An Integrated Workflow for Chemical EOR Pilot Design

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Summary

After primary and secondary production of oil from a petroleum reservoir, more than half of the oil is often left in place. In order to improve the process displacement efficiency – so that one can recover some of this remaining capillary-trapped or water-by-passed oil –, it is necessary to apply enhanced oil recovery (EOR) techniques such as surfactant flooding, either Surfactant (S), Surfactant-Polymer (SP) or Alkaline-Surfactant-Polymer (ASP).

This paper describes a complete workflow for optimizing S, SP or ASP processes for chemical EOR. The workflow consists in successive steps: reservoir fluid and rock characterizations, formulation screening, core flood validation and simulation including sensitivity studies.

Introduction

For a majority of oil reservoirs, large amount of oil are still left after extensive water flooding (today average worldwide recovery factor is 32%). Chemical EOR technology is the most promising tertiary recovery technique to both improve sweep and displacement efficiency. The well known process to improve reservoir sweep efficiency consists in injecting low concentration of polymer that viscosifies water. This process known as polymer flood has been extensively used at large scale especially at the Daqing field in China. More complex chemical enhanced oil recovery processes use both surfactant to reduce oil-water interfacial tension and polymer to improve sweep efficiency (SP). The addition of alkali to surfactant flooding, known as Alkaline-Surfactant-Polymer (ASP) flooding process, reduces the amount of surfactant required to reach performance. Key step in those processes consists thus in designing and testing ability of low to ultra-low interfacial tension formulations to effectively displace oil trapped in porous media.

Here we report a workflow developed jointly by Rhodia and IFP for the optimization and validation of Surfactant-Polymer (SP) and Alkali-Surfactant-Polymer (ASP) mixtures in a chemical EOR study. Such development capitalizes on both “Rhodia” recognized expertise in microfluidics and High Throughput Screening (HTS) tests and IFP large experience in the field of EOR.
Figure 1 presents the different steps, Rhodia and IFPEN have identified to fulfil a chemical EOR pilot design.

![Fig 1: Chemical EOR workflow for a pilot design](image)

**Process and material selections**

Reservoir information is critical to evaluate the feasibility of a chemical EOR project as well as the nature of chemicals that can be used. Obviously, temperature, brine composition, oil & rock properties must be known. Besides this basic information, a detailed picture of the reservoir characteristics must be drawn including heterogeneities.

Reservoir temperature orients surfactant selection to fulfill thermal stability requirements. A salinity window must be defined as well as the injection strategy for coreflood experiments. Crude oil is characterized by physico-chemical data (API degree, SARA analysis, Acid Number) and empirical equivalent alkane carbon number scale (EACN). Together with the salinity window, this information is used to pre-select surfactant candidates. Rock properties such as permeability, porosity and clay content are also primordial. From these data, we can evaluate if a given reservoir is a good candidate for surfactant flooding and define a strategy for a chemical EOR design study.

Chemical EOR surfactants reported in the literature include: olefin-based surfactants, alkylaryl sulfonates, alcohol based non-ionics and sulfated/sulfonated alkoxylated alcohols. It is now well established that there is a very strong structure/performance relationship for all these surfactant families. Critical criteria include raw material selection (alkyl chain length distribution, branching…) as well as synthesis conditions.

Rhodia has developed a range of chemical EOR surfactants. All those chemicals have been mapped through a performance salinity/temperature/EACN matrix in order to properly preselect surfactants for a given reservoir conditions.

**Chemical Formulation Optimization**

The objective of the formulation process is to optimize a surfactant mixture in order to guarantee a good injectivity and high oil recovery in a reservoir core. Large oil recovery is related to both InterFacial Tension (capillary number) and mobility ratio. The following paragraph describes a high throughput (or combinatorial) workflow we used to design surfactant formulations using a robotic platform. High Throughput Screening (HTS) tools and combinatorial methodologies are used to screen a large set of parameters by miniaturization and parallelization. The main features of our formulation workflow have been described in previous publications (Morvan et al., 2008, Moreau et al., 2009).
**EOR formulation: phase behaviour & solubility**

