text{ads}}\left(\frac{C}{55.5}\right)(1 - \theta) \tag{1.14}$$

where k_{ads} is the rate constant for adsorption.

The rate of desorption is proportional to the fraction of surface covered θ,

$$\text{Rate of desorption} = k_{\text{des}}\theta \tag{1.15}$$

At equilibrium, the rate of adsorption is equal to the rate of desorption and the $k_{\text{ads}}/k_{\text{des}}$ ratio is the equilibrium constant K, that is,

$$\frac{\theta}{(1 - \theta)} = \frac{C}{55.5}K \tag{1.16}$$

The equilibrium constant K is related to the standard free energy of adsorption by

$$-\Delta G_{\text{ads}}^{o} = RT \ln K \tag{1.17}$$

R is the gas constant and T is the absolute temperature. Equation (1.17) can be written in the form

$$K = \exp\left(-\frac{\Delta G_{\text{ads}}^{o}}{RT}\right) \tag{1.18}$$

Combining Eqs. (1.3) and (1.5),

$$\frac{\theta}{1 - \theta} = \frac{C}{55.5}\exp\left(-\frac{\Delta G_{\text{ads}}^{o}}{RT}\right) \tag{1.19}$$

Equation (1.6) applies only at low surface coverage ($\theta < 0.1$) where lateral interaction between the surfactant ions can be neglected.

At high surface coverage ($\theta > 0.1$) one should take the lateral interaction between the chains into account, by introducing a constant A, for example, using the Frumkin–Fowler–Guggenheim equation [5],

$$\frac{\theta}{(1-\theta)}\exp(A\theta) = \frac{C}{55.5}\exp\left(-\frac{\Delta G_{ads}^0}{RT}\right) \tag{1.20}$$

Various authors [6, 7] have used the Stern–Langmuir equation in a simple form to describe the adsorption of surfactant ions on mineral surfaces,

$$\Gamma = 2rC\exp\left(-\frac{\Delta G_{ads}^0}{RT}\right) \tag{1.21}$$

Various contributions to the adsorption free energy may be envisaged. To a first approximation, these contributions may be considered to be additive. In the first instance, ΔG_{ads} may be taken to consist of two main contributions, that is,

$$\Delta G_{ads} = \Delta G_{elec} + \Delta G_{spec} \tag{1.22}$$

where ΔG_{elec} accounts for any electrical interactions and ΔG_{spec} is a specific adsorption term which contains all contributions to the adsorption free energy that are dependent on the "specific" (nonelectrical) nature of the system [5]. Several authors subdivided ΔG_{spec} into supposedly separate independent interactions [6, 7], for example,

$$\Delta G_{spec} = \Delta G_{cc} + \Delta G_{cs} + \Delta G_{hs} + \cdots \tag{1.23}$$

where ΔG_{cc} is a term that accounts for the cohesive chain–chain interaction between the hydrophobic moieties of the adsorbed ions, ΔG_{cs} is the term for the chain/substrate interaction whereas ΔG_{hs} is a term for the head group/substrate interaction. Several other contributions to ΔG_{spec} may be envisaged, for example, ion–dipole, ion–induced dipole, or dipole–induced dipole interactions.

Since there is no rigorous theory that can predict adsorption isotherms, the most suitable method to investigate adsorption of surfactants is to determine the adsorption isotherm. Measurement of surfactant adsorption is fairly straightforward. A known mass m (g) of the particles (substrate) with known specific surface area A_s ($m^2 g^{-1}$) is equilibrated at constant temperature with surfactant solution with initial concentration C_1. The suspension is kept stirred for sufficient time to reach equilibrium. The particles are then removed from the suspension by centrifugation and the equilibrium concentration C_2 is determined using a suitable analytical method. The amount of adsorption Γ (mol m^{-2}) is calculated as follows:

$$\Gamma = \frac{(C_1 - C_2)}{mA_s} \tag{1.24}$$

The adsorption isotherm is represented by plotting Γ versus C_2. A range of surfactant concentrations should be used to cover the whole adsorption process, that is, from the initial low values to the plateau values. To obtain accurate results, the solid should have a high surface area (usually $> 1\,m^2$).

