

Application of Ultrashort Hydrophobe Surfactants with Cosolvent Characters for Heavy Oil Recovery

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ABSTRACT: A new class of ultrashort hydrophobe surfactants with cosolvent characters was investigated as a sole additive to conventional polymer flooding for heavy oil recovery. No alkali was used for emulsification. The surfactants were composed of a short hydrophobe (phenol in this research) extended by propylene oxide (PO) and ethylene oxide (EO) units to achieve a sufficient level of surface activity and aqueous stability: phenol-*x*PO-*y*EO. Results are presented for the selection of ultrashort hydrophobe surfactants, aqueous stability, emulsion phase behavior, and oil displacement through a glass-bead pack at 368 K. Results show that 2 wt % phenol-4PO-20EO was able to reduce the interfacial tension between oil and NaCl brine to 0.39 dyn/cm, in comparison to 11 dyn/cm with no surfactant, at 368 K. Water flooding, 40 cp polymer flooding, and surfactant-improved polymer flooding were conducted for displacement of 276 cp heavy oil through a glass-bead pack that represents the clean-sand facies of a heavy oil reservoir in Alberta, Canada. The oil recovery after 2.0 pore volumes of injection (PVI) was 84% with the surfactant-improved polymer flooding, which was 54 and 22% greater than the water flooding and the polymer flooding, respectively. Results suggest a new opportunity of enhanced heavy oil recovery by adding a slug of one nonionic surfactant with cosolvent characters to conventional polymer flooding.

1. INTRODUCTION

The U.S. Geological Survey estimated that there exists more than 3300 billion bbls of heavy oil and 5500 billion bbls of bitumen resources in the world, and approximately 34% of the total heavy oil and bitumen resources are distributed in North America.¹ The efficiency of heavy oil recovery is strongly affected by the viscosity of in situ reservoir oil ranging from 50 to 50 000 cp.² Canadian extra-heavy oil or bitumen is even more viscous.³ Widely used recovery methods for heavy oil include cyclic steam stimulation and steam-assisted gravity drainage. However, these methods may be inefficient and/or impractical for shallow and/or thin reservoirs, including many heavy oil reservoirs in Alaska and Canada.^{2,4}

Polymer flooding is another method that has been widely used for heavy oil recovery, in which the displacing phase with an increased viscosity improves the conformance control under reservoir heterogeneity and lowers the mobility ratio for oil displacement. Field pilots of polymer flooding include East Bodo, Suffield Caen, and Seal in Canada.^{5–7} Large-scale polymer flooding was successfully conducted in Pelican Lake in Canada.⁸ In the Pelican Lake case, the incremental oil recovery after polymer flooding was 10–25% of the original oil in place (OOIP), in which heavy oil of 800–10 000 cp was displaced by a polymer of 20–25 cp.⁹ Polymer flooding was performed in an offshore heavy oil field in Bohai Bay in China.¹⁰ After 3 years of polymer flooding, however, the incremental oil recovery was reported to be approximately 4%. Thereafter, surfactant-polymer (SP) flooding was implemented.¹¹

Heavy oils typically contain acidic hydrocarbon components, a part of which can be used as natural surfactants after the mixing and reaction with alkalis, such as sodium carbonate, sodium hydroxide, ethanolamine, and ammonium hydrox-

ide.^{12–14} Therefore, alkali-surfactant-polymer (ASP) flooding has been studied for heavy oil recovery. ASP flooding is designed to achieve Winsor type III microemulsion phase behavior during the oil displacement,¹⁵ with in situ natural surfactants, synthetic surfactants, cosolvent, and other additives.^{16,17} Optimal ASP flooding achieves a high displacement efficiency by microemulsion phase behavior with ultralow interfacial tension (IFT) and a high volumetric sweep efficiency by the use of the polymer.

Conventional screening criteria indicate that ASP flooding can be used effectively when the oil viscosity is below 200 cp.¹⁸ Sheng reported 32 field projects of ASP flooding, most of which were in China (19 projects) with oil viscosities lower than 50 cp.¹⁷ ASP flooding, however, has been also studied for more viscous oil. Laboratory experimental results show substantial incremental oil recovery by ASP flooding for oils with viscosities from 320 to 500 cp,^{19–21} 2000 cp oil,²² and 16 000 cp oil.²¹ ASP floods for heavy oil in Canada include Taber South (Husky), Crowsnest (Husky), Suffield (Cenovus), and Mooney (BlackPearl). The ASP flooding resulted in an incremental recovery of 11.1% of the OOIP for 120 cp oil in Taber South,²³ 10% for 480 cp oil in Shuffield,²⁴ and 9% for 440 cp oil in Mooney.^{25,26}

