Physicochemical Properties of Microemulsions and their Uses in Enhanced Oil Recovery

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Abstract—Use of microemulsion in enhanced oil recovery has become more attractive in recent years because of its high level of extraction efficiency. Experimental investigations have been made on characterization of microemulsions of oil-brine-surfactant/cosurfactant system for its use in enhanced oil recovery (EOR). Sodium dodecyl sulfate, propan-1-ol and heptane were selected as surfactant, cosurfactant and oil respectively for preparation of microemulsion. The effects of salinity on the relative phase volumes and solubilization parameters have also been studied. As salinity changes from low to high value, phase transition takes place from Winsor I to Winsor II via Winsor III. Suitable microemulsion composition has been selected based on its stability and ability to reduce interfacial tension. A series of flooding experiments have been performed using the selected microemulsion. The flooding experiments were performed in a core flooding apparatus using uniform sand pack. The core holder was tightly packed with uniform sands (60-100 mesh) and saturated with brines of different salinities. It was flooded with the brine at 25 psig and the absolute permeability was calculated from the flow rate of the through sand pack. The sand pack was then flooded with the crude oil at 800 psig to irreducible water saturation. The initial water saturation was determined on the basis of mass balance. Waterflooding was conducted by placing the coreholder horizontally at a constant injection pressure at 200 psig. After water flooding, when water-cut reached above 95%, around 0.5 pore volume (PV) of the above microemulsion slug was injected followed by chasing water. The experiments were repeated using different composition of microemulsion slug. The additional recoveries were calculated by material balance. Encouraging results with additional recovery more than 20% of original oil in place above the conventional water flooding have been observed.

Keywords—Microemulsion Flooding, Enhanced Oil Recovery, Phase Behavior, Optimal salinity

I. INTRODUCTION

The application of enhanced oil recovery (EOR) methods has been investigated with major purpose of responding to the requirements of energy supply when the conventional techniques start to become unprofitable. Therefore, EOR methods mainly focus on the segment that corresponds to 70-75% of the original oil detected, which is the mean percent nailing in the reservoirs after conventional extraction. Microemulsions are isotropic, transparent or translucent, thermodynamically stable dispersions of surfactant, alcohol, oil and water, and have been used in various fields, such as EOR, pharmaceutics, nanoparticle synthesis, liquid–liquid extraction, cosmetic, detergency and other chemical engineering, due to their very low interfacial tension, nanometer-sized droplets, good solubilization capacity, etc. [1]-[4].

Microemulsion in EOR is an efficient tool because of its high level of extraction efficiency of residual oil from natural oil reservoir [5]-[8]. Ultra low interfacial tension (IFT) can be obtained by creating a middle phase microemulsion using brine, oil, surfactant and cosurfactant. The phase behavior of surfactant-brine-alcohol-oil systems is of immense importance for surfactant flooding in EOR due to the well-established relationship between the IFT and microemulsion phase behavior [9]-[13]. The phase behavior of surfactant-brine-alcohol-oil system is one of the key factors in interpreting the performance of chemically EOR by microemulsion process [14]. The tertiary oil recovery is mainly dependent on the properties of oil-water-rock interfaces. These are capillary forces, contact angle, wettability, viscous forces and interfacial tension. These properties are related to a dimensionless quantity, called Capillary number, \(N_c\) that is a measure of the mobilization of the occluded oil to enhance the oil recovery and well represented by as:

\[
N_c = \frac{\mu \nu}{\sigma \cos \theta}
\]

where, \(\mu\) is the dynamic viscosity of the liquid, \(\nu\) is the velocity, \(\theta\) is the contact angle and \(\sigma\) is the interfacial tension (IFT) between oil and water phases.

