Chapter

CO_2-Philic Surfactants Structural Morphology Prerequests for CO_2 Philicity for Foam Durability for EOR Applications

Muhammad Sagir, Muhammad Bilal Tahir, Muhammad Pervaiz, Muhammad Hassan Qasim, Sami Ullah and Reema Ansar

Abstract

In oil fields CO_2-EOR have extravagant interest because of its increasing microscopic sweep efficiency. As a balance and dense solution over a huge range of temperature and pressure, carbon dioxide can improve viscosity reduction and oil swelling because of all partial miscibility with heavy oils and proportion miscibility with light oils, and also carbon dioxide has mutual solubility with water and hydrocarbons that these properties result in increasing microscopic sweep efficiency in mechanism of CO_2 injection. However, due to CO_2 lower viscosity than water and oil, CO_2-EOR efficiency is limited that causes near well-bore conformance issue and mobility contrast problem such as gravity override and fingering. The carbon dioxide philic surfactant blends traditionally includes foam booster, foam stabiliser and foaming surfactant. An integrated property-performance analysis of blends of anionic surfactants includes carbon dioxide philic groups such as twin-tailed carbonyl group, propylene-oxide and methyl group of CO_2-philic groups under the circumstances of reservoir showed that carbon dioxide philic surfactants can be the mixture of CO_2 problems. Here we will underline that modifying the surfactant tail can be a proper path to surpass foaming performance.

Keywords: EOR, foam, CO_2-philic surfactants

1. Introduction of foam

Foam is the gas dispersion in liquid. The liquid phase is called exterior stage and the stage of gas is spread in interior stage. We can see the foam formation in **Figure 1**. We called thin fluid film lamella. In Foam we can separate a lamella into internal gas bubbles. The Point where the lamella contact with each other is called 'Plateau border. It is shown in **Figure 1**. There is a density difference between the medium and gas bubbles due to which the system rapidly split in to two layers and the gas bubbles moved to the top [1]. Pure liquid could not foam. They only foam when they have a surface-active material [1, 2]. We find that whenever a bubble of gas is injected under the surface of liquid, its outburst instantly. If we use diluted surfactant solution then a restoring force is created that effort to launch the equilibrium,

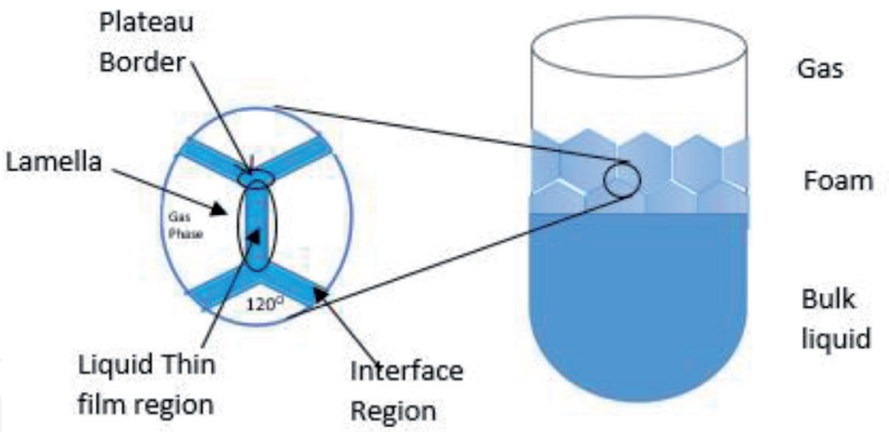

Figure 1.
A schematic of three bubbles meeting at a plateau border.