Reported issues of ASP flooding include insufficient injectivities caused by calcite and silica scales, which were attributed partly to the injected alkalis.^{27,28} For example, Alberta Energy Regulator reported the scale plugging and injectivity problems in the ASP flooding projects in Taber

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South (Husky) and Suffield (Cenovus).²⁹ To avoid the problems of alkali injection, there are a limited number of laboratory scale experimental studies of SP flooding for heavy oil recovery.^{28,30} They used self-assembled betaine surfactants and a mixture of olefin sulfonates, alkyl aryl sulfonates, alkyl ether sulfates, and alkyl glyceryl ether sulfonates that created ultralow IFT microemulsions with their heavy oil without using alkali.^{28,30}

ASP flooding may involve a large number of chemicals to be injected, which tends to make the implementation of ASP flooding more complicated and costly. Alkali-cosolvent-polymer (ACP) flooding has been recently studied as a simpler alternative for heavy oils, in which only alkali and cosolvent were injected with no synthetic surfactant.^{19,31,32} They used isobutanol (IBA), alkoxyated IBA (e.g., IBA-2EO, IBA-5EO, IBA-10EO, and IBA-2PO), alkoxyated phenol (phenol-1PO-2EO) as cosolvents. Their results show ultralow IFT microemulsions at experimental conditions and highly efficient corefloods.

Upamali et al. recently investigated the potential advantage of using short hydrophobe cosolvents and surfactants.³³ They used alkoxyated IBA (IBA-3EO, IBA-10EO, IBA-30EO, and IBA-1PO-2EO) and alkoxyated phenol (phenol-1PO-2EO, phenol-1PO-5EO, phenol-2EO, and phenol-4EO) as a cosolvent for conventional surfactants and achieved ultralow IFT type III microemulsion phase behavior. They also used 2-ethylhexanol- x PO sulfate as a surfactant along with a conventional surfactant to show ultralow IFT type III microemulsion phase behavior. According to their study, the advantages of short hydrophobe cosolvents and surfactants include short equilibrium time for microemulsion formation, low microemulsion viscosity, and low retention in cores.

Previous studies of short hydrophobe cosolvents and surfactants were focused on ASP or ACP flooding that achieves an ultralow IFT between the displaced and displacing phases.^{19,31–33} Their aqueous formulations consisted of an alkali, one or more surfactants, cosolvents for ASP flooding, and an alkali with one or more cosolvents for ACP flooding.

This paper presents the first investigation into the application of ultrashort hydrophobe surfactants as a sole chemical additive that improves the displacement efficiency of polymer flooding for heavy oil recovery. Use of an ultrashort hydrophobe surfactant with no alkali is not expected to achieve ultralow IFT with heavy oil. Hence, the proposed method may be more properly denoted as “surfactant-improved polymer flooding” than SP flooding which achieves ultralow IFT between the displacing and displaced phases.

Section 2 describes the materials used for this research. Section 3 presents the phase behavior of heavy oil emulsification with new surfactants. Results of oil-displacement experiments and fractional flow calculation are presented in Section 4. The potential advantage of ultrashort hydrophobe surfactants is summarized in Section 5. Finally, key conclusions are given in Section 6.

2. MATERIALS

This section describes the materials for two types of experiments: phase behavior and displacement experiments. Materials for phase behavior experiments include oil, brine, and surfactants. In addition to these, a porous medium and polymer are explained for the displacement experiments.

2.1. Oil. Dehydrated Athabasca bitumen was used as heavy oil in this research. The experiments were conducted at 368 K, at which the

oil viscosity was measured to be 276 cp. The SARA composition is 24.5 wt % saturates, 36.6 wt % aromatics, 21.1 wt % resins, and 17.8 wt % asphaltene (*n*-pentane insoluble). The acid number of bitumen was measured to be 3.56 mg-KOH/g-oil based on the method of Fan and Buckley.³⁴ More data of this oil sample can be found in Baek et al.^{3,35}

2.2. Brine. The initial and injection water were 5 wt % NaCl and 0.1 wt % NaCl, respectively. The simple brine composition with no hardness allowed us to focus on evaluating the effect of the surfactant on heavy oil recovery.

2.3. Surfactants. Ultrashort surfactants were made by alkoxylation of phenol, that is, phenol- x PO- y EO, where x is the number of propylene oxide (PO), and y is the number of ethylene oxide (EO). In this research, x and y were set to be 4–7 and 5–40, respectively. Phenol- x PO- y EO surfactants were provided by Harcros Chemicals. Below is an explanation of the selection of this ultrashort hydrophobe surfactant for this research.

