

CHAPTER 11

Surface Chemistry in the Petroleum Industry

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1 INTRODUCTION

It is well recognized that the energy consumption per capita and the standard of living of a society are interrelated. Among various sources of energy, fossil fuels or crude oils play an important role in providing the energy supply of the world. Crude oil is the most readily exploitable source of energy available to humankind, and is also a source of raw materials for feed stocks in many of the chemical industries on which our present civilization relies. The field of surface chemistry is intricately connected to most

(if not all) processes of petroleum technology – from the drilling of crude oil to petroleum refining and petrochemical processing – as well as to allied and dependent applications and industries. All of these processes involve interfacial phenomena and surface chemical interactions.

In the context of petroleum technology, surface chemistry deals with the surface properties of crude oil/air, crude oil/brine (or water) and crude oil/solid surfaces. Thus, surface tension, interfacial tension (IFT), contact angle, wetting and surface charge (zeta potential) are the parameters that one measures for surface

chemical studies. The next section deals with the fundamental aspects of surface chemistry and how they relate to the petroleum industry. Following this discussion, we will describe several major areas in the petroleum industry – enhanced oil recovery, corrosion inhibition, oil spill clean-up, fluidization of bitumen, asphaltic emulsions, oil/water separation and crude oil dehydration – where knowledge of surface chemistry plays a vital role.

2 FUNDAMENTALS

A surfactant molecule has two functional groups, namely a hydrophilic (water-soluble) or polar group and a hydrophobic (oil-soluble) or non-polar group. The hydrophobic group is usually a long hydrocarbon chain (C₈–C₁₈), which may or may not be branched, while the hydrophilic group is formed by moieties such as carboxylates, sulfates, sulfonates (anionic), alcohols, polyoxyethylenated chains (nonionic) and quaternary ammonium salts (cationic) (1). Crude oil contains organic acids and salts, alcohols and other natural surface-active agents. When crude oil is brought in contact with brine or water, these natural surfactants accumulate at the interface and form an adsorbed film which lowers the interfacial tension of the crude oil/water interface.

Depending on the type of crude oil, the adsorbed film at the interface can be either fluid or very viscoelastic and able to form a skin. Depending on the properties of the crude oil (e.g. API gravity (2), sulfur, salt and metals content, viscosity, pour point, etc.), the structure of the film can vary significantly. Therefore, the molecular packing, surface viscosity, surface elasticity and surface charge of the adsorbed film are very important parameters that determine various phenomena such as coalescence of emulsion droplets, as well as oil drop migration in porous media.

2.1 Adsorbed films

Adsorption is an entropically driven process by which molecules diffuse preferentially from a bulk phase to an interface. Due to the affinity that a surfactant molecule encounters towards both polar and non-polar phases, thermodynamic stability (i.e. a minimum in free energy or maximum in entropy of the system) occurs when these surfactants are adsorbed at a polar/non-polar (e.g. oil/water or air/water) interface. The difference between solute concentration in the bulk and that at the interface is the *surface excess* concentration. The latter

is related to surface and interfacial tension by the *Gibbs Adsorption Equation* (3–5), which in its practical form, is as follows:

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln C} \quad (11.1)$$

where Γ is the surface excess per unit area (moles/cm²) of surfactant measured, R the universal gas constant, T the temperature (in kelvin), γ the surface tension (often replaced by σ for interfacial tension), and C the bulk concentration of surface-active species. Once the surface excess Γ is known, the area per molecule of adsorbed surfactant can be calculated by using the following equation:

$$\text{Area per molecule}(\text{\AA}^2) = \frac{10^{16}}{N_A \Gamma} \quad (11.2)$$

with units of area/molecule in \AA^2 /molecule, and where N_A is the Avogadro constant (6.023×10^{23} molecules per mole).

The Gibbs adsorption equation allows for calculation of area per molecule from very simple measurements of surface (or interfacial) tension versus surfactant concentration in the solution. This calculation, in turn, enables one to study the relative area/molecule of a surfactant. Tighter molecular packing in the adsorbed film lowers the interfacial tension.

In addition, for very surface-active molecules, a slight increase in bulk phase concentration produces a dramatic reduction in the interfacial tension.

With the use of specific surfactants, and with appropriate physico-chemical conditions, the interfacial tension of a crude oil/water interface can drop as low as 10^{-4} mN/m (6). As will be discussed below, such ultra-low interfacial tensions are very important in technologies such as enhanced oil recovery processes for recovering crude oil from depleted oil wells.

The presence of surfactant molecules at an interface leads to a dramatic change in many surface properties, including surface and interfacial tensions (as discussed above), contact angle, wettability, surface charge and surface rheology (i.e. surface viscosity). Surfactants can also act as a barrier when they adsorb at an interface, thus influencing mass and heat transfer between the adjacent phases as well as dispersion stability (1).

2.2 Self-assembly of surfactant molecules

The adsorption of surface-active molecules from a bulk phase to a surface or interface is governed by an equilibrium rate constant, and the adsorption occurs at any

concentration. If the concentration of a soluble surfactant in water is increased gradually, the surface concentration also increases and reaches a maximum level at a specific bulk concentration. Beyond this concentration, individual surfactant monomers begin to aggregate with their hydrophilic heads pointing outwards towards the solution and the hydrophobic tails pointing inwards away from the water in order to minimize the free energy (i.e. maximize the entropy) of the system. The concentration at which this aggregation occurs is called the critical micelle concentration (CMC), and the aggregates are called micelles. In general, micelles are spherical aggregates of surfactant molecules about 4–10 nm in diameter that are in equilibrium with single surfactant monomers in the bulk aqueous solution (Figure 11.1). The critical micelle concentration depends upon the structure of surfactant molecules, as well as physico-chemical conditions such as temperature, pH and the ionic composition of the solution.

As total surfactant concentration is further increased, other cylindrical, hexagonal-packed and lamellar

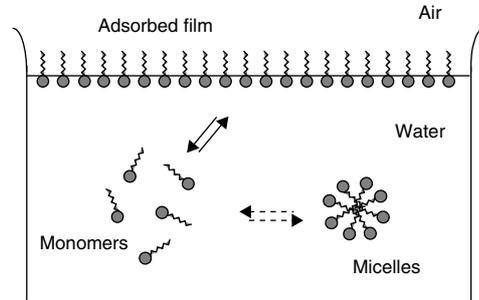


Figure 11.1. Schematic representation of the three environments (monomer, micelle and adsorbed film) in which surfactant molecules reside in water above the CMC

structures may form, depending on the surfactant structure and physico-chemical conditions (Figure 11.2). If the bulk phase is non-aqueous, reverse micelles may form with polar heads pointing inwards into a water core and hydrophobic tails pointing outwards into the oil.