In microemulsion systems, a variety of phases can exist in equilibrium with another phase, with each phase having different structure. Microemulsion phases are changed from Winsor type I to Winsor type II through Winsor type III by systematic variation of salinity at a particular temperature and pressure [15], [16]. The commonly observed Winsor-type systems indicate that the microemulsions can remain in equilibrium with excess oil, excess water, or both. The factors that affect the phase transition between different types of systems and physicochemical properties include salinity, temperature, molecular structure and nature of the surfactant and cosurfactant, nature of the oil and the water-oil ratio (WOR) [17]-[20]. Under adequate conditions, the microemulsion system is miscible with both oil and water. Optimum salinity and the amounts of solubilized oil and water contained in a microemulsion play important roles in obtaining low IFTs and higher oil recoveries in chemical EOR. Since IFTs are having minimum value at optimal salinity and solubilization parameters are related to IFT, estimation of both properties is of great importance in designing economical microemulsion flooding [21], [22]. Microemulsion flooding involves the injection of surfactant solution with hydrocarbon, alcohol and water/brine that causes the interfacial tension of oil-aqueous phase drop from 30 mNm\(^{-1}\) to zero by the order of \(10^{-3} \text{ to } 10^{-4} \text{ mNm}^{-1}\). This decrease in interfacial tension allows spontaneous emulsification and displacement of the oil [23], [24]. In microemulsion flooding a small chemical slug (5-30% pore volume) is injected into oil reservoir during the process. This slug is displaced through the reservoir by a polymer bank, which in turn is displaced by drive water.
In microemulsion flooding surfactant adsorption in the reservoir rocks is one of the most restrictive factors that have an affect on the efficiency of the oil recovery process [25]-[27]. Microemulsion flooding prefers a high concentration of surfactant solution to form micelles that can solubilize or dissolve the reservoir oil and the process takes place via incorporation of small oil droplets in micelle core, effectively causing miscibility in the system [28]. Some researchers carried out flooding experiments with microemulsions and they observed a linear relationship between the values of injected pore volume (PV) and the oil recovery, typically reaching 40-50% of residual oil recovery by injecting 5-10 PV of microemulsion [5], [29], [30].

The objectives of the present study are the formation and characterization of microemulsion that are stable at the reservoir temperature. The formation of stable microemulsion using minimum amount of surfactant is the biggest challenge for its use in enhanced oil recovery. Thus, a complete study on phase behavior and physicochemical properties of microemulsion comprising of sodium dodecyl sulfate, brine, Propan-1-ol and heptane have been investigated as a function of salinity. Relative phase volumes of different components in microemulsions are very sensitive to the salinity. Pseudo-quaternary phase diagrams have been drawn to identify the microemulsion region. A series of flooding experiments have been performed using the prepared microemulsion. The additional recoveries were calculated by material balance. Encouraging results with additional recovery more than 20% of original oil in place above the conventional water flooding have been observed.

II. EXPERIMENTAL SECTION

A. Materials
Anionic surfactant, Sodium dodecyl sulfate (SDS) of 98% purity was purchased from Fisher Scientific, India. Sodium Chloride (NaCl) with 98% purity procured from Qualigens Fine Chemicals, India, was used for preparation of brine. Reverse osmosis water from Millipore water system (Millipore SA, 67120 Molsheim, France) was used for preparation of solutions. Propan-1-ol (98% pure) was used as cosurfactant. It was supplied by Otto-kemi Pvt. Ltd., India. In this study n-heptane (with purity >99%) was used as oil and purchased from MERCK, India. The entire chemicals were used without further purification.

B. Experimental Procedures
1. Phase Diagram of Microemulsion System
The phase diagram has been established by a conventional titration method for determination of microemulsion region. At a fixed cosurfactant (CS) to surfactant (S) ratio of two (CS/S=2) different amount of heptane was taken and it was stirred by Remi magnetic Stirrer by gradual addition of brine solutions (4 wt% NaCl solution) from micropipette till the turbidity appeared. All mixtures were prepared by weight; and compositions are expressed as weight percent to draw the phase diagram. The experiments have been performed at 29°C and the data have been reproduced by repeating the experiments.