Phenol was selected as the basis for the surfactant's hydrophobicity. Its aromatic structure is known to be compatible with asphaltene-rich heavy oil because the steric effect of the benzene ring can reduce the size of asphaltic components' aggregation.³⁶ Larichev et al. presented that planar molecules (e.g., cyclic structures) could fit into the asphaltene structure and replace asphaltene molecules with relatively small hydrocarbons.³⁶

The alkoxylation of phenol causes surfactant properties and aqueous stability. The PO and EO groups are related to hydrophobicity and aqueous stability of a surfactant, respectively. A larger number of PO results in a higher level of hydrophobicity. Depending on brine salinity, brine hardness, and temperature, EO number should be adjusted for aqueous stability. Chang et al. discussed details of alcohol alkoxyated and other surfactants along with cosolvents.³⁷

In this research, we attempt to minimize the PO and EO numbers added to phenol because the main objective of this study is to test ultrashort hydrophobe surfactants for improved polymer flooding for heavy oil recovery. Phenol-1PO- x EO studied by Upamali et al. and Sharma et al. did not give desirable emulsion phase behavior with the heavy oil studied in this research.^{32,33} It was found that four is the minimum PO number to create oil-in-water (o/w) emulsions with the heavy oil studied. Therefore, the PO numbers of 4 and 7 were investigated. Then, the EO numbers ranged from 5 to 30 for phenol-4PO- y EO and from 5 to 40 for phenol-7PO- y EO.

2.4. Polymer. Hydrolyzed polyacrylamide (HPAM) polymer, Flopaam 3630S, was used for polymer flooding and improved polymer flooding with the glass-bead pack described below. The polymer concentration was 0.22 wt %, which gave a viscosity of approximately 40 cp at injection conditions, corresponding to the field conditions of interest (seven times less viscous than the displaced oil). Figure 1 gives the measured viscosities of the polymer solution at different shear rates at 368 K. The polymer solution viscosity clearly decreased with increasing brine salinity. The effect of the surfactant addition on the polymer solution viscosity was not observed.

2.5. Glass-Bead Pack. A cylinder was packed with glass beads as a porous medium. The cylinder is 50 cm long, and its internal volume is 8.2 mL. The porous medium contained particles with diameters ranging from 106 to 125 μ m (sieve number 120). The porosity and permeability of the porous media were measured to be 33% and 9.5 darcy, respectively, representing the clean-sand facies of a heavy oil reservoir in Alberta, Canada.

3. PHASE BEHAVIOR EXPERIMENTS

An optimal surfactant was selected among phenol-4PO- y EO ($y = 5, 10, 15, 20, 25,$ and 30) and phenol-7PO- y EO ($y = 5, 10, 15, 20, 30,$ and 40) by conducting aqueous stability tests first and then emulsion phase behavior tests at 368 K. Phenol-4PO-20EO was eventually selected for subsequent displacement experiments (Section 4). This section presents the main results in these screening steps.

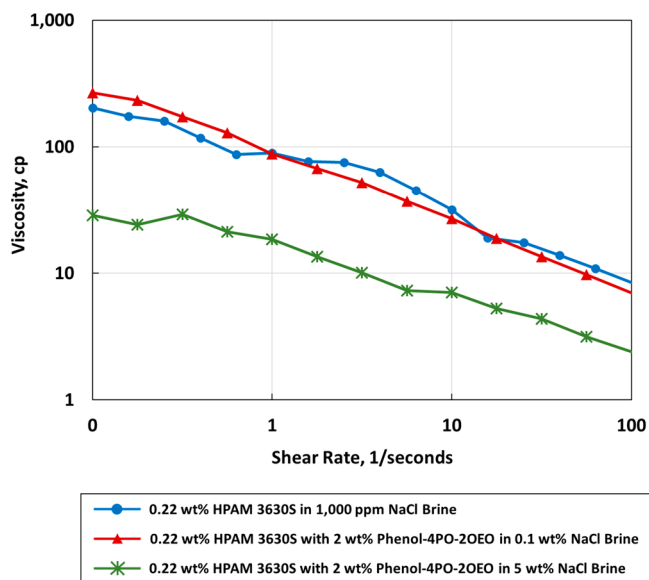


Figure 1. Polymer solution viscosity at 368 K. 0.22 wt % Flopaam 3630S was used for polymer flooding and surfactant-improved polymer flooding. The target viscosity of polymer solution was about 40 cp at an estimated shear rate for the injection rate. The polymer solution viscosity clearly decreased with increasing brine salinity. The effect of the surfactant addition on the polymer solution viscosity was not observed.

A total of 12 surfactants were subjected to aqueous stability tests at three surfactant concentrations (0.5, 1, and 2 wt %) in the injection brine (0.1 wt % NaCl). Samples were aged at four different temperatures (298, 313, 353, and 368 K) for 2 days. Aqueous stability was confirmed by visual observation as to whether the solution was clear or cloudy (opaque), and whether it showed any phase separation. Table 1 shows that six surfactants passed the aqueous stability test at 368 K, the temperature for the subsequent displacement experiments. They are phenol-4PO-*y*EO (*y* = 15, 20, 25, and 30) and phenol-7PO-*y*EO (*y* = 30 and 40).

