Alkali-Surfactant-Gas/\(\text{CO}_2\) (ASG) Flooding for Enhanced Oil Recovery: Screening of Chemical Slug

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Abstract

The objective of the present study was to screen chemical formulations for the combined chemical-gas Enhanced Oil Recovery (EOR) process of Alkali-Surfactant-Gas (ASG) Flooding. Phase behavior tests are inexpensive, rapid and effective means to screen chemical formulations for a specific application. Phase behavior tests were performed with various combinations of surfactants, co-solvent (Isopropyl Alcohol), alkali \((\text{Na}_2\text{CO}_3)\) and soft brine together with crude oil (31³ API) of Upper Assam Basin at reservoir temperature \((70^\circ \text{C})\). Three types of surfactants were used: SDS (anionic), TX-100 (non-ionic) and a natural surfactant (Black Liquor). Foam stability test were done to select suitable concentrations of surfactant for preparation of formulation. The foamability and stability of bulk foam increased with increasing surfactant concentration. Best oil recovery in chemical floods and increased foam stability is observed when a negative salinity gradient is imposed in injected fluids. The formation water of the reservoir under study has a salinity of 3800 ppm, so optimum salinity of around 3000 ppm was targeted for the chemical formulations. The optimum salinity was taken as the salinity of the solution where Winsor type III microemulsion was observed. Three best performing formulations were screened based on the results of phase behaviour and foam stability tests.

Keywords: Phase behavior, Surfactants, Microemulsion, Optimum salinity, Foam

1. INTRODUCTION

Alkaline Surfactant Gas (ASG) flooding is a chemical & gas synergetic enhanced oil recovery process. In ASG process, foam is formed in the porous media by the co-injection or alternate injection of surfactant solution and gas. Foam acts as a mobility control agent by reducing the relative permeability of the injected chemical slug that forms micro-emulsion at ultra-low oil-water IFT. Although foam can be formed in the porous media, clay minerals in rock matrix adsorbed the surfactants and reduced the efficiency of the foaming process. So alkali is added to the chemical slug where it works as a clay stabilizer.

Injection of surfactants solution into the reservoir leads to the formation of microemulsions (ME) at the interface between crude oil and water. ME are thermodynamically stable, isotropic dispersions of oil and water stabilized by surfactants (and/or cosurfactants). By creating a middle phase ME using brine, oil, surfactant, and/or cosurfactant, it is possible to obtain ultra-low IFT [1]. The formation & phase behaviour of ME when brine, oil & surfactant are mixed was first described by Winsor (1954). The phase behaviour of ME are dependent on the nature & concentration of surfactants, co-surfactant, oil, brine, co-solvents, temperature etc [2,3,4]. For particular ME system, phase behaviour is strongly affected by the salinity or concentration of electrolyte. ME phase behavior is described as Winsor type I, type II, and type III. The middle phase ME or Winsor type III is important in EOR because of its ultra-low IFT \((<10^{-3} \text{mN/m})\). By systematically varying the salinity at a particular temperature and pressure, phase transition from Winsor type I to Winsor type II through Winsor type III can be observed.

Phase behavior tests are inexpensive, quick and effective means to screen chemical formulations, minimizing the need for relatively expensive core flood tests [5]. These are performed with various combinations of surfactants, co-solvents and alkalis with a particular crude oil at the reservoir conditions. Phase Behavior tests includes the aqueous stability test & salinity scan. Salinity scan helps to determine the optimum salinity, which is one of the most important parameter in the surfactant flooding process. It is salinity at which IFT between ME & water is equal to the IFT between ME & oil. Healy et. al. 1977 concluded that the optimum salinity is also the salinity at which maximum oil recovery was obtained from core flooding experiments [6]. Foam stability test is another way to select suitable concentrations of surfactant for preparation of formulation. In this type of test, surfactants are tested for their ability to form stable foam and to provide suitable concentration for preparation of formulation. The solubilization parameter \(V_o/V_s\) and \(V_w/V_s\) are functions of salinity. \(V_o/V_s\) increases with salinity, while \(V_w/V_s\) decreases with salinity, and they intersect at optimum salinity. The amount of oil and brine solubilized in the surfactant phase are approximately equal at optimum salinity [7].