It is essential to wet both the external and internal surfaces (pores inside agglomerates).

Wetting of the external surface requires surfactants that lower the liquid/air interfacial tension, γ_{LA}, efficiently, in particular under dynamic conditions (dynamic

surface tension measurements are more informative). Wetting of the internal surface requires penetration of the liquid into the pores that is determined by the capillary pressure which is directly proportional to γ_{LA}.

A useful concept for assessment of powder wetting is to measure the contact angle θ at the solid/liquid interface, which when combined with the surface tension γ_{LA} can give a quantitative measure of wetting and penetration of the liquid into pores.

1.1.2
Breaking of Aggregates and Agglomerates into Individual Units

This usually requires the application of mechanical energy. High-speed mixers (which produce turbulent flow) are efficient in breaking up the aggregates and agglomerates, for example, Silverson mixers, UltraTurrax. The mixing conditions have to be optimized: heat generation at high stirring speeds must be avoided. This is particularly the case when the viscosity of the resulting dispersion increases during dispersion (note that the energy dissipation as heat is given by the product of the square of the shear rate and the viscosity of the suspension). One should avoid foam formation during dispersion; proper choice of the dispersing agent is essential and antifoams (silicones) may be applied during the dispersion process.

In order to maintain the particles as individual units, it is essential to use a dispersing agent that must provide an effective repulsive barrier preventing aggregation of the particles by van der Waals forces. This dispersing agent must be strongly adsorbed on the particle surface and should not be displaced by the wetting agent. The repulsive barrier can be electrostatic in nature, whereby electrical double layers are formed at the solid/liquid interface [8, 9]. These double layers must be extended (by maintaining low electrolyte concentration) and strong repulsion occurs on double-layer overlap. Alternatively, the repulsion can be produced by the use of nonionic surfactant or polymer layers which remain strongly hydrated (or solvated) by the molecules of the continuous medium [10]. On approach of the particles to a surface-to-surface separation distance that is lower than twice the adsorbed layer thickness, strong repulsion occurs as a result of two main effects: (i) unfavorable mixing of the layers when these are in good solvent conditions and (ii) loss of configurational entropy on significant overlap of the adsorbed layers. This process is referred to as steric repulsion. A third repulsive mechanism is that whereby both electrostatic and steric repulsion are combined, for example, when using polyelectrolyte dispersants.

1.1.3
Wet Milling or Comminution

The primary particles produced after dispersion are subdivided into smaller units by milling or comminution (a process that requires rupture of bonds). Wet milling can be achieved using ball mills, bead mills (ceramic balls or beads are normally

used to avoid contamination), or colloid mills. Again the milling conditions must be adjusted to prevent heat and/or foam formation. The role of the dispersing agent (surfactant) in breaking the primary particles is usually described in terms of the "Rehbinder" effect, that is, adsorption of the dispersing agent molecules on the surface of the particles (which lowers their surface energy) and in particular in the "cracks" which facilitate their propagation.

1.1.4
Stabilization of the Resulting Dispersion

The particles of the resulting dispersion may undergo aggregation (flocculation) on standing as a result of the universal van der Waals attraction. Any two macroscopic bodies (such as particles) in a dispersion attract each other as a result of the London dispersion attractive energy between the particles. This attractive energy becomes very large at short distances of separation between the particles. As mentioned above, to overcome the everlasting van der Waals attraction energy, it is essential to have a repulsive energy between the particles. Two main repulsive energies can be described: electrostatic repulsive energy is produced by the presence of electrical double layers around the particles produced by charge separation at the solid/liquid interface. The dispersant should be strongly adsorbed to the particles, produce high charge (high surface or zeta potential), and form an extended double layer (that can be achieved at low electrolyte concentration and low valency) [8, 9]. The second repulsive energy, steric repulsive energy, is produced by the presence of adsorbed (or grafted) layers of surfactant or polymer molecules. In this case the nonionic surfactant or polymer (referred to as polymeric surfactant) should be strongly adsorbed to the particle surface and the stabilizing chain should be strongly solvated (hydrated in the case of aqueous suspensions) by the molecules of the medium [10]. The most effective polymeric surfactants are those of the A–B, A–B–A block, or BA_n graft copolymer. The "anchor" chain B is chosen to be highly insoluble in the medium and has strong affinity to the surface. The A stabilizing chain is chosen to be highly soluble in the medium and strongly solvated by the molecules of the medium. For suspensions of hydrophobic solids in aqueous media, the B chain can be polystyrene, poly(methylmethacrylate), or poly(propylene oxide). The A chain could be poly(ethylene oxide) which is strongly hydrated by the medium.