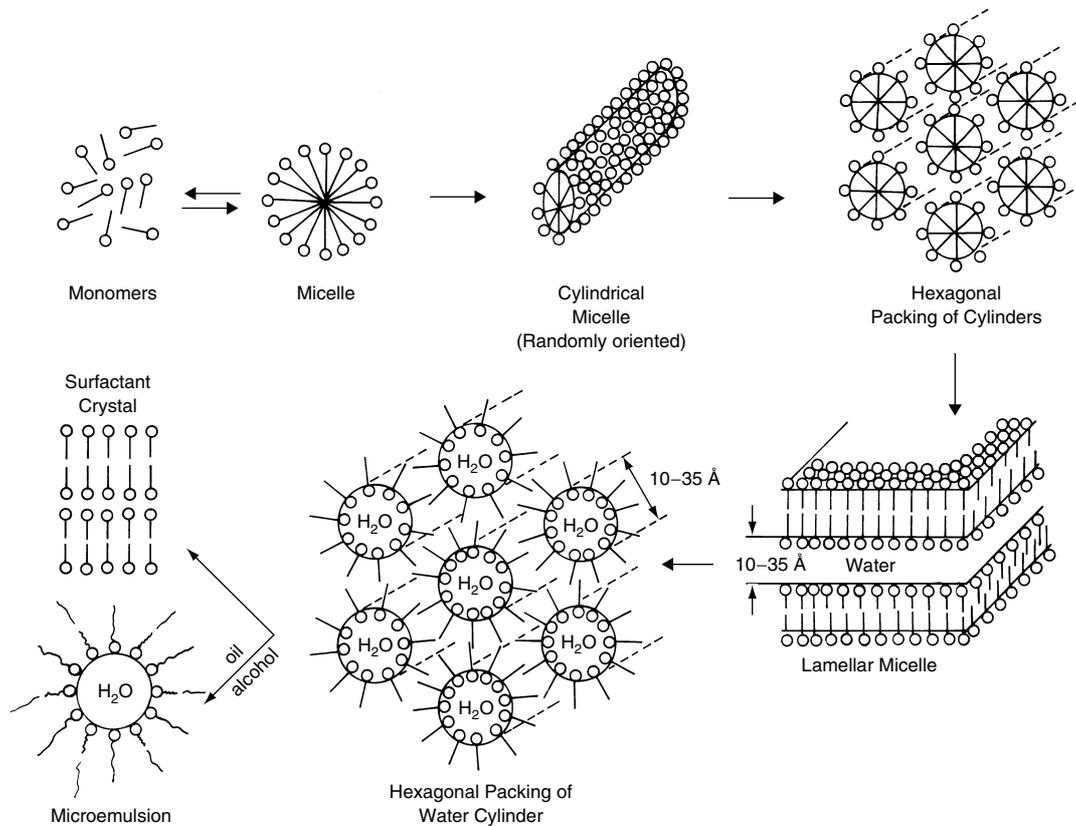


Figure 11.2. Possible structures formed in a surfactant solution

When an oil phase is present in contact with the aqueous phase, the water/oil partition coefficient of the surfactant, degree of surface activity and molecular structure determine whether an oil-in-water (o/w) emulsion, water-in-oil (w/o) emulsion, or liquid crystalline structure is formed (1).

Surfactant aggregates are dynamic systems. Thermal energy and coulombic forces keep surfactant monomers and aggregates in motion, and influence the rates of formation and break-up of these structures. Micellar systems, for example, exhibit two characteristic “relaxation” times, known as τ_1 and τ_2 , corresponding to the rate at which single monomers enter and exit a micellar aggregate, and to the rate of formation and break-up of an entire micelle, respectively. The kinetics of micellization has been shown to strongly affect such interfacial phenomena as wetting time, foamability, emulsion droplet size, oil solubilization rate and detergency (7).

2.3 Contact angle and wetting

The wetting of a surface by a liquid and the ultimate extent of spreading of that liquid are very important aspects of practical surface chemistry. Porous media in a petroleum reservoir can be water-wet or oil-wet, depending on the chemical composition of the solids and the crude oil. The extent to which crude oil wets the porous media is directly related to the work required to bring this oil to the surface, as will be seen later. Wetting of a solid surface by a liquid is determined by the contact angle (measured through the liquid) that this liquid makes with the surface (Figure 11.3). Usually, complete wetting means that the contact angle between a liquid and a solid is zero, or so close to zero that the liquid spreads on the solid spontaneously. Non-wetting occurs when the angle is greater than 90° , so that the liquid beads up like water on a waxy surface (8).

Young’s equation, as follows:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (11.3)$$

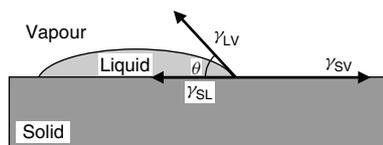


Figure 11.3. Force balance among the three surface tensions (Young’s equation) acting at each point in the contact line; θ is the contact angle of the liquid with the solid surface

describes the relationship between contact angle (θ) and the solid–vapour (γ_{SV}), solid–liquid (γ_{SL}) and liquid–vapour (γ_{LV}) interfacial tensions. This equation is usually helpful and sufficient for describing wetting equilibria in most circumstances. However, sometimes it is useful to determine thermodynamically whether wetting will occur. For a spontaneous process (such as spreading) to occur, the free energy of the process must be negative (8). In terms of surface tensions, we define the *spreading coefficient*, $S_{L/S}$, where:

$$S_{L/S} = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} \quad (11.4)$$

Spontaneous spreading occurs when $S_{L/S} > 0$. Thus, to encourage wetting, γ_{LV} and γ_{SL} should be made as small as possible. This is achieved by adding a surfactant to the liquid phase to decrease the solid/liquid and liquid/vapour interfacial tensions.

Contact angle and wetting are closely related to the interaction of crude oil with the rock surface and solid particles in the reservoir porous media. The silica in sand, for example, is preferentially water-wet so that oil will not wet its surface. Silica is negatively charged, and the negative charges found in the adsorbed film around crude oil droplets leads to repulsion and a beading effect between the water-wet solid and oil. On the other hand, limestone, having a net positive charge, will preferentially bind to the negatively charged surfactants from crude oil such as organic acids. Hence, the surfactant tail will be facing outward and the oil can spread on the limestone. Both excessive beading (non-wetting) and complete wetting of porous media by a crude oil make it very difficult to coalesce oil droplets and move oil ganglia through porous media to the surface.

Figure 11.4 shows how the wettability of a water-wet solid surface in contact with an oil droplet can change when surfactant molecules adsorb on to it. As is shown, if the solid surface has some negative sites where cationic surfactants can be adsorbed, the hydrophobic tails of these molecules will point towards the oil, thus making the solid surface more wettable by the oil droplet.

2.4 Foams

For a liquid to produce a foam, it must be able to (i) expand its surface area so as to form a thin film around gas bubbles, (ii) possess the correct rheological and surface properties to retard thinning of the lamellae leading to bubble coalescence or collapse, and

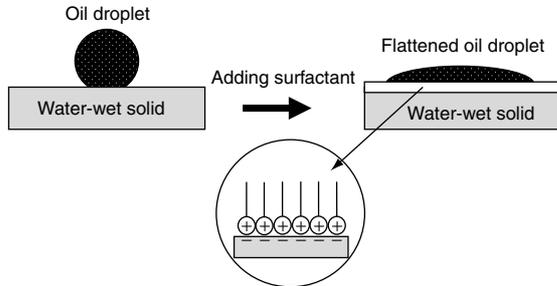


Figure 11.4. The wettability of a water-wet solid surface in contact with an oil droplet increases when surfactant molecules adsorb on to the surface

(iii) retard the diffusion of trapped gas from small to large bubbles or to the surrounding atmosphere. Foaming does not occur in pure liquids because such a system cannot meet the above three criteria. When surface-active molecules or polymers are present in the liquid, however, rheological effects and adsorption of molecules aid in stabilizing the interface, thus impeding the diffusion of gas through the lamellae, and resulting in a more mechanically stable system (Figure 11.5) (9).

