Fuel 215 (2018) 484–491

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Surfactant-less alkali-cosolvent-polymer floods for an acidic crude oil

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ARTICLE INFO

Keywords:
Alkali
Cosolvent
Polymer
Surfactant
Enhanced oil recovery
Interfacial tension

ABSTRACT

Alkali-surfactant-polymer floods can increase the oil recovery in many reservoirs by lowering interfacial tension (IFT). Surfactants are the most expensive chemicals in these processes. However, surfactant requirement is low in case of crude oils which contain naphthenic acids. These acids with the addition of an alkali generate in-situ soap which results in lowering the oil-water IFT. The goal of this work is to investigate if surfactants can be eliminated from the formulation in case of sufficiently acidic crude oils to reduce the cost. Low IFT formulations were obtained by varying the alkali concentration in the absence of synthetic surfactants. A cosolvent was added to lower the viscosity of microemulsions and to obtain the low IFT region in the desired salinity range. Various cosolvents were systematically tested to obtain the desired phase behavior. For comparison, alkali-surfactant-polymer (ASP) and alkali-cosolvent-polymer (ACP) formulations were developed for the same crude oil using synthetic surfactants. One-dimensional ASP and ACP corefloods were performed in sandstone cores to test these formulations. The ASP coreflood showed 84.5% oil recovery and 0.1 mg/g-rock surfactant retention in a Berea core. ACP corefloods showed 80–90% oil recovery in Berea cores and minimal cosolvent retention, and 97% recovery in a Boise core. The study shows that comparable oil recoveries could be obtained from ASP and ACP corefloods for a sufficiently acidic crude oil, provided the cosolvent selection is performed carefully.

1. Introduction

It is well-known that a substantial amount of oil is left unrecovered after secondary floods in oil reservoirs due to large capillary forces. Surfactants that can lower the oil-water interfacial tension (IFT) and thus improve the recovery, have been investigated for many decades. Several laboratory surfactant floods, as well as few pilot studies, showed a substantial increase in oil recovery on injecting surfactants [1–5]. In addition, recent studies have reported much lower surfactant retentions in surfactant floods as compared to those reported in the past, thus making surfactant floods more economical than before [6]. Many new surfactants have been found to be suitable under extreme conditions of high temperature, salinity, and hardness, thus extending the application of surfactant floods to such reservoirs [7–11]. The polymer is added to surfactants to promote stable displacement and improve the sweep efficiency. Hydrolyzed polyacrylamide (HPAM) and Xanthan gum are most commonly used polymers. Significant advances have been made to develop polymers which have improved stability under extreme conditions of high temperature and high hardness. Polyacrylamide based polymers containing additional functional groups such as N-Vinyl Pyrrolidone (NVP) and Acrylamido-tert-butyl-sulfonate (ATBS) are more tolerant of high salinity and high temperature conditions [12,13]. In addition, improved biopolymers such as Scleroglucan have been investigated for chemical EOR applications [14]. An alkali is often added to surfactants and polymers in chemical formulations. Alkalis help in lowering the surfactant adsorption on rock surfaces. In addition, it generates in-situ soap on reacting with the naphthenic acids present in the crude oil [15–17]. Sodium hydroxide (NaOH), sodium silicate (Na_2SiO_3) and potassium hydroxide (KOH) were first used for alkali floods [18,19]. However, these alkalis interacted strongly with reservoir rocks resulting in scaling issues. Sodium carbonate was found to be less reactive and has since become the standard alkali in chemical floods [20]. Recently, new alkalis have been investigated which were found to be advantageous over conventional alkalis in special situations [21–24].

Although significant advances have been made towards improving the understanding of surfactant floods and making them more robust and economical, the current low oil price situation makes it challenging to apply these processes in some fields. The objective of this study is to develop a cheaper alternative to ASP flood for an acidic crude oil. ACP floods have recently been developed for viscous oils [25,26]. In this process, an alkali is added to generate soap on interaction with the acidic components of the crude oil, which in-turn lowers the IFT. A small amount of cosolvent is added to lower the viscosity of the microemulsion phase and obtain the low IFT region in the desired salinity window [27]. In addition, cosolvents help in obtaining a favorable

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https://doi.org/10.1016/j.fuel.2017.11.079
Received 17 November 2017; Accepted 21 November 2017

Nomenclature

ACP	Alkali-cosolvent-polymer
AMPS	2-Acrylamide-2-methylpropane sulfonic acid (AMPS)
ASP	Alkaline-surfactant-polymer
ATBS	Acrylamido-tert-butyl-sulfonate
CO_2	Carbon dioxide
DI	Deionized water
HPAM	Hydrolyzed polyacryamide
HPLC	High performance liquid chromatography
IBA	Isobutyl alcohol
IFT	Interfacial tension
IOS	Internal olefin sulfonate
KOH	Potassium hydroxide
md	Millidarcy
NaCl	Sodium chloride
Na_2CO_3	Sodium carbonate
NaOH	Sodium hydroxide
Na_2SiO_3	Sodium silicate
NVP	N-vinyl pyrrolidones
OOIP	Original oil in place
ppm	Parts per million
PV	Pore volume
TDS	Total dissolved solids

salinity gradient. The polymer is added to obtain a stable displacement and improve the sweep efficiency. Cosolvents are typically low molecular weight alcohol-based compounds having about six carbons. These compounds are cheaper compared to traditional surfactants [25,28].

