
Microemulsion in Enhanced Oil Recovery

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Abstract

The success of surfactant flooding for enhanced oil recovery (EOR) process depends on the efficiency of designed chemical formula. In this chapter, a thorough discussion on Winsor Type III microemulsion was included which is considered the most desirable condition for achieving an ultra-low interfacial tension during surfactant-flooding process. A brief literature review on chemicals, experimental approaches, and methods used for the generation of the desirable phase was presented. Phase behavior studies of microemulsion are a very important tool in describing the interaction of an aqueous phase containing surfactant with hydrocarbon phase to form the Type III microemulsion. Microemulsion highly depends on brine salinity and the interfacial tension (IFT) changes as microemulsion phase transition occurs. At optimal salinity, Type III microemulsion forms, whereas salinity greater or lower than optimal value causes a significant increase in the IFT, resulting in insufficient oil displacement efficiency. Type III microemulsion at optimum salinity is characterized by ultra-low IFT, and extremely high oil recovery can be achieved. In addition, this chapter also stated various other mechanisms relating to oil entrapment, microemulsion phase transition, and surfactant loss in porous media.

Keywords: surfactant, microemulsion, type III, enhanced oil recovery

1. Introduction

Existing oil fields are maturing day by day, and finding new reserves have become more exigent. An average of about 35% of total oil can be recovered naturally from the reservoir while the rest remains entrapped [1, 2]. Secondary recovery is applied after the diminishing of natural recovery in which the reservoir is flooded with water and only one-third (35–50%) of original oil can be recovered [1]. The remaining oil after water flooding is indispensable and cannot be ignored at this time of high-energy demand. Further enhancements in oil recovery can be made after water flooding using various enhanced oil recovery (EOR) techniques.

EOR is the oil recovery by injection of chemicals or gases and/or thermal energy into the reservoir to recover the remaining entrapped oil. Several techniques have emerged for EOR, and their selection depends on the complete evaluation of reservoir and economics. Chemical flooding, miscible displacement, and thermal recovery are the three major types of EOR techniques. These techniques change the viscous and capillary forces of the fluid present in the reservoir [2]. These forces are responsible for oil entrapment during water flooding [3]. Chemical flooding is considered as the most attractive EOR technique that mobilizes the remaining oil by reducing the capillary forces [4]. These forces conclude that interfacial tension (IFT) at the crude oil and brine interface plays a dominant role. A reduction of IFT for an increasing capillary number is an efficient and economically feasible approach [2, 5, 6].

In water flooding, the typical value of IFT is 10–30 dynes/cm. However, the chemical enhanced oil recovery (CEOR) can reduce the IFT value to 10^{-3} dynes/cm, which gives a significant reduction in residual oil saturation (ROS) [5, 7–9]. This ultra-low IFT can be achieved by surfactant flooding but the hurdle in the implementation of this method is the high cost of chemicals involved [10–12]. The designing of efficient chemicals involved in surfactant flooding, which is technically and economically suitable, is the need of time [10–12].

Surfactant flooding in the reservoir produces microemulsion after the interaction of surfactant with crude oil and brine [1, 6]. Microemulsions are thermodynamically stable, optically transparent, isotropic dispersion of hydrocarbon and aqueous phase stabilized by interfacial film of surfactant molecules [1, 9]. Micelles are formed after critical micelles concentration (CMC) due to the aggregation of surfactant molecules among themselves. When water is used as a solvent, larger quantities of crude oil can be dissolved in surfactant solutions with a concentration above the CMC [5]. The micelles formed have oil in their interior and are termed as swollen micelles [13, 14]. However, micelles in a hydrocarbon solvent will solubilize water and enhance the water solubility in the solution significantly. In this case, micelles formed will contain water in their interior and are called reverse micelles [14]. When there is a large amount of solubilized materials, which may be either oil in water or water in oil, the solution is frequently called a microemulsion [5, 6].

In 1954, Winsor characterized microemulsion phase behavior as Type I (oil in water), Type II (water in oil), and Type III (a bicontinuous oil/water phase known as middle-phase microemulsion) [5, 15, 16]. Type III microemulsion has been found suitable for reducing residual oil saturation due to its unique properties, that is, ultra-low IFT, thermodynamic stability, and the ability to solubilize oil and water [15–18]. Salinity greater than optimal begins to lower oil-microemulsion IFT to trap surfactant in residual oil (i.e., surfactant loss) and increases water-microemulsion IFT, which reduces oil mobilization [1, 7]. Whereas salinity lower than optimal begins to lower the water-microemulsion IFT to keep surfactant in the water phase and increases oil-microemulsion IFT, which tends to reduce oil mobilization [7, 17–19]. IFT between oil, water, and microemulsion is dependent on several factors, that is, salinity, temperatures, effect of divalent ions, surfactant structure, and oil composition [1, 5]. These factors are responsible for the phase transition between different phases of microemulsion. Accounting for these factors yields efficient chemical formulation design [1, 7, 20, 21].