Nelson et. al. 1978 found that best oil recovery in chemical floods occur when a negative salinity gradient is imposed in injected fluids [8]. Liu 2007 study also confirmed that negative salinity gradient improve recovery [2]. A negative salinity gradient means the slug formulation is selected at an optimal salinity lower than the in situ reservoir brine salinity.
The drive, which follows the slug, salinity is lower than the salinity of slug. This negative salinity gradient reduces surfactant retention and also leads to the increasing the oil recovery. Srivastava et. al. 2009 also concluded that a negative salinity gradient assists ASG process by increasing foam stability [9, 10].

The primary objective of the present study is to prepare an optimum chemical formulation that will be capable of achieving of ultra-low IFT with a crude oil of Upper Assam Basin. The formation water of the reservoir under study has a salinity of 3800 ppm NaCl, so optimum salinity of around 3000 ppm NaCl was targeted for the chemical formulations.

2. EXPERIMENTAL DESCRIPTION

2.1 Materials: A nonionic surfactant Triton X-100 (TX-100), polyoxyethylene tereoctylphenyl ether, two anionic surfactants Sodium Dedocyl Sulfate (SDS) & Alfa Olefin Sulphonate (AOS) and a natural surfactant Black Liquor (BL) were used. Triton X-100, purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, Sodium dodecylsulphate (SDS) (with 98% purity), was purchased from Merck (India). Sodium Alfa Olefin Sulphonate 32% a yellowish transparent liquid was supplied by a local vendor. The natural surfactant BL is an anionic water soluble surfactant, whose main constituent is Na-lignosulphonate and an effluent from Nowgong paper Mill, Jagiroad, Assam. Sodium carbonate (Na\(_2\)CO\(_3\)), a conventional alkali, purchased from Merck Specialities Pvt. Ltd., Mumbai was used in the study. Sodium chloride, which adjusts the brine salinity, was purchased from Merck Specialities Pvt. Ltd., Mumbai. Co-solvents used in phase behaviour test are usually small carbon chain (C\(_3\) to C\(_5\)) alcohols. Alcohol reduce ME viscosity, prevents gel formation, and reduces equilibrium time. Isopropyl alcohol (IPA) was used as co-solvent in the experiments purchased from Merck Life Sciences Pvt. Ltd., Mumbai. The crude oil used was from a reservoir of Upper Assam Basin having a dead oil viscosity and density of 4.1 cP and 31 API, respectively.

2.2 Methods:

2.2.1 Phase Behavior Study

The concentrated stock solutions of surfactants, IPA, Na\(_2\)CO\(_3\), and NaCl were initially prepared. The stock solutions and distilled water (DW) were mixed in different ratios to obtain the solutions with a range of salinities. The solutions were mixed in the following particular order to prevent phase separation [2, 11, 12]:

(i) NaCl, Na\(_2\)CO\(_3\), & IPA
(ii) Distilled Water
(iii) Surfactant Solution

2 ml of the mixed aqueous solutions were dispensed taken in 5 ml borosilicate pipettes (tips of which were heat-sealed) over which 2 ml of crude oil was added (WOR=1:1). The pipettes were sealed and arranged in order of increasing salinity in racks and placed in an oven. After 20-30 minutes when the samples reached the temperature of the oven (maintained at average reservoir temperature of 65°C), the pipettes were gently inverted several times in order to facilitate mixing of oil and aqueous phase [2,8,9,10]. The pipettes were then left in the oven to equilibrate and the fluid interfaces were inspected at intervals of hours, days and weeks. Prior to adding crude oil to pipettes, aqueous stability tests were conducted to determine the clarity and homogeneity of all dispensed aqueous solutions. After dispersing in each pipette, aqueous volumes were agitated and settled for one hour, and aqueous stability was tested by visually inspecting any cloudiness and/or phase separation. Only those mixtures were selected for phase behavior studies which were found to be stable without cloudiness or precipitation occurring. In this workable salinity range were identified for the chemical formulations.

Initially coarse salinity increments between pipettes were used to identify the optimal salinity region. The salinity of formation water was 3800 ppm NaCl and for applying negative salinity gradient concept during the flooding process, the optimal salinity (OS) target was fixed around 3000 ppm, NaCl. Then additional test with different combination of chemicals with finer salinity increments were conducted to focus on target salinity region for more accurate assessment. The goal was to screen a chemical formulation for conducing further oil recovery experiment utilizing negative salinity gradient. In addition, performance evaluation of the phase behaviour tests were made by comparing the microemulsion parameters i.e. optimal solubilisation ratio, equilibrium time, gellation etc. Chemical formulation having optimal solubilisation ratio greater than 10, quick equilibrium time and optimal salinity around 3000 ppm NaCl were selected. A typical flow chart of phase behavior test is shown in Fig. 1.
2.2.2 Foam Stability Test

In foam stability test, surfactants are tested for their ability to form stable foam and to provide suitable concentration for preparation of formulation. Foaming tests are simple and provide quick-preliminary estimate of the ability of surfactants to form stable foam. But in these tests, the effects of different phenomenon, like capillary pressure, dispersion and adsorption, present in an actual reservoir cannot be ascertained [9].