These surfactants were subject to emulsion phase behavior tests with mixtures of oil/surfactant/brine. The objective was to find low-IFT o/w emulsions at 368 K. For each sample, 4 mL of the solution was prepared in an 8 mL borosilicate test tube. Samples were prepared at three different surfactant concentrations (0.5, 1, and 2 wt % in the aqueous phase) with six different salinities (0, 0.1, 0.5, 1, 2, and 3 wt % NaCl). The water–oil ratio was fixed at 7:3 (i.e., 70 vol % aqueous phase and 30 vol % oil). Samples were aged at 368 K for 5 days before reporting the phase behavior.

Table 2 presents that 13 samples with four surfactants resulted in low IFT o/w emulsions: phenol-4PO-*y*EO, where *y* = 20 and 25, and phenol-7PO-*y*EO, where *y* = 30 and 40. Figure 2 shows these o/w emulsion samples. The emulsions in this figure are macroemulsions that are not stable. They were separated into the oil and water phases by the 7th day after mixing. Emulsion samples were evaluated by visual observation in terms of fluidity, color, and droplet size in the emulsion phase. It was determined that phenol-4PO-20EO and phenol-7PO-30EO were the most suitable surfactants, but the former was selected for further analysis because of the shorter hydrophobe. The solution of 2 wt % phenol-4PO-20EO with 0.1 wt % NaCl brine was selected as the injection surfactant

Table 1. Aqueous Stability Test of New Surfactants^a

surfactant	surfactant concentration (wt %)	stability: S (stable), C (cloudy), PS (phase separation)			
		temperature			
		298 K	313 K	353 K	368 K
phenol-4PO-5EO	0.5	S	S	C	C
	1	S	C	C	C
	2	S	C	C	PS
phenol-4PO-10EO	0.5	S	S	S	C
	1	S	S	C	C
	2	S	S	C	C
phenol-4PO-15EO	0.5	S	S	S	S
	1	S	S	S	C
	2	S	S	S	C
phenol-4PO-20EO	0.5	S	S	S	S
	1	S	S	S	S
	2	S	S	S	S
phenol-4PO-25EO	0.5	S	S	S	S
	1	S	S	S	S
	2	S	S	S	S
phenol-4PO-30EO	0.5	S	S	S	S
	1	S	S	S	S
	2	S	S	S	S
phenol-7PO-5EO	0.5	S	C	PS	PS
	1	C	C	PS	PS
	2	C	C	PS	PS
phenol-7PO-10EO	0.5	S	S	PS	PS
	1	S	C	PS	PS
	2	S	S	PS	PS
phenol-7PO-15EO	0.5	S	S	C	PS
	1	S	S	S	PS
	2	S	S	S	PS
phenol-7PO-20EO	0.5	S	S	S	PS
	1	S	S	S	PS
	2	S	S	S	PS
phenol-7PO-30EO	0.5	S	S	S	S
	1	S	S	S	S
	2	S	S	S	S
phenol-7PO-40EO	0.5	S	S	S	S
	1	S	S	S	S
	2	S	S	S	S

^aAqueous brine salinity was 0.1 wt % NaCl.

solution viscosified by the polymer for the subsequent displacement experiments.

The critical micelle concentration (cmc) for phenol-4PO-20EO was measured to be 0.008 wt % by the pendant drop method, as shown in Figure 3. The IFT between the selected surfactant solution and oil was measured to be approximately 0.39 dyn/cm at 368 K by the spinning drop method. In comparison, the IFT between oil and 0.1 wt % NaCl brine at 368 K is approximately 11 dyn/cm.³⁸

The IFT measurement for the surfactant solution and oil was repeated with the 0.05 wt % HPAM polymer in the aqueous phase and resulted in 0.41 dyn/cm, which is close to IFT with no polymer. It was not possible to measure the IFT at higher polymer concentrations because an oil droplet did not elongate properly in the viscous phase surrounding it. Previous studies indicated that the effect of the polymer on the IFT between the aqueous and oleic phases depends on oil

