

Wettability alteration in enhanced oil recovery process using new amphoteric and cationic surfactants

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ABSTRACT

Over time, production of hydrocarbons decreases due to sequential producing and nowadays using Enhanced oil recovery (EOR) methods is a necessity. One of the methods in order to improve the oil recovery is altering the rock wettability toward water-wet by using Surfactant flooding. Surfactants have a variety of applications in the petroleum industry due to their remarkable ability to lower the oil-water interfacial tension and alter wettability. In this study new cationic and amphoteric surfactants synthesis and investigation of wettability alteration in EOR process is described. The goal of this work is to compare the wettability of a carbonate rocks from oil (mixed)-wet towards water-wet. Changing the wettability to preferentially water-wet condition will reduce the residual oil saturation (Sor). Wettability alteration is measured based on the contact angle method.

KEY WORDS: EOR, PETROLEUM, WETTABILITY, CTAB, HABSA

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INTRODUCTION

Oil recovery from a reservoir can be divided into three steps which are primary recovery, secondary recovery and tertiary recovery. Further discussion will be well served by a brief review of the “primary”, “secondary” and “tertiary” terms. These terms are generally understood and accepted (although a formal definition of these terms does not exist, either). They reflect and describe the natural progression of oil production from its inception to the point where economic production is no longer feasible. Production depends on the natural energy of the reservoir itself. The natural energy varies from pressure decline and the accompanying evolution of dissolved gas, to the expansion of gas cap, or the influx of water. The key element forces are “natural”. When natural drive energy is depleted, or too small for economic oil recovery, energy must be added to the reservoir to permit additional oil recovery. That additional energy is usually in the form of injected water or gas. The process depends mainly on physical displacement to recover additional oil. It can be said that it mimics the natural process of water influx or gas expansion. The key element forces are not natural; rather they are physical, as opposed to thermal, chemical, solvent, interfacial tension, etc. One could think of these as being a physical augmentation of the natural drive mechanism, (Stosur et al 2003 and Ge and Wang, 2015).

When secondary recovery is no longer economic, supplemental energy of a different kind permits additional oil recovery. A critical distinction that should be noted is that this energy (ies) is (are) in addition to, or in lieu of the natural or physical displacement mechanisms of the primary or secondary methods. Enhanced fluid flow conditions within the reservoir are usually induced by addition of heat, chemical interaction between the injected fluid and the reservoir oil, mass transfer, and/or changing of oil properties in such a way that the process facilitates oil movement through the reservoir. Tertiary recovery processes generally include *thermal, chemical, gas miscible and microbial*. They are also often referred to as enhanced oil recovery (EOR) processes. Almost half of the world’s discovered oil reserves are located in carbonate fractured formations, which are mostly oil-wet. These oil reservoirs are good candidates for enhanced oil recovery if the wettability of the matrixes is altered more toward water-wetness. Sandstone reservoirs are more complex than carbonate reservoirs. The wettability of sandstone reservoirs may vary widely from strongly water-wet to strongly oil-wet states. Neutral or intermediate wettability is also common, (El Mofty 2012, Ge and Wang 2015 Mohammed and Babadagli 2015).

Buckley and Leverett (1942) published one of the first papers on the effect of wettability on oil recovery.

Since then, studies have continuously debated the optimum wettability that provides maximum oil recovery. Recently, Enhanced Oil Recovery methods based on chemically-induced wettability alteration have gained a great deal of attention. Yong Zhu et al. (2012) investigated the adsorption of cationic-nonionic mixed surfactant (HDPB/TX100) onto bentonite and showed the cationic surfactant improved the adsorption of TX100 and total adsorbed amount significantly, indicating the good synergistic effect between HDPB and TX100. The co-adsorption of the cationic and nonionic surfactants increased the ordering conformation of the adsorbed surfactants on bentonite, but decreased the thermal stability of the organo bentonite system. The goal of this study is to describe the wettability of reservoirs and some surfactants, in addition to their measures and method. The motivation behind this approach is to keep the injection architecture similar to that of waterflood.

MAIN SUBJECTS

Wettability is defined as “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids. Types of wettability are divided into 3 classes: (1) Strong Wettability, (2) Neutral Wettability and (3) Fractional Wettability which is described below: *Strong Wettability*: this class is divided into 2 types as below: *Water-Wet*: When the rock is water-wet, there is a tendency for water to occupy the small pores and to contact the majority of the rock surface Anderson (1986). *Oil-Wet*: Similarly, in an oil-wet system, the rock is preferentially in contact with the oil; the location of the two fluids is reversed from the water-wet case, and oil will occupy the small pores and contact tie majority of the rock surface. *Neutral Wettability*: When the rock has no strong preference for either oil or water, the system is said to be of neutral (or intermediate) wettability. *Fractional Wettability*: Besides strong and neutral wettability, a third type is fractional wettability, where different areas of the core have different wetting preferences (Fall 2016).