Surfactant solutions are prepared at different concentration. Equal volumes (2ml) of these surfactants solutions are dispensed in test-tube. Equal volume of light paraffin oil (2ml) was then added to each test-tube. The test tubes were then shaken with equal intensity, which resulted in the formation of foam at the top of the liquid column. After foam generation, the stability of foam are characterized by $V_i$ and $t_{1/2}$. Surfactants and their concentration with the best foam ability in the presence of oil will exhibit higher $V_i$ & $t_{1/2}$.

3. RESULTS & DISCUSSIONS

3.1 Foam Stability Test

For Triton X-100 surfactants, the foamability and stability of bulk foam increased with increasing surfactant concentration (Fig. 2 & Fig. 5). Higher initial foam volume and half-time for dewater are indications of good foamability and stability of foam. For SDS, the initial foam volume increased with increasing surfactant concentration and remained nearly constant after 0.2 wt% (Fig. 3). Both for Triton X-100 & SDS, generated foam was strong and stable for more than 1 hour. For SDS, foam stability increased by increasing the surfactant concentration with the highest stability shown at 0.3 wt% (Fig. 6). BL being a weak surfactant, the initial volume of foam formed was less (Fig. 4). For BL also the initial foam volume increased with increasing surfactant concentration and remained nearly constant after 6 wt% (Fig. 7).
Fig. 2 Initial foam volume of TX-100 with increasing concentration.

Fig. 3 Initial foam volume of SDS with increasing concentration.

Fig. 4 Initial foam volume of BL with increasing concentration.
3.2 Phase Behavior Tests: Screening of chemical formulations

A series of phase behaviour tests were performed with different formulations prepared by changing the concentrations of surfactant, co-surfactant, co-solvent and alkali within a range of salinities. The pipettes were observed for Type III microemulsion formation and the solubilisation parameters were calculated. The concentrations of the chemicals were varied to obtain formulations having the optimal salinity around 3000 ppm and optimal solubilisation ratio greater than 10.

From the aqueous stability tests, it was observed that at higher salinities (greater than 40000 ppm) the chemicals used were unstable showing precipitation with visible signs of cloudiness. Below 20000 ppm, no precipitation or visible signs of cloudiness was observed confirming the compatibility of chemicals in the aqueous solution within the salinity range from 0 to 20000 ppm. Alkali concentration of 0.5 to 1 wt% was found to sufficient to provide suitable pH and satisfy alkali consumption in the core by previous authors [5]. Co-solvent concentration should be low to reduce overall chemical costs. The IPA concentration was varied from 0.5 to 1 wt%. SDS with concentration ranging from 1 to 5 wt% were used in the phase behavior tests. The Critical Micellar Concentration (CMC) of BL is 5 wt% and the favourable concentration of BL from foam stability test was 6 wt% [13]. So, BL concentration in the range of 4 to 6 wt% was tested in the formulation. BL, being a weaker surfactant, was used along with co-surfactants. TX-100 concentration was kept at 0.1 & 0.3 wt% and AOS concentration at 1 to 2 wt% in preparing the formulation. The optimal salinity was observed to increase with the total surfactant concentration [5]. The equilibrium time for most of the tests was about 1 day, in fact no change in interface was observed after 16 hours. One exception in the case where no co-solvent was used when the equilibrium time increased to 3 days (Table 1). Co-solvent like alcohol was observed to lower optimum solubilization ratio and thereby increase interfacial tension (IFT) due to the established relation between IFT & optimum solubilization ratio [10]. Three well performing chemical formulations were selected based on the phase behavior results. The photograph of the phase behaviour tests of these formulation is shown the Fig. 8 and the solubilisation data in the Fig. 9.
### Table 1 Summary of Crude Oil Phase Behavior Parameters and Equilibrium Time