As previously discussed, the Gibbs adsorption equation demonstrates how an increase in the amount of surface-active material will result in a decrease in the surface tension of a liquid. Because the Gibbs adsorption equation was derived on a thermodynamic basis, the surface tension is an equilibrium value that does not take into account the time necessary for molecules to diffuse and adsorb to an interface. The instantaneous, or dynamic surface tension of a newly created interface is always higher than the equilibrium surface tension value(s). In the laboratory, the dynamic surface tension of an adsorbed film can be obtained by

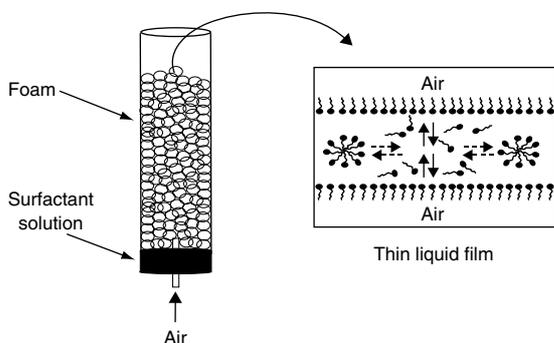


Figure 11.5. Schematic representation of the adsorption of surfactant on the newly created air/water interface during foam generation

measuring the maximum pressure realized within a soap bubble as a function of the bubble lifetime (Figure 11.6). If the interface (i.e. bubble) formation time is long, surfactants have time to flow from the bulk solution to the interface. Given enough time, the dynamic surface tension approaches an equilibrium value. However, if the interface is created very quickly (by a very small bubble lifetime), surfactants do not have the opportunity to diffuse from the bulk to the interface and hence higher values of the dynamic surface tension are observed.

The effect on surface tension by surfactant adsorption from the bulk solution (Gibbs effect) and by diffusion along an interface (Marangoni effect) is often referred to as the combined Gibbs–Marangoni effect (Figure 11.7).

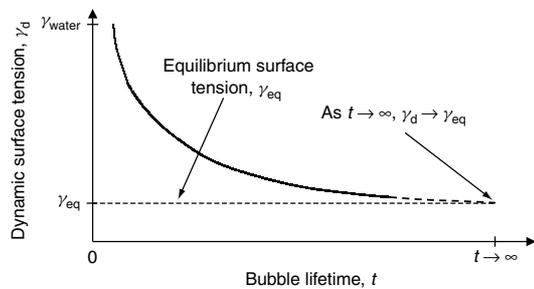


Figure 11.6. Dynamic surface tension of a newly created interface as a function of bubble lifetime

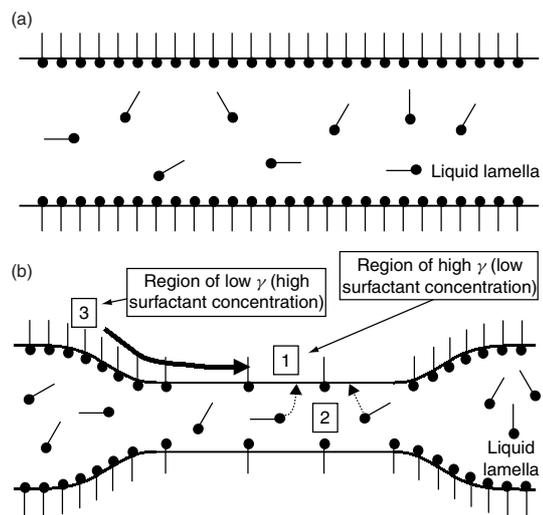


Figure 11.7. Schematic representation of the Gibbs–Marangoni effects. (a) Unstretched film. (b) Stretched film. Film stretching causes localized areas of high surface tension, γ [1]. Surfactant molecules flow from the bulk phase [2] to the surface (Gibbs effect) and along the interface [3] (Marangoni effect) to “heal” the stretched film [1]

As a foam lamella is stretched (e.g. by gravity, agitation, thermal fluctuation or drainage), it becomes thinner and a new surface is generated having a lower transient surfactant concentration at the surface, and consequently a higher surface tension, than its neighbouring surface. The surface tension gradient that is generated results in the flow of surfactant (and associated boundary layer water) from areas of low γ to those of high γ , thereby opposing film thinning. Likewise, the diffusion of surfactant molecules with associated water also occurs from the bulk in the direction of the newly created surface. These mechanisms can be thought of as producing a “healing” effect at the site of thinning. While the Gibbs and Marangoni effects are complementary, each of them are generally important in different surfactant concentration regimes. However, both mechanisms rely on the presence of a surface tension gradient and are ineffective at very low and very high surfactant concentrations. At very low surfactant concentrations, not enough surfactant monomers exist in the bulk or interface to diffuse to the thinning film. At very high concentrations, so many monomers are present in the system that an adequate concentration gradient is not established between the thinning film and the bulk and neighbouring surfaces.

Other factors can also affect the stability of foam; among these are temperature, surfactant structure, surface viscosity, rate of drainage and bulk viscosity.

2.5 Emulsions

Working with emulsion systems is nothing new to people in the petroleum industry. Historically and economically, the most important problems in the oil industry have been in the area of breaking up o/w emulsions formed within reservoirs. However, the breaking and formation of emulsions plays a very important role in other technological applications in the oil industries. Because of their wide-ranging practical importance, it is necessary to discuss the fundamental aspects and methods of characterization of emulsions.

An emulsion (sometimes referred to as a macroemulsion in order to distinguish it from a microemulsion) is defined as a thermodynamically *unstable* mixture of two immiscible liquids, one existing as a dispersed phase and the other as a continuous phase. Note that emulsions are formed from surfactant, oil, and water at concentrations found in the two-phase and three-phase regions of the surfactant/oil/water phase diagram (Figure 11.8). However, emulsions are not thermodynamically stable and thus are not labelled on the phase diagram. The

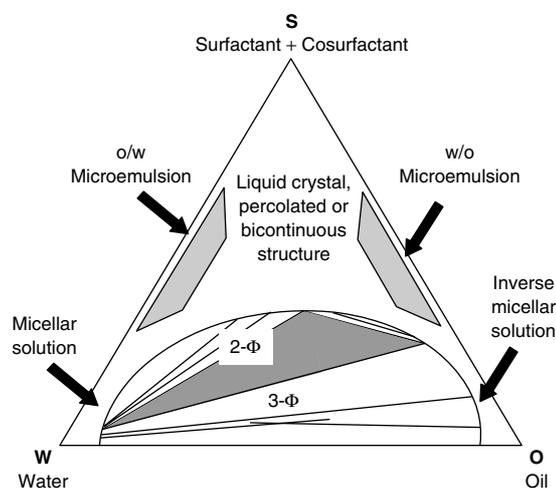


Figure 11.8. Typical phase diagram for the Oil (O)/Water(W)/Surfactant + Cosurfactant (S) system. Emulsions are formed from surfactant, oil and water at concentrations found in the two-phase (2- Φ) and three-phase (3- Φ) regions of the diagram

common types of emulsions relevant to the petroleum industry are oil-in-water (o/w) and water-in-oil (w/o) emulsions, although water-in-oil-in-water (w/o/w) and oil-in-water-in-oil (o/w/o) multiple emulsions are sometimes encountered. The thermodynamic instability of an emulsion system dictates that the suspension will separate over time into water and oil. This phase separation is dependent, among other factors, upon the rate of emulsion droplet coalescence. The level of emulsion stability required in a process is dependent upon application of the emulsion system. For example, microemulsions formed with brine and crude oil within a reservoir aid in mobilizing the oil trapped in the porous medium and in pumping the oil to the surface. However, it is preferred that once the emulsion has been brought to the surface, it quickly and easily (i.e. inexpensively) breaks up into its individual oil and water phases. On the other hand, sometimes it is required that emulsions be stable for a long time, such as in the case of Orimulsion[®], a low-viscosity (150–350 CP) o/w emulsion made from heavy crude oil (10).