Almost all minerals in a natural, clean state exhibit water-wet behavior. Certain components, primarily heavy asphaltene and the resin fractions of crude oil, can alter the wettability of the original water-wet rock. Components carrying a charged group, such as an acid or a base, significantly affect wettability during the formation of the reservoir. Additional significant components include oil and mineral composition, water solubility of polar oil components, capillary pressure and thin film forces. Mohammed and Babadagli (2012). Temperature, salinity, pressure and initial water saturation can affect the degree of wettability alteration as well.

Many different methods have been proposed for measuring the wettability of a system. They include

quantitative methods such as contact angles, imbibition and forced displacement (Amott), and USBM wettability method and qualitative methods such as imbibition rates, microscope examination, flotation, glass slide method, relative permeability curves, permeability/saturation relationships, capillary pressure curves, capillary metric method, displacement capillary pressure, reservoir logs, nuclear magnetic resonance, and dye adsorption. Although no single accepted method exists, three quantitative methods generally are used: (1) contact-angle measurement, (2) the Amott, and (3) the USBM method. The contact angle measures the wettability of a specific surface, while the Amott and USBM methods measure the average wettability of a core (Anderson 1986).

This is an imbibition-based method to measure the wettability of a core. The principle is that the wetting fluid will spontaneously imbibe into a core and displace the non-wetting fluid. The experiment begins with a restored state core sample at irreducible water saturation (S_{wirr}) and high initial oil saturation. In this method drainage and imbibition capillary pressures are measured through centrifuge tests. The sample is saturated initially with water. The water is then displaced by oil to irreducible water saturation (S_{wi}) using the centrifuge. Afterward, the sample which contains initial oil saturation and irreducible water saturation (S_{wi}) is then centrifuged in water to residual oil saturation (S_{or}). Qualitative methods for wettability measurement are: imbibition rates, microscope examination, flotation, glass slide method, relative permeability curves, permeability/saturation relationships, capillary pressure curves, capillary metric method, displacement capillary pressure, reservoir logs, nuclear magnetic resonance and dye adsorption. In below explain some important qualitative methods for wettability measurement:

Wettability alteration

Changing the wetting state of materials is a growing field of research in many areas of engineering and science. In the oil industry, the term wettability alteration usually refers to the process of making the reservoir rock more water-wet. This is of particular importance in naturally hydrophobic carbonates, fractured formations, and heavy-oil systems. This shift in wettability enhances oil recovery in oil-wet and weakly water-wet reservoirs and eventually increases the ultimate oil recovery. Wettability alteration process in each reservoir is a unique process and requires the understanding of the mechanisms that caused a reservoir to be oil-wet. Wettability alteration may increase oil recovery by gravity or capillary imbibition, (Mohammed and Babadagli 2012).

Surfactants may be one of the best options to improve recovery from geologically challenging reservoirs. During recent years, depressed oil prices have limited sur-

factant consideration. However, surfactant recovery can be economically attractive for reservoirs where recovery is dominated by gravity and imbibition processes. Surfactant is an abbreviation for surface active agent, which literally means active at a surface Holmberg *et al.*, (2002).

It is common practice to divide surfactants into the categories anionics, cationics, non-ionics and zwitterionics as following classification: Anionics are used in greater volume than any other surfactant class. Important facts about anionic surfactants: 1. They are by far the largest surfactant class. 2. They are generally not compatible with cationics (although there are important exceptions). 3. They are generally sensitive to hard water. Sensitivity decreases in the order carboxylate > phosphate > sulfate ~ sulfonate. 4. Sulfates are rapidly hydrolysed by acids in an autocatalytic process. The other types are stable unless extreme conditions are used Holmberg *et al.*, (2002).

Nonionic surfactants come as a close second with about 45% of the overall industrial production. They do not ionize in aqueous solution, because their hydrophilic group is of a non-dissociable type, such as alcohol, phenol, ether, ester, or amide. Important facts about nonionic surfactants: 1. They are the second largest class of surfactant. 2. They are normally compatible with all other types of surfactants. 3. They are not sensitive to hard water. 4. Contrary to ionic surfactants, their physicochemical properties are not markedly affected by electrolytes. 5. The physicochemical properties of ethoxylates are very temperature dependent. Contrary to most organic compounds they become less water soluble – more hydrophobic – at higher temperatures (Holmberg *et al.*, 2014).