1.1.5
Prevention of Ostwald Ripening (Crystal Growth)

The driving force for Ostwald ripening is the difference in solubility between the small and large particles (the smaller particles have higher solubility than the larger ones). The difference in chemical potential between different sized particles was given by Lord Kelvin [11],

$$S(r) = S(\infty)\exp\left(\frac{2\sigma V_\mathrm{m}}{rRT}\right) \tag{1.25}$$

where $S(r)$ is the solubility surrounding a particle of radius r, $S(\infty)$ is the bulk solubility, σ is the solid/liquid interfacial tension, V_m is the molar volume of the dispersed phase, R is the gas constant, and T is the absolute temperature. The quantity $(2\sigma V_m/rRT)$ is termed the characteristic length. It has an order of ~1 nm or less, indicating that the difference in solubility of a $1\,\mu$m particle is of the order of 0.1% or less. Theoretically, Ostwald ripening should lead to condensation of all particles into a single. This does not occur in practice since the rate of growth decreases with the increase of the particle size.

For two particles with radii r_1 and r_2 ($r_1 < r_2$),

$$\frac{RT}{V_m} \ln\left[\frac{S(r_1)}{S(r_2)}\right] = 2\sigma\left[\frac{1}{r_1} - \frac{1}{r_2}\right]$$

(1.26)

Equation (1.26) shows that the larger the difference between r_1 and r_2, the higher the rate of Ostwald ripening.

Ostwald ripening can be quantitatively assessed from plots of the cube of the radius versus time t,

$$r^3 = \frac{8}{9}\left[\frac{S(\infty)\sigma V_m D}{\rho RT}\right]t$$

(1.27)

where D is the diffusion coefficient of the disperse phase in the continuous phase.

Several factors affect the rate of Ostwald ripening and these are determined by surface phenomena, although the presence of surfactant micelles in the continuous phase can also play a major role. Trace amounts of impurities that are highly insoluble in the medium and have strong affinity to the surface can significantly reduce Ostwald ripening by blocking the active sites on the surface on which the molecules of the active ingredient can deposit. Many polymeric surfactants, particularly those of the block and graft copolymer types, can also reduce the Ostwald ripening rate by strong adsorption on the surface of the particles, thus making it inaccessible for molecular deposition. Surfactant micelles that can solubilize the molecules of the active ingredient may enhance the rate of crystal growth by increasing the flux of transport by diffusion.

1.1.6
Prevention of Sedimentation and Formation of Compact Sediments (Clays)

Sedimentation is the result of gravity–the particle density is usually larger than that of the medium. The particles tend to remain uniformly dispersed as a result of their Brownian (thermal) motion (of the order of kT; k is the Boltzmann constant and T is the absolute temperature). The gravity force is $(4/3)\pi R^3 \Delta\rho g L$ (R is the particle radius, $\Delta\rho$ is the buoyancy or the density difference between the particle and the medium, g is the acceleration due to gravity, and L is the length of the container). When $(4/3)\pi R^3 \Delta\rho g L > kT$, sedimentation of the individual particles will occur. The particles in the sediment will rotate around each other (as a result of the repulsive forces between them) producing a compact sediment (technically referred to as a "clay"). The compact sediments are very difficult to redisperse (due