It is well established that ultra-low interfacial tensions are required to mobilize additional oil when a reservoir has been waterflooded. This has been the subject of a large number of articles (Stegemeier G.L., 1976; Green D. W. and Willhite G.P., 1998, Bavière M., 1991). A process based on phase behavior screening has been described for evaluating potential EOR surfactants (Levitt D.B. et al., 2006). This approach is based on a well established relationship between low interfacial tension and a microemulsion phase behavior. When oil, water and surfactant are mixed, at low surfactant concentrations, solutions separate into microemulsion as originally described by Winsor (Winsor, 1954). Microemulsions are either type I (oil in water - WI), type II (water in oil - WII) or type III (bicontinuous oil and water - WIII).

Interestingly, surfactant solubility in brine has been investigated only by a limited number of authors. This aspect, often by-passed is critical when it comes to injectivity issues. Our HTS platform allows probing both phase behaviour and solubility in different brines. Objective is to ensure that ultra-low IFT is achieved while maintaining appropriate brine solubility.

All experiments have been performed on a fully automated Genesis Tecan robotic platform. During one experiment, 48 formulations can be prepared in 8 ml glass vials. Dispense of liquids by the robot is volume based. For viscous liquids, targeted volumes and actually dispensed weight often differ significantly, so that a calibration is required. Images of our samples are taken in batch sessions where the gripper of the robot sequentially positions all vials in front of a Digital Camera (Nikon D70). Samples are kept in a temperature controlled rack and hence each imaging session yields a set of unique image files for a given temperature. The principle of the screening relies on identifying surfactant formulations which yield to typical middle phase microemulsions.

This is illustrated in Fig. 2 where both solubility (Figure 2a) and phase behaviour (Figure 2b) at different salinities are reported for an olefin-based formulation. In this example, we used dodecane as model oil and temperature has been set at 80°C. A clear transition from Winsor I to Winsor III has been observed above 43 g/L NaCl. The solubilisation ratio (Vo/Vs = Vw/Vs ∼ 15) is indicative of an ultra-low interfacial tension at optimal salinity for this system. In this salinity range, the surfactant solubility is good, reducing injectivity hurdles.

In order to precisely assess the injectivity of the final formulation, a simplified injectivity test has also been set. Typically 5 pore volumes of optimized surfactant formulation are injected in small model ceramic cores with controlled properties (permeability, pore morphology). Pressure drops are recorded at different flow rates and compared to predicted values.

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**Fig. 2:** a) Solubility and b) phase behaviour screening for an olefin-based formulation against dodecane as a function of salinity. Temperature is set at 80°C. Digits reported on test tubes represent brine salinity (NaCl, g/L TDS). The surfactant concentration is 8 g/L. The aqueous stability is good up to 55 g/L NaCl. The phase behaviour clearly shows the Winsor I to Winsor III transition around 43 g/L NaCl. The optimal salinity is in the range 49-52 g/L. Optimum solubilization ratio is above 10 (ultra-low IFT ∼ 10-3 mN/m)
Static and dynamic adsorption-retention tests

An estimate of surfactant adsorption is essential regarding the economics of a surfactant flooding process. Clay is usually responsible for surfactant adsorption and thus we have used kaolinite clay to define adsorption tests (Zhang, 2006).

Two methods have been developed to characterize surfactant adsorptions: static & dynamic tests. Static adsorption is determined from mass balance between surfactant concentration before and after contact with Na-kaolinite. In our experiments the solid to liquid ratio is 0.2 (wt %) and the surfactant is titrated with Hyamine 1622.

For the dynamic test, a sandpack made of sand (95%) and kaolinite (5%) has been prepared and water saturated. The surfactant injection is performed at 10 cm³/h and effluents are collected for surfactant titration with Hyamine. The surfactant adsorption, calculated from a mass balance, is governed by the competition between attractive forces i.e. Van der Waals interactions, and electrostatic forces that can be either repulsive or attractive. Considering sand surface is negligible compared to the kaolinite one (sand surface area < 0.05 m²/g; kaolinite surface area ~ 20 m²/g) adsorption values are all reported on a kaolinite basis.

