1
General Introduction

Several classes of formulations of disperse systems are encountered in the chemical industry, including suspensions, emulsions, suspoemulsions (mixtures of suspensions and emulsions), nanoemulsions, multiple emulsions, microemulsions, latexes, pigment formulations, and ceramics. For the rational preparation of these multiphase systems it is necessary to understand the interaction forces that occur between the particles or droplets. Control of the long-term physical stability of these formulations requires the application of various surfactants and dispersants. It is also necessary to assess and predict the stability of these systems, and this requires the application of various physical techniques.

A brief description of the various formulation types is provided in the following sections.

1.1
Suspensions

These are by far the most commonly used systems for the formulation of insoluble solids. The solid can be hydrophobic, such as most organic materials that are used in pharmaceuticals, agrochemicals, and paints; the solid can also be hydrophilic, such as silica and clays. With some pigments and inks the particles need to be very small – that is, in the nanosize range – and these are referred to as nanosuspensions. Latexes may also be considered as suspensions, particularly if the particles are solid-like at ambient temperatures. With many of the latexes that are used in paints the particles are liquid-like at below and ambient temperature, but when applied to a surface these liquid-like particles coalesce to form a uniform film. The system may then be considered as an emulsion.

For the formulation of suspensions, the hydrophobic or hydrophilic solid is dispersed in a aqueous or nonaqueous medium to produce a system that covers a wide particle size range, typically 0.1–5 μm. This process requires the presence of a surfactant (dispersant) that satisfies four criteria: (i) wetting of the powder by the liquid; (ii) the dispersion of aggregates and agglomerates into single units; (iii) comminution of the large particles into smaller units; and (iv) stabilisation

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of the resulting dispersion against flocculation and crystal growth. The choice of wetting/dispersing agent is crucial for achieving this control.

1.2
Latexes

As mentioned above, latexes may be considered as suspensions and are prepared using two main processes:

(i) Emulsion polymerisation: In this case the monomer, for example styrene or methylmethacrylate, is emulsified in water using an appropriate surfactant. An initiator such as potassium persulphate is then added and the system is heated to produce the polymer particles. Initiation mostly occurs in the monomer swollen micelles, and the number of particles produced and their size depends on the number of micelles.

(ii) Dispersion polymerisation: The monomer is dissolved in a solvent in which the resulting polymer particles are insoluble. An initiator that is soluble in the solvent is added to start the polymerisation process. A protective agent that strongly adsorbs onto the particle surface (or becomes incorporated in the particle) is simultaneously added to prevent aggregation of the particles. The protective agent is a block (A-B or A-B-A) or graft (Ban) copolymer. B is the ‘‘anchor’’’ chain that is chosen to be insoluble in the medium and has a strong affinity to the surface, while A is the stabilising chain that is highly soluble in the medium and is strongly solvated by its molecules. This provides a strong steric repulsion.

1.3
Emulsions

These are dispersions of liquid drops in an immiscible liquid medium. The most common systems are oil-in-water (O/W) and water-in-oil (W/O). It is also possible to disperse a polar liquid into an immiscible nonpolar liquid, and vice versa; these are referred to as oil-in-oil (O/O) emulsions. In order to disperse a liquid into another immiscible liquid, a third component is needed that is referred to as the emulsifier. Emulsifiers are surface-active molecules (surfactants) that adsorb at the liquid/liquid interface, thus lowering the interfacial tension and hence the energy required for emulsification is reduced. The emulsifier plays several other roles: (i) it prevents coalescence during emulsification; (ii) it enhances the deformation and break-up of the drops into smaller units; (iii) it prevents flocculation of the emulsion by providing a repulsive barrier that prevents close approach of the droplets to prevent van der Waals attraction; (iv) it reduces or prevents Ostwald ripening (disproportionation); (v) it prevents coalescence of the drops; and (vi) it prevents phase inversion.

1.4
Suspoemulsions

These are mixture of suspensions and emulsions that can be produced by mixing two separately prepared suspensions and emulsions. Suspoemulsions may also be produced by the emulsification of an oil into a prepared suspension, or dispersing a solid an emulsion. Several instability processes may occur in these systems: (i) homoflocculation, whereby the suspension particles and emulsion drops form separate flocs; (ii) heteroflocculation, whereby the suspension particles and emulsion drops form combined flocs; and (iii) phase transfer and crystal growth. The solid particles can enter the emulsion droplets, but when they leave the droplets they may grow to form large crystals.