The chemical formulation typically contains surfactant, cosurfactant, water, and electrolyte. Phase behavior studies are one of the most important criteria for surfactant testing and

selection. The phase behavior experiments permit qualitative observations such as the presence of undesirable microemulsions, the viscosity of the phases, and the equilibrium time, which is correlated well with good flood performance [16, 17]. Chemical phase behavior tests are therefore conducted with different surfactants and other additive such as electrolytes, cosurfactant, and cosolvent in order to achieve the most desirable Type III microemulsion [16].

2. Surfactants

Surfactants are surface-acting agents that influence interfacial and surface properties. Surfactants are extensively used chemicals having various applications in the oil industry. In petroleum recovery and processing industry, surfactants are used at various stages, for example, injection in reservoir, oil well drilling, production, and plant process [22]. Surfactant consists of polar (hydrophilic) and non-polar (lipophilic or hydrocarbon loving) portion as shown in **Figure 1** [1, 5]. The hydrophobic portion or the non-polar portion is often called tail, whereas the polar portion or the ionic portion is known as the head of surfactant molecule [1, 23]. When there are two immiscible phases, that is, oil and water, surfactant molecules start to arrange themselves at the interface by arranging their heads in water and tails in oil. Due to this dual nature, molecules of surfactants reside at the interface between oil and water, and forming different types of microemulsion [5].

2.1. Types of surfactants

According to the charge present on the head of surfactant molecule, surfactants are classified into different types as discussed subsequently [1, 5].

2.1.1. Anionic surfactants

Anionic surfactants are known by having a negative charge on their heads when they are in aqueous solution. They are widely used surfactants in EOR processes as they have a relatively good stability, a low adsorption on sandstone rock, and can be prepared economically [5, 24]. Examples of anionic surfactants are sodium dodecyl sulfate, alkyl sulfate, alkyl ether sulfate,

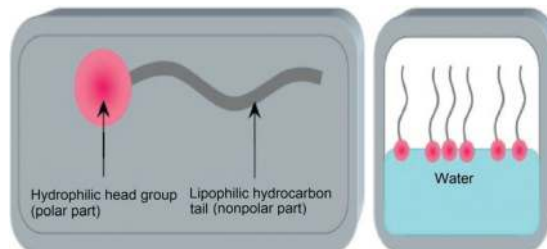


Figure 1. A schematic of surfactant molecule and its orientation in water [1].

alkyl phosphate, and so on. Alcohol alkoxy sulfate (AAS), internal olefin sulfonate (IOS), and alpha olefin sulfonate (AOS) are mostly used anionic surfactants in EOR application nowadays [7, 19].

2.1.2. Nonionic surfactants

In aqueous solution, nonionic surfactants do not have any charge on their head, that is, they do not ionize. IFT reduction of nonionic surfactant is less as compared to anionic surfactants which restrict them to be used as primary surfactant in EOR applications [5]. However, they proved themselves as a cosurfactant due their high salinity tolerance. Propoxylated and ethoxylated alcohols are examples of this class of surfactant [8].

2.1.3. Cationic surfactants

Cationic surfactants have positive charges on their heads when they are in the aqueous phase. Cationic surfactants give high adsorbance in sandstone reservoir and hence cannot be used for EOR application [1, 5]. However, these surfactants can be used for wettability alteration from oil-wet to water-wet in carbonate reservoir. Dodecyltrimethylammonium bromide, ammonium salts of fatty acids, and alkyl amine salts are the common examples of this type of surfactants [23].

2.1.4. Zwitterionic surfactants

These surfactants consist of two opposite charge active groups. Zwitterionic surfactant can be anionic, nonionic, anionic-cationic or nonionic-cationic [5]. They are also called amphoteric surfactants [6]. The charge on the head of zwitterionic surfactant is reliant on the pH of solution. Betaine, amine oxide, and amidobetaine are the examples of zwitterionic surfactants [8].

3. Surfactant in EOR application

The use of surfactant in EOR application is very effective in recovering a large amount of residual oil after water flooding, which could be about 60% of original oil in place [25]. The injection of surfactant in the reservoir is not a new method for EOR, and it has been used since 1920s [25, 26]. Later in 1970s, during the oil crisis, this method of EOR was investigated heavily, and phenomena associated with it were understood and presented by many researchers, which helped the development in surfactant flooding [15, 26, 27].

Surfactant flooding is used to reduce the capillary forces to mobilize the trapped residual oil after water flooding. When the surfactant solution is flooded in the reservoir, the hydrophobic tail of surfactant interacts with the residual oil and hydrophilic head interacts with the brine, and this interaction causes a strong reduction in IFT [5, 28]. A decrease in IFT in reservoir reduces the resistance to flow, which tends to mobilize the residual oil and gives high oil recovery [29]. A proper selection of surfactant is an important factor causing the IFT to reduce

to 10^{-3} dynes/cm and helps in 10–20% recovery of that original oil in place which cannot be recoverable technically and economically by any other technique [29].