Cationic Surfactants are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums. Important facts about cationic surfactants: 1. They are the third largest surfactant class. 2. They are generally not compatible with anionics (although there are important exceptions). 3. Hydrolytically stable cationics show higher aquatic toxicity than most other classes of surfactants. 4. They adsorb strongly to most surfaces and their main uses are related to *in situ* surface modification (Holmberg *et al.*, 2014).

Zwitterionic surfactants contain two charged groups of different sign. Whereas the positive charge is almost invariably ammonium, the source of negative charge may vary, although carboxylate is by far the most common. Zwitterionics are often referred to as *amphoterics*. Important facts about zwitterionic surfactants: 1. They are the smallest class of surfactant (partly due to high price). 2. They are normally compatible with all other types of surfactants. 3. They are not sensitive to hard

water. 4. They are generally stable in acids and bases. The betaines, in particular, retain their surface activity at high pH, which is unusual. 5. Most types show very low eye and skin irritation. They are, therefore, well suited for use in shampoos and other personal care products (Holmberg *et al.*, 2014),

MATERIALS AND METHODS

Two surfactants, one new amphoteric and one cationic surfactant are considered in this study. Initial surfactant is hexadecylaminobenzenesulfonic acid (HABSA) which recognized amphoteric surfactant. HABSA formulation is (C₁₆H₃₃C₆H₃NH₂SO₃H) that show, when it dissolves in water, it contains two charged groups of different sign at its head and a long alkyl tail. The second surfactant is Cetrimonium bromide ((C₁₆H₃₃)N(CH₃)₃Br, cetyltrimethyl ammonium bromide, hexadecyl trimethyl ammonium bromide, CTAB) which is one of the components of the topical antiseptic cetrimide. The cetrimonium cation is an effective antiseptic agent against bacteria and fungi. It is a cationic surfactant. Its uses include providing a buffer solution for the extraction of DNA. It has been widely used in synthesis of gold nanoparticles (e.g., spheres, rods, and bipyramids). It is also widely used in hair conditioning products. Because of Property soapy this is a good candidate for chemical oil recovery in world (Ito *et al* 2016).

Experimental procedures

Synthesis of new surfactants: Two different surfactants are considered in this study that synthesized in PUT lab in Ahwaz: New amphoteric surfactant (hexadecylaminobenzenesulfonic acid (C₁₆H₃₃C₆H₃NH₂SO₃H), HABSA) A cationic surfactant (hexadecyltrimethylammonium bromide ((C₁₆H₃₃)N(CH₃)₃Br), CTAB)

Synthesizing procedure of HABSA:

5 mL of concentrated hydrochloric acid and 54 mmol of ortho-sulfanilic acid are added to 250 mL beaker (A) with 125 mL water. It is stirred until a homogenous solution is obtained. 6.5 mL (69 mmol) of acetic anhydride is added to this mixture. To another 250 mL beaker (B), 5.6 g (69 mmol) of sodium acetate is dissolved in 35 mL of water. Then the content of beaker A is added to beaker B and the mixture is vigorously stirred in an ice bath. A white precipitate (compound 1) is obtained. It is collected by filtration and dried in vacuum oven at 80 °C. Anhydrous aluminum chloride (0.13 g, 1.0 mmol) is weighed into an aluminum weighing boat in the fume hood and quickly transferred to a clean dry 100 mL round bottom flask containing a magnetic stir bar. The flask is stoppered and brought to the bench where it is fitted with a Claisen adaptor, a dropping funnel, and a condenser

vented to a gas trap. 3.46 g (15 mmol) of the aforementioned white product (1) and 20 mL of acetonitrile are added to the flask. While rapidly stirring the mixture, 15 mmol hexadecyl bromide is added slowly drop wise over a period of about 10 minutes. After the addition is completed, the stirring is continued at reflux temperature for an additional 24 h. Then the reaction mixture is cooled to room temperature. The resulting product (2) is collected by filtration and dried under reduced pressure at 80 °C. Into a 100 mL round-bottomed flask equipped with a condenser and a magnetic stirring bar, 7.6 mmol of compound 2 and 17 mL of a 5.0 M hydrochloric acid solution are added and refluxed. After 10 minutes, the reaction mixture is cooled to room temperature. On completion of the reaction, the solution is neutralized with 25% w/w sodium hydroxide solution, and a precipitate is formed slowly. (Yield = 80%, m.p. 283-284 °C).