to the small distances between the particles). Production of "clays" must be prevented by several processes [3]: using "thickeners" which can produce a "gel" network in the continuous phase. At low stresses (which are exerted by the particles) these "gel" networks produce a high viscosity preventing particle sedimentation. In most cases, the particles and the "thickener" produce a "three-dimensional" structure that prevents separation of the dispersion. In some cases, "controlled" flocculation of the particles (self-structured systems) may be used to prevent sedimentation. The most widely used "thickeners" for prevention of sedimentation in aqueous suspensions are high molecular weight water soluble polymers such as hydroxyethylcellulose (HEC) or xanthan gum (a polysaccharide with a molecular weight $>10^6$). These polymers show non-Newtonian (shear thinning) behavior above a critical concentration C^* at which polymer coil overlap occurs. Above C^* the residual (or zero shear) viscosity show a rapid increase with the further increase in polymer concentration. These overlapped coils form a "three-dimensional" gel network in the continuous phase, thus preventing particle sedimentation. Alternatively, one can use finely divided "inert" particles such as swellable clays (e.g., sodium montmorillonite) or silica that can also produce a three-dimensional gel network in the continuous phase. In most cases, a mixture of high molecular weight polymer such as xanthan gum and sodium montmorillonite is used. This gives a more robust gel structure that is less temperature dependent.

1.2
Particle Dimensions in Suspensions

It is necessary to define the lower and upper limit of particle dimensions. This is by no means exact, and only an arbitrary range of dimensions may be chosen depending on the range of properties of the system with the change of size. For example, the lower limit may be set by the smallest aggregate for which it is meaningful to distinguish between "surface" and "interior" molecules; this is arbitrarily taken to be about 1 nm. Simple considerations show that when matter is subdivided into particles with dimensions below 1000 nm (1 μm) a substantial proportion of the atoms or molecules come close to the surface and make contributions to the energy that differ from those made by the molecules in the interior. This is sometimes set as the upper limit of the colloidal state, and therefore solid/liquid dispersions within the size range 1 nm–1 μm may be referred to as colloidal suspensions. It is difficult to set an upper limit for the size of particles in suspensions, but generally speaking particles of diameters tens of micrometers may be encountered in many practical systems.

1.3
Concentration Range of Suspensions

The particle concentration in a suspension is usually described in terms of its volume fraction ϕ, that is, the total volume of the particles divided by the total

volume of the suspensions. Volume fractions covering a wide range (0.01–0.7 or higher) are encountered in many practical systems. It is difficult to define an exact value for ϕ at which a suspension may be considered to be "dilute" or "concentrated." The most convenient way is to consider the balance between the particles' translational motion and their interparticle interactions. At one extreme, a suspension may be considered "dilute" if the thermal motion of the particles predominate over the imposed interparticle forces [12, 13]. In this case the particle translational motion is large, and only occasional contacts occur between the particles, that is, the particles do not "see" each other until collision occurs, giving a random arrangement of particles. In this case the particle interactions can be described by two-body collisions. Such dilute suspensions show no phase separation when the particle sizes are in the colloid range and the density of the particles is not significantly larger than that of the medium (e.g., polystyrene latex suspension). Moreover, the properties of the suspension are time independent, and therefore any time-averaged quantity such as viscosity or light scattering can be extrapolated to infinite dilution to obtain the particle size.

As the particle number is increased in a suspension, the volume of space occupied by the particles increases relative to the total volume of the suspension and a proportion of space is excluded in terms of its occupancy by a single particle. Moreover, the probability of particle–particle interaction increases and the forces of interaction between the particles play a dominant role in determining the properties of the system. With the further increase in particle number concentration, the interactive contact between the particles produces a specific order between them, and a highly developed structure is obtained. Such ordered systems are referred to as "solid" suspensions. In such cases, any particle in the system interacts with many neighbors. The particles are only able to vibrate within a distance that is small relative to the particle radius. The vibrational amplitude is essentially time independent, and hence the properties of the suspension such as its elastic modulus are also time independent.