3.1. Mechanism of surfactant flooding

When the surfactant is injected into the reservoir, it reduces the IFT between crude oil and brine and results in the coalescence of trapped droplets of oil and mobilizes it. In this way, the saturation of oil increases and mobile bank of oil begins to form [29]. **Figure 2** illustrates the typical chemical flood after water flooding. In **Figure 2**, region 1 is the residual oil saturation after secondary recovery, that is, water flooding, oil present is immobile, and only water is flowing. Region 2 is the oil bank with both oil and water flowing formed due to surfactant flooding. Surfactant slug in region 3 decreases the IFT between crude oil and brine and causes immiscible displacement of oil. Whereas region 4 is the polymer drive controlling the mobility and giving a smooth displacement of surfactant slug in the reservoir [22, 29].

3.2. Important factors associated with surfactant flooding

When more than one fluid is present in the reservoir, the flow conditions change. This results in the dynamic rock properties affected by fluid–fluid interaction and rock–fluid interaction [1]. Flooding of surfactant drastically decreases the forces inside capillaries, which facilitates immobile oil, and changes the properties of brine, oil, and reservoir rock [5]. Several factors involved in oil entrapment and the effect of surfactant on them are discussed subsequently.

3.2.1. Interfacial tension

The molecules at the liquid surface undergo imbalance attractive forces. Inward pull is exerted on the surface molecules by other molecules of the same liquid, whereas the vapors do not have the same strong attraction. The surface area of the liquid reduces due to this imbalance. The intensity of this force, which is acting on the surface of the liquid, is called surface tension [30]. In general, the surface tension is the tension between the liquid and the gas or atmosphere, and if the tension is at the interface of two dissimilar liquid, then it is known as interfacial tension (IFT) [30]. IFT is similar to surface tension in which cohesive forces are involved, but in IFT, adhesive forces are the main acting force at the interface. High IFT consequences the immiscibility of water and oil, and due to this reason, water could not drive

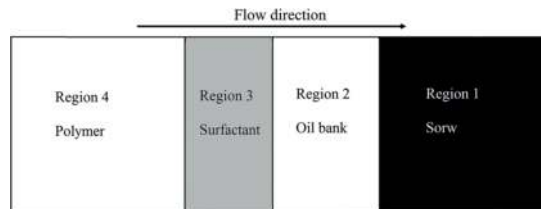


Figure 2. A schematic of the different phases in a typical chemical flood [22].

the remaining oil properly during water flooding or secondary recovery [3]. A decrease in IFT favors in high mobilization of oil. It is generally considered in EOR that the reduction of IFT to 10^{-3} dynes/cm helps in achieving a high mobilization of residual oil [3]. This ultra-low IFT can be achieved when the surfactant flooding generates the most desirable microemulsion (i.e., Type III) in the reservoir [1, 7, 31] as discussed later in Section 7.

3.2.2. Capillary pressure

Capillary pressure is the key factor that controls the distribution of fluid in reservoir, and all the EOR techniques except thermal recovery aim at eliminating or reducing it. Reservoir pores behave like capillary tubes having two different fluid phases that are immiscible. When two different immiscible fluids come in contact in capillary, an interface forms between them due to IFT. This interface is not straight but curved due to the difference of pressure between the two fluids. The pressure at the convex side is lesser than the pressure at the concave side, and the difference of pressure between the concave and the convex sides of interface is termed as the capillary pressure [32]. As the two fluids are immiscible having different wetting property, that is, one preferentially wets the surface of the tube known as wetting fluid, while the other is termed as non-wetting fluid [33].

The geometry of reservoir is complex consisting of a large number of capillaries. According to the Young-Laplace equation, the capillary pressure inside the capillary is directly proportional to IFT and contact angle and inversely proportional to the radius of the capillary as shown in Eq. (1) [33]

$$P_c = \frac{2\gamma \cos \theta}{r} \quad (1)$$

where P_c is the capillary pressure, γ is the interfacial tension, θ is the contact angle, and r is the radius of pore. Hence, according to Eq. (1), IFT should be low to reduce the capillary pressure.

3.2.3. Capillary number

The recovery of oil is dependent on the capillary and viscous forces present in the reservoir. The ratio of capillary forces to the viscous forces is called the capillary number. The capillary number is dimensionless value and is expressed as follows in Eq. (2) [1]

$$N_c = \frac{v\mu_w}{\gamma_{ow} \cos \theta} \quad (2)$$

where N_c is the capillary number, μ_w the displacing fluid (water) viscosity, v is the interstitial velocity of water, γ_{ow} is the IFT between crude oil and water (i.e., displacing fluid), and θ is the contact angle between oil and water.

The capillary number is in the range of 10^{-7} – 10^{-6} for a mature water flood, which is quite low, and a substantial amount of oil remain behind [1]. Residual oil after water flooding can be recovered by EOR methods in which the capillary number is increased. According to Eq. (2), the capillary number can be increased by increasing the viscosity of displacing fluid or by

reducing the IFT between the displacing fluid and the crude oil. An increase in the interstitial velocity of displacing fluid is not practically possible in the reservoir. The most feasible approach is the reduction of IFT with the help of surfactant flooding [8, 34].

