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A triblock copolymer for polymer flood in porous media

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ABSTRACT

High molecular weight polymers are used in petroleum reservoir polymer floods to enhance oil recovery. The objective of this work is to evaluate small polymeric surfactants for their viscosifying capacity in reservoir brines and oil displacement ability. The phase behavior and viscosity of a triblock copolymer (P123) are studied as a function of brine salinity and temperature. Its flow through a porous rock and oil displacement is evaluated and compared with that of a Newtonian fluid (glycerol) and a non-Newtonian fluid with a high molecular weight polymer (HPAM) of similar viscosity. P123 forms cylindrical micelles in brine to give high viscosity. The viscosity increases with salinity at a low salinity, but decreases at a higher salinity. In the secondary mode, both the polymers (P123 and HPAM) and glycerol solutions increase the oil recovery significantly over the water flood. The oil recovery is similar for the three viscous fluids. In the tertiary mode, none of the viscous fluids increased oil recovery over the waterflood at typical field rates. Pressure drop during P123 flood is significantly lower than the pressure drop during HPAM and glycerol floods of similar initial viscosity. Viscosity of the aqueous P123 solution decreases when it is equilibrated with oil. Some of the cylindrical micelles are converted to spherical micelles in the presence of solubilized oil. P123 is not as cost effective as HPAM because it is slightly more expensive and needs a higher concentration for a similar viscosity.

1. Introduction

Since less than half of the original oil in a subterranean petroleum reservoir is produced through primary (depressurization) and second recovery (mostly water flooding) techniques, it is necessary to utilize enhanced oil recovery (EOR) techniques to increase the ultimate recovery of oil (Lake, 1989). Chemical, miscible gas, and thermal recovery techniques are being developed to increase oil recovery. One of the promising techniques within chemical methods is polymer flooding. Typically a high molecular weight (about 10–20 million Dalton) polymer is mixed with brine and injected (Sorbie, 1991). Polymer flooding increases oil recovery by increasing the sweep efficiency and decreasing water fractional flow because of favorable viscosity ratio between the oil and the polymeric solution (Green and Willhite, 1998). It is suitable for viscous oils because waterflood sweep efficiency is low due to viscous fingering and permeability heterogeneity. Polymer flooding typically does not increase the microscopic displacement efficiency of light oils, though recent studies show that viscoelastic polymeric solution may be able to improve the microscopic displacement efficiency over that of the waterflood (Delshad et al., 2008; Wang et al., 2010).

The typical polymers used for polymer flood are synthetic polymer hydrolyzed polyacrylamide (HPAM) and biopolymer Xanthan gum. There are temperature and salinity limits for the use of these polymers. Chemical, mechanical, and biological degradations must be avoided during the use of these polymers (Molloy et al., 2000; Levitt and Pope, 2008, 2010). The viscosity of the solution increases as the molecular weight increases at constant polymer concentration. The molecular weight of the typical polymers used is in the range of 10–20 million Dalton (Donaldson et al., 1985). The hydrodynamic radius of these polymers is of the order of microns and they have difficulty flowing through low permeability porous rocks (e.g. 10 mD or lower).

It is possible to viscosify water with small molecules if they associate. Some cationic surfactants, such as hexadecyltrimetrimethylammonium bromide (CTAB) (Rehage and Hoffmann, 1991; Lin et al., 1994; Candau and Oda, 2001) and nonionic (Acharya and Kunieda, 2003) surfactants, as well as some triblock polymers (Chu, 1995; Hamley, 2001; Nakashima and Bahadur, 2006; Aswal et al., 2007; Dreiss, 2007) can self-assemble into long, flexible cylindrical micelles to impart useful viscoelastic properties. Unlike ordinary polymers, cylindrical micelles are in equilibrium with their monomers, and micellar chains can reversibly break and recombine and are therefore called “living polymers” (Candau et al., 1985) or “equilibrium polymers”. It would be useful to identify an assembled system which could break into smaller aggregates and pass through the pore throats of low permeability rocks as well as aggregate in pore bodies and give high viscosity.

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Nomenclature

CTAB	hexadecyltrimetrimethylammonium bromide
IFT	interfacial tension
OOIP	original oil in place
WOR	water to oil ratio
HPAM	hydrolyzed polyacrylamide
NaCl	sodium chloride
$CaCl_2$	calcium chloride
$MgCl_2$	magnesium chloride
cP	centipoise
CTAB	hexadecyltrimetrimethylammonium bromide
pv	pore volume
Soi	initial oil saturation
WF	water flood
PF	polymer flood
RRF	residual resistance factor
Sor	residual oil saturation
THF	tetrahydrofuran

Triblock copolymers such as Pluronics (EOm–POn–EOm) are small molecules (MW < 10,000); they are called "polymeric surfactants" because of their amphiphilic nature. Ethoxy (EO) blocks are hydrophilic, whereas the propoxy (PO) blocks are hydrophobic and this hydrophobicity increases with temperature. The aqueous solution of P123, a Pluronic, starts to become cloudy at about 50 °C (Ganguly et al., 2005; Chaibundit et al., 2008) and phase separates at about 93 °C (Bharatya et al., 2007). Because of their amphiphilic nature triblock copolymers form micelles in water at certain temperatures. In a salinity and temperature range, these micelles are cylindrical which leads to increased viscosity of the aqueous solution. The goal of this work is to evaluate the applicability of these small block copolymers as a viscosifying agent for polymer floods in porous rocks.