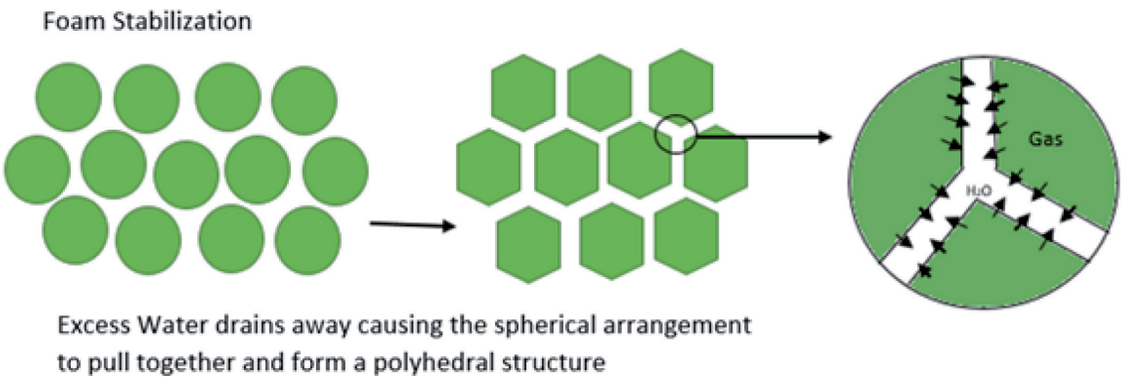

Figure 2.
Foam stabilisation and formation of polyhedral structure foam.

as the air/liquid interface enlarge the surface equilibrium changes, this leads to form polyhedral structure as shown in **Figure 2**.

2. Types of foam

According to the structure, a foam may be distinguished in two main types [2, 3]:

2.1 Spherical foam

We can say it as a provisional dilute dispersion of bubbles in the liquid. It involves of gas bubbles separated by thick films of viscous liquid formed in recently prepared systems.

2.2 Polyhedral gas cells

In polyhedral gas cells thin flat "walls" are produced on ageing with connection points at plateau borders [2].

Mainly, the spume can be categorised as:

2.2.1 Bulk foam

The bulk foam is an "agglomeration of gas bubbles parted from One another by thin liquid films. In bulk foam the total volume of gas (discontinues phase) is

relatively much larger than the thin liquid films (continues phase). It is regarded as a single stage of homogenous. The gas content in bulk foams is high which 60–97% is usually. In bulk form foams are produced when gas links a liquid in the presence of powered agitation.

2.2.2 Foam in porous media

In porous media foam occurs as a distinct micro gas bubbles which is contact along the wetting fluid of aperture walls. Thin liquid films (lamella) make the bridge between these micro gas bubbles in order to separate them. In permeable media, the behaviour of spume and bubble size reliant on pore throat and pore size distribution. Mostly foam spread as bubble train in matrix of reservoir rock. In many cases, specific foam bubbles in reservoir matrix rock may be numerous pore bodies in length. Foam bubbles are mostly larger than pore bodies in porous media. As Foam present in the form of bubble trains in reservoir-rock porous media where the Plateau border of the foam lamellae is made at the pore wall and has, for stationary non flowing foam in the pore body, an angle of about 90° in the middle of the liquid lamellae and the pore wall [4–6].

Foam may also have classified as:

- Transient foam: All foams are thermodynamically unstable reason is the high interfacial free energy. Affording to breakdown kinetics of foam films, the foam films may be of two types: The foams having very short life time only in seconds are called unstable foams. They are mostly produced using "mild" surfactants, e.g., pine oil, phenol. Short-chain alcohols, aniline [7, 8].

- Stable foam: Second type of foam is permanent type with lifetime of hours, called metastable foams. These foams are generated by using good foaming agents (surfactants) proteins solid particles or long-chain fatty acids.

3. Condition to form foam

To create a foam three condition are required.1st Condition is the mechanical work so that the surface area is increased. This can be done by, dispersing a high volume of gas in the liquid, agitation, or inserting a gas in the liquid [9, 10].

The second condition is surfactants that must be available so that surface tension decreases. And the last is foam must be produced more rapidly than it break.