4. Micellization and solubilization

In surfactant flooding, the oil displacement generally involves the interaction among three components, that is, water, surfactant, and crude oil. Surfactant molecule has the affinity for both water and oil. When the surfactant is added in the solution, its molecules disperse as monomers. Due to their surface-active character, the monomers of surfactant accumulate and form a monolayer at the interface of water and adjacent fluids such as oil. When the surfactant concentration increases to a certain value, the monomers begin to associate among themselves to form micelles [1, 35]. Micelles are an aggregation of molecules which usually consists of 50 or more surfactant molecules [35]. The critical micelle concentration (CMC) is defined as the lowest concentration above which monomers cluster to form micelles [1, 35]. Above the CMC, a further increase in surfactant concentration would only increase the micelle concentration and not change monomer concentration much. A plot of surfactant monomer concentration versus total surfactant concentration is shown in **Figure 3**. The IFT of the aqueous solution of a pure surfactant does not change much beyond the CMC. If water is the solvent, surfactant solutions with concentrations above CMC can dissolve considerably larger quantities of organic materials than can pure water or surfactant solutions at concentrations below the CMC because the interior of the micelles is capable of solubilizing the organic compounds. Similarly, micelles in a hydrocarbon solvent will solubilize water and enhance the water solubility in the solution significantly. When there is a large amount of solubilized materials, which may be either oil in water or water in oil, the solution is frequently called a microemulsion [6].

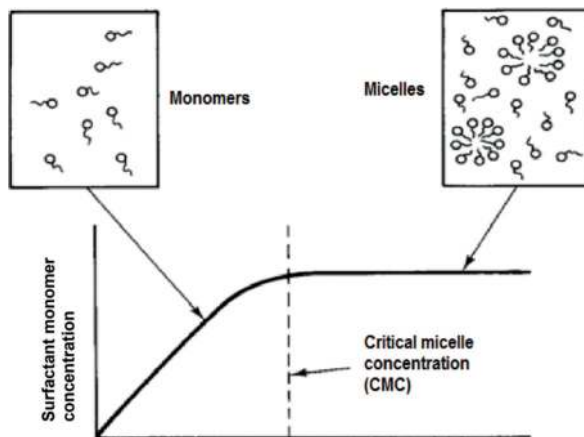


Figure 3. A schematic definition of the critical micelle concentration [6].

5. Microemulsion

A microemulsion is a thermodynamically stable dispersion of oil and water, which contains substantial amounts of both oil and water, stabilized by surfactant. Microemulsions are typically clear solutions, as the droplet diameter is approximately 100 nm or less [6].

Oil is nonpolar and consists of hydrocarbon molecules having no interaction with polar molecules, that is, water. When the crude oil and water are mixed and stirred, emulsion forms which destabilize rapidly and again separate into two phases due to high IFT of water and oil droplets. The stability of these emulsion increases with the addition of surfactant due to the decrease of interfacial energy; as a result, a stable emulsion or a microemulsion forms [36]. By contrast, microemulsion is thermodynamically stable due to zero interfacial energy. The IFT between the microemulsion and excess phase can be extremely low. The final microemulsion state does not depend on the order of mixing, and energy input only determines the time it takes to reach the equilibrium state [37].

Microemulsions have many application in numerous fields, such as EOR, cosmetic, nanoparticles synthesis, detergency, and pharmaceuticals [36]. Microemulsion gives low IFT and has a good solubilizing ability, and due to this reason, it is found quite suitable for EOR application. It lowers the IFT between brine and crude oil and mobilizes the remaining trapped oil after water flood [36].

5.1. Types of microemulsion

Winsor (1954) characterized the microemulsion as three types, that is, Type I (lower phase), Type II (upper phase), and Type III (middle phase) as shown in **Figure 4** [67]. Type I microemulsion is an oil-in-water microemulsion in which a portion of oil is solubilized by surfactant. Type I microemulsion is in equilibrium with excess oil phase. Type II is a water-in-oil

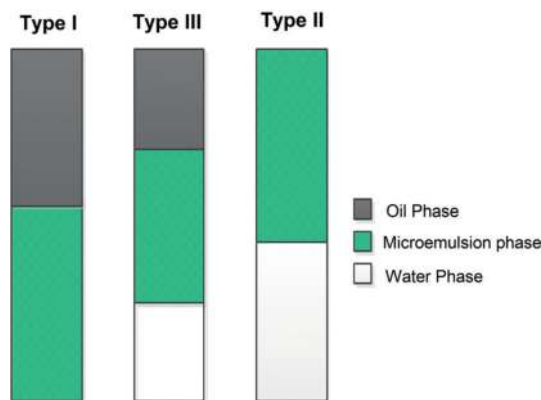


Figure 4. Types of microemulsion [15].

microemulsion in which a portion of water is solubilized by surfactant and microemulsion is in equilibrium with excess water phase. In Type III microemulsion, both oil and water are solubilized by surfactant and is often assumed to be bicontinuous because it is in equilibrium with excess oil and water [5].

Out of three microemulsion types, Winsor Type III microemulsion reflects the most favorable condition for surfactant flooding [38]. All microemulsions are thermodynamically stable and in theory never separate out into their oil and water constituents [1, 5, 24].

