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Alteration of Wettability by Cationic Gemini and Conventional Surfactants for Carbonate Reservoirs

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Abstract

Carbonate reservoir properties are complicated to understand. Out of these properties altering wettability is an important property to be considered for oil recovery. The aim of this research work is to compare the amount of oil recovered by applying cationic gemini and its original form. An investigation was conducted on Cationic gemini form of Cetyl Tri Alkyl Bromide (CTAB) and its conventional form on carbonate cores for wettability alteration. The concentrations for surfactants were selected on the basis of conductivity test. During core flooding oil recovery through these surfactants has been compared. Gemini 16-3-16,2Br has shown 0.35 pore volume additional recovery than CTAB.

Keywords: Adsorption, Cationic Surfactant, CMC, Gemini Surfactant, Wettability

1. Introduction

Carbonate reservoirs have specific characteristics tending more and more challenges for production. Their complex network in pore system makes difficult in selecting a recovery method. Apart from complexities in porosities wettability is another important parameter to be considered. Mostly, carbonate reservoirs are mixed wet to oil wet. So, production of oil from these reservoirs is not so easy[1]. Understanding the properties of carbonate reservoirs to alter is being a major challenge in today's research. Limited research work has been carried in carbonate reservoirs due to technical and economic constraints[2]. Recovery mechanism in carbonate reservoirs was successful by water flooding and gas injection methods[3]. A few were carried under polymer flooding[4].

Apart from field projects, research work has been carried much in laboratories by application of surfactants. EOR surfactants were specially designed by considering factors like wettability alteration, mixing with emulsions and stable at high temperatures. These surfactants were applied to alter oil wet carbonate reservoir to water wet[5]. Spontaneous imbibition is a process to extract oil by imbibition of water into water wet reservoir pores. But, in oil wet reservoirs it is not effective. The recovery can be improved only by wettability alteration through the application of surfactants and its classes.

1.1 Gemini Surfactants

These are new class surfactants having two hydrophobic tails with hydrophilic heads connected by a hydrophobic spacer. They posses better surface activities than conventional surfactants. Stability is dependent on the spacer length. Hydrophobic chains may be of same length or differ. Same length tails will provide better surface properties. Its ability to make low CMC values will make a good solubilizer. The CMC ranges of Gemini surfactants are lower than conventional surfactants. DTAB (Dodecyl Trimethyl Ammonium Bromide) and CTAB cetyltrimethyl ammonium bromide) with C12 and C16 configurations has shown CMC of $1.5–1.6*10^{-2}$ M and 10^{-3} M respectively, but Gemini surfactant of same molecules, that is 12-3-12,2 Br_, and 16-3-16,2 Br_has shown $9.1–9.6*10^{-4}$ M and $2.50–2.55*10^{-5}$ M respectively[6].

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1.1.1 Wettability Alteration

Alteration of Wettability for carbonate reservoirs depends upon the electrostatic charge on the surface. These rocks posses mostly mixed to oil wet. Wettability is an important factor for fluid transfer form fracture to matrix. In oil wet fractured reservoir the flow of oil and water will be faster compared to matrix. Gravity drainage will help to produce oil when the block size is big enough to accept negative capillary pressure. Even though less pressure gradient in the matrix blocks for fluid flow, altering wettability will overcome these effects and makes fluid to flow.

Cationic surfactants were chosen based on charge of the carbonate mineral for wettability alteration. If the charges were similar on surfactants and surface of carbonate rock then there is less chance of adsorption and better chance of altering wettabillity[7].

2. Methodology

2.1 Preparation of Gemini Surfactant

A long chain alkyle group of nitrogen of 2RN $(CH_3)_2$ has been refluxed for 4 hours with methelene bromide $Br(CH_2)_4Br$ to form gemini surfactant as $RN^+(CH_3)_2(CH_2)4N^+(CH_3)_2R2Br^-$.

2.1.1 Conductivity Measurement

Conductivity of surfactants will be measured by conductivity cell, where we can determine Critical Micelle Concentration (CMC). CMC is the level of concentration where micelles are formed in aqueous and organic phases. Above this concentration, further addition of surfactants will increase number or aggregation of micelles. At the level of CMC ultralow Interfacial tension can be achieved between oil and water.

Different concentrations of surfactants for conventional and Gemini were chosen to measure CMC.

2.1.2 Core Flooding

Core flooding is an apparatus where we can simulate reservoir by analyzing core. Core from the reservoir will be shaped to fit inside core holder. It will be cleaned, dried and aged by oil. Water will be injected to displace oil from core simulated as recovery from waterflooding.

Figure 1. Conductivity Cell.

Figure 2. Ranges of surfactant concentration.

Following those chemicals will be injected for additional recovery. This is specially designed equipment where pressures can be recorded at all times.

3. Results and Observation

Eight number of different concentrations were tested on both cationic conventional and Gemini types shown in Table 1.