4. Stability of foam

Lamella's stability is the stability of foam. It depends on different factors which are rate of capillary drainage, mechanical deformations, surfactant concentration, like gas diffusion, aqueous phase salinity, anti-foaming effect of oil, disjoining pressure [1, 4, 11–13].

4.1 Drainage of film

In film drainage process the lamella undergoes a thin method. Which goes toward the super thin or rupture of liquid films.it is also called structure of black spot. Gravity drainage and capillary suction can be done by two means. The drainage of gravity is usually occur in lamella that is thick .in this process due to

the gravity the film is moved downward .we can slow this process by decreasing the liquid in the foam and increasing the bulk viscosity. The two indicators are the lamella's time to reach the crucial broadness and the limited broadness beneath which the lamella coalesces. The signals reliant on different factors like viscosity, surfactant solubility, elasticity of surface, adsorption on the plane and ratio of gas to liquid. Usually as the attentiveness of the surfactant extended, the critical thickness decreases [14, 15].

4.2 Gas diffusion

With the side pressure of lamella could not be equal so the gas is dissolved in lamella the by diffusion it escape .it is common when the porous media trapped the bubbles. When the moving lamella is reshaped continuously then the inter bubble diffusion is complicated. In high flow rates the gas diffusion may be negligible. The main foam film drainage tool is capillary drainage. The reason of the occurrence is the capillary tube (at plateau border suction). The curvature at centre of film is comparatively higher than the radius of the curvature at the plateau border. The reason is the fact at the middle of foam lamella the film border is nearly equal. While, at plateau boundary, the curvature is further curved [16].

4.3 Oil effect

The oil-foam contacts are significant as the oil occurrence has incompatible belongings on stability of foam. However, the damaging consequence on spume strength by the oil is prevalent. Oil interaction with surfactant creates some problems like it causes in lamellae liquid depletion which brings alteration in wet ability and this scattering of oil on lamella become reasons for destabilisation of the interface. Surfactant and oil solution makes the emulsion and they break the structure of foam. Three coefficients typically used to describe the mechanisms of oil destabilising foam. The spreading coefficient, S: the entering coefficient E, and the bridging coefficient B. Coefficients are described as: [17–21].

Spreading (S), entering (E), and bridging (B) coefficients are described to assess the possibility of oil droplet to enter the gas-water surface. Eqs. 1–3 explaining the foam destabilisation.

$$E = \sigma_{gw} + \sigma_{ow} + \sigma_{og} \tag{1}$$

$$S = \sigma_{gw} - \sigma_{ow} - \sigma_{og} \tag{2}$$

$$B = \sigma^2{}_{gw} + \sigma^2{}_{ow} + \sigma^2{}_{og} \tag{3}$$

where, σ_{gw}, σ_{ow}, and σ_{og} stand for gas/water, oil/water, and gas/oil surface.

If the E, entering coefficient is in positive, a drop of oil is predicted to be drawn up in the lamellar area among two bubbles. This will breaching the air/water interface causes the film to drop the foam become stable ability and skinny to rupture point. When bridging coefficient, B, is positive, the oil droplet bridges the lamellar area among the two neighbouring bubbles. When the spreading coefficient, S, is positive, the droplet of oil in the lamella area is predicted to extent like a lens above a foam. The extent of a droplet of oil above a foam lamella reasons the lamella's foam to break (**Figure 3**).

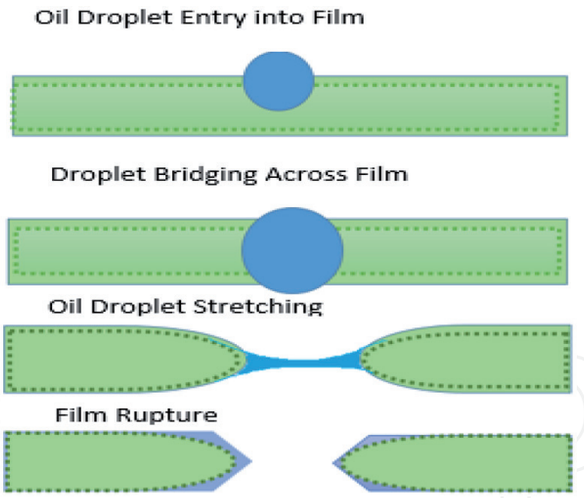

Figure 3.
Oil destabilising foam mechanism.