Common emulsion properties such as droplet size distribution, emulsion type, stability, and rheological properties depend on many factors, including the following:

- chemical composition (molecular structure and concentration) of oil
- chemical composition (types and concentrations of salts present) of water

- chemical composition (nonionic, anionic, cationic, zwitterionic and polymeric) and concentration of surfactants
- structure and concentration of cosurfactants (e.g. short-chain alcohols)
- number and types of finely divided particles present
- temperature and pressure of the system
- order of mixing of emulsion constituents
- energy input.

It is clearly evident that emulsions are very complicated systems. Progress has been made on theoretical studies attempting to clarify the complexities of these systems. However, the majority of predictions of the type and stability of emulsions derives more from empirical observation than from theory. Emulsion formulation is still considered to be an art rather than a scientific method in many circles of industry (11).

2.5.1 Hydrophilic–lipophilic balance (HLB)

A very useful numerical rating scheme, known as the *hydrophilic–lipophilic balance* (HLB) number, was introduced by Griffin (12). In this empirical method, surfactants are assigned a number based on their solubility behaviour in water (Table 11.1). This method correlates well with Bancroft's rule, which states that the external (continuous) phase of an emulsion will be that in which the emulsifying agent (surfactant) is the most soluble (13). Each surfactant is then rated according to this scale. Surfactant mixtures are assigned an HLB number on a weight-pro-rated basis. Molecular functional groups (e.g. $-\text{OH}$, $-\text{COONa}$, $-\text{CH}_2-$, etc.) have also been assigned HLB numbers (14). The empirical HLB number is calculated by adding 7 to the algebraic sum of the functional group numbers given in Table 11.2. For example, the calculated HLB number for sodium laurate

Table 11.1. The hydrophilic–lipophilic balance (HLB) scale

Surfactant solubility/ Behaviour in water	HLB number	Application
No dispersibility in water	{ 0 2	–
	4 }	W/O emulsifier
Poor dispersibility	{ 6 }	
Milky dispersion, unstable	{ 8 }	
	{ 10 }	Wetting agent
Milky dispersion, stable	{ 12 }	
Translucent-to-clear solution	{ 14 }	Detergent
	{ 16 }	Solubilizer
Clear solution	{ 18 }	O/W emulsifier

Table 11.2. Group HLB numbers^a

Hydrophilic group	HLB	Lipophilic group	HLB
$-\text{SO}_4\text{Na}$	38.7	$-\text{CH}-$	-0.475
$-\text{COOK}$	21.1	$-\text{CH}_2-$	
$-\text{COONa}$	19.1	$-\text{CH}_3-$	
Sulfonate	~ 11.0	$-\text{CH}=\text{}$	-0.15
$-\text{N}$ (tertiary amine)	9.4	$-(\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-)$	
Ester (sorbitan ring)	6.8		
Ester (free)	2.4		
$-\text{COOH}$	2.1		
$-\text{OH}$ (free)	1.9		
$-\text{O}-$	1.3		
$-\text{OH}$ (sorbitan ring)	0.5		

^aTo calculate the HLB number for a given surfactant, add 7 to the algebraic sum of the group numbers.

(C₁₁H₂₃COONa) would be:

$$7 + 11(-0.475) + 19.1 = 20.9$$

The HLB empirical approach is still very popular because of its extreme simplicity, but it does not take into account the effects of the kind and concentration of electrolyte, temperature and other factors.

2.5.2 Winsor's R ratio

The introduction by Winsor (15) of the theoretical concept that an emulsion formulation could be represented by a single parameter relating the "ratio of the interaction energies" between adsorbed surfactant molecules and the oil and water in the system was the next step in understanding emulsion formulation. It was shown that the state and properties of a system at equilibrium were directly related to a particular combination of the interactions between surfactant, water and oil. This combination of interactions was expressed as the ratio R . A ratio $R < 1$ means that the interactions between surfactant and oil are stronger than those between surfactant and water. In this case, the surfactant/oil/water systems have a tendency to form w/o emulsions. When $R = 1$, the surfactant–oil and surfactant–water interactions are balanced. Such a system forms a thermodynamically stable bicontinuous microemulsion. Finally, $R > 1$ means that the interactions between the surfactant and water molecules are stronger than the interactions between the surfactant and oil molecules, which thus leads to o/w emulsions.

A major drawback to this method, however, is that Winsor's so-called R ratio could not be numerically calculated as in the HLB method, which made it difficult to use for practical emulsion formulations.

2.5.3 Phase-inversion temperature

The *phase-inversion temperature* (PIT) is the temperature at which the continuous and dispersed phases of an emulsion system are inverted (e.g. an o/w emulsion becomes a w/o emulsion, and vice versa). This phenomenon, introduced by Shinoda (16), occurs for emulsion systems containing nonionic surfactants, and can be a valuable tool for predicting the emulsion behaviour of such systems. The phase inversion occurs when the temperature is raised to a point where the interaction between water and the nonionic surfactant molecules decreases and the surfactant partitioning in water decreases. Hence, surfactant molecules

begin to partition in the oil phase beyond this temperature. The PIT phenomenon does not occur with ionic surfactants, where a normal temperature–solubility relationship exists (i.e. solubility increases with increased temperature), so its use is limited. However, emulsion formulations are quite often stabilized by a mixture of both ionic and nonionic surfactants, where the PIT may still be important.

2.5.4 Surfactant affinity difference

Enhanced oil recovery research in the 1970s led to the development of empirical correlations that numerically describe the conditions for attaining ultra-low interfacial tension and maximum oil mobilization. The correlation, the *surfactant affinity difference* (SAD), is a measure of the difference between the standard chemical potentials or the Gibbs free energy of surfactant in the oil and water phase, as follows:

$$\text{SAD} = \mu_w^* - \mu_o^* = \Delta G_{\text{oil} \rightarrow \text{water}} = -RT \ln K_p \quad (11.5)$$

where K_p is the partition coefficient of the surfactant between water and oil at the corresponding temperature, a value that can be measured. At a SAD = 0, the surfactant affinity for the water phase exactly equals its affinity for the oil phase, thus resulting in the optimum formulation (i.e. an ultra-low interfacial tension). The sign of the SAD indicates the dominant affinity of the surfactant, whereas the value denotes the magnitude of deviation from an optimum formulation. A SAD < 0 means that surfactant–oil interactions dominate, while a SAD > 0 indicates that surfactant–water interactions prevail.

2.5.5 Microemulsions

Under certain conditions, the oil or water droplets in emulsions can be made small enough (< 100 nm) that the emulsions appear transparent. Such dispersions are called microemulsions. Three types of microemulsions can be formed, namely oil-in-water, water-in-oil, and middle-phase microemulsions. The latter microemulsions occur when the Winsor's ratio $R = 1$, and when the SAD = 0. All microemulsions are thermodynamically stable, which implies that they form spontaneously at certain concentrations of oil, water and surfactant, and the formation is limited only by the diffusion of the molecules. It has been reported (17) that the change in free energy of dispersions shows a minimum at an equilibrium droplet size in the range of 100–1000 Å for

microemulsion systems. Microemulsions require a relatively large amount of surfactant in order to stabilize the large interfacial area created by the nano-droplets. They also often require the addition of cosurfactants such as short-chain alcohols to attain an appropriate interfacial fluidity or surface viscosity of the oil/water interface.

3 APPLICATIONS

3.1 Drilling mud

The drilling mud used in prospecting for petroleum is a complex system made from a variety of materials used to perform several functions in the drilling process: water, with its high heat capacity, removes the heat generated by friction between the rocky material and the drilling tip, oil lubricates the drilling tip, clay provides the appropriate rheology, and salts of heavy metals increase the density of the mud, so that the particles of rock (debris) can rise with the mud up to the ground level, where they are separated. Dispersant and emulsifying surfactants are used to stabilize this complex mixture. It is important to mention that drilling mud is formulated for each region, because of the variation in geology and physico chemical conditions from one place to another (18).