1.5
Multiple Emulsions

These are complex systems of emulsions of emulsions. Two types may be identified:

(i) Water-in-Oil-in-Water (W/O/W), whereby the oil droplets of an O/W emulsion contain emulsified water droplets. These are generally produced via a two-step process: a W/O emulsion is first prepared using a low-hydrophilic–lipophilic-balance (HLB) which is then emulsified into an aqueous solution of a high-HLB surfactant.
(ii) Oil-in-Water-in-Oil (O/W/O), where an O/W emulsion that has been prepared using a high-HLB surfactant is emulsified into an oil solution of a low-HLB surfactant.

It is also possible to prepare multiple emulsions consisting of nonpolar oil droplets with emulsified polar oil droplets which are dispersed in an aqueous solution or another polar oil. With W/O/W multiple emulsions it is essential to control the osmotic balance between the internal water droplets and the external continuous phase.

Several breakdown processes may be identified with multiple emulsions:

- Expulsion of the water droplets from the multiple emulsion drop to the external phase. This may result in the production of an O/W emulsion.
- Coalescence of the water droplets in the W/O/W multiple emulsion or the oil droplets in the O/W/O system.
- Flocculation of the multiple emulsion drops that would be accompanied by an increase in the viscosity of the system.
- Coalescence of the multiple emulsion drops with the ultimate formation of a W/O emulsion.
- Diffusion of the active ingredients from the internal droplets to the external continuous phase.

1.6
Nanosuspensions

These are suspensions with a size range of 20 to 200 nm. Like suspensions, they are kinetically stable but, due to the small size of the particles, they have much longer physical stability: (i) an absence of sedimentation, as the Brownian motion is sufficient to prevent separation by gravity; and (ii) an absence of flocculation, as the repulsive forces (electrostatic and/or steric) are much larger than the weak van der Waals attraction.

Nanosuspensions can be prepared by two main process:

(i) Top-up processes, whereby one starts with molecular components that can grow by a process of nucleation and growth process.
(ii) Bottom-down processes, whereby the large particles are subdivided by application of intense energy, for example using high-pressure homogenisers or bead milling.

The resulting nanosuspensions must be maintained colloidally stable by using surfactants and/or polymers that provide an effective energy barrier against flocculation.

1.7
Nanoemulsions

These are emulsion systems with a size range of 20 to 200 nm. Like emulsions, they are only kinetically stable but, due to the very small size, they have much longer physical stability:

- The very small droplets prevent any creaming or sedimentation, as the Brownian diffusion is sufficient to prevent separation by gravity.
- The small droplets have much smaller van der Waals attraction, and flocculation is prevented. This is particularly the case with sterically stabilised systems.
- The small droplets prevent coalescence, as surface fluctuation is not possible and the liquid film between the droplets that has an appreciable thickness prevents any thinning or disruption of that film.

The major instability process of nanoemulsions is Ostwald ripening, which results from the difference in solubility between the small and larger drops. The smaller droplets with a higher curvature have a greater solubility than the larger droplets. On storage, the droplet size distribution shifts to larger sizes and, ultimately, the nanoemulsion will become an emulsion with larger sizes. Nanoemulsions can be transparent, translucent or turbid, depending on two main parameters: the droplet size distribution and the difference in refractive index between the disperse and continuous phases.

1.8
Microemulsions

These are transparent or translucent systems covering the size range from 5 to 50 nm. Unlike emulsions and nanoemulsions (which are only kinetically stable), microemulsions are thermodynamically stable as the free energy of their formation is either zero or negative. Microemulsions are better considered as swollen micelles: normal micelles can be swollen by some oil in the core of the micelle to form O/W microemulsions. Reverse micelles can be swollen by water in the core to form W/O microemulsions.

The driving force for microemulsion formation is the ultra-low interfacial tension which is normally obtained by using two surfactants: one which is predominantly oil-soluble (such as a medium-chain alcohol) and one which is predominantly water-soluble (such as an anionic surfactant). The low tension results in a low interfacial energy which can be overcompensated by the entropy of dispersion. Microemulsions require the use of a high surfactant concentration. For example, for a 20% microemulsion the surfactant concentration will be in the range 10–20%.

1.9
Pigment and Ink Dispersions

Pigments are used in many industrial applications, such as paints and dyestuffs. One of the most widely used white pigments is titanium dioxide, which is applied in white paints (undercoat and overcoat) and in sunscreens (for protection against UV light). Several dispersions of titanium dioxide are formulated that require an optimum particle size distribution for particular application. In paints, the particle size distribution is controlled to give maximum hiding power (high reflection of light), whereas for sunscreens the particle size distribution is controlled to give maximum UV adsorption. Both, aqueous and nonaqueous titanium dioxide dispersions are formulated, and these require the use of efficient dispersing agents. Several other coloured pigments of inorganic and organic materials are also formulated both for dyestuff, paint and ink jet applications. These dispersions are generally in the submicron size (nanodispersions), and they require the use of efficient wetting, dispersing and milling agents. It is also essential to control the physical stability of these nanosuspensions, both on storage and on application. Strong repulsive barriers, whether electrostatic, steric and/or electrosteric (a combination of electrostatic and steric), are essential to prevent any aggregation.

