ISSN: 0976-3376

Available Online at http://www.journalajst.com

ASIAN JOURNAL OF
SCIENCE AND TECHNOLOGY

Asian Journal of Science and Technology
Vol. 06, Issue, 08, pp. 1652-1655, August, 2015

RESEARCH ARTICLE

LOW COST SURFACTANTS FOR WETTABILITY ALTERATION STUDIES

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ARTICLE INFO

Article History:
Received 21st May, 2015
Received in revised form
06th June, 2015
Accepted 30th July, 2015
Published online 31st August, 2015

Key words:
Surfactants,
Wettability alteration,
Spontaneous imbibition,
Enhanced oil recovery.

ABSTRACT

Surfactants possess the ability to alter rock wettability which will improve oil& gas well productivity, however the cost of chemicals that serve as wettability alteration agent can be a major constraint to exploring the option for improved oil recovery. The goal of this study is to develop a surfactant from locally sourced and readily available reagents at low cost, with favourable potency levels, which can compete with synthetic surfactants. The core sample used for this experiment is water wet in nature. The sample was treated and aged for a specific period followed by physical property measurements and spontaneous imbibition experiment. Rate of imbibition before and after treatment had varying times indicating that the wettability of the core sample was altered from water-wetting to otherwise. Hence the anionic surfactant used in the study can be considered for improving recovery from multiphase petroleum reservoirs.

INTRODUCTION

Multiphase fluids in petroleum reservoirs exhibit dynamic behaviour during pressure drop under production. The dynamic behaviours are explained by evolution and expansion of dissolved gas at bubble point pressure and condensates drop out at dew point pressure. Depending on the rock physical characteristics, the phase changes and mass transfer can be beneficial or detrimental. For instance, the decline in recovery rate in Gas Condensate Reservoirs attributed to liquid banking around wellbore region is due to unfavourable interplay of microscopic forces in the porous media i.e. capillary forces and interfacial phenomena. These forces dictate the flow and relative permeability of each phase which determines the recovery from multiphase reservoirs. The foundation of enhanced and improved recovery is in the ability to modify and re-adjust the character of viscous and capillary forces, and interfacial phenomena to suite the displacement of reservoir fluids. Enhanced and improved recovery schemes have helped in the sustenance and continuity of brownfields majorly. Surface-active agents (surfactants) are one of the injection chemicals mostly used for EOR/IOR operations. Surfactants recovery mechanisms are lowering the interfacial tension between immiscible fluids and Altering rock wettability. Wettability alteration mechanism has been proposed and studied extensively to improve productivity in gas reservoirs (Fan *et al.,* 2006, Rocke *et al.,* 2008, Tang and Firoozabadi, 2000, Li and Firoozabadi, 2000, Li *et al.,* 2011).

Wettability alteration agents used for EOR/IOR programmes are synthetic, highly specialised chemicals designed and manufactured by chemical companies and multinational labs under patent laws. They are designed specifically for reservoir rocks under specified conditions to exploit certain recovery mechanisms. These factors make them expensive which is a major discouragement for chemical enhanced oil recovery projects. If surfactants or wettability alteration agents can be developed from readily available reagents and these chemicals will compete favourably with synthetics in terms of potency and performance, then it should serve as an encouragement for considering CEOR for major EOR projects. This research effort aims to Identify and design a particular surfactant, evaluate its performance and Compare it with already recognised WA agents.

Literature Review

Kewen Li and Abbas Firoozabadi (2000) used two chemicals for their wettability alteration studies: an inexpensive cationic surfactant which was water soluble and a polymer which was very expensive and had selective solubility. The purpose of their research was to alter the wetness of a porous media from liquid wetting to gas wetting and investigate its effect on liquid imbibition, oil drainage and relative permeabilities. They made use of Berea cores and cores from a chalk reservoir. Normal decane was used as the oil phase, air as the gas phase and brine as water phase. Glass capillary experiments revealed wettability alteration from 50° to 90° and 0° to 60° by the cationic surfactant for water-oil systems and oil-air systems respectively.

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Imbibition was considerably reduced for both water and decane. The effect of the polymer was more pronounced with alterations of 50° to 120° and 0° to 60° for water-air systems and air-oil systems respectively. Imbibition did not take place thus showing that it's more potent. Guo-Qing Tang and Abbas Firoozabadi (2000) compared the polymers used in the previous work to another polymer which was twenty times less expensive. Their experiments were designed specifically for gas condensate systems, measuring injectivity and relative permeability. Both chemicals demonstrated just about the same level of potency with wettability alteration treatments highly successful increasing both gas and liquid phase permeabilities.