Results of dynamic experiments show the striking effect of brine composition on the adsorption (Fig. 3). A set of static and dynamic data are compared in Table 1. Both methods are consistent and the adsorption follows the well-known trends:
- Adsorption increases with brine hardness;
- Adsorption decreases with alcohol addition;
- Adsorption strongly decreases in alkaline conditions.

| Table 1: Comparison between static and dynamic adsorption of olefin surfactants on model rocks |
|-----------------------------------------------|-----------------------------------------------|
| Adsorption on Na-kaolinite mg/g | 2 g/L Surfactant 10 g/L NaCl | 2 g/L Surfactant 10 g/L Na₂CO₃ 10 g/L 2-butanol | 2 g/L Surfactant Dilute Sea Water at 10 g/L 10 g/L 2-butanol |
| Static adsorption | 5.8 | 1.2 | 13.1 |
| Dynamic adsorption | 6.0 | 1.4 | 8.9 |

Fig. 3: Comparison of the surfactant concentration profile in various conditions of salinity and alkalinity in the dynamic adsorption test (Sandpack).

For surfactant formulations, i.e. containing mixtures of several surfactants, the static method cannot be used because of lack of representativity. Indeed, potential chromatographic effects make the adsorption more complex with a fractionation of the chemical components (Trogus, 1979). We thus recommend the use of the dynamic test. The test performed by continuous
injection is stopped only when the injected surfactant concentration is recovered in the effluents, making sure that complete adsorption is satisfied.

According to Table 1, we clearly see the benefit of adding an alkaline to a surfactant formulation. In the following paragraph we describe surfactant positioning and formulation selection in the framework of an ASP process.

**Surfactant positioning**

As stated above, our setup is fully automated, allowing the formulation and characterization of a large number of surfactant mixtures. Main objective is to optimize efficiency and cost by minimizing surfactant concentration and adjusting ratio between each component. All images are stored and automatically processed using a specific procedure detailed in a separate reference (Morvan M., 2008). Combining series of data, clear surfactant positioning can be extracted. An example of interfacial tension screening obtained for an olefin based formulation is presented in Error! Source du renvoi introuvable.. The optimal salinities of a given formulation for different oils are plotted versus the oil EACN at different temperatures. The optimal salinity follows the typical relationship (Salager J.L., 1978):

$$\ln(S) = K.EACN + a_\tau.(T-T_0)$$  \hspace{1cm} (1)

This approach is convenient for the surfactant pre-positioning to address given reservoir conditions.

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**Fig. 4:** a) Solubility and microemulsion behaviour of an olefin-based formulation with different oil (from heptane to hexadecane). b) Optimal salinity of an olefin-based formulation as a function of temperature versus different oils from heptane (dark circles) to hexadecane (white circles). c) Solubilization ratio for a selected olefin based formulation using dodecane as model oil.
From those set of data we have selected an olefin based formulation for an ASP coreflood experiment. Solubilization ratios as a function of salinity for this formulation are presented in figure 4c.

Core flood experiments

A first coreflood has been performed to determine adsorption-retention of chemicals. This is an important step to evaluate surfactant loss in the core.

The second set of corefloods has been conducted to evaluate the oil recovery efficiency. Constant salinity was the rule in the past while now, it is clearly evidenced that salinity gradient is a very promising way for maximizing oil recovery (Flaaten, 2008). In a simple approach of the salinity gradient concept, surfactant mixture in formation water exhibits a WII type while salinity of the injected formulation corresponds to a WI type. Therefore, WIII type conditions, occurring at an intermediate salinity between formation and injection water salinity, are encountered during flooding. A polymer drive with a decreasing salinity gradient gives further advantage by promoting the release of the adsorbed surfactant and a supplementary oil recovery can be obtained if low interfacial tensions are encountered. Different salinity gradients can be envisioned including preflushes and surfactant slug salinity management in order to increase control on the phase behaviour (e.g. injection of WII surfactant formulation with decreasing salinity gradient). Nevertheless this approach is restricted to limited number of pilots as it can lead to surfactant stability issues (for heavy oils) and require appropriate water management facilities.