6. Phase behavior of microemulsion

The phase behavior of microemulsions is very important to enhanced oil recovery. This is because it can be used as an indicator of ultra-low IFT [1, 31, 36, 39, 40]. Phase behavior screening helps in quickly evaluating favorable surfactant formulations. Winsor (1954) first described the phase behavior of microemulsion for surfactant, oil, and brine system [16, 17]. The phase behavior of a microemulsion system is a function of surfactants, cosurfactants, oil, brine, alcohol, temperature, and so on [5, 16]. In a particular microemulsion system containing an ionic surfactant, the concentration of the electrolyte is an important impact factor on the phase behavior of microemulsion.

When the salinity in the aqueous phase increases, the solubility of anionic surfactants in the aqueous phase decreases. With the increase in salinity, surfactants are driven out of brine and contribute to the middle or upper phase and cause the transition of microemulsion from Type I to Type II through Type III (Figure 5) [1, 5, 14, 16].

Healy et al. described the phase behavior of a simple or an ideal microemulsion system and the effect of brine salinity on phase behavior [15]. As discussed in the previous section that the main mechanism by which salinity affects microemulsion phase behavior with ionic surfactants is the electrostatic forces. For instance, those between charged surfactant

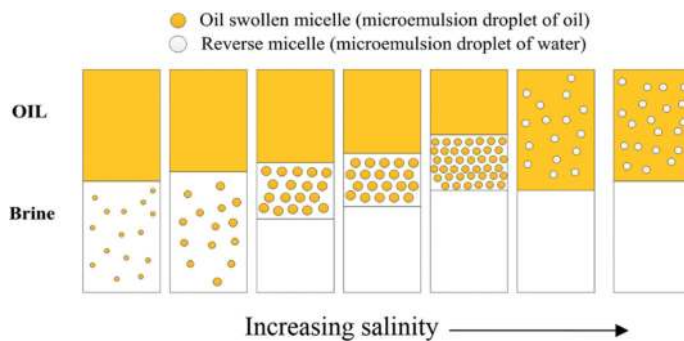


Figure 5. Schematic illustration of middle phase formation and microemulsion phase transition as a function of salinity [14].

head groups in surfactant films covering the surfaces of microemulsion drops [41]. These forces will spontaneously change the curvature of the drops which in turn determines the type and solubilization capacity of the microemulsions. Healy et al. [15] found for their ideal system that the multiphase behavior divides into three basic classes as shown in **Figure 6**.

At low salinities, the microemulsion is an oil-in-water microemulsion that coexists with nearly pure excess oil [1, 5, 15]. The system would appear as shown on the left side of **Figure 6**. Since the density of this kind of microemulsion is higher than the oil, therefore it is below the oil and is called “lower-phase” microemulsion [1]. Also, it is named as Winsor Type I or Type II (-) because the slope of the tie lines of lower-phase microemulsion is negative in the two-phase region. In this microemulsion, the radius of microemulsion drop will become larger and solubilization of oil will be enhanced with the increase of salinity and the repulsion between the charged head groups decreases [41].

When the salinities are very high, the electrostatic forces from the electrolytes will change the sign of the drop curvature so that the water-in-oil microemulsion forms [41]. It is called an “upper-phase” microemulsion because the microemulsion is lighter than the water and is present above the water phase [1]. The system would appear as shown on the right side of **Figure 6**. The upper-phase microemulsion is also named Winsor Type II [1, 5, 16].

At intermediate salinities, three phases coexist and the microemulsion formed is in equilibrium with both excess oil and brine and lies in the middle as shown in **Figure 6**. This microemulsion, which is called “middle-phase” microemulsion, contains almost all the surfactant in it. This type of microemulsion is of great importance in EOR because of its ultra-low IFT, a large interfacial area, thermodynamic stability, and the ability to solubilize excess amount of both oil and water [1, 15–18].

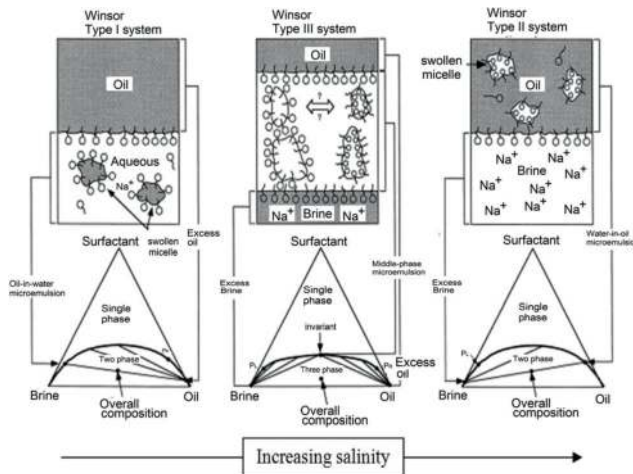


Figure 6. Microemulsion ternary phase diagram for different salinities [15].

7. Relationship between IFT, solubilization, and salinity

IFT between different phases of microemulsion and solubilization of oil and water changes as a function of salinity. The relationship between IFT, solubilization, and salinity is discussed as follows.