3.2 Enhanced oil recovery

One of the most attractive energy sources today is the petroleum remaining in a depleted oil well, where it is trapped in the reservoir's porous media by capillary and viscous forces. To recover this trapped oil, several technologies based on enhanced oil recovery (EOR) processes have been developed. Examples of these technologies (also referred to as "tertiary oil recovery") are surfactant-polymer flooding, foaming and acid fracturing (6, 19–22). However, the presence of many interfaces and the complexity of the physico-chemical and geological characteristics of the reservoirs make enhanced oil recovery an immense scientific and technological challenge. A detailed knowledge of the petroleum reservoir, transport through porous media, and various interfacial phenomena are required. Furthermore, enhanced oil recovery technologies are usually very expensive because enormous quantities of costly chemicals are injected into an oil well and are completely lost during the process.

In spite of the above-mentioned difficulties, enhanced oil recovery technologies are appealing since indeed the

depleted oil wells still contain approximately 65% of the original oil in place.

3.2.1 Surfactant-polymer flooding

This present section will deal in a general way with all of those technologies referred to as "surfactant-polymer flooding" or "chemical flooding". Basically, the purpose of surfactant-polymer flooding is to produce oil from an exhausted petroleum well by injecting into the reservoir a slug of surface-active agents capable of mobilizing the residual oil (Figure 11.9) (6, 19–22). Figure 11.10 shows schematically the surfactant-polymer flooding process. The first step is to inject a solution (preflush) to condition the reservoir by eliminating undesirable salts that would otherwise bind to the valuable surfactants and render them ineffective (20, 23–26). Next, a surfactant solution is injected to decrease the interfacial tension of the oil ganglia (6, 19–22, 27), and to mobilize the ganglia through narrow necks of the pores (6, 21), thus forming an oil bank (as shown in Figure 11.11). The formation of an oil bank is indispensable, since it will allow the efficient mobilization of the trapped crude oil. The surfactant slug is driven by a slug of thickened aqueous polymer solution that is in turn driven by a water slug (6, 20, 21). The viscous polymer slug prevents fingers of water from penetrating the oil bank, which would otherwise make the process less effective (22).

In order to optimize the surfactant-polymer flooding process, the oil bank formed must be propagated through the porous media while the oil ganglia continue to coalesce with the leading edge of the oil bank. The volumetric coverage of the process is optimized by adjusting the mobility of each slug (Figure 11.11) (6, 22). This is accomplished by maintaining the ultra-low interfacial tension at the oil bank/surfactant slug interface (6, 28).

There also exists a need to avoid surfactant aggregate structures such as lamellar liquid crystals which exhibit high viscosity (29–32). System parameters should be such that mixing between the fluids in the surfactant, oil and polymer slugs does not occur. A dispersion of surfactant and oil would form an undesired emulsion, while a dispersion of surfactant and polymer, if incompatible, could lead to phase separation, which would decrease the effectiveness of the process. Other points to take into account are (i) the mass transfer of surfactant to the oil bank can change the interfacial tension, and (ii) surfactant-polymer incompatibility leads to a phase separation, which would reduce the efficiency of the process (30, 31).

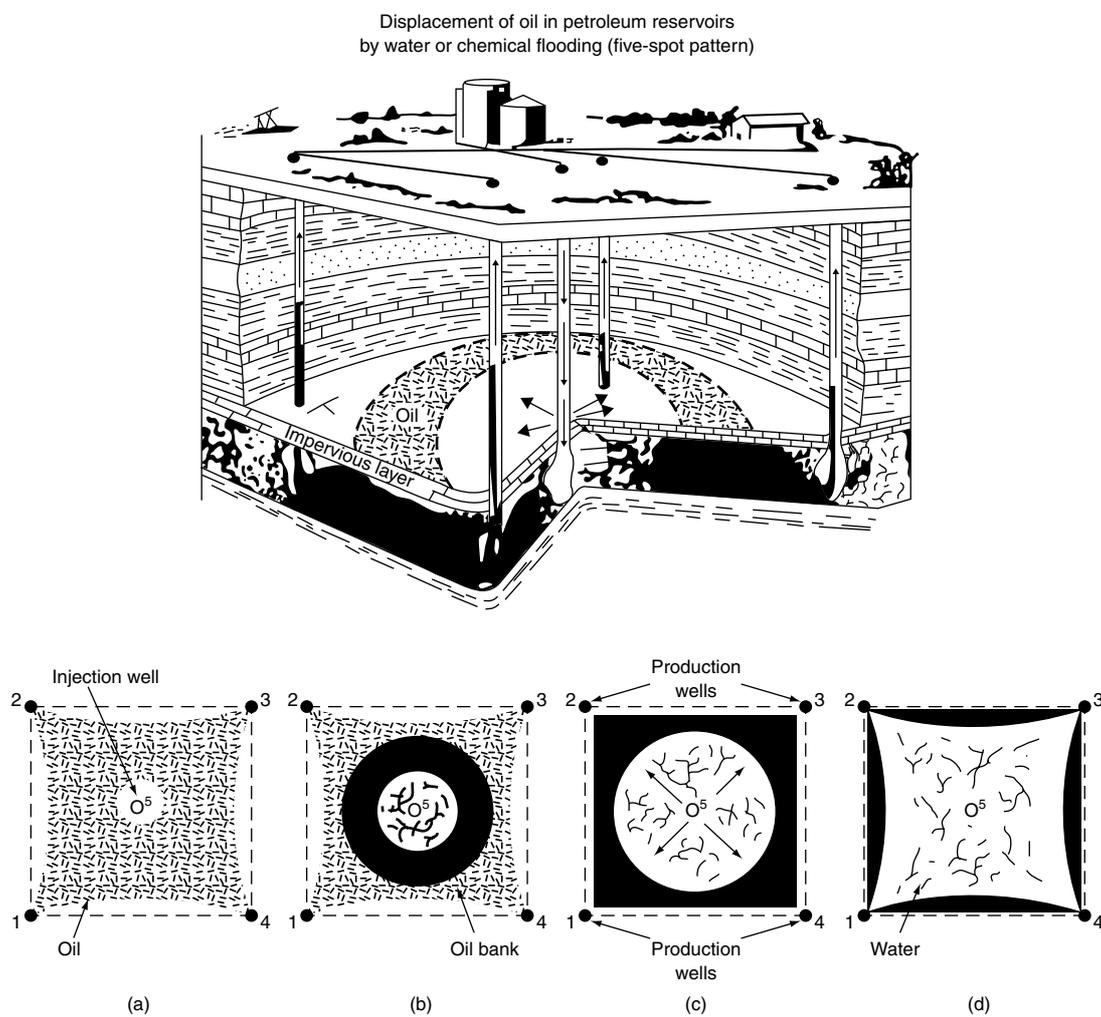


Figure 11.9. Schematic representation of an oil reservoir and the displacement of oil by water or chemical flooding