4.4 Effect of temperature

The stability of foam depends on temperature. A high temperature results in decreased foam drainage time and therefore causing the foam stability decrease with the temperature increase.

5. Role of surfactant in foam generation and stability

The generation is not the serious challenge alone; the important ones are foam quality, form and its stableness mainly when it is in proximity with oil. Surfactants is used for foam spread have low endurance with salinity and results in extreme adsorption on carbonate rocks. The surfactants are capable of playing central roles in enhancement of oil recovery, not only in foam generation but also in IFT reduction. The modern type of surfactants CO_2-phillic surfactants are used for CO_2 control application movability and for the stability of foam in the creation. As the traditional surfactants, these have two surfactants that have well defined areas, tail and head; nonetheless, surfactants tail has a capability for stabilising the CO_2 gas. The reference of foam stability, surfactants that are non-iconic are minor but their stability at high temperatures is a problem. A foam usually absorbs on the rock matrix, deteriorates over time, and has a higher deterioration at high temperatures in the existence of oil. When the Carbon dioxide gas is used the problems become more severe. This phenomena was particularly created to produce fresh surfactants with an affinity for CO_2 gas under controlled conditions and to defeat the problems that arise from traditional surfactants. The surfactants novel can produce much balance spume at a higher temperature and in the existence of oil with less adaption problems.

6. Problems with conventional surfactants in foam stability

The creation of spume, alone, is not a serious problem; the highlighted ones are quality of spume, formation of spume and its balance is particularly when it is in contact with oil. The surfactants used for spume creation have low endurance with salinity and result in extreme adaption on rocks of carbonate. With reference to stability of foam, the surfactants of non-ionic are lesser but the problem is their

stability at high temperatures. Usually, a foam that absorbs on the rock matrix becomes worse over time, and has a higher decay at increased temperatures if present with oil. These problems become worse when the CO_2 gas is present. This phenomena was particularly created to produce fresh surfactants with an affinity for CO_2 gas under controlled conditions and to defeat the problems linked with surfactants that is conventional. The surfactants of novel can produce much balance foam at an increased temperature and in the existence of oil with lesser adaption problems.

7. CO_2-philic surfactants

Like conventional surfactants, the surfactants of carbon dioxide phallic are pure amphophilic compounds but rather than lipophilic and hydrophilic parts, they are made up of carbon dioxide-phobic fragments and carbon dioxide philic. Usually the ends of these surfactants are attracted toward CO_2, and are known as the surfactants of CO_2-philic segments, and CO_2-phobic parts are head group of the surfactant [22]. Phobic segments of carbon dioxide are usually selected as a traditional group of hydrophilic, formerly we have identified the segment of tail of the carbon dioxide-philic surfactant. The distinctive form of a carbon dioxide philic surfactant is illustrated in **Figure 4**.

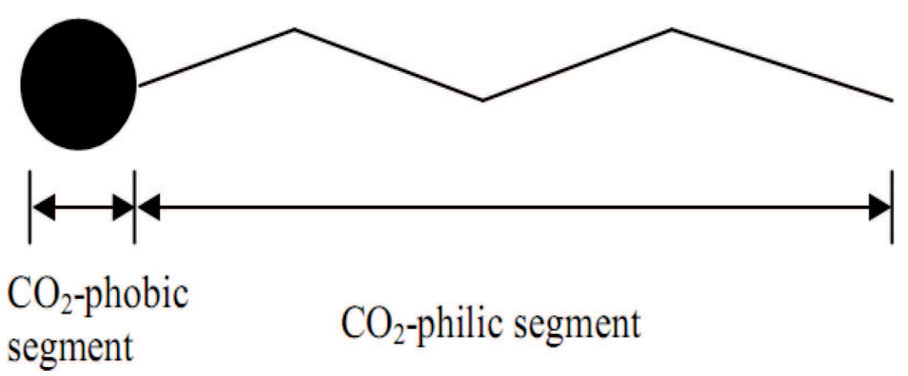

Figure 4.
Structure of a CO_2-philic surfactant.