The aqueous phase behavior of a triblock copolymer is studied in brines typical of oil fields. The viscosity behavior is observed as a function of brine salinity. The phase behavior of the equilibrated oil–brine-triblock copolymer is evaluated. The rheology of the aqueous solution is studied during flow in a porous rock. Then a viscous oil is displaced by this block copolymeric solution in a porous rock and this behavior is compared with those by the traditional HPAM polymeric solution and a glycerol solution (Newtonian) of about the same viscosity. The next section outlines the methodology. The third section describes the results followed by the conclusions.

2. Experimental methodology

2.1. Materials

A tri-block copolymer P123 (PEO20–PPO70–PEO20) and glycerol (from Sigma Aldrich) were obtained at 99% purity. Hydrolyzed polyacrylamide (HPAM3330) was obtained from SNF. Its molecular weight was 8×10^6 and it has 25–30% degree of hydrolysis. Sodium chloride (NaCl), calcium chloride ($CaCl_2$), and magnesium chloride ($MgCl_2$) were obtained from Fisher Scientific. Except glycerol, all the other chemicals were solid and were prepared in distilled water. The base brine composition was set to 5 wt% NaCl, 1 wt% $CaCl_2$, and 0.5 wt% $MgCl_2$, typical of many oil reservoir brines. Oil was obtained from a petroleum reservoir and had a viscosity of 103 cP at 25 °C.

2.2. Physical properties

Polymer P123 was added to the brine and its phase behavior was studied as a function of salinity and temperature. 2 ml oil was mixed with 2 ml P123 solution in a thin, graduated, 5 ml borosilicate glass pipette, which was flame sealed at the top. If not stated otherwise, the P123 solution refers to 1 wt% P123 in brine with 5 wt% NaCl, 1 wt% $CaCl_2$ and 0.5 wt% $MgCl_2$. The sample was equilibrated by shaking from time to time. The interfacial tension (IFT) between oil and P123 solution was measured by in a Ramé-Hart Goniometer by using the pendent drop method. Viscosity of aqueous solutions was measured with a Contraves low shear viscometer at 1 s^{-1} and with an ARG2 rheometer as a function of shear rate from 1 to 100 s^{-1}. Particle size within the aqueous phase was measured by a Delsa™ Nano C particle analyzer using dynamic light scattering.

2.3. Core preparation

All 3 cores (Berea #1–#3) approximately 1 ft long and 1.5 in. in diameter were drilled, dried, and weighed. A vacuum pump was used to evacuate air from the core and several pore volumes of CO_2 were flushed to remove the air. Next, the cores were flooded with brine containing 65,000 ppm total dissolved solids including 50,000 ppm NaCl, 10,000 ppm $CaCl_2$ and 5000 ppm $MgCl_2$. Pressure data were recorded and brine permeability was calculated. The core #2 and #3 were then flooded with a viscous oil (103 cP) at a high pressure gradient (~100 psi) until no water was produced in the effluent. Table 1 describes the composition of brine and polymer solutions used and Table 2 lists the properties of all Berea sandstone cores. All coreflood experiments were performed at 25 °C.

2.4. Core flood

Seven different core floods were performed. One core flood was conducted for P123 solution single phase flow in the absence of oil. For each viscosifying agent (P123, HPAM, and Glycerol) core floods were performed in similar cores, and under similar conditions. Three floods were conducted under secondary condition, i.e., the core was at high oil saturation with connate brine when the viscous solution was injected. Three corefloods were conducted in tertiary conditions, i.e., viscous solutions were injected after a water flood. Capillary end effect was minimal because of water-wet conditions, one-foot long cores, and high pressure drops.

2.4.1. Single phase flow

The Berea #1 core was injected with brine at the rate of 1 ft/day, 2 ft/day, 4 ft/day, and 8 ft/day and the pressure drops were measured. After brine flow, P123 solution was injected at the

Table 1
Composition of brine and polymer solutions for core flood.

Chemical/viscosity	Brine (wt%)	P123 (wt%)	HPAM (wt%)	Glycerol (wt%)
Polymer		1	0.28	60
NaCl	5	5	5	5
$CaCl_2$	1	1	1	1
$MgCl_2$	0.5	0.5	0.5	0.5
Viscosity (cP) @ 10 s^{-1}	1	11	11	11