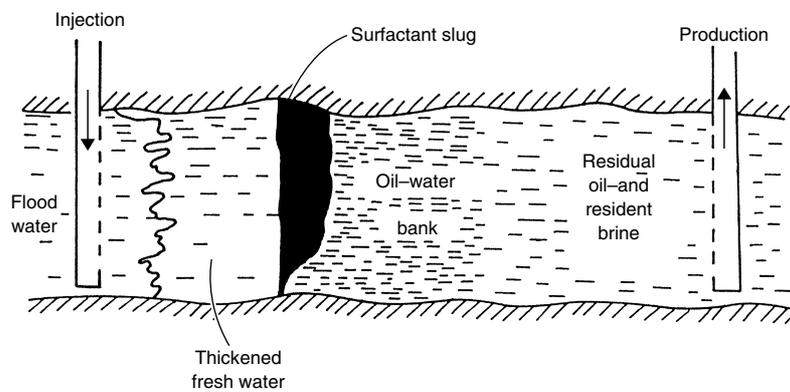


Figure 11.10. Schematic representation of the surfactant-polymer flooding process

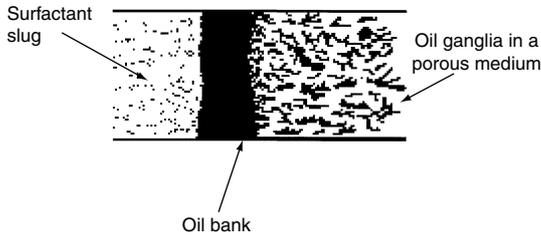


Figure 11.11. Schematic representation of the role of ultra-low interfacial tension on the formation of the oil bank

After secondary oil recovery (water flooding), the oil ganglia are trapped inside the pores by viscous and capillary forces, the magnitude of which can be accounted for by the capillary number, N_c , which is defined as follows:

$$N_c = \left(\frac{\mu_w v_w}{\gamma_{ow}} \right) \quad (11.6)$$

where μ_w is the viscosity of water, v_w is the water velocity and γ_{ow} is the oil/water interfacial tension (6, 19–22). At this stage in the oil recovery process, the capillary number is about 10^{-6} , which means that the forces trapping the oil ganglia are enormous. As indicated by equation (11.6), to overcome these forces it is necessary to increase the capillary number by three orders of magnitude to 10^{-3} by increasing the viscosity or velocity of the fluid, or by decreasing the interfacial tension from 30 to 10^{-3} – 10^{-4} mN/m. Any attempt to increase the fluid velocity involves the use of high pressures which can collapse the rock structure, thus

creating preferred paths of high porosity, and possibly leading to channelling (22). Increasing the viscosity is also impractical (try blowing honey through a straw!). Therefore, in order to increase the capillary number, one must decrease the interfacial tension (IFT) of the entrapped oil.

Interfacial tensions can reach ultra-low values at low as well as high surfactant concentrations (Figure 11.12) (6, 21). At low surfactant concentrations, the system appears to be a two-phase one, namely oil and brine in equilibrium with each other. A small change in the surfactant concentration around this region could strongly affect the interfacial tension. Such a change in surfactant concentration might occur due to adsorption of surfactant molecules on to surfaces of the reservoir porous media. On the other hand, in high-surfactant-concentration systems (approximately 4–8 wt% surfactant), a microemulsion middle phase exists in equilibrium with the excess oil and brine phases. These high-concentration systems are close to the optimal formulation (i.e. the concentration at which the most oil can be mobilized), and are therefore preferred to low-concentration systems (Figure 11.13).

Surface charge density is another parameter that can strongly and favourably affect the displacement efficiency of oil ganglia by changing the interfacial tension, surface viscosity and electrical repulsion of the ganglia entrapped in the porous media (Figure 11.14) (6, 21, 22, 33).

Figure 11.15 indicates that there exists an optimal salinity where the high surfactant concentration formulations exhibit a minimum interfacial tension

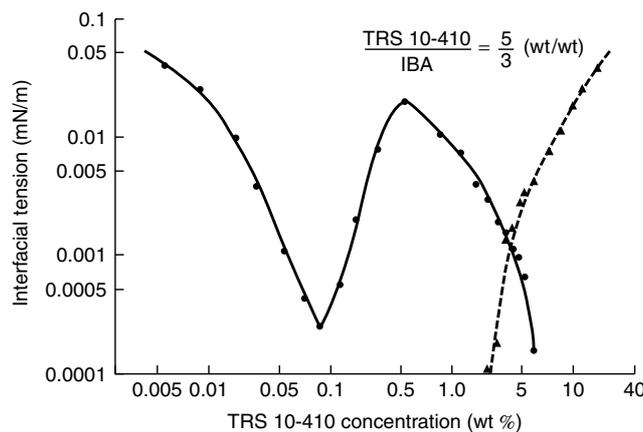


Figure 11.12. Effect of surfactant concentration on the interfacial tension (IFT) of TRS 10-410 (a petroleum sulfonate surfactant) + isobutyl alcohol (IBA) in 1.5% NaCl with dodecane. An ultralow IFT can occur at low or high surfactant concentrations: ●, interfacial tension of o/w micro emulsion; ▲, interfacial tension of w/o micro emulsion. A three-phase system (oil-continuous, water-continuous and middle-phase regions) exists where the (●) and (▲) data overlap

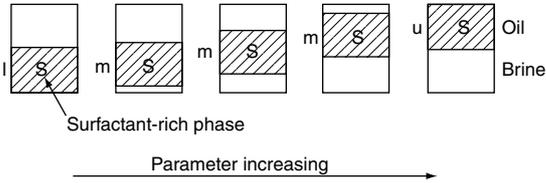


Figure 11.13. Factors that can affect the partitioning of surfactant from the water to the oil phase. The transition from the lower to the middle to the upper phase (l–m–u) can occur by (a) increasing the salinity, (b) decreasing the oil chain length, (c) decreasing the temperature, (d) increasing the total surfactant concentration, (e) increasing the brine/oil ratio, (f) increasing the surfactant solution/oil ratio, or (g) increasing the molecular weight of the surfactant

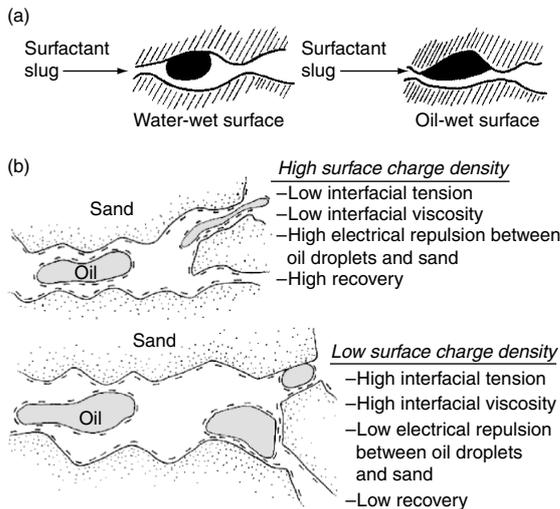


Figure 11.14. (a) Shape of an oil drop on a water-wet or an oil-wet surface. (b) The role of surface charge in the oil displacement process

between oil and water, a middle-phase microemulsion formation with equal oil and water solubilized in the middle phase, a minimum loss of surfactant in the porous media, and a minimum phase separation time of the three phases, as well as a minimum pressure buildup while pumping these multiphase systems through the porous media, and a maximum oil displacement efficiency. This figure also suggests that these are all interrelated interfacial phenomena.