7.1. Relationship between solubilization ratio and salinity

As the transition of microemulsion takes place from Type I to Type III to Type II, the volume of oil and water solubilized in the microemulsion phase changes. Healy et al. [15] developed a relationship between oil and water solubilization ratios and the salinity. Oil and water solubilization ratios were defined as follows:

$$\text{Oil solubilization} = \frac{V_o}{V_s} \tag{3}$$

$$\text{Water solubilization} = \frac{V_w}{V_s} \tag{4}$$

where V_o and V_w are oil and water volume solubilized in microemulsion, respectively, and V_s is the volume of surfactant used. All the surfactant was assumed to partition into the microemulsion phase [15, 16, 42].

Figure 7 shows the plot of oil and water solubilization ratio versus salinity. It illustrates that at low salinity, water solubilization ratio is high and constant because all the water is solubilized in microemulsion, whereas solubilization ratio of oil is too low. Hence, at low salinity, Type I microemulsion forms with the solubilization of a little amount of oil. When the salinity increases, the solubilization ratio of oil also increases, while the solubilization ratio of water

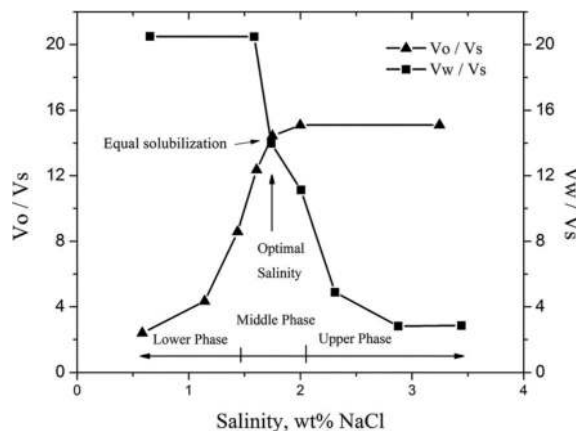


Figure 7. The plot of oil and water solubilization ratio versus salinity [1].

decreases. At intermediate salinity, middle-phase Type III microemulsion forms with both oil and water solubilized in it. The intersection point of oil and water solubilization ratio curves versus salinity gives the optimal salinity (S^*) and optimal solubilization ratio (σ^*) as shown in **Figure 7**. Optimal salinity is the salinity where equal volume of oil and water is solubilized in microemulsion [14, 15, 17–19, 21, 43]. A further increase in salinity above optimal shifts the system to the upper phase where all the oil is solubilized in microemulsion phase with very low water solubilization.

7.2. Relationship between IFT and salinity

Microemulsion can have one or two different interfaces (i.e., oil microemulsion or/and water microemulsion) depending on the type of microemulsion. IFT value at these interfaces changes as a function of salinity. Healy et al. [15] presented a strong relationship between phase behavior of microemulsion and IFT. Both phase behavior and IFT were found as a function of salinity, and the plot of IFT between the equilibrium phases versus salinity is shown in **Figure 8**. In this figure, IFT between microemulsion and excess oil phase is represented by γ_{mo} whereas IFT between microemulsion and excess water phase is represented by γ_{mw} . It can be seen in **Figure 8** that when the salinity increases, γ_{mw} decreases and γ_{mo} increases. The value of salinity where γ_{mo} is equal to γ_{mw} was named optimal salinity as shown in **Figure 8**. This optimal salinity (shown in **Figure 8**) is close to the optimal salinity where oil solubilization ratio is equal to water solubilization ratio (shown in **Figure 7**) and can be correlated [1, 42, 44]. **Figure 8** shows that salinity lowers than optimal, begins to lower the water-microemulsion IFT to keep surfactant in the water phase, and increases oil-microemulsion IFT, which tends to reduce oil mobilization. So in Type I, surfactants are concentrated in the lower phase causing the IFT of oil microemulsion to be higher. Salinity greater than optimal begins to lower oil-microemulsion IFT to trap surfactant in residual oil (i.e., surfactant loss) and increases water-

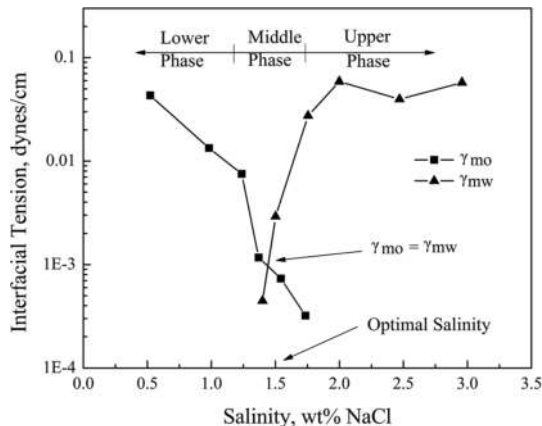


Figure 8. Interfacial tension versus salinity [1].

microemulsion IFT, which reduces oil mobilization. It can be concluded from **Figure 8** that the lowest IFT for both oil and water microemulsion simultaneously occurs at optimal salinity condition [15, 18–20].