Table 2. General Phase Behavior of Oil Emulsification with New Surfactants^a

phenol-4PO-xEO					phenol-7PO-xEO				
EO #	salinity [wt %]	surfactant concentration [wt %]			EO #	salinity [wt %]	surfactant concentration [wt %]		
		0.5	1.0	2.0			0.5	1.0	2.0
15	0	N			30	0	N	o/w	o/w
	0.1	N				0.1	N	o/w	o/w
	0.5	N				0.5	N	N	N
	1	N				1	N	N	N
	2	N				2	N	N	N
	3	N				3	N	N	N
20	0	N	o/w	o/w	40	0	N	o/w	o/w
	0.1	N	o/w	o/w		0.1	N	N	N
	0.5	N	N	N		0.5	N	N	N
	1	N	N	N		1	N	N	N
	2	N	N	N		2	N	N	N
	3	N	N	N		3	N	N	N
25	0	N	o/w	o/w	30	0	N	N	N
	0.1	N	N	o/w		0.1	N	N	N
	0.5	N	N	N		0.5	N	N	N
	1	N	N	N		1	N	N	N
	2	N	N	N		2	N	N	N
	3	N	N	N		3	N	N	N
30	0	N	N	N	30	0	N	N	N
	0.1	N	N	N		0.1	N	N	N
	0.5	N	N	N		0.5	N	N	N
	1	N	N	N		1	N	N	N
	2	N	N	N		2	N	N	N
	3	N	N	N		3	N	N	N

^aSamples were aged at 368 K. Only four surfactants resulted in low IFT o/w emulsion (o/w = o/w emulsion/N = no emulsion/blank = not tested).

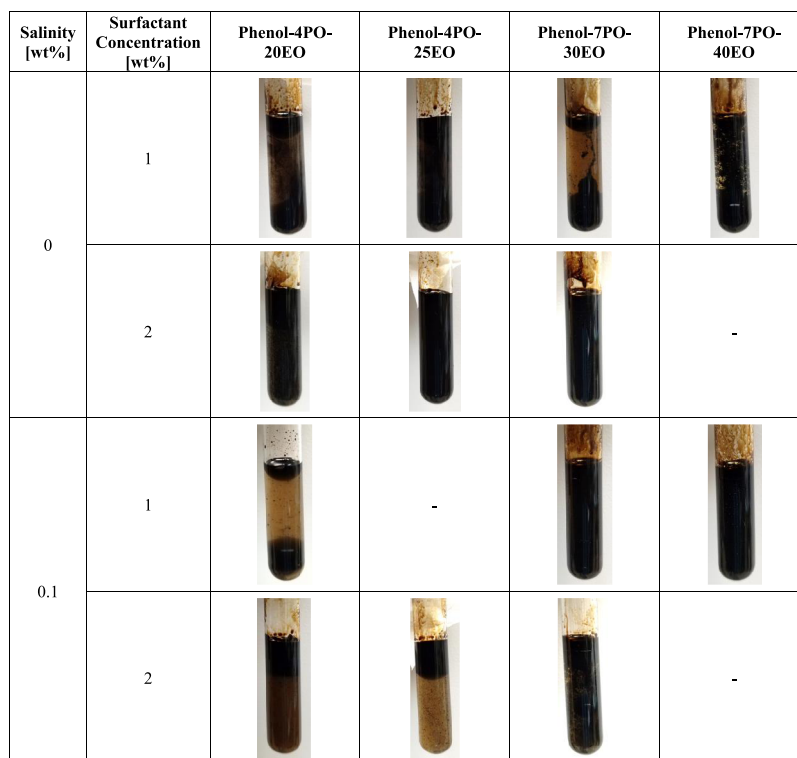


Figure 2. Emulsion phase behavior with new surfactants at 368 K. Phenol-4PO-20EO and phenol-7PO-30EO resulted in desired o/w emulsions.

composition, surfactant(s), and polymer among many other factors. Khan et al. found that the surface tension of an anionic surfactant (sodium dodecyl sulfate or sodium dodecylbenzene

sulfonate) solution increased with increasing polymer concentration (polyacrylamide, partially HPAM, or xanthan gum).³⁹ However, the range of cmc did not change significantly in their

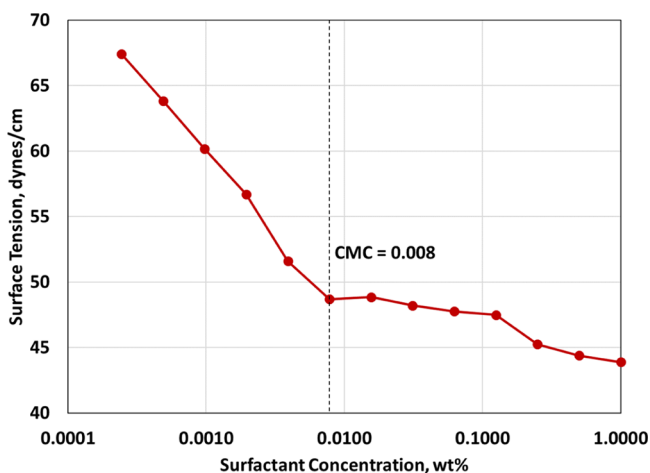


Figure 3. cmc of phenol-4PO-20EO was estimated to be 0.008 wt %. The IFT was measured by the pendant drop method.

research.³⁹ SiTu et al. reported that the IFT between *n*-decane and the mixture of benzyl-substituted alkyl sulfobetaine and polyether nonionic surfactant solution increased with increasing polymer concentration.⁴⁰ They used partly HPAM, hydrophobically modified polyacrylamide, and copolymer.⁴⁰ However, SiTu et al. also found that the HPAM polymer did not change the IFT between Daqing crude oil and the surfactant solution likely because of acidic components in the crude oil.⁴⁰ In this research, the acid number (3.56 mg-KOH/g-oil) and the IFT values measured with/without the 0.05 wt % HPAM polymer indicate that the IFT is approximately 0.4 dyn/cm between heavy oil and 2 wt % phenol-4PO-20EO solution with/without the HPAM polymer.