2. Determination of Relative Phase Volume and Solubilization Parameters
Microemulsion phase behavior was determined by equilibrating the surfactant and cosurfactant mixture with equal volumes of oil and brine solution and measuring the volume of the microemulsion phase and excess oil and/or excess brine phase at constant pressure and temperature. All the samples were prepared with 47 wt% water, 47 wt% oil, 4 wt% alcohol and 2 wt% surfactant. For all systems, a constant water-oil ratio (WOR) was maintained (WOR=1). The details procedure of the experiment was stated in our previous paper [31]. The volume of oil and brine that can be solubilized in microemulsion is of interest in characterizing solubilization capacity of the surfactant (SDS). The volumes of oil and water solubilized per unit volume of surfactant in microemulsion phase have been considered as solubilization parameters ($V_o/V_s$ and $V_w/V_s$) of oil and water respectively. $V_o$, $V_s$ and $V_w$ represent the volume of surfactant, oil and water respectively in the microemulsion phase. The solubilization parameters were calculated with the assumption that the total surfactant was contained in the microemulsion phase [32].

3. Experimental Apparatus and Methods for Microemulsion Flooding
The experimental apparatus is composed of a sand pack holder, cylinders for chemical slugs and crude oil, positive displacement pump, measuring cylinders for collecting the samples. The detail of the apparatus is shown in Fig 1. The displacement pump is one set of Teledyne Isco syringe pump. Control and measuring system is composed of different pressure transducers and a computer. The physical model is homogeneous sand packing model vertically positive rhythm. The model geometry size is $L= 35$ cm and $r= 3.5$ cm. Sandpack flood tests were employed for the evaluation of the effectiveness of microemulsion flooding. For uniform sandpacks, 60−70 mesh sand was poured in to the coreholder which was vertically mounted on a vibrator and filled with corresponding brines for different floodings. The coreholder was fully filled at a time and was vibrated for one hour. The wetpacked sandpack was flooded with the heavy oil until water production ceased (water cut was less than 1%). The initial water saturation was determined on the basis of mass balance. The wetpacked sandpack was flooded with the Crude oil at 400 psig to irreducible water saturation. The initial water saturation was determined on the basis of mass balance. Waterflooding was conducted horizontally at a constant injection flow rate. The same injection flow rate was used for all the displacement tests of this study. After water flooding, ~0.5 PV microemulsion slug was injected followed by ~2.0 PV water injection as chase water flooding. The same methods are followed for different microemulsion systems at various salinities. The effective permeability to oil ($k_o$) and effective permeability to water ($k_w$) were measured at irreducible water saturation ($S_{wi}$) and residual oil saturation ($S_{ro}$), respectively, using Darcy’s law equation. The permeability of the sand...
packs was assessed with the Darcy equation, Eq. (1), used with fluid flow in porous materials. For a horizontal linear system, flow rate is related with permeability as follow:

\[ q = \frac{k \frac{dP}{dx}}{\mu} \quad (2) \]

where, \( q \) is volumetric flow rate (cm\(^3\)/sec.), \( A \) is total cross-sectional area of the sand pack (cm\(^2\)), \( \mu \) is the fluid viscosity (CP), \( \frac{dP}{dx} \) is the pressure gradient (atm/cm) and \( k \) is Permeability in Darcy.

\[ \text{Volume of oil remaining in the sand pack} = \text{Volume (oil injected)} - \text{Volume (oil expelled)} \]

(b) The second step is performed with the objective of recovering any amount of oil still stored in the sand pack, under high interfacial tensions and lacking any chemical interaction. The amount recovered is calculated via a mass balance:

\[ \text{Volume of oil remaining in the sand pack} = \text{Volume (oil injected)} - \text{Volume (oil expelled)} \]

The recovery factor was calculated by two methods, either using a secondary oil displacement procedure or by means of a tertiary oil displacement technique, overall comprising two steps:

(a) The first step, corresponding to the secondary recovery method, involves the injection of brine into the sand pack, as described in the procedure above. At this point, a certain amount of oil is recovered and another remains in the sand pack. The brine only pushes away the oil found in the sand pack, under high interfacial tensions and lacking any chemical interaction. The amount recovered is calculated via a mass balance.

\[ \text{Volume of oil remaining in the sand pack} = \text{Volume (oil injected)} - \text{Volume (oil expelled)} \]

(b) The second step is performed with the objective of recovering any amount of oil still stored in the sand pack, which corresponds to the implementation of a tertiary recovery method, whereby microemulsion is injected in the fourth step of the process. This solution works by reducing interfacial tensions between the contacting fluids and, as a result, the volume of recovered oil increases.