Huh [20] derived a theoretical relationship between IFT and optimal solubilization ratio shown in Eq. (5) [1, 16, 20, 31, 44, 45]

$$\gamma = \frac{0.3}{(\sigma^*)^2} \quad (5)$$

where γ is the interfacial tension and σ^* is the optimal solubilization ratio. Eq. (5) shows that optimal IFT is inversely proportional to solubilization ratio. A solubilization ratio greater than 10 reduces the IFT to ultra-low value, that is, 0.003 dynes/cm. The ultra-low IFT results in high capillary number which gives significant reduction in residual oil saturation [1, 46]. Estimating IFT from Eq. (5) is much quicker than direct measurement and sufficiently accurate for screening purposes [18, 21, 47].

8. Effect of chemicals used in microemulsion formation

8.1. Effect of surfactant

Surfactant provides the force necessary to part two liquids which act on the interface. Surfactant provides the solubilization of oil and water into the microemulsion under some conditions by changing the interfacial properties of surface. Surfactants generally consist of lipophilic tail, hydrophilic head, and intermediate neutral group [1, 5, 17].

The tail of surfactant has a significant effect on phase behavior of microemulsion. Surfactant with a branched carbon chain is preferred due to reduced packing at the oil/water interface, giving a lower viscosity microemulsion and less-ordered oil/water structures that decrease the formation of liquid crystal or gel [1, 19, 48]. Longer carbon chain of surfactant increases oil solubilization but decreases optimal salinity [49]. However, microemulsion viscosity and equilibrium time increase with the increase of carbon chain length of surfactant [5]. Surfactant having extreme branching with two different carbon tails attached to the head group has shown a very good performance in terms of solubilization ratio and optimal salinity [19, 48, 50].

According to the charge of head group, surfactants are classified into four types, that is, anionic, cationic, nonionic, and zwitterionic discussed in Section 2. Anionic surfactants are found to be most suitable for surfactant flooding because their adsorption is low [49, 51]. Surfactant tail and head are joined by the intermediate groups. They are neither strongly hydrophobic nor hydrophilic and often neutral in nature. They provide the stability at oil/water interface. They give a very good salinity tolerance and a high optimal salinity. They also prevent the precipitation of surfactant. Ethylene oxide (EO) and propylene oxide (PO) are the

mostly used intermediate groups. PO groups are neutral in nature, whereas EO groups are hydrophilic. PO groups provide high tolerance for divalent cations and also help in reducing IFT by increasing the area and size of surfactant molecule without making it too hydrophilic. EO groups give high tolerance to salinity and divalent cations [1, 8, 19, 52].

Alcohol sulfates, that is, alcohol ethoxy sulfates (AES) and alcohol propoxy sulfates (APS), are commercially available branched surfactants and have the ability to give gel and liquid crystal-free microemulsion. The number of EO and PO groups attached tell about the hydrophilicity and hydrophobicity of the surfactant [19, 21, 22, 44].

Properties of surfactant are also dependent on hydrophile–lipophile balance (HLB) number. It indicates the ability of surfactant to form water-in-oil or oil-in-water microemulsion and also tells about the relative solubilization. The range of HLB number is from 0 to 20. When the HLB number is 0, the molecule of surfactant becomes completely hydrophobic and gives no solubilization of water. When the HLB number increases, molecules become less hydrophobic and more hydrophilic. Therefore, an increase in HLB allows surfactant to be more soluble in water and less soluble in oil. When the formation salinity is high, a high HLB surfactant should be chosen and vice versa [5, 48].

8.2. Effect of cosurfactant

Primary surfactant is the surfactant which directly plays a role in the formation of microemulsion. Sometimes, cosurfactant is necessary to target the desired microemulsion at some desired conditions. Cosurfactant is often molecularly dissimilar to the primary surfactant, but yet it is sufficiently similar to form micelles and avoid phase separation [1]. Molecular dissimilarity helps in changing the optimal salinity of surfactant mixture and decreases microemulsion viscosity and gel formation [1]. Molecularly dissimilar surfactant actually creates disorder in microemulsion structure by aligning at oil/water interface of microemulsion droplet. Due to this disordering, microemulsion destabilizes and a reduced viscosity microemulsion is obtained [7, 49]. Recent study has proven that internal olefin sulfonate (IOS) is a high-performance cosurfactant when used in combination with alcohol alkoxy sulfates (a primary surfactants) [16, 19, 44, 53].