3.2.2 Foams in enhanced oil recovery

In the petroleum industry, foam finds applications mainly in the area of enhanced oil recovery. The basic

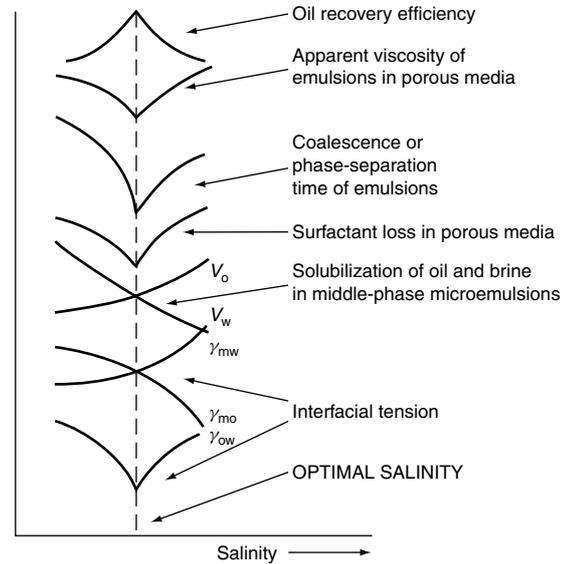


Figure 11.15. The various phenomena occurring at optimal salinity in relation to enhanced oil recovery

concept involves the use of the unique rheological properties of foam in porous media to block highly permeable areas (from where the oil has already been swept) and to allow oil to be recovered from the low-permeability zones.

Carbon dioxide is often used in the foaming process as a displacing fluid. The carbon dioxide fluid is miscible in all proportions with the lighter hydrocarbons. This behaviour is very different from that of displacement by water, where a significant amount of oil remains trapped because of the immiscibility of the two phases. Another advantage of using carbon dioxide is that it has limited solubility in water, so nearly all of the CO_2 injected can be used to solubilize the oil, and little is wasted by dissolving into the water.

Surfactants are used to overcome some of the disadvantages that the CO_2 flooding system offers. The crucial disadvantage of CO_2 flooding is the low viscosity of liquid CO_2 when compared to the heavy fractions in the oil. A low viscosity implies a higher mobility and this means a possibility of CO_2 leakage via finger formation or channelling. Surfactants are used to decrease this higher mobility by enhancing foam stability.

Steam is also used as a foaming fluid. The problem in this case is similar to that of the CO_2 system, i.e. a high mobility of the steam. Once again, surfactants with or without non-condensable gas are used to increase the foam stability. Since the operating temperatures involved are high, the surfactant system must be

designed to remain effective over a wide range of temperatures. The adsorption of surfactants on to reservoir rock surfaces is minimal at high temperatures, unless ionic species are present. If the foam is made out of "pure" steam (saturated steam in equilibrium with water as the lamella), according to Kelvin's equation, the smaller bubbles, which have a higher pressure, will collapse and be absorbed by larger bubbles, thus resulting in decreased foam stability. Small amounts of non-condensable gas are added to increase the foam stability by decreasing the rate of steam condensation and foam collapse.

The text by Schramm (34) covers most aspects of the use of foams in the petroleum industry, ranging from fundamentals to enhanced oil recovery. It also provides field data from several oil fields along with the "in-laboratory" experimental methods that are used to correlate field data to proposed theories.

3.2.3 Acid fracturing for oil well stimulation

Acid fracturing is an oil well stimulation process in which acid (HCl or HF, depending on the rock structure) is injected into an oil well at sufficiently high pressure to fracture the porous media or to widen existing natural fractures. Various principles of surface chemistry are employed in this process in order to avoid excessive and costly fluid loss, and to decrease the rate of acid spent.

For controlling fluid loss, surfactants are used as thickeners which gel the acid by forming micelles. These gelled acids are shear-stable because micellar chains can quickly reform following shearing. The advantages of surfactants as thickeners is that they can be designed to provide high viscosity to "live" (i.e. active) acid solutions, while at the same time providing low viscosity to the spent acid. This is possible because of the disruption of the micellar structure due to the increased concentration of reaction products formed during spending of acid. The decreased spent acid viscosity aids in recovery of the treating fluids (35).

The employment of foamed acid and acid-external emulsions (oil as the dispersed phase and gelled acid as the continuous phase) are other methods used to control the loss of acid solutions. The disadvantage of using oils is that a large concentration of oil is required to increase the viscosity of the emulsion formulation, which reduces the acid concentration and, therefore, the amount of acid available for fracture etching. Foaming the acid also reduces the amount of acid available for etching since less acid is present per unit volume injected.

To control the reaction rate of the acid, retarders such as alkyl sulfonates, alkyl phosphonates and alkyl amines are used to form hydrophobic films on carbonate surfaces. These protective films act as a barrier to slow acid attack. Another method involves the use of foaming agents to stabilize the carbon dioxide foam that is created when CO₂ is released as a product of the acid-etching reaction. This CO₂ foam acts as a barrier to slow acid attack. Yet another method for controlling the acid activity in an oil well is the use of emulsions containing kerosene or diesel as the continuous oil phase and hydrochloric acid as the dispersed aqueous phase. Acid-in-oil emulsions are most commonly used because oil separates the acid from the carbonate surface (and from machine parts, thus reducing the level of corrosion). Moreover, acid reaction rates can be further decreased by surfactant retarders that increase the wettability of the carbonate surface for oil.

3.3 Antifoaming and defoaming

Foam shows peculiar properties that are useful in enhanced oil recovery. However, foam turns out to be a major problem in all downstream processing of the recovered crude oil. The causes of foaming are usually related to naturally occurring impurities and corrosion products found in process streams. Antifoaming and defoaming agents are added in all major unit operations to avoid foaming. Antifoaming agents are added to prevent the formation of new foam, while defoamers are added to destroy the existing foam (34). Hydrophobic silicas, silicone oils, glycol-based polymers, amides, mineral oils and fatty acids are common antifoaming agents (34).

3.4 Corrosion inhibition

The petroleum industry does not remain unaffected by corrosion (as was alluded to in the discussion on acid-in-oil emulsions above). Indeed, corrosion is a common phenomenon endured by almost every industry. The metallic parts used everywhere from oil wells to refineries and petrochemical plants are susceptible to corrosion. In 1999, in the USA alone, corrosion was held responsible for approximately \$300 billion of lost revenue, of which more than one third could have been saved by using available methods of corrosion control (36).

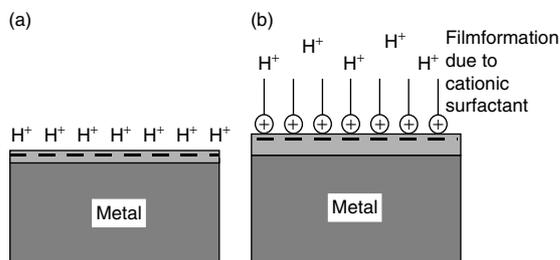


Figure 11.16. Schematic representations of (a) a Bare metal surface, and (b) a surface where the Presence of a surfactant film acts as a barrier to corrosion

The most commonly observed corrosion in the oil industry begins with the adsorption of protons on metallic surfaces, followed by an irreversible electrochemical reaction between the protons and the metallic atoms. Metallic cations may either dissolve in the aqueous phase or react with anions such as sulfur, thus exposing more metallic surface for subsequent attacks.

Surface chemistry provides an important corrosion control method (Figure 11.16). Ohmic inhibitors, also known as filming inhibitors, are cationic surfactants that have a tendency to preferentially adsorb to all available negative sites on the metallic surface, forming a compact and hydrophobic film. This low-permeability film will (i) decrease the wettability of the surface to water and brine, (ii) decrease the mobility of various ions, (iii) lessen the spread of conductive bridges between the anode and cathode, and (iv) reduce the possible chemical interactions of oxidizing agents (e.g. protons, acids, etc.) with negative sites on the metallic surface.

Robinson (18) describes in detail the possible solutions to corrosion-related problems which are encountered in the various steps of petrochemical operations.