Stanley Wu and Abbas Firoozabadi (2010) concentrated on permanent wettability alterations in low permeability reservoirs. Varieties of chemical with differing functional groups were used for the study and the degree of wettability alteration was noticed to be a function of WA agent's concentration and functionality. The WA agents were fluorinated polymeric chemicals produced by DuPont Company (Wilmington, DE). The permanent alteration was confirmed using compositional analyses from gas chromatography-mass spectrometry (GCMS) and inductively coupled plasma-mass spectrometry (ICPMS). The analyses demonstrated that chemical reaction between chemical and rock substrate is responsible for wettability alteration.

Li *et al.* (2011) also concentrated on wettability alteration studies for low permeability reservoirs using actual rock cores. The cores were obtained from Dongpu field, a gas condensate reservoir. They used a new and cheaper chemical with the aim of looking at the possibility of economical deployment for full field application. The chemical was effective for high salinity reservoirs and also thermally stable. These were demonstrated through spontaneous imbibition tests and relative permeability experiments. Thus, gas production was enhanced greatly due to wettability alteration. Salehi *et al.* (2006) studied wettability alteration of carbonate rocks using a Bio-surfactant produced from high-starch agricultural effluents. They assessed wettability alteration using two-phase separation, water flotation techniques and surfactant loss due to retention and adsorption by the rock. They assessed the effectiveness of the surfactin, compared to a commercially available surfactant. Qingjie *et al.* (2004) studied the effects of altered wettability on permeability for oil-wet reservoirs. They used an unsteady state method test with constant pressure, and brine with different concentrations spread over the core samples, measuring the interfacial tension between layers. Their results indicated that both water and oil permeabilities are affected by wettability alteration. They found that relative permeability curves for water are lowered as wettability was altered from oil wet to intermediate wet. Recovery efficiency was also improved and water cut lowered

MATERIALS AND METHODS

Materials

Core Sample

A core sample was acquired from the Chad basin specifically for this study and reservoir rock properties were determined in a standard reservoir engineering laboratory. It's cylindrical in shape, 33.7mm long with a diameter of 23.3mm and weighs 32.55g. The porosity of the core sample was measured using a gas porosimeter to be 24.30%. The core sample itself is brownish in colour.

Chemicals

The target surfactant is an anionic soap. The reagents used for making it, which were acquired at cheap rates from local chemical suppliers, are sulphonic acid, nitrosol ($Ca(NO_3)_2$), sodium lauryl ether sulphate, soda ash and caustic soda. The main reaction during compounding is the reaction between the organic acid and sodium ion to give the anionic surfactant which will be used for altering the wettability of the rock. The surfactant is whitish in appearance and highly viscous. A solution of the surfactant was prepared using the following procedure:

1. 50ml of surfactant was measured into 100ml beaker.
2. Distilled water was added to the beaker until it reached 100ml volume/volume.
3. Stirring to dissolve surfactant completely and have a homogeneous solution.
4. This gives a concentration value of 50% of surfactant.

Experiments

Core Treatment

The core was saturated with the surfactant for exactly four hours after which it was transferred to an aging cell and put in an oven. This is to allow the chemical adsorb onto the solid surface. It spent exactly 12 hours in the oven at 75°C to mimic reservoir conditions. It was then aged further more outside the oven for another 3 days. After treatment with surfactant the core sample physical properties were measured again, the weight increasing to 33.4g.

Spontaneous Imbibition

A simplified method of performing spontaneous imbibition test was carried out on the core sample before and after the core treatment with surfactant. This is by measuring the time it will take a droplet of water to imbibe completely unto the solid surface under controlled ambient conditions. Here, the change in weight is also noted. After imbibition it was dried in an oven at 150^{o}c for thirty minutes in preparation for treatment with surfactant.