Although it is not ultralow, the IFT value of 0.39 dyn/cm is much lower than when the surfactant is not used. Indeed, it was observed that the emulsion and excess oil phases (Figure 2) mixed quite easily when it was flowing. Based on the method introduced in Kumar et al.,⁴¹ the excess oil phase in the sample was confirmed to be oil-external because it was dissolved in toluene but not in water.

The oil concentration in the emulsion phase with 2 wt % phenol-4PO-20EO was measured to be less than 1 vol %. The emulsion phase was actually transparent, light brown liquid. It is likely that the viscosity of this emulsion is similar to the viscosity of the external phase (brine or polymer).

Table 3. Summary of Oil Displacement Experiments

experiment		water flooding	polymer flooding	improved polymer flooding
glass-bead pack	porosity (%)	33	33	33
	permeability (darcy)	9.65	9.49	9.45
	oil viscosity at 368 K (cp)	276	276	276
	initial brine salinity	5 wt % NaCl	5 wt % NaCl	5 wt % NaCl
injection fluids (secondary flooding)	brine	0.1 wt % NaCl	0.1 wt % NaCl	0.1 wt % NaCl
	polymer	N/A	0.22 wt % Flopaam 3630S	0.22 wt % Flopaam 3630S
	surfactant	N/A	N/A	2 wt % phenol-4PO-20EO
	viscosity at shear rate 8 s ⁻¹	N/A	40 cp	40 cp
injection rate (mL/h)	0.2	0.2	0.2	
capillary number	3.4 × 10 ⁻⁸	4.4 × 10 ⁻⁶	1.2 × 10 ⁻⁴	
pore volume injection (PVI)	2	2	2	
water breakthrough (PVI)	0.2	0.5	0.7	
oil recovery at 1.0 PVI (%)	27	50	79	
oil recovery at 2.0 PVI (%)	30	62	84	

4. OIL DISPLACEMENTS AND FRACTIONAL FLOW CALCULATION

This section first presents the results of oil displacement experiments. Then, the fractional flow analysis will be presented to explain the experimental results.

4.1. Oil Displacements. Water flooding, polymer flooding, and improved polymer flooding by adding phenol-4PO-20EO were conducted. With the objective of quantifying the incremental recoveries by polymer and by surfactant-improved polymer, all displacements were conducted in the secondary-recovery mode. Table 3 lists the injection fluids for three cases. The short hydrophobe surfactant was injected as a part of two pore volumes of polymer solution for the surfactant-improved polymer flooding in this experiment, but it would be a slug for oil-displacement fronts in field applications.

Figure 4 shows a schematic of the experimental setup. There were three accumulators for oil, initial reservoir brine (5.0 wt %

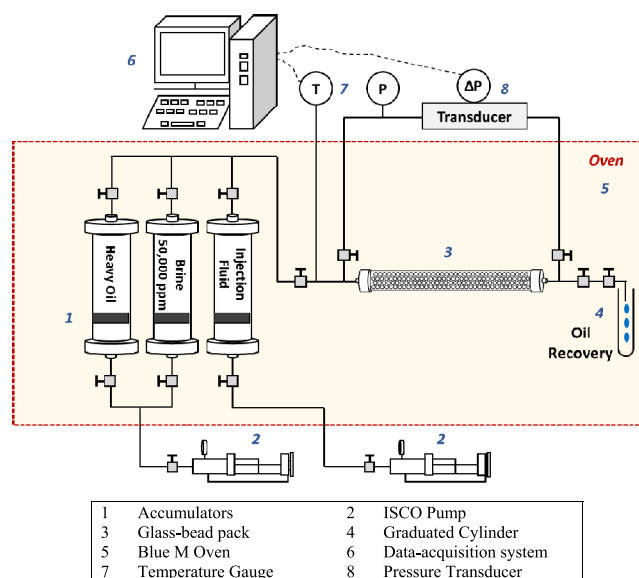


Figure 4. Schematic of the experimental setup for oil displacements.