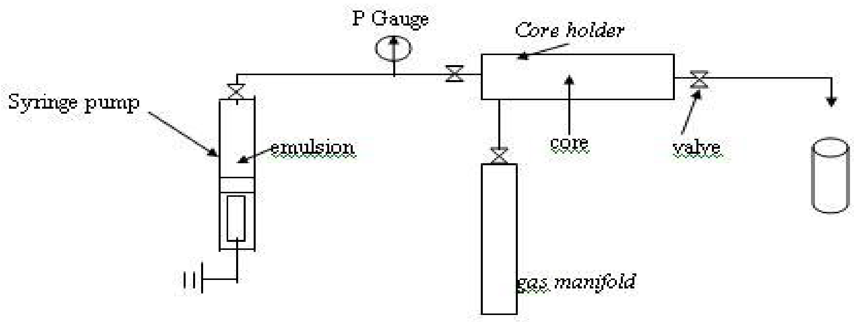

Figure 3. Core flooding apparatus.

Table 1. Conductivity vs Concentration

S.no.	Gemini CTAB 10^{-5}ppm	Conductivity mS/cm	Conventional CTAB 10^{-3}ppm	Conductivity mS/cm
1	1	0.5	1	2.5
2	2	2.5	2	5.0
3	3	4.8	3	7.5
4	4	5.0	4	7.8
5	5	5.05	5	8.0
6	6	5.1	6	8.2
7	9	5.4	9	10
8	12	6.0	12	10.1

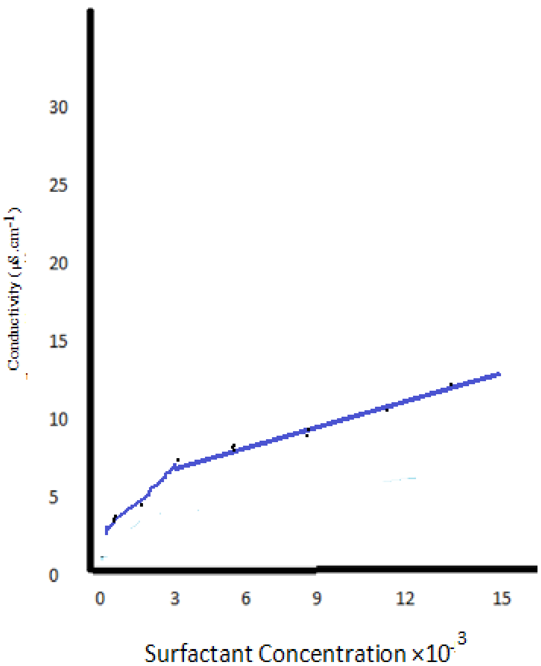

Figure 4. CMC for gemini

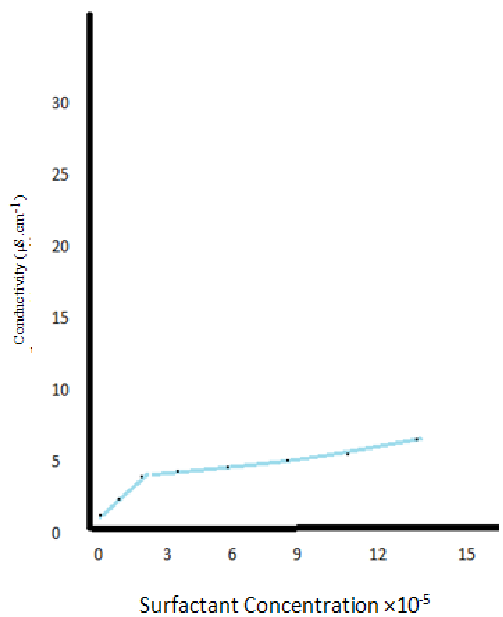

Figure 5. CMC for CTAB.

On the both graphs sharp break have been observed. Formation of micelles will form at these concentrations. Where hydrophobic and hydrophilic phases were separated. And these two concentrations were selected for flooding core. 3×10^{-5} ppm shown in Figure 4 from Gemini and 2.8×10^{-3}ppm shown in Figure 5 from conventional was chosen for wettability alteration.

Carbonate core was selected from 1108.3 ms Depth for core flooding apparatus. Initially it was aged with crude oil for seven days. Then flooded with water at the rate of two pore volumes per day. After that, residual oil have been recovered by conventional CTAB of nearly 0.5 Pore Volume, the same experiment was repeated by Gemini surfactant. The recovery has improved to 0.85 pore volume with 2.05mg/g adsorption.

4. Conclusion

A comparative investigation has been conducted on carbonate reservoirs for wettability alteration. A conventional cationic surfactant CTAB and its gemini form 16-3-16,2Br- have been tested on carbonate reservoir. CMC's for both surfactants were determined by conductivity test. The CMC for gemini surfactant that is 3×10^{-5} ppm was lower than conventional surfactant 2.8×10^{-3} ppm. This is because organic spacer and double tail chain. Less concentration is enough to form micelle compared with single tail chain. The recovery of residual oil by gemini surfactant is 0.35 pore volume more than conventional one because less cocnetration CMC of gemini surfactants are easily soluble than conventional surfactants in acqueous medium which could contact much surface of reservoir and interface to reduce Interfacial Tension (IFT). The adsorption of cationic surfactants on both forms is due to clay content inside core.

5. References

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