The goal of this study is to develop ACP formulations for a light acidic crude oil and compare the performance to an ASP formulation for the same oil. Surfactant phase behavior experiments were performed first to develop an ultralow ASP formulation. An ASP coreflood was conducted in a sandstone reservoir core to evaluate the oil recovery. This result serves as the base case for this study. ACP formulations were developed with the same crude oil to obtain ultralow IFT formulations with low microemulsion viscosities. The type and amount of cosolvent were varied systematically. Based on the phase behavior results, three ACP formulations were chosen for oil recovery corefloods in sandstone cores. ACP corefloods were performed using these formulations and the results were compared with the results of the ASP coreflood. The experiments conducted in this study are listed in Table 1.

2. Methods and materials

2.1. Materials

Chemical agents used in this study consisted of salts, alkalis, surfactants, polymers, and cosolvents. Laboratory grade salts such as sodium chloride (NaCl) and alkalis such as sodium carbonate (Na_2CO_3) were obtained from Fisher Scientific. Internal olefin sulfonate (IOS) and alcohol propoxy sulfate surfactants were obtained from Shell chemicals. Some cosolvents such as isobutyl alcohol (IBA) were obtained from Huntsman chemicals, while other cosolvents such as IBA ethoxylates and Phenol ethoxylates were obtained from Harcros chemicals. Polymers such as Flopaam 3330S and Flopaam 3630S were obtained from SNF (Cedex, France). The cores used in this study consisted of outcrop and reservoir sandstone cores. The outcrop cores were obtained from Kocurek industries (Caldwell, Texas). The crude oil used was an acidic crude oil having the viscosity of 14 cP at 59 °C and an acid number of 2.0 mg KOH/g oil.

2.2. Phase behavior experiments

Phase behavior experiments were performed to identify ultralow IFT formulations for conducting ASP and ACP corefloods. The phase behavior experiments with surfactants involved mixing oil and aqueous solutions in a ratio. The aqueous solution consisted of a fixed amount of surfactant (with or without a cosolvent), a fixed amount of base formation brine and varying amounts of sodium carbonate. The sodium carbonate concentration was systematically increased in increments of 0.25 wt% or 0.5 wt%. Keeping the sodium carbonate concentration constant, the oil to water ratio was changed from 1:9 to 1:1. Phase behavior experiments for different oil-to-water ratios were performed to study the effect of in-situ soap (generated on adding sodium carbonate). Different combinations of alcohol alkoxy sulfate and IOS surfactants were tested to identify an ultralow IFT surfactant formulation with aqueous stability at the optimum salinity. In addition, the slope on the activity map guided the selection of surfactants. A negative slope is desirable to effectively achieve a negative salinity gradient in corefloods. After preparing the phase behavior samples in 4 mL glass pipettes, argon was passed through the samples and the tubes were sealed using a propane torch. The samples were equilibrated at 59 °C and mixed from time to time. The solubilization ratios of oil and water were obtained after the samples were equilibrated. Alkali-surfactant-cosolvent samples, which did not contain oil, were prepared similarly to obtain the aqueous stability information of surfactant formulations.

Phase behavior experiments were similarly conducted to obtain ultralow IFT ACP formulations. In these experiments, no surfactant was added to the aqueous phase, so the aqueous phase consisted of salts, alkalis, and cosolvent. Cosolvent concentrations in these phase behavior experiments were typically set to 0.4–0.5 wt%. The type of cosolvent was systematically varied to obtain an ultralow IFT formulation which was aqueous stable at the reservoir condition and gave a reasonable slope on the activity map. IFT values (between microemulsion-aqueous phases) of ACP formulations around optimum salinity were measured by a Kruss spinning drop tensiometer.

2.3. Oil recovery corefloods

Oil recovery corefloods were performed at 59 °C in outcrop sandstone cores to test ASP and ACP formulations. The dimensions and mass of a core were recorded, after which it was placed in a coreholder and an overburden pressure of about 700 psi was applied. Air porosity and permeability were measured. The air from the core was removed next by applying many vacuum/CO_2 cycles. The core was then placed in a convection oven and saturated with formation brine. Next, brine

Table 1
List of experiments.

Phase Behavior Experiments	
A1	ASP phase behavior experiment using $C_{12\text{-}13}$-PO-SO_4 and IOS surfactants
A2	ACP phase behavior experiment using 0.5% IBA as the cosolvent
A3	ACP phase behavior experiment using 0.5% IBA-2PO as the cosolvent
A4	ACP phase behavior experiment using 0.5% Phenol-1PO-2EO as the cosolvent
Oil Recovery Corefloods	
B1	Oil recovery ASP coreflood in Berea sandstone core using the ASP formulation A1.3
B2	Oil recovery ACP coreflood in Berea Sandstone using the ACP formulation A2
B3	Oil recovery ACP coreflood in Berea Sandstone using the ACP formulation A3
B4	Oil recovery ACP coreflood in Boise Sandstone using the ACP formulation A4
B5	Oil recovery ACP coreflood in Berea Sandstone using the ACP formulation A4
B6	Oil recovery ACP coreflood in Berea Sandstone using the ACP formulation A4