Here we report the results of a coreflood performed under a salinity gradient design. We applied an ASP formulation with a slug of surfactant and alkaline followed by a polymer drive. The coreflood is fully analyzed with measurements of surfactant recovery and retention as well as pH profile. Petrophysical data such as, relative permeabilities and polymer mobility, are extracted form pressure drop measurements. These data are of prime importance for up-scaling the surfactant process from lab to the pilote stage.

The workflow comprises the following steps:

- Core characterization & preparation;
- Oil recovery test and optimization.

Coreflood characterization and preparation

A large range of tools are used to investigate heterogeneities and characterize core samples. CT scan is used to select appropriate cores from full size samples. High Pressure Mercury Injection (HPMI) is the conventional method used to determine pore size distribution of the sample. This analysis is usually completed with Nuclear Magnetic Resonance (NMR) to characterize sample heterogeneities. Oil could indeed be trapped in the small pore network and very difficult to extract even with surfactants, leading to poor recovery factors. Cores with low permeability regions or high permeability anisotropy are discarded.

A special methodology has been developed to restore wettability when it is necessary. Core is set at irreducible water saturation (Swi) by drainage at reservoir conditions and then water flooded to reach the residual oil saturation (Sor). Special equipment with X-Ray acquisition may be used to monitor the in-situ saturation (ISSM) as a function of chemical agents injected and time.

In the example presented below, sandstone cores from Clashach material are used. Clashach sandstone is considered as representative of North Sea reservoirs. The core is set up in a Hassler coreholder or epoxyed for tests carried out at low temperature.

Oil recovery test

A conventional set-up for two phase flow is used to investigate formulation performance in reservoir conditions with crude oil (Fig. 5). The core flood methodology is in three steps:
• Permeability measurements and water saturation;
• Drainage followed by imbibition with the synthetic formation water;
• Injection of the chemical slug followed by polymer or chase water.

Results presented below illustrate a salinity gradient process to maximize oil recovery. The injection rate is around 2 ft/day. The salinity is continuously decreased from 50 g/L in the waterflooding water up to 25 g/L in the chase water. The surfactant slug is 0.5 PV at a surfactant concentration of 8 g/l in 30 g/L NaCl and 10 g/L Na₂CO₃. The surfactant slug is in a WI type. The polymer drive is at a salinity of 25 g/L NaCl + 10 g/L Na₂CO₃. The polymer used is a 30% hydrolysed polyacrylamide with a molecular weight given close to 8 million Daltons (Floopam 3330S - SNF). The optimal salinity is at 36 g/L NaCl + 10 g/L Na₂CO₃.

Coreflood results are summarized in (Fig. 6). The oil breakthrough occurs around 0.3 PV, as a first indication of low surfactant retention. The oil recovery is in two banks. The first bank corresponds to the surfactant injection whereas the second bank is recovered during the polymer displacement. It is strongly believed that the second bank is the result of the surfactant desorption at the rear of the surfactant slug. Surfactant concentrations in the effluent are large, meaning we can lower the surfactant concentration significantly for a pilot design. Finally, the oil saturation after the injection of the chemical slugs is 18% which compares favorably with the initial 48 % of oil left after waterflooding. This is a satisfactory performance when considering both the relatively low surfactant concentration and the use of model oil. Indeed, with a reactive crude oil, lower interfacial tensions are expected due to in-situ generation of surface active soaps (Nelson, 1984).
Surfactant concentration has been determined by Hyamine titration. It must be emphasized that a mass balance on surfactant effluents shows retention of 0.16 mg/g of rock, well below the retention amount measured with the dynamic adsorption test previously described (0.42 mg/g of kaolinite). This is consistent with the relatively low clay content in Clashach sandstone. This value is also lower than the one measured during the single-phase dynamic adsorption test on Clashach core. This is due to the salinity gradient which is known to lower adsorption and phase retention. The displacement is thus occurring within a WII to WI type system without surfactant trapping, giving a clear indication of a well-designed formulation.