8.3. Effect of cosolvent

Cosolvent is a small carbon chain (i.e., C3 to C5) alcohols and acts at the interface of microemulsion droplet [16]. It reduces the viscosity of microemulsion and the formation of gel and liquid crystals. Short-chain alcohol molecules reduce the packing of micelles by separating the longer chain of the surfactants [1, 39, 54]. It gives the flexibility to the interface of microemulsion droplet to form a spherical shape. When the microemulsion is prepared in the absence of a cosolvent, the solubilizing capability of micelles becomes unlimited [5]. This may reverse the type of microemulsion as the inner phase expands. The expansion of inner phase can be controlled by the addition of cosolvent, and the desired type and properties of microemulsion can be achieved [5]. Hence, the addition of cosolvent increases the stabilization of microemulsion and decreases the equilibrium time [19, 55]. A higher carbon number crude

oil requires higher carbon number surfactants to solubilize oil and hence a higher carbon number cosolvent to give the desired phase behavior [44]. With the addition of hydrophilic cosolvents, the aqueous solubility of surfactant solution increases, whereas optimal solubilization ratio decreases [5, 16, 48]. Short-chain alcohols such as propanol gives a high optimal salinity for sulfonate surfactants, whereas alcohol with longer carbon chain such as hexanol and pentanol reduces optimal salinity [5].

8.4. Effect of electrolyte

Electrolyte is a compound that ionizes when dissolved into solvent such as water. As the electrolyte concentration increases, the solubility of anionic surfactant in aqueous phase decreases [15]. At low salinity, Type I microemulsion forms with very low oil solubilization. However, at high salinity, the Type II microemulsion is produced with a very small amount of water solubilized by surfactant. At intermediate brine concentration, Type III microemulsion forms by the solubilization of both oil and water. However, at optimal salinity, an equal volume of oil and water is solubilized by surfactant and is obtained by conducting phase behavior experiments with salinity gradient [1]. Mostly used electrolyte in phase behavior experiment is sodium chloride (NaCl).

9. Equilibrium time of microemulsion/microemulsion coalescence

The time after which no further coalescence of oil and water takes place is known as equilibrium time or coalescence time. Formulation with a rapid equilibrium produces microemulsion of less viscosity [47, 56]. However, lengthy equilibrium time occurs when macroemulsion or gel is found, which is not desirable [47]. Therefore, a chemical formulation should be screened for fast equilibrium so as to remove all these undesirable phases. Macroemulsion and high-viscosity microemulsion transport poorly and result in the retention of surfactant in the porous media causing unfavorable condition for microemulsion flooding [16, 19].

10. Surfactant loss mechanism in reservoir

The success of chemical flooding depends on the loss of elimination or reduction of surfactant loss in the reservoir. Surfactant concentration in the injected slug decreases as it transports through the reservoir. Surfactant loss takes place in reservoir due to various mechanisms, that is, surfactant adsorption, surfactant precipitation, surfactant degradation, surfactant polymer mixing, and surfactant partitioning in residual oil phase [57].

When surfactant slug comes in contact with the reservoir rock, the adsorption of surfactant takes place on the rock surface. Due to adsorption, the surfactant concentration in the injected slug reduces and the amount remaining behind is not sufficient to achieve ultra-low IFT and to mobilize the trapped residual oil [58]. The effect of microemulsion composition on the amount of surfactant adsorb on Berea sandstone was studied. It was observed that petroleum sulfonate

(a preferentially oil-soluble surfactant) adsorbs more from water external microemulsion than from oil external microemulsion [57, 59].

Divalent cations such as Ca^{++} and Mg^{++} present in connate water cause the surfactant to precipitate. When the surfactant starts precipitating, IFT between brine and oil will be altered, and the efficiency of surfactant flood reduces. Ethoxy group (EO) was found having a high tolerance to divalent cations (e.g., Mg^{++} and Ca^{++}) [60]. Other researchers have also presented that ethoxylated surfactants and alcohols give a high salt tolerance and hence precipitate less [57, 61].

Surfactant intended to be flooded should be stable at reservoir temperature. Anionic surfactants are found to be resistant to high temperature as compared to nonionic surfactants. Different surfactants have different workable temperature ranges. Most of them are sufficiently stable at a normal temperature range [57, 62]. Sulfate surfactants are used for a low-temperature condition, that is, up to 60°C , whereas sulfonate surfactants are stable up to 80°C , and some sulfonates (i.e., internal olefin sulfonates) are stable up to 200°C .

Results of core floods have proved that most of micellar fluids are incompatible with the polymer. Surfactant slug gives multiple phases when mixed with polymer. If the IFT between these multiple phases is high, the phase trapping occurs in the reservoir, which increases the chemical requirement and lowers the recovery efficiency. The interaction of surfactant with polymer can be reduced if the salinity of a polymer slug is lesser than that of surfactant [5, 57, 63–65].

When the surfactant slug is injected, it moves through the reservoir and comes in contact with crude oil [66]. If surfactant partitions in oil, then IFT will be sufficiently high which results in the phase trapping of oil phase. The trapped phase also contains surfactant, and thus loss of surfactant takes place [57].

11. Conclusion

This chapter discussed surfactants, their chemistry, and application in EOR. Various phenomena associated with surfactant-flooding process were presented in detail. It deals with the phase behavior studies of microemulsion and the effect of different chemical additives to generate the most desired Type III microemulsion for EOR. The phase transition of microemulsion due to salinity addition and IFT behavior during different microemulsion phase shifting was explained in detail. Finally, a brief literature on oil entrapment and surfactant loss mechanism in porous media was discussed.

Conflict of interest

The authors declare no conflict of interests.

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