1.10
Foams

Foams are gas-in-liquid dispersions that may be obtained as either aqueous or nonaqueous forms. In some cases a highly stable foam is required, for example in fire-fighting foams and in many food products, whereas in other cases the destruction of a foam may be required, for example during the preparation of suspensions or emulsions. An antifoaming agent or a defoamer is required to prevent foam formation. Several theories are available that can describe the stability/instability of foams. One of the most acceptable of these is the production of a high interfacial elasticity (Gibbs dilational elasticity) which promotes the flow of liquid between the air bubbles (Marangoni effect). The concept of a disjoining pressure, as described by Deryaguin, has also been introduced to explain foam stability.

This book, on the formulation of disperse systems, is organised as follows. Chapter 2 will provide a brief description of the various surfactant classes that are used in the formulations, while Chapter 3 describes the physical chemistry of surfactant solutions, with emphasis placed on the process of micellisation. Chapter 4 summarises the various dispersants and polymers used for stabilisation of disperse systems, and the criteria for an effective dispersant are described. Chapter 5 describes the adsorption of surfactants at the air/liquid, liquid/liquid, and solid/liquid interfaces, together with details of the adsorption process and its effect on the surface, interfacial and solid/liquid tensions. The theoretical analysis of the adsorption process, using the Gibbs and Langmuir adsorption isotherms and area occupied by a surfactant molecule is described. Measurement of the surfactant adsorption at various interfaces is also described. Chapter 6 provides an account of the adsorption of polymeric surfactants at the solid/liquid interface, and the general behaviour of polymer adsorption and its irreversibility are also emphasised. Theories of polymer adsorption and the experimental determination of adsorption parameters are also briefly described. Chapter 7 describes the colloid stability of disperse systems containing electrical double layers. Various models of the electrical double layer at charged interfaces are described, and this is followed by a description of the interaction between particles or droplets containing electrical double layers. The van der Waals attraction between particles or droplets is analysed, and the combination of electrostatic repulsion with van der Waals attraction is used to describe the theory of colloid stability. The parameters that determine the stability/instability of disperse systems are summarised, and this is followed by a section on the flocculation of dispersions, with both fast and slow flocculation processes being described. Chapter 8 describes the stability of disperse systems containing adsorbed nonionic surfactants or polymers, referred to as steric stabilisation. The interaction between particles or droplets containing adsorbed nonionic surfactants or polymers is described in terms of mixing and elastic (entropic) interactions. A combination of the mixing and elastic terms with van der Waals attraction describes the theory of steric stabilisation and the criteria for its effectiveness. The flocculation of sterically stabilised dispersions both weak and strong is described. Chapter 9 describes the formulation of solid/liquid dispersions (suspensions), and details are provided of the preparation of suspensions by condensation (nucleation and growth) and dispersion methods. The factors affecting each process and the role of surfactants are also briefly described, and the process of powder wetting and dispersion, and their evaluation, is analysed in terms of the surface forces involved. The stabilisation of suspensions, using electrostatic and/or steric repulsion, is described in terms of the various interaction forces. The properties of concentrated suspension and their states on storage are described. Ostwald ripening (crystal growth) and its prevention is described. The distinction between colloid and physical stability is described in terms of the interaction forces and the effect of gravity. The final part of the chapter describes the process of sedimentation of suspensions and methods for its prevention. Chapter 10 deals with the formulation of liquid/liquid dispersions (emulsions), and the description of emulsion systems and their classification, depending on the nature of the emulsifier or the structure of the system, is discussed. This is followed by a section on the thermodynamics of emulsion formation and stability. The methods of emulsification and the role of the surfactant are also described, as are the various methods that can be applied for the selection of emulsifiers. This followed by analysis of the stability/instability of emulsions, namely creaming or sedimentation, flocculation, Ostwald ripening, coalescence, and phase inversion. The methods that can be applied for the prevention of emulsion instability are given. Chapter 11 describes the formulation of suspoemulsions (mixtures of suspensions and emulsions), with the application of suspoemulsions in agrochemicals, cosmetics and paints being briefly described. The various interactions in suspoemulsions, namely homoflocculation and heteroflocculation, coalescence and crystallisation are described. The reduction of heteroflocculation using polymeric surfactants, and the prevention of creaming and sedimentation and recrystallisation in suspoemulsions is also described. Chapter 12 deals with the formulation of multiple emulsions, notably W/O/W and O/W/O systems. The structure of multiple emulsions and their breakdown processes are also described, and this is followed by a section on the preparation of multiple emulsions using a two-stage process. The characterisation of multiple emulsions using droplet size analysis and rheology is also described. Chapter 13 describes the methods of preparation