The recovery factor is obtained by summing up the amounts of oil recovered in each step (secondary and tertiary oil displacement process) and is expressed in percentage (%)

\[ \text{RF}_{\text{Total}} = \text{RF}_{\text{SM}} + \text{RF}_{\text{TM}} \]

where, \( \text{RF}_{\text{Total}} \) = Total recovery factor (%), \( \text{RF}_{\text{SM}} \) = Recovery factor obtained by secondary method (%), \( \text{RF}_{\text{TM}} \) = Recovery factor obtained by tertiary method (%).

III. RESULTS AND DISCUSSION

A. Phase Diagram of Microemulsion System

The pseudo ternary phase diagram of sodium dodecyl sulfate/brine/propan-1-ol/heptane system has been constructed and shown in Fig. 2, where water and NaCl salt considered as a single pseudo-component and (S+CS) is another single component so that the apexes represent oil, brine and (S+CS). The importance of the construction of this type of phase diagram is to determine the composition of the microemulsion. Fig. 2 depicts the phase diagram of surfactant, cosurfactant, Oil and brine at a constant CS/S ratio of 2. It is also important to prepare microemulsions with low concentrations of surfactant from the economical point of view. In the Fig. 2, the shaded areas represent the two-phase microemulsion region and out of the shaded areas imply single-phase microemulsion regions (Winsor IV). From the figure the composition of the microemulsion has been determined to prepare a large amount of microemulsion for flooding experiments. A point was chosen inside the single phase microemulsion region and the compositions of the point in wt% were as follows: CS/S- 20%, oil-53%, and 27% brine.

B. Effect of Salinity on Phase Behavior

Relative volume fraction of various phases of Winsor I, Winsor III and Winsor II are plotted in the Figs. 3 as a function of salinity. Experimentally it has been found that the relative phase volumes of microemulsion system are largely affected by salinity and it changes from Winsor I to Winsor II through Winsor III phase. In Fig. 3, relative phase volumes are plotted as a function of salinity. This type of dataset is known as “salinity scan”. From Fig. 3 it is cleared that at lower salinity region only two phases exist, i.e. water-external microemulsion at the bottom and excess oil phase at the top. This is called Winsor type I phase behavior. With increasing salinity, a bi-continuous microemulsion (B.C.µE) phase is formed. At moderate salinity, three phases coexist simultaneously. This type of phase is considered as Winsor type III. When the salinity further increases, the relative volume of middle phase converted to Winsor type II with oil-external microemulsion at the top and excess water at the bottom. The dependency of phase behavior of oil-water surfactant system on salts can be explained by interfacial energy. Salting out phenomena also plays an important role microemulsion phase. As the salt concentration is increased, some of the water molecules are attracted by the salt ions, which decreases the number of water molecules available to interact with the charged part of the surfactant. As a result of the increased demand for solvent molecules, the interactions

\[ \text{Volume of oil remaining in the sand pack} = \text{Volume (oil injected)} - \text{Volume (oil expelled)} \]

[Fig. 1 Schematic diagram of experimental set-up for Microemulsion Flooding in sandpacks]

[Fig. 2 Pseudoternary phase diagram of oil–brine-surfactant-cosurfactant microemulsion system at 4 wt% NaCl]
between the hydrophilic head groups become stronger than the solvent-solute interactions; the surfactant molecules are precipitated by forming hydrophobic interactions with each other. The interfacial film curvature turns from positive value to zero to negative one, corresponding to phase transition from O/W to bi-continuous phase to W/O structure [16].

C. Solubilization Parameters of Oil and Water in Microemulsion

Fig. 4 shows the salinity dependence phase behavior of SDS microemulsion system at 303 K to characterize the surfactants' solubilization capacities. For characterization of the surfactants' solubilization capacities, the solubilization parameters (or phase uptakes) are commonly used. Healy and Reed [14] first introduced the terms,

\[ SP_i = \frac{V_i}{V_o} \]  

where \( i \) refer to water or oil and \( s \) refers to the surfactant.