In between the random arrangement of particles in "dilute" suspensions and the highly ordered structure of "solid" suspensions, one may loosely define concentrated suspensions [12, 13]. In this case, the particle interactions occur by many-body collisions and the translational motion of the particles is restricted. However, the translational motion of the particles is not reduced to the same extent as with "solid" suspensions, that is, the vibrational motion of the particles in this case is large compared with the particle radius. A time-dependent system arises in which there will be spatial and temporal correlations.

1.4
Outline of the Book

The text is organized as follows: Chapter 2 deals with the fundamentals of wetting with particular reference to the contact angle concept. The thermodynamic treatment of the contact angle and Young's equation is presented. This is followed by

the analysis of the spreading pressure, adhesion tension, work of adhesion, and cohesion. The Harkins definition of spreading coefficient is discussed. Finally, the contact angle hysteresis and its reasons are discussed in terms of surface roughness and surface heterogeneity.

Chapter 3 deals with the concept of critical surface tension of wetting, its measurement, and its value in characterizing solid surfaces. The role of surfactants on powder wetting is analyzed in terms of its adsorption and effect on the contact angle. A distinction is made between the dynamic and equilibrium processes of surfactant adsorption. A section is given on the analysis of the dynamics of adsorption and its measurement. An analysis is given of the process of dispersion wetting. The process of wetting of the internal surface and the capillary phenomena is described. This is followed by the analysis of the rate of penetration of liquids into pores between aggregates and agglomerates. The assessment of wettability using sinking time test and contact angle measurements is described. This is followed by classification of wetting agents for hydrophobic solids in aqueous media.

Chapter 4 deals with the structure of the solid/liquid interface and electrostatic stabilization. It starts with the description of the origin of charge on surfaces and creation of the electrical double layer. The structure of the electrical double layer following Gouy–Chapman–Stern–Grahame pictures is given. Analysis of the double-layer extension and electrostatic repulsion is described at a fundamental level. The effect of electrolyte concentration and valency on double-layer extension and repulsion is described. Analysis of the van der Waals attraction is given in terms of the London dispersion forces. The expressions for the London van der Waals attraction and the effect of the medium are described. The combination of electrostatic repulsion and van der Waals attraction gives the total energy of interaction between particles as a function of their surface-to-surface separation. This forms the basis of the theory of colloid stability due to Deryaguin–Landau–Verwey–Overbeek (DLVO) theory. Energy–distance curves are given with particular reference to the effect of electrolyte concentration and valency. The main criteria for effective electrostatic stabilization I are given. This is followed by a section on suspension flocculation as a kinetic process. Both fast and slow flocculation are described followed by the concept of stability ratio. This leads to the definition of critical coagulation concentration (CCC) and its dependence on electrolyte valency as described by the Schultze–Hardy rule.

Chapter 5 deals with the electrokinetic phenomena and the zeta potential. The process of charge separation in the region between two adjoining phases is described. The arrangement of charges on one phase and the distribution of charges in the adjacent phase result in the formation of the electrical double layer described in Chapter 4. When one of these phases is caused to move tangentially past the second phase leads to the phenomena of electrokinetic effects which can be classified into four main topics, namely, electrophoresis, electro-osmosis, streaming potential, and sedimentation potential. A brief description of each of these effects is given. Particular emphasis is given to the process of electrophoresis that is commonly applied for suspensions. The concept of surface of shear is

described and hence the definition of electrokinetic or zeta potential. The calculation of the zeta potential from electrophoretic mobility using Smoluchowski, Huckel, Henry and Wiersema, Loeb, and Overbeek theories is described. This is followed by the experimental techniques of measurement of electrophoretic mobility and zeta potential. Both microelectrophoresis and electrophoretic light scattering (Laser-Doppler method) or laser velocimetry are described.