of nanosuspensions, and the application of nanosuspensions in cosmetics and drug delivery is outlined. The preparation of nanosuspensions by top-up (starting from molecular units) and bottom-down (by the comminution of larger particles) processes is described, with emphasis placed on the factors determining each process: nucleation and growth (top-up process), wetting, dispersion, and the comminution of larger particles (bottom-down process). The role of surfactants and dispersants in each process and maintenance of the stability of nanoparticles against flocculation and crystal growth is also described. Chapter 14 deals with the formulation of nanoemulsions and the factors that control their transparency. The advantages of nanoemulsions in personal and health care are summarised, and this is followed by a section on the preparation of nanoemulsions using high-pressure homogenisers and low-energy emulsification methods, including phase inversion composition (PIC) and phase inversion temperature (PIT) methods. The origin of the high kinetic stability of nanoemulsions is described in terms of the interaction forces between the droplets, and this is followed by a section on the Ostwald ripening of nanoemulsions, and its reduction. Examples of nanoemulsions based on nonionic and polymeric surfactants are given. Chapter 15 deals with the formulation of microemulsions and the surfactant composition. The definition of microemulsions and the origin of their thermodynamic stability is described; this is followed by a section on the phase diagrams of ternary (water-surfactant-cosurfactant) and quaternary (water-oil-surfactant-cosurfactant) systems and identification of the microemulsion region. Theories of the stability of microemulsions are also briefly described, as are the characterisation of microemulsions using scattering methods, conductivity and NMR. Chapter 16 deals with the formulation of foams, starting with the factors responsible for foam formation; the stability/instability of foams and the role of surfactants are also described. This is followed by a section on the theories of foam stability, and a description of antifoamers and defoamers is given. Applications of foam in the food industry, mineral flotation, wall insulation and enhanced oil recovery are illustrated. Chapter 17 describes the formulation of latexes and the methods of their preparation by emulsion and dispersion polymerisation; both, aqueous and oil-based latexes are described. The commonly used surfactants in emulsion and dispersion polymerisation are described, together with their role in each process. The application of latexes in paints and coatings is described, with particular reference to the factors affecting film formation. Chapter 18 deals with the formulation of pigments and inks. The various pigment types and their general properties are outlined, and the particle size and shape of pigments and the nature of the pigment surfaces are described. The wetting of pigment powders, and their deagglomeration and comminution, is described at a fundamental level, with particular reference to the role of surfactants and dispersants. The colloid stability of pigment dispersions in terms of electrostatic, steric and electrosteric forces is described. The application of pigment dispersions in paints, sunscreens and colour cosmetics is briefly described. Chapter 19 describes the methods of evaluation of formulations after dilution. The chapter starts with optical microscopy and particle size distribution using image analysis, phase contrast, differential interference contrast and polarising microscopies. A brief summary of scanning and transmission electron microscopies, confocal laser scanning microscopy, and atomic force microscopy is given. This is followed by the various scattering methods, including time average light scattering, turbidity, light diffraction, dynamic light scattering and back-scattering techniques. Chapter 20 describes the methods of evaluation of formulations without dilution, namely rheological techniques. The steady-state shear stress-shear rate measurements and the flow curves are described, together with the models that can be applied for fitting the flow curves and the evaluation of rheological parameters. The time effects during flow (thixotropy) and methods of their evaluation are described. The constant stress (creep) measurements and measurement of the residual (zero shear) viscosity are also described, followed by the investigation of stress relaxation after the sudden application of strain. The dynamic (oscillatory) methods and evaluation of the elastic and viscous components are described, with particular emphasis on calculation of the cohesive energy density of the structure formed. Chapter 21 deals with the methods that can be applied for the assessment and prediction of creaming or sedimentation, flocculation and coalescence. The accelerated tests for the evaluation of stability using temperature changes and centrifugation, and their limitations, are described. The rheological methods that can be applied for the prediction of creaming or sedimentation are described, showing a correlation of the rate with the residual (zero shear) viscosity. The prediction of formulation separation (syneresis), using modulus and cohesive energy density measurements, is described, and this is followed by the application of steady-state measurements for the prediction of formulation flocculation. The application of creep tests and dynamic (oscillatory) techniques for the prediction of flocculation is described, as is the measurement of emulsion coalescence rate by following the droplet number or average droplet size with time. The correlation of coalescence with a reduction of viscosity in the absence of flocculation and/or Ostwald ripening is also shown. Finally, the application of dynamic (oscillatory) methods for the prediction of emulsion coalescence is illustrated.

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