8. CO_2-philic surfactants for foam

The leading group of researchers have informed that non-fluorinated, hydrocarbon-based systems can be created in a way that they are CO_2-philic in nature. These surfactants resolve the above mentioned foam problems [23–26]. Since CO_2 is a weak solvent, the polar and high molecular weight substances are only partially soluble, but CO_2 can dissolve in other few volatile and low molecular weight solvents. The carbon dioxide is a Lewis acid because it has an accepting electron nature, in spite of the fact that it has low polarisable properties [27]. The CO_2 can take part in Lewis acid–base interactions because of CO_2 having an electron accepting property. Many researchers have proved this kind of carbon dioxide bonding with other stuff like polymers and surfactants, etc. Fin and Lei Hong have expressed this kind of collaboration in their phenomena.

Fin also stated in his work that ab initio molecular simulation research have shown that the O_2 (ester or ether) in the side chain play an major role in promoting philicity of carbon dioxide because of the carbonyl oxygen. They recognised the three different ways the CO_2 linked with a hydrocarbon end of the molecule.

They need the Isopropyl acetate molecule as a sample. In the picture below, the red colour imitate oxygen, black represents carbon and white is used for atoms of hydrogen [17, 28–32].

9. Requirements for CO_2-philic surfactants for CO_2-philicity

Maximum attraction with the CO_2 and minimum intermolecular attractions are the basic requirements involved in designing a CO_2-philic molecule. Few of the Carbon dioxide philic appearance are splitting, less molecular weight hydrophobes, tip tail, and presence of groups of carbonyl, methyl, propylene oxide (PO), tert-butyl tip and a minimum number of methylene groups [22, 27, 33, 34]. A detailed discussion of the important factors that favour the carbon dioxide philicity of a surfactant will be followed in the next few sections.

9.1 Branches

The surfactants branching *is* a key factor for the carbon dioxide philicity of the hydrophobic part. It is because of the effect that when chain length decreases, the CMC (aqueous) increases; while, an increase in branching increases the solubility in CO_2. According to Ben Tan branching in the diacid as well as diol moiety has the increasing effect on solubility, and acyl chains branching increases the solubility up to 20 times.

9.2 Number of tails

It is observed that in case of CO_2-philic compounds the solubility is greatly affected by the tail number. With the increase in the number of tails the dissolved surfactants in the carbon dioxide increases. A huge and emergent part of literature is fixated on the phenomena of interfacial of the carbon dioxide/H_2O interface and proposes that there should be more contact with the interface for a double tail surfactant and as a result offers more stability for the micro emulsion. When a third chain is added in the surfactant structure the surfactant's solubility is increased in carbon dioxide even more [35–38].

9.3 Tail length and tip

In the past the relationship of CO_2-philicity with the tail length has been widely studied and the interdependency of CO_2-philic properties and surfactant tail structure was observed. At various temperature and pressure values, different double tail fluorinated surfactants have been studied for the phase behaviour [6, 7, 39]. This study leads to specifications for the optimization of tail length which is suitable for the maximum water/carbon dioxide emulsion formation at micro level. The phase behaviour for the oligomers is altered by the end-group modification of the oligomer PVAc-OH. Audrey DuPont examined P and T phase stability, chain structure effect and the aggregation structure. Surfactant free volume and surfactant packing are the parameters to view the effects of the chain lengths. Carbon dioxide solubility in esters is significantly affected by small structural changes in them. Depending upon the number of carbon atoms we can observe even/odd effects on solubility of carbon dioxide. According to observations made by Bray Christopher the acyl chain length is important with the carbon dioxide solubility for the molecule. With the increase in length of the chain by 10 carbon atoms the solubility increases in a systematic way. The influence of minor structural changes to the solubility of CO_2

molecule proposes that a qualitative as well as quantitative study of property–structure relationship is possible, that leads to the ability to predict properties associated with carbon dioxide solubility of molecules [8, 16].