Porosimeter Measurements

This experiment is to investigate the effect of the wettability agent on the flow property of the porous media in terms of porosity and indirectly on absolute permeability. A gas porosimeter was used for the experiment using the following procedures: The following expressions are used for calculating the porosity of rock sample

$$\phi = \frac{V_p}{V_b} \times 100\% \qquad \text{……………………………………} (1)$$

$$V_b = \frac{\pi d^2 L}{4} \qquad \text{………………………………………} (2)$$

$$\phi = \frac{V_b - V_g}{V_b} \qquad \text{………………………………………} (3)$$

RESULTS AND DISCUSSION

Spontaneous Imbibition

The core sample used for this experiment is naturally water-wet since the water droplet imbibed completely unto the rock surface. Water droplet imbibition unto the core sample before treatment with surfactant took 27mins 46secs while after treatment it took 1hr 30mins 15secs to imbibe. It is safe to say that during imbibition water displaced air in the porous media since the core sample is originally saturated with air. Before treatment the droplet displaced air from the sample easily because the core itself is water-wetting. However After treatment with surfactant, the grain surface properties were altered and it became more difficult to displace air present in pore spaces because the surfactant had increased the threshold pressure needed for imbibition. This indicates that the surfactant being a surface active agent has been able to alter the surface properties of fluid-fluid and fluid-rock interfaces. The displacement of air by water during imbibition is a two-phase displacement process which is highly dependent on capillary forces in the likes of interfacial tension and wettability as depicted in the equation below

$$P_c = \frac{\sigma \cos \theta_p}{\sqrt{\frac{k}{\phi}}} \quad \text{……S………………………………}(4)$$

Wettability alteration of a rock is strictly a function of the type of surfactant, surface charge of rock minerals, degree of adsorption and the strength of bonds formed through reaction with the wettability alteration agent. Thus, the nature and kind of surface matters because while a surface active-agent might be suitable for adsorption at liquid-liquid interfaces, they might not be able to influence any change at solid-liquid interfaces for the same reasons. Imbibition occurs more rapidly for cores that have high relative permeabilities to the invading fluid. This is due to the ability of the wetting phase to completely take over the pores of a core sample because they are highly permeable. Wettability alteration affects the rate of imbibition and relative permeability. Both water and oil relative permeabilities are highly dependent on wetting phases in a reservoir. The rapid imbibition of wetting phase would enhance the displacement of the non-wetting phase thereby increasing its relative permeability. However, it can lead to flow ‘choking’ as it can increase the competition of flow in pore spaces as noticed in liquid banking in condensate reservoir. Hence, readjusting the capillary forces by altering the wettability will influence the release of non-wetting phase, therefore improving well deliverability in the case of gas condensate reservoirs.

Porosimeter Measurements

Porosity is a measure of void spaces in a material and is a fraction of volume of voids over the total volume. The initial porosity of the core sample before treatment was calculated to be 24.3% while after treatment with surfactant it was calculated to be 22.06%. This shows damage to the core. Damage to reservoir rocks during EOR/IOR processes can be incurred via two common mechanisms which are adsorption of injected fluids in pore spaces and precipitation on solid grains from complex reactions of chemical agents and rock minerals. In this case, it’s most likely a result of surfactant physical adsorption unto grain surfaces. Although there was wettability alteration, significant reduction in porosity connotes decrease in absolute permeability of rock sample which is could be detrimental to the hydraulic conductivity of the core. Likening this to real field case, if the damage caused by the surfactant is reversible when a post-flush solvent or buffer is used, then it is a suitable wettability alteration agent, otherwise it will incur more cost in terms of damage to the reservoir rock when it introduces skin. Pre-flush conditioners also will aid in controlling the rate of adsorption by rendering the pH and salinity condition conducive for surfactant injection.

Conclusion

The following conclusions and recommendations can be made based on this study:

1. Cheap and cost-effective surface-active chemicals are enough justification for considering chemical methods for improved recovery schemes as option for reservoir management. In this particular study, the surfactants are relatively cheap and will be a viable option for large scale production in pilot scale or full field applications.
2. Surfactant type and potency are very important criteria for selection in chemical EOR/IOR design. A fore-knowledge of the chemical properties of the minerals of the reservoir rock under consideration as well as the surface charge of the grains will serve as a good guide in designing the surface-active agent
3. Most chemical EOR/IOR agents have the potential to cause formation damage when used alone.

However, the ability to reverse this damage by buffer solutions and pre-conditioners is a very important design factor, thus, the damage reversibility of the anionic surfactant can be investigated to further test its applicability to petroleum reservoirs.

4. The displacement capability of the anionic surfactant can further be studied in addition to imbibition experiments using standard relative permeability tests for multiphase fluids.

Nomenclature

d	Core Diameter
k	Absolute Permeability
L	Core Length
P_c	Capillary Pressure
V_b	Bulk Volume of Core Sample
V_g	Grain Volume of Core Sample
V_p	Pore Volume of Core Sample
ϕ	Porosity
θ_p	Pseudo Contact Angle
σ	Surface Tension

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