Fig. 7 shows the pressure drop across the whole core versus pore volume injected. The maximum pressure drop was reached after 0.3 to 0.4 pore volumes of fluid injected corresponding to the beginning of oil recovery. The pressure drop measured at the final state of the polymer injection is consistent with the water permeability measured after chase water injection. Viscosities of the injected fluids are measured to evaluate mobility ratios during the displacements. Taking also into account the pressure drop measured at the end of the polymer injection, the estimated relative permeability to water (Kr) at this stage is 0.6. From this Kr, a value of the mobility reduction (Rm=4.75) can be determined after the 0.5 pore volume of polymer injected. This value is consistent with the relative viscosity of the polymer solution (ηr=4.55). From those data, it is clear that chemical injection did not damage to the core.

**Simulation**

In this section, we investigate, within the context of numerical simulation, the tertiary oil recovery performance of an ASP coreflood. Clearly, the final objective of an ASP process feasibility study is to forecast pilot-scale oil recovery performance. Prior to this, the very first step consists in matching laboratory coreflood results with numerical modelling. The work presented hereafter encompasses this first building block, namely the numerical simulation of a real ASP coreflood experiment, with a real reservoir core saturated with real reservoir oil and brine.

The modeling is performed with an in-house numerical simulator named SaripCH. The physics of SaripCH is currently being implemented in the commercial reservoir simulator PumaFlow within the OpenFlow platform, in order to enlarge the ability to simulate full-field chemical EOR processes. SaripCH is a tridimensional diphasic black-oil simulator with mass balance equations for chemicals.

The oil recovery mechanism is modeled by the introduction of a relationship between the residual oil saturation and the capillary number, \( N_c = \frac{(\eta u)_{w}}{\gamma_{ow}} \), where \((\eta u)_{w}\) is the viscous driving force of the water phase (\(\eta_{w}\) being the viscosity of the displacing water phase and \(u_{w}\) its Darcy
velocity) and $\gamma_{ow}$ the oil-water interfacial tension. This relationship $S_o = f(N_c)$ is often referred as to the Stegemeier or capillary desaturation curve. As illustrated on Fig. 8(a) and 8(d), increase of $N_c$ over several orders of magnitude results in a significant residual oil saturation reduction. The capillary number is calculated for each time step by using a table giving $\gamma_{ow}$ as function of surfactant concentration and salinity. This relationship is introduced as a table in the simulator, the capillary number and the resulting oil saturation being calculated at each time step. Finally, the water-oil relative permeabilities are linearly interpolated as a function of the capillary number. To summarize, the inputs required by Sarip are the following:

- (i) Surfactant, polymer and alkaline adsorptions,
- (ii) The relationship between the interfacial tension, salinity and surfactant concentration,
- (iii) The relationship between residual oil saturation and the capillary number,
- (iv) End points of the relative permeability curves.

Additional features are alkaline/rock reactions through ion exchange and dissolution/precipitation. Alkaline, polymer and surfactant adsorptions are represented with a conventional Langmuir isotherm, whose plateau adsorption depends on salinity for polymer and both on salinity and pH for surfactant [see Figure 8(c)].

Table 2: ASP coreflood injection schedule.

<table>
<thead>
<tr>
<th></th>
<th>Slug size (PV)</th>
<th>$C_{\text{saturant}}$ (g/L)</th>
<th>$C_{\text{polymer}}$ (ppm)</th>
<th>$C_{\text{alkaline}}$ (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical slug</td>
<td>4.6</td>
<td>2</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>Chase water</td>
<td>9.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
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Fig. 8: Main coreflood features: (a) capillary desaturation curve, (b) relative permeabilities (see the text), (c) surfactant adsorption, (d) oil-water interfacial tension as a function of surfactant concentration (diamond symbols represent experimental measurements).