9.4 Methyl groups, PO groups and methylene groups

CO_2-philicity is also favoured by the increase in methyl group number. Other factors that are considered in surfactant development are a smaller chain length, low molecular weight, lower no. of methylene and the propylene oxide groups.

9.4.1 Carbonyl groups

Beckman and Styranec have formulated CO_2-philic compounds by the use of only oxygen, hydrogen and carbon comprising precursors. They observed the polyether solubility was significantly influenced by the side chain or by adding the carbonyl group in its backbone. Addition of acetate group in the side chain gives an increase in solubility to a certain limit after that limit the solubility tends to decrease. According to the studies of Fink et al., the solubility of CO_2-philic compounds in carbon dioxide was significantly influenced by the addition of a good number of ester-functional side chains. The effect of numerous fluorine and vinyl-acetate groups in the side chain was studied by Bilal Baradie. He observed the polyether solubility was strongly changed with the side chain or with the addition of the carbonyl group [9, 40].

9.4.2 Molecular weight

A lot of research studies have claimed that carbon dioxide solubility greatly depends on the MW (weight of molecular) of the compound, as PVAc. At low pressures oligomer PVAc-OH (Mw < 3000 g/mol) is found to be dissolved in carbon dioxide but as the molecular weight increases it decreases in solubility. It was determined by Tan et al. Polymer's solubility such as PEC and PEE is significantly dependent upon their molecular weight as well as chemical structure of those polymers. A series of trials was conducted by Matthew B. Miller* by the mixing of different solvents with various extents of carbon dioxide to measure the compatibility for both mixture components having bubble point as basis. It is observed that species with low MM (molar mass) having minimum one atom of O_2 in ether, acetate groups/or carbonyl would have most favourable interaction with carbon dioxide through Lewis base/Lewis acid interactions [17].

10. CO_2-philic surfactants as potential CO_2 gas mobility control agent

Although carbon dioxide has many advantages as being not-toxic, inexpensive, and gas that is not flammable overall process wipe-out efficiency is limited by the minimum viscosity, low density and the increase movement of the carbon dioxide. Most significantly, the poor process sweep efficiency that is caused due to the low density resulting in high velocity of carbon dioxide gas results in sticky fingering, an soon breakthrough of the inserted carbon dioxide gas and override of gravity. This undesired ratio of movement brings the process to a week wipe-out efficiency and subsequently oil recovery is less anticipated.

To reach the high recovery of oil, concerns regarding carbon dioxide movement have to be solved. By the use of foam the carbon dioxide movement can be efficiently controlled [7–10]. The velocity of carbon dioxide can be reduced

by foam and it brings down the breakthrough of the inserted gas along with the reduction in the production of gas cap gas. With many advantages of foam it also has a few disadvantages, as instability beneath reservoir situation, For example, maximum salinity, maximum temperature, and particularly in the existence of oil. Incorporation of CO_2-philic surfactants promotes the foam stability. Surfactants are very distinctive molecules having a H_2O soluble part (head) as well as an oil soluble part (tail). From the generation of foam to IFT reduction, the surfactants tends to play vital roles in increasing oil recovery. For stable foam generation in carbon dioxide mobility control applications the CO_2-philic surfactants are employed. Like the other surfactants, these surfactants also have two different parts, tail and head; therefore, the tail for these surfactants has an empathy for carbon dioxide gas to balance the spume [41–45].

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