Today, consumer paints are predominantly water-based. Such systems offer easy application, quick dry, low odour and easy clean-up. Environmental concern, especially low VOC requirements, has increased the industrial awareness of latex polymers. The popularity of water-based surface coatings has sharply focused the need of chemists to understand the processes involved in forming latex polymers.

18.1 TERMINOLOGY

An emulsion is a mixture of two immiscible liquids—one, the dispersed phase, existing as discrete droplets dispersed throughout the other, the continuous phase. In the case of emulsion polymerization the continuous phase is comprised mainly of water and is therefore termed the aqueous phase. However, an emulsion polymer is actually a dispersion of solid, or semi-solid, polymeric particles in a continuous aqueous phase, and is, therefore in fact described as a colloidal suspension.

The polymeric particles develop once an appropriate initiator has been added to a system emulsified in an aqueous surfactant system. This is the process referred to as emulsion polymerization, although the term is something of a misnomer as it could be taken to imply the loci of the polymerization is within the monomer droplets, which, as will be seen, is not the case.

The end-products of emulsion polymerization utilized in the industry are sometimes themselves referred to as emulsions, but modern surface coatings literature tends to favour the more accurate term latexes.

18.2 INGREDIENTS FOR EMULSION POLYMERIZATION

The traditional emulsion polymerization system initially consists of four components: water, monomer, surfactant and initiator.

18.2.1 Water

Water is used as the dispersing medium in emulsion polymerization. The aqueous phase provides an excellent heat sink for the exothermic polymerization reaction, while it also provides a low-viscosity product even at high conversion of monomer to polymer. Water acts as the solvent for the stabilizing surfactant and initiator.

The aqueous phase supports the early reactions in the formation of an emulsion polymer. The system needs to be relatively clean to allow stable and reproducible products to be
formed. In particular, polyvalent metal ions can reduce the effectiveness of surfactants or inhibit the initiation process. For these reasons deionized water is often used.

### 18.2.2 Monomer

Emulsion polymerization is an example of a free radical mechanism. In order for polymerization to occur, the monomers involved require a degree of unsaturation. There are a large number of possible monomer structures. The most common structure is of the form $\text{CH}_2 = \text{CX}_1\text{X}_2$, where $\text{X}_1$ and $\text{X}_2$ may be of a variety of substituents. Such species are called vinyl monomers, for example:

- vinyl acetate $\text{CH}_2 = \text{CH} \longrightarrow \text{O} \longrightarrow \text{C} \longrightarrow \text{CH}_3$
- vinyl chloride $\text{CH}_2 = \text{CHCl}$
- styrene $\text{CH}_2 = \text{CH} \longrightarrow \text{C}_6\text{H}_5$
- methyl methacrylate $\text{CH}_2 = \text{C} \longrightarrow \text{C} \longrightarrow \text{OCH}_3$

### 18.2.3 Surfactants

Formation of a stable monomer emulsion in water can be difficult in the absence of any surface active agent. High-speed dispersion can produce an emulsion, but often this is unstable and two distinct layers eventuate. The large interfacial area between the liquids (monomer and water) implies that the emulsion has a high free energy compared with the separated phases. The addition of a soap, or surface active agent (surfactant), can lower the interfacial tension, thus forming a more stable emulsion. Furthermore, the use of surfactants stabilizes the growing polymer latex particles and the final latex.

Surfactants are molecules that can bridge an interfacial surface. They are composed of a hydrophilic portion, orientated into the aqueous phase, and a hydrophobic portion, orientated into a monomer droplet, polymer particle or micelle.

Surfactants have limited solubility in water. At the critical micelle concentration (cmc) clusters of 50–100 surfactants molecules form, exposing only their hydrophilic portion to the aqueous phase. These clusters are known as micelles. Traditional latex systems are formulated above the cmc.

Surfactant molecules can be classified as either anionic, cationic or non-ionic. A latex is also classified in this way, depending on the surfactant type employed. The use of either anionic or cationic surfactants means that the growing polymer particles are separated by coulombic forces. The degree of latex stability will be determined by the strength of the electrical double layer around the polymer particles. Non-ionic surfactants stabilize the latex through steric forces. Steric stabilization is less affected by impurities such as large metal ions. In practice, most commercial latexes are produced using a combination of anionic and non-ionic surfactants.

### 18.2.4 Initiators

The initiator system in emulsion polymerization must generate a free radical to commence the polymerization process. The initiator is usually water-soluble, although monomer-soluble