NaCl), and injection fluids. The injection fluids were 0.1 wt % NaCl brine for water flooding, 0.22 wt % polymer in 0.1 wt % NaCl brine for polymer flooding, and 2 wt % phenol-4PO-20EO with 0.22 wt % polymer in 0.1 wt % NaCl brine for

improved polymer flooding. Pressure and flow rate of these fluids were controlled by ISCO pumps. The system temperature was kept at 368 K in a Blue M oven. System pressure and temperature were monitored and recorded by a data-acquisition system.

The general experimental procedure is described here. First, the porous medium and all flow lines were cleaned with toluene and dried at 368 K for one day. Next, the system was evacuated for at least 2 h. Then, the glass-bead pack was saturated with reservoir brine (5.0 wt % NaCl). Based on the volume injected, the pore volume of the glass-bead pack was measured. Reservoir brine was injected for several pore volumes to calculate the permeability of the glass-bead pack with Darcy's equation. Thereafter, the oil was injected. Reservoir brine was collected from the outlet during the oil injection. Oil breakthrough and water recovery were measured to determine the initial oil and water saturations for the subsequent oil-displacement experiment. Several pore volumes of oil were injected to estimate the end-point relative permeability to oil.

After the preparation, each oil-displacement experiment used 2.0 pore volumes of injection (PVI) at an injection rate of 0.2 mL/h, which corresponds to 1.0 ft/day in the porous medium. The corresponding shear rate in the porous medium was approximately 8 s^{-1} based on the correlation of Cannella et al.⁴² Oil recovery was measured by a graduated cylinder at the effluent. After 2.0 PVI, more than 200 mL of injection fluid was additionally injected to estimate the end-point relative permeability to the injection fluid.

The capillary number of the water flooding was 3.4×10^{-8} , which is in the normal range of water flooding.¹⁶ The capillary number of the polymer flooding was 4.4×10^{-6} because of the increased viscosity of the displacing fluid. The capillary number of the improved polymer flooding was 1.2×10^{-4} because of the IFT reduction by the surfactant (2 wt % phenol-4PO-20EO).

The three rows from the bottom in Table 3 give a summary of results from the oil displacements. Figure 5 presents the cumulative oil recovery for each flooding experiment. The water flooding case defines the basis for evaluating the polymer

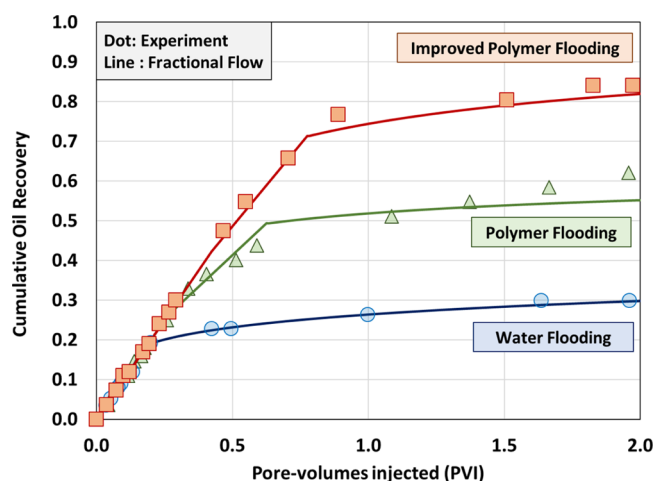


Figure 5. Oil displacement results: the cumulative oil recovery factors at 2 PVI was 30% for water flooding, 62% for polymer flooding, and 84% for surfactant-improved polymer flooding. The oil recovery data were matched by fractional flow calculation by using the parameters given in Figure 6.

flooding, which in turn gives the basis for evaluating the surfactant-improved polymer flooding. The oil recovery at 1.0 PVI was 27% for the water flooding case, 50% for the polymer flooding case, and 79% for the surfactant-improved polymer flooding. The oil recovery at 2.0 PVI was 30% for the water flooding case, 62% for the polymer flooding case, and 84% for the surfactant-improved polymer flooding. The surfactant added to the polymer solution yielded an incremental recovery of 29% in comparison to the polymer flooding case at 1.0 PVI.