Experimental results show that the change of salinity from lower to a higher value leads to the transition of microemulsion phase from WI to WII via WIII. During the transition, the solubilization parameter for oil (\( SP_o \)) increases while water solubilization parameter (\( SP_w \)) decreases as shown in Fig. 4. The salt concentration corresponding to the situation where both the solubilization parameters for oil and water are same is called the optimal salt concentration or optimal salinity. The point of optimal salinity has immense importance because several physical properties (e.g. solubilization parameters, IFT etc.) attain either a maximum or minimum at or near this point [33].

D. Microemulsion Flooding and Recovery

The sand pack was flooded with microemulsion slug after water flooding and the Fig. 5 shows the oil recovered with pore volume injected into sand pack. The figure of waterflood oil recovery shows an early breakthrough and channel flow which caused much lower oil recovery. During injection of microemulsion slug, water-cut declines gradually, and then again reaches 100% at the end of flooding. After the injection of microemulsion slug, the trapped oil droplets or ganglia are mobilized due to a reduction in interfacial tension between oil and water. The coalescence of these drops leads to a local increase in oil saturation. Behind the oil bank, the surfactant now prevents the mobilized oil from being retrapped. The effectiveness of the microemulsion at different brine concentration on enhanced oil recovery was tested with three sets of flooding experiments performed in the sandpack systems. The concentration of brine to be used for microemulsion flooding is related to the optimal salinity concept which has been determined from the phase behavior and solubilization parameter study. In the present work, the experiments were carried out in sand pack, the water flood recovers almost 50% of the original oil in place (OOIP) because of higher porosity (~37%) and permeability. During water flooding, as the water cut reaches above 95%, it was subsequently flooded with microemulsion slugs, followed by chase water. The recovery of oil and water cut with pore volume (PV) injected for three different microemulsion systems is presented in Fig. 5. It has been found that water begins to break through when the injected volume of water reaches 0.15 PV, and then water cut sharply increases above 90% for each case. During injection of microemulsion slug, the water cut declines gradually and then reaches 100% at the end of flooding. Fig. 5 also shows that the cumulative oil recovery by microemulsion flooding is higher in the case of microemulsion prepared at optimal salinity on because of significant physicochemical properties of microemulsion at that salinity. The microemulsion shows ultra-low IFT between oil and water at optimal salinity. If the IFT is low enough, residual oil in a water-wet core could be emulsified and move downstream. The mechanism results in a reduced water mobility that improves both vertical and areal sweep efficiency. The additional recovery of oil over water flooding is 22.63, 24.88, and 22.87% when microemulsion slugs with 2 wt%, 4 wt%, and 9 wt% brines were used respectively. However, the proper design of the microemulsion slug should be performed by feasibility analysis, considering the operating costs and market value of the crude.
Phase behavior and physicochemical properties of microemulsions comprising of sodium dodecyl sulfate/brine/propan-1-ol/heptane and its structural changes with the salinity have been investigated for the application of microemulsion in enhanced oil recovery. Salinity plays important roles on the relative phase volume and solubilization parameters in microemulsions. Pseudoternary phase diagram is the one of the crucial step for microemulsion flooding in enhanced oil recovery. The results of the present study show that as salinity changes from low to high, phase transition takes place from Winsor I to Winsor II via Winsor III. A series of flooding experiments have been performed using the prepared microemulsion. The additional recoveries were calculated by material balance. Encouraging results with additional recovery more than 20% of original oil in place above the conventional water flooding have been observed. Microemulsion at optimal salinity (4 wt% brine) shows highest efficiency to recover the additional oil.

IV. CONCLUSION

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial assistance provided by University Grant Commission [F. No. 37-203/2009(SR)], New Delhi to the Department of Petroleum Engineering, Indian School of Mines, and Dhanbad, India. Thanks are also extended to all individuals associated with the project.

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