Chapter 6 gives the general classification of dispersing agents and adsorption of surfactants at the solid/liquid interface. The dispersing agents can be ionic or nonionic surfactants, polymeric surfactants, and polyelectrolytes. The process of surfactant adsorption is described at a fundamental level using the Stern–Langmuir analysis of surfactant adsorption and its modification by Frumkin–Fowler–Guggenheim for high surface coverage. The adsorption of ionic and nonionic surfactants on hydrophobic and hydrophilic solids is described with emphasis on the free energy of surfactant adsorption. The concept of hemi-micelle formation on solid surfaces is described. This is followed by the different adsorption isotherms of nonionic surfactants on solid surfaces and the structure of the adsorbed layers.

Chapter 7 deals with the process of adsorption of polymers at the solid/liquid interface. The complexity of the process of polymer adsorption and the importance of the configuration (conformation) of the polymer at the solid/liquid interface are described with particular reference to the polymer/surface and polymer/solvent interaction. The conformation of homopolymers, and block and graft copolymers at the solid/liquid interface is described. For characterization of polymer adsorption one needs to determine the various parameters that determine the process. The theories of polymer adsorption are briefly described. This is followed by the description of the experimental methods for determination of the various adsorption parameters.

Chapter 8 deals with the process of stabilization of suspensions using polymeric surfactants and the theory of steric stabilization. The interaction between particles containing adsorbed polymer layers is described in terms of interpenetration and/or compression of the adsorbed layers. The unfavorable mixing of the stabilizing chains when these are in good solvent conditions is described at a fundamental level. The entropic, volume restriction, or elastic interaction is described. The combination of mixing and elastic interaction gives the total steric interaction. The combination of steric repulsion with van der Waals attraction shows the resulting energy–distance curve for sterically stabilized suspensions. The role of the adsorbed layer thickness in determining the energy–distance curve is described. This is followed by the main criteria for effective steric stabilization. The conditions for flocculation of sterically stabilized dispersions are described. Both weak (reversible) and strong (incipient) flocculation can be produced depending on the conditions. Particular attention is given to the role of the solvency of the medium for the stabilizing chains.

Chapter 9 deals with the properties of concentrated suspensions. A distinction can be made between "dilute," "concentrated," and "solid" suspension in terms of the balance between Brownian diffusion and interparticle forces as discussed above. The states of suspensions on standing are described in terms of interpar-

ticle interactions and the effect of gravity. Three main systems can be distinguished: colloidally stable, coagulated, and weakly flocculated suspensions. The colloidally stable systems are those where the net interaction between the particles is repulsive, whereas coagulated systems are those with net attraction between the particles. Weakly flocculated suspensions are produced with a relatively smaller attraction and in this case the flocculation is reversible. Three systems could be distinguished: weakly flocculated suspension with net attraction in the secondary (shallow) minimum, flocs produced by bridging with polymer chains that are weakly adsorbed on the particle surfaces, and weakly flocculated suspensions produced by addition of "free" (nonadsorbing) polymer in the continuous phase.

Chapter 10 deals with sedimentation of suspensions and prevention of formation of dilatant sediments. It starts with the effect of particle size and its distribution on sedimentation. The sedimentation of very dilute suspensions with a volume fraction $\phi \leq 0.01$ and application of the Stokes law is described. This is followed by the description of sedimentation of moderately concentrated suspensions (with $0.2 \geq \phi \geq 0.1$) and the effect of hydrodynamic interaction; sedimentation of concentrated suspensions ($\phi > 0.2$) and models for its description; sedimentation in non-Newtonian liquids and correlation of sedimentation rate with residual (zero shear) viscosity; and role of thickeners (rheology modifiers) in prevention of sedimentation: balance of density, reduction of particle size, and use of thickeners and finely divided inert particles. The application of depletion flocculation for reduction of sedimentation is described. The use of liquid crystalline phases for reduction of sedimentation is also described.