Synthesizing procedure of CTAB:

10 ml of hexadecyl bromide (C₁₆H₃₃Br) is placed in a 250 mL round-bottomed flask, and 5 ml of tri Methylamine [(CH₃)₃N] and 100 ml of solvent acetonitrile (CH₃CN) are added to the flask. A magnetic stirring rod is placed in the flask. The flask content is heated under reflux and stirred using a magnetic stirrer for 24 hours. The solution is cooled to room temperature. The product is formed as a white precipitated. The product is collected with small amount of acetonitrile then air dried.

RESULTS AND DISCUSSION

There are many ways in which CMC could be determined. The CMC is the narrow concentration range over which amphiphilic or surfactant solutions show an abrupt change in a physical property such as electrical conductivity, surface tension, osmotic pressure, density, light scattering or refractive index (Hoolmberg *et al* (2002). The conductance of a solution, can give important quantitative information regarding the ionic composition of a sample. Conductance is a measure of a sample's ability to pass a current and strongly depends on the concentration, mobility, and charge of ions in solution (Settle 2017).

The Jenway model 4510 Conductivity/temp meter with dual display and TDS range is easy to use with a flexibility that will enable it to meet the broadest range of applications. Set-up menu options include cell constant, temperature coefficient and reference temperature. With automatic range selection and endpoint detection, readings can be taken quickly and with minimum intervention. For applications where greater accuracy is required the 4510 has automatic conductivity standard recognition which can be overridden by entry of user

specific values. This setup includes following issues:

- Auto ranging to give best resolution
- Simultaneous display of conductivity or TDS and temperature
- Calibration to cell constant or standard solutions
- Auto Standard recognition with manual override
- 32 location memory
- Bi-directional RS232 link to printer or PC

Technical specification, (Fall 2016).

When conductivity meter is used to find the CMC, conductivity of the solution increases linearly with total surfactant concentration. However, the slope of the lines has an inflection point that indicates the CMC. The pellets and plug are cleaned by Toluene with Soxhlet extractor. Two main reasons to clean core are: To remove all liquids from the core so that porosity, permeability, and fluid saturations can be measured. To clean the core as a first step in restoring the wettability of cores are altered. Distilled water is used as the aqueous phase for contact angle, flooding tests and solutions. One of the best wettability measurement methods when pure fluids and artificial cores are used is the contact angle.

In the sessile drop method the flat surface of pellet is suspended horizontally in the oil (kerosene) and placed a drop of water on the surface of the pellet. Then the contact angle between water drop, slice surface and oil is measured. When θ is between 0° and 60° to 75° in such a system, it is defined as water-wet. When θ is between 105° to 120° and 180° the system is defined as oil-wet. In the range of a 75° to 105° contact angle, the system is neutral-wet.

After preparing and cleaning the core sample, it is saturated with distilled water by vacuumed pump. Then the core is placed in the rubber sleeve in the core holder. This sleeve is used as a connection to exert overburden pressure on the rock. In these experiments the overburden pressure is provided by water (2500 psi). To reach S_{wi} , injection of oil is continued until no water is detected at the outlet. Volume of discharged water is measured and the S_{wi} is calculated by: $S_{wi} = 1 - (\text{Volume of produced water}/\text{Pore volume})$. Now to reach residual oil saturation S_{or} , distilled water is injected into the core plug at constant flow rate of 1 cc/min until no oil is produced at the out let. Difference between injected oil volume and produced oil divided to total pore volume indicates residual oil saturation, S_{or} . The core sample is flooded with two surfactants (at CMC). At this step, core holder is connected to another transfer vessel and surfactant solution is injected into the core with a constant rate. The oil produced would be measured to calculate the oil recovery.

CONCLUSION

This study was conducted to compare wettability alteration in EOR process, using new amphoteric and cationic

surfactants. New cationic and amphoteric surfactants synthesis and investigation of wettability alteration in EOR process is described. The goal of this work is to compare the wettability of a carbonate rocks from oil (mixed)-wet towards water-wet. Changing the wettability to preferentially water-wet condition will reduce the residual oil saturation (S_{or}). Wettability alteration is measured based on the contact angle method. Cationic Surfactants are in general more expensive than anionic ones, because of the high pressure hydrogenation reaction to be carried out during their synthesis. As a consequence, they are only used in two cases in which there is no cheaper substitute.

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