Coreflood experimental data are the following: the core is 6.30 cm long, its diameter is 3.91 cm, its porosity is 22% and its absolute permeability is 20 mD. Core length is represented with 30 cells;
we performed a sensitivity study considering several cells numbers (10, 100, 300 and 400), and checked that the results presented below in Fig. 9 do not significantly vary within reasonable accuracy. The injection history is summarized in Table 2. Initial oil and water saturations are straightforwardly obtained after the waterflooding. Experimental oil-water relative permeabilities are fitted with Corey power laws $K_w = c_w(s_w)^a$ and $K_o = c_o(s_o)^b$ where $c_w$ and $c_o$ are the maximum water and oil relative permeabilities, $s_w = (S_w-S_{wi})/(1-S_{wi}-S_{or})$, $s_o = (1-S_w-S_{or})/(1-S_{wi}-S_{or})$, $a = 1.635$ and $b = 5$ [see Figure 8(b), where starred quantities refer to chemical flooding]. Oil and water viscosities are 3.50 and 0.6 cP, respectively. The maximum surfactant adsorption is $q_{max} = 0.38$ mg/g [see Figure 9(c)], whereas the alkaline one is 0.07 mg/g; polymer adsorption is negligible within experimental errors. Two sets of relative permeabilities have been used [see Figure 9(b)]: the first one is the waterflooding reference corresponding to a capillary number of $6.2 \times 10^{-8}$ $(\ln N_c = -16.6)$; the second set is drawn for the value of a capillary number of $9.1 \times 10^{-4}$ $(\ln N_c = -7)$, corresponding to the ASP experiment. The intermediate sets are interpolated depending on the current value of the capillary number.

The main features of the displacement are reproduced in Figure 9. The simulated tertiary oil recovery is in excellent agreement with the experimental values, as well as the pH [see Figures 9(a) and 9(d)]. In addition, the surfactant-mobilized oil bank breakthrough reported in Figure 9(c) is in excellent agreement with the recovery factor shown in Figure 9(a), without any significant time (or injected pore volume) shift. The surfactant recovery is well represented although the surfactant breakthrough occurs slightly earlier in the modeling [see Figure 9(b)].

The results of Figure 9 have been checked for several cell numbers, reasonable time steps and numerical material balance constraints, without noticing any relevant difference: they have been obtained straightforwardly from the measured experimental data without any adjustable parameter(s) tuning or numerical cooking, which proves not only the ability of Sarip$^{14}$ to match a
complex ASP coreflood in a rather simple manner, but also the simulator’s predictability and reliability, which look pretty good. Indeed, as explained above, the final objective of an ASP process feasibility study is to forecast pilot-scale oil recovery performance, which first clearly means being able to predict one production history without any adjustable parameter(s) unrealistic tuning: clearly, this very first but touchy step is fully achieved with SaripCH.

The ASP laboratory coreflood is successfully modeled with SaripCH taking into accounts the aqueous reactions, alkali/rock interactions, and phase behavior of surfactant. Such modelling can help to improve the oil recovery and screen the major factors responsible of the relatively low performance. Surfactant is still recovered in the effluent, meaning that surfactant adsorption is not the limiting factor. However interfacial tensions are not low enough to mobilize the residual oil. Improvements should be achieved by optimizing surfactant formulation/injection scheme. The very low permeability must also be remembered. A forthcoming paper will present a pilot-scale ASP process feasibility study, including five-spot numerical simulations and process optimization.

Conclusions

We have reported an integrated workflow for designing optimal conditions for chemical EOR operations, relying on complementary expertise between IFP and Rhodia in different domains: physico-chemistry, high throughput screening technics, experienced core flood instrumentation and analysis, simulations using the right physics.

Our chemical EOR workflow is based on:

- A fast identification of the best chemicals suitable for given field conditions using robotized technics that enable fast and accurate solubility screening, phase diagram and interfacial tension screening for optimal formulation design.
- An extensive optimization study in order to closely adjust chemical composition and ensure overall formulation efficiency and robustness;
- Core flood experiments for adsorption measurement and oil recovery determination which validate performances of selected chemical formulation(s) and define simulation input data.
- An insight into the propagation of the various chemical additives in the core and aid in future coreflood and field-scale ASP designs.
- Simulations using a detailed physics that simulate very accurately experimental results. Only a limited number of easily accessible experimental data are necessary, almost no fitting data are used; this make theses simulations easily predictive.
- An optimization of injection strategy and extrapolation to pilot design.

References