Chapter 11 deals with characterization of suspensions and assessment of their stability. It gives a brief description of the various techniques that can be applied for measurement of the particle size distribution. This starts with optical microscopy and improvements using phase contrast, differential interference contrast, and polarizing microscopy. The use of electron and scanning electron microscopy for assessment of suspensions is also described. Techniques such as confocal scanning laser microscopy and atomic force microscopy are also briefly described. The various scattering techniques that can be applied for particle size determination are described. They start with application time average and dynamic light scattering. The use of light diffraction techniques that are commonly in practice is also discussed. For assessment of concentrated suspensions backscattering techniques are described.

Chapter 12 describes the methods of evaluation of suspensions without dilution, in particular the application of rheological techniques. The various rheological methods that can be applied are described. The first method is steady-state shear stress–shear rate measurements that can distinguish between Newtonian and non-Newtonian flow. The various rheological models that can be applied for the analysis of the flow curves are described. This is followed by the description of constant stress (creep) measurements and the concept of residual (zero shear) viscosity and critical stress. The last part deals with dynamic or oscillatory techniques and calculation of the complex, storage, and loss moduli. This allows one to obtain information on the structure of the suspension and the cohesive energy

density of the flocculated structure. A section is devoted to the use of rheology for the assessment and prediction of the physical stability of the suspension. Chapter 13 describes the rheology of concentrated suspensions which depends on the balance between Brownian diffusion, hydrodynamic interaction, and interparticle forces. An important dimensionless number is the ratio between the relaxation time of the suspension and the applied experimental time and this is defined as the Deborah number. The Einstein equation for very dilute suspensions ($\phi \leq 0.01$) and its modification by Batchelor for moderately concentrated suspensions (with $0.2 \geq \phi \geq 0.1$) are described. Rheology of concentrated suspensions ($\phi > 0.2$) is described. It starts with hard-sphere suspensions where both repulsion and attraction are screened. The models for the analysis of the viscosity versus volume fraction curves are described. This is followed by electrostatically stabilized suspensions where the rheology is determined by double-layer repulsion. The rheology of sterically stabilized suspensions is described with particular reference to the effect of the adsorbed layer thickness. Finally, the rheology of flocculated suspensions is described and a distinction is made between weakly and strongly flocculated systems. The various semiempirical models that can be applied for the analysis of the flow curves are described.

References

1 Tadros, T. (2005) *Applied Surfactants,* Wiley-VCH Verlag GmbH, Weinheim, Germany.

2 Parfitt, G.D. (ed.) (1977) *Dispersion of Powders in Liquids,* Applied Science Publishers, London.

3 Tadros, Th.F. (ed.) (1987) *Solid/Liquid Dispersions,* Academic Press, London.

4 Gibbs, J.W. (1928) *Collected Works,* vol. 1, Longman, New York, p. 219.

5 Hough, D.B., and Randall, H.M. (1983) *Adsorption from Solution at the Solid/ Liquid Interface* (eds G.D. Parfitt and C.H. Rochester), Academic Press, London, p. 247.

6 Fuerstenau, D.W., and Healy, T.W. (1972) *Adsorptive Bubble Separation Techniques* (ed. R. Lemlich), Academic Press, London, p. 91.

7 Somasundaran, P., and Goddard, E.D. (1979) *Mod. Aspects Electrochem.,* **13**, 207.

8 Deryaguin, B.V., and Landau, L. (1941) *Acta Physicochem. USSR,* **14**, 633.

9 Verwey, E.J.W., and Overbeek, J.Th.G. (1948) *Theory of Stability of Lyophobic Colloids,* Elsevier, Amsterdam.

10 Napper, D.H. (1983) *Polymeric Stabilisation of Dispersions,* Academic Press, London.

11 Thompson, W. (Lord Kelvin) (1871). *Phil. Mag.,* **42**, 448.

12 Ottewill, R.H. (1982) *Concentrated Dispersions* (ed. J.W. Goodwin), Royal Society of Chemistry, London. Chapter 9.

13 Ottewill, R.H. (1983) Concentrated dispersions, in *Fundamental Considerations of Science and Technology of Polymer Colloids,* vol. II (eds G.W. Poehlin, R.H. Ottewill, and J.W. Goodwin), Martinus Nijhoff, Boston/The Hague, p. 503.