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Surfactant</th>
<th>Surfactant Co-solvent IPA (wt%)</th>
<th>Alkali Na₂CO₃ (wt%)</th>
<th>Salinity NaCl (ppm)</th>
<th>Opt. Sol. Ratio</th>
<th>Opt. Salinity NaCl (wt%)</th>
<th>Eq. Time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>SDS</td>
<td>0.5</td>
<td>0.8</td>
<td>0 to 20000</td>
<td>undet.</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>SDS</td>
<td>0.5</td>
<td>0.8</td>
<td>0 to 20000</td>
<td>8</td>
<td>7000</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>SDS</td>
<td>0.5</td>
<td>0.8</td>
<td>0 to 10000</td>
<td>5</td>
<td>1500</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>SDS</td>
<td>0.5</td>
<td>0.8</td>
<td>0 to 8000</td>
<td>8</td>
<td>3100</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>SDS</td>
<td>0.8</td>
<td>0.8</td>
<td>0 to 7000</td>
<td>13</td>
<td>3100</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>BL</td>
<td>0.1</td>
<td>TX</td>
<td>0.8</td>
<td>0.5</td>
<td>0 to 20000</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>BL</td>
<td>0.1</td>
<td>TX</td>
<td>0.8</td>
<td>0.5</td>
<td>0 to 10000</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>BL</td>
<td>0.1</td>
<td>TX</td>
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<td>0.5</td>
<td>0 to 10000</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>BL</td>
<td>0.3</td>
<td>TX</td>
<td>0.8</td>
<td>0.5</td>
<td>0 to 7000</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>BL</td>
<td>2</td>
<td>AOS</td>
<td>0.8</td>
<td>0.5</td>
<td>0 to 10000</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>BL</td>
<td>1</td>
<td>AOS</td>
<td>1</td>
<td>0.5</td>
<td>0 to 7000</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>BL</td>
<td>1</td>
<td>AOS</td>
<td>0.8</td>
<td>0.5</td>
<td>0 to 7000</td>
</tr>
<tr>
<td>13</td>
<td>4</td>
<td>BL</td>
<td>2</td>
<td>AOS</td>
<td>1</td>
<td>0.5</td>
<td>0 to 7000</td>
</tr>
<tr>
<td>14</td>
<td>4</td>
<td>BL</td>
<td>2</td>
<td>AOS</td>
<td>1.5</td>
<td>0.5</td>
<td>0 to 7000</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>BL</td>
<td>1</td>
<td>AOS</td>
<td>1</td>
<td>0.5</td>
<td>0 to 7000</td>
</tr>
</tbody>
</table>

### Table 2 Summary of chemical formulation screened

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Formulation</th>
<th>Formulation ID</th>
<th>Optimum Salinity (wt%NaCl)</th>
<th>Optimum Solubilization Ratio (cc/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3 wt% SDS, 0.8 wt% Na₂CO₃</td>
<td>F1</td>
<td>3100</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>5 wt% BL, 0.3 wt% TX-100, 0.8 wt% IPA, 0.5 wt% Na₂CO₃</td>
<td>F2</td>
<td>3100</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>5 wt% BL, 1 wt% AOS, 0.8 wt% IPA, 0.5 wt% Na₂CO₃</td>
<td>F3</td>
<td>3200</td>
<td>12</td>
</tr>
</tbody>
</table>

Fig. 8 Photograph of phase behavior tests of the three selected formulations
4. CONCLUSION

This paper presents the screening of chemical formulation for ASG core flooding experiments. The foam stability tests, aqueous stability, and phase behavior tests were used to screen 3 best performing chemical formulations (Table 2). The anionic surfactants like SDS, BL & AOS has shown good performance to achieve the targeted optimal salinity. The phase behaviour mixtures of the selected formulations were also gel free, had free flowing interfaces, had optimum solubilization ratio > 10 and had quick equilibrium time. The work is a supplementary study for the combined gas-surfactant enhanced oil recovery of a depleted reservoir of Upper Assam Basin. This selected formulation will be used in the ASG core flooding experiments.

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NOMENCLATURE

\( V_o/V_s \) Solubilisation parameter of oil in microemulsion which is the ratio of oil to surfactant in microemulsion

\( V_w/V_s \) Solubilisation parameter of water in microemulsion which is the ratio of water to surfactant in microemulsion

\( V_i \) Initial foam volume.

\( t_{1/2} \) Time for dewater half volume from foam.
REFERENCES