3.5 Oil spill clean-up

The introduction of petroleum into the marine environment is a direct consequence of the production and transportation of crude oil and refined products. Oil spills have justifiably earned ill fame for polluting the environment by being responsible for some of the worst environmental disasters in (recent) human history. Oil spills jeopardize the dissolved oxygen-dependent aquatic life because the oil film acts as a barrier for oxygen transport across the air–water interface. Seabirds are unable to fly or even float on water once oil wets their feathers, thus leading to their untimely death. In addition to aesthetic and ecological concerns, coastal regions

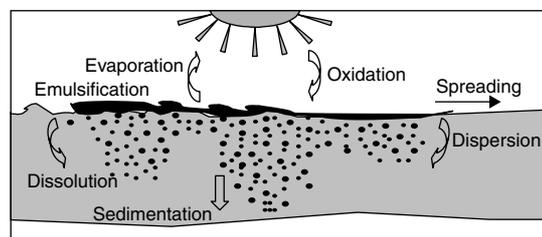


Figure 11.17. Schematic showing some of the phenomena governing the fate of an oil spill after a spillage at sea

can suffer economically from damage done by oil spills to recreational areas, harbours and vessels, commercial shellfish grounds and intake sources for desalination and power plants. Figure 11.17 shows some of the phenomena that decide the fate of spilled oil on the sea surface.

For removal of spilled oil, a surfactant solution (a dispersant) is added along the circumference of the oil (sprayed from boats and aircraft), which creates a surface tension gradient that forces the oil to contract to the centre of the oil lens, so making the job of removal of the oil easier. The effectiveness of this process depends on sea conditions and application techniques, as well as the chemical nature of both the oil and dispersant. The time elapsed after an oil spill remains one of the critical factors in this process, because with weathering, the viscosity of oil increases rapidly, hence resulting in slower migration of surfactant to the oil/water interface and a decreased dispersion effectiveness.

Once the oil is collected, it is then pumped to on-ship coalescers that use surfactants and oil-wet or water-wet filters to break the crude oil–brine emulsion.

Even after removal of the bulk of the spilled oil, a thin layer of oil still exists – this remains a barrier for oxygen absorption. Moreover, the native microbial populations cannot degrade it. It then becomes imperative to break this film into tiny droplets so as to quicken the oil degradation and to increase oxygen transport from the atmosphere to the water. This is achieved by adding a surfactant solution to the oil lens.

The surfactants traditionally used as dispersants are not without their share of problems. Lately, there has been some debate on the toxicological impact of these dispersants on marine organisms and the coastal environment, and so the search for new, less toxic formulations remains ongoing.

The interested reader is referred to ref. (37) for further studies on the chemistry and physics of dispersants and dispersed oil, methods for toxicological testing and the techniques employed, logistics, monitoring and

application strategies for using various dispersants in the United States.

3.6 Fluidization of bitumen

Bitumen is a naturally occurring hydrocarbon that exists in a semi-solid or solid phase in natural deposits. The most important reservoirs of bitumen are found in Canada and Venezuela. Among the problems encountered when recovering bitumen, its high viscosity is one of the greatest. Natural bitumen has a viscosity greater than 10 000 mPa, measured on a gas-free basis at its original temperature in the deposit and atmospheric pressure (38, 39).

Current technology has made possible the recovery and use of this huge source of energy (38–41). Moreover, since the extraction process of this raw material requires much less energy than the refining process required for other fossil fuels, (the bitumen extraction industry is flourishing.) Gas-oil, which is an intermediate product created during the refining of crude oil, is pumped into the oil well to reduce the viscosity of the bitumen and allow it to be pumped from underground to a flow station (at ground level.)

A commercial product known as Orimulsion[®] is an example of the application of surface chemistry to the technology of conferring special properties to heavy crude oil¹. This is an oil-in-water emulsion made from bitumen stabilized by a nonionic surfactant, which decreases the viscosity of the bitumen from 10⁵ to less than 10² mPa, and reduces the NO_x emissions while still maintaining a high combustion performance (42).

It is worth mentioning here that to optimize the low viscosity of an emulsion, two emulsions of different drop size distributions are mixed, with the smaller one being about 25% and the larger one about 75% of the total concentration (43).

3.7 Asphaltic emulsions

Another very important application of surface science in the petroleum industry that has recently been receiving much attention is the creation of oil-in-water asphaltic emulsions (asphalt dispersed in a brine continuous phase) which are used to pave roads (44). The idea is to decrease the viscosity of asphalt, while at the same time avoiding the use of gasoline. The latter is presently

being used to fluidize asphalt, but has high economic and environmental costs.

For this technological application, the main types of surfactants used have been cationics, since most rock surfaces are negatively charged. By using this method, when the asphaltic emulsion contacts the ground, surfactant molecules migrate from the surface of the asphalt droplets to the rock surfaces, which results in the breaking of the asphaltic emulsion and a permanent spread of asphalt on to the rock surfaces. Cationic surfactants are preferred, despite their high cost, because they promote faster breakup of the asphalt emulsion, which is often necessary to prevent the possibility of rain washing away the asphalt before it has solidified. However, work is currently being carried out to incorporate non-ionic surfactants into the emulsion in order to reduce costs and to improve the mechanical properties of the asphalt.

3.8 Oil/water separation and crude oil dehydration

Oil-water emulsion systems are often desirable in cases such as the transportation of crude oil and increased fuel efficiency of light oil fractions. By the same token, these systems are undesirable for distillation and catalytic cracking of crude oil. More than 50% of all of the petroleum recovered is in the form of water-in-oil emulsions. These emulsions are formed because crude oil contains natural surfactants and the oil and water are emulsified as they pass through mechanical devices such as pumps or valves. Water must be removed before any refinery operation can be performed on this oil material. It is not economically viable to distill crude oil in emulsion form because of the incremental energy costs that would be encountered when producing fractions in the established standard viscosity range. Moreover, water may poison or reduce the activities of the catalysts used in catalytic cracking processes further down the processing line.

In earlier days, the method used to destabilize a crude oil/water emulsion was gravity-heating sedimentation. Nowadays, however, chemical de-emulsification and improved electromagnetic and gravitational techniques are the main methods used to break down an emulsion.

Such methods take advantage of inexpensive de-emulsifying chemicals to enable the collision and fusion of droplets that ultimately lead to oil/water phase separation. This is achieved by adjusting the surface charge density, counterion concentration and temperature. Polymers are also added to promote flocculation. A detailed

¹ Note: Orimulsion[®] is a trademark of INTEVEP, SA, a branch company of Petróleos de Venezuela, SA (PDVSA).

discussion of the electrostatic phenomena used in this process can be found in ref. (45).

The coagulants (typically multivalent counterions) commonly used are the salts of aluminium and iron and salts or the bases of calcium and magnesium. The transition from stabilized to destabilized emulsions on changing the temperature is very sharp at the critical flocculation temperature (CFT) when nonionic surfactants are used. Generally, aqueous dispersions destabilize upon increasing temperature, while non-aqueous dispersions destabilize with decreasing temperature.

To dissolve the stabilizing agent, the use of cosolvents such as carbon disulfide, carbon tetrachloride, acetone and ether is in current practice. For specific examples of oil/water separations and for further details about the use of dissolved air floatation, deep bed filtration, and the selection and sizing of various equipment, the interested reader is referred to ref. (46).

4 SUMMARY

Surfactants have very special qualities that make them invaluable to the petroleum industry. The relevance of various interfacial phenomena, such as adsorbed surfactant films, self-assembly, contact angle, wetting, foams and emulsions, in nearly every process in the industry has been discussed. In addition, this chapter summarized the importance of the adsorption and aggregation behaviour of surfactants with regard to drilling, enhanced oil recovery, antifoaming, corrosion inhibition, oil spill clean-up, oil/water separation and fluidization of highly viscous materials.

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