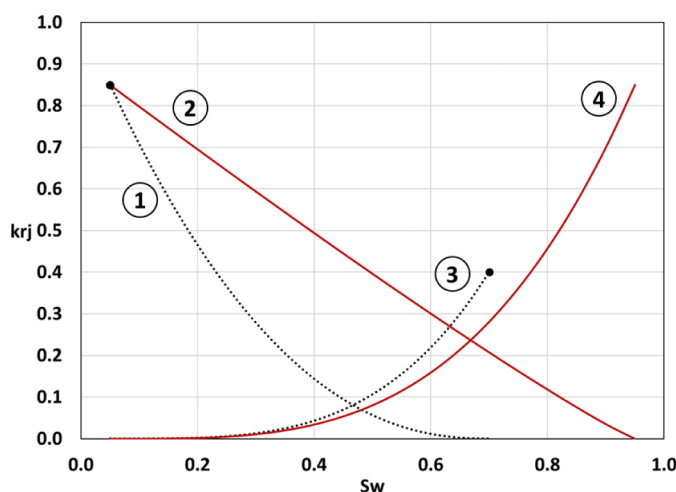
The water flooding showed the water breakthrough at 0.2 PVI, which resulted from the adverse effect of low-viscosity water on the efficiency of oil displacement by water. The polymer flooding case showed a delayed breakthrough around 0.5 PVI, which resulted in a two-fold increase in oil recovery at 2.0 PVI in comparison to the water flooding case. The surfactant-improved polymer flooding showed the breakthrough around 0.7 PVI resulting in the aforementioned increase in oil recovery in comparison to the polymer flooding. This improvement by the surfactant addition to polymer was attributed to the lowered IFT (Section 3) because this is the main difference from the polymer-alone injection. The effect of lowered IFT on polymer flooding was confirmed by matching experimental results with fractional flow theory in the following section.

4.2. Fractional Flow Calculation. Results from the oil displacement experiments were matched by fractional flow theory.⁴³ The main purpose was to evaluate the effect of the reduced IFT on the improved polymer flood in comparison to the water and polymer floods.

It was assumed that there was no oil in the emulsion phase during the improved polymer flooding. This assumption was validated by the phase behavior test that resulted in less than 1 vol % of oil in the emulsion phase (Section 3). Therefore, the viscosity of the displacing fluid for the improved polymer flooding was the same as the polymer solution viscosity.

Figure 6 presents the relative permeability curves required to match the data for water flooding, polymer flooding, and improved polymer flooding. The end-point relative permeabilities for heavy oil and brine (dots) were measured during the experiment. The end-point relative permeability for the SP solution and the exponent of each curve were calibrated to match the breakthrough times and oil recoveries.

The capillary end effect for each oil displacement was estimated by Rapoport and Leas number.⁴⁴ The scaling coefficient for the polymer flooding and the improved polymer flooding was $42.3 \text{ cp}\cdot\text{cm}^2/\text{min}$, indicating no capillary end effect. The scaling coefficient of the water flooding was $0.33 \text{ cp}\cdot\text{cm}^2/\text{min}$ that might indicate the possibility of the capillary end effect. Therefore, the fractional flow was matched with the polymer flooding first. The water flooding was matched with the same relative permeability curves that were used for the polymer flooding. Next, a new set of relative permeability curves was constructed with the lowered residual oil saturation for the improved polymer flooding from 0.3 to 0.05. This residual oil saturation reduction was attributed to the reduced IFT by the surfactant addition, which is the main difference between the polymer flood and the improved polymer flood. Figure 5 shows that the fractional flow curves are in good agreement with the cumulative oil recovery data. In particular, the agreement in terms of water and polymer breakthrough times can be confirmed by the changes in the oil production rate (changes in slope in Figure 5). Figure 5 also shows the agreement in terms of the ultimate oil recovery factors.



1	k_{ro} (Water flooding, Polymer flooding)	3	k_{rw} (Water flooding, Polymer flooding)
2	k_{ro} (Improved polymer flooding)	4	k_{rw} (Improved polymer flooding)

	Water Flooding Polymer Flooding	Improved Polymer Flooding
S_{wr}	0.05	0.05
S_{or}	0.3	0.05
k_{rw}^o	0.4	0.85
k_{ro}^o	0.85	0.85
n_w	3.6	3.4
n_o	2.3	1.1

Figure 6. Relative permeability for the fractional flow calculation (Section 4.2). The same relative permeability curve was used for water flooding and polymer flooding. A relative permeability curve was constructed for improved polymer flooding. The shaded parameters in the table were measured and shown as dots in the figure. The other parameters were determined by matching the oil-displacement results.

5. POTENTIAL ADVANTAGE OF ULTRASHORT HYDROPHOBE SURFACTANTS

The improved polymer flooding results suggest a potential opportunity of enhanced heavy oil recovery by using a simple nonionic surfactant as a sole additive to widely used polymer flooding. Results so far indicate that the proposed method relies on the effect of ultrashort hydrophobe surfactants on oil displacement efficiency. The ultrashort hydrophobe surfactants are designed to have multiple functions in one compound. It has characters of cosolvent (i.e., phenol in this paper), and its PO and EO units, respectively, give the hydrophobicity and hydrophilicity. The aqueous stability of the surfactant at the desired temperature and brine composition can be found by changing the EO number. As shown with phenol- x PO- y EO in this paper, the optimal selection of surfactants for given oil displacement can be performed in a systematic manner.

Unlike the conventional SP and ASP flooding, the proposed method of enhanced heavy oil recovery does not achieve ultralow IFT (e.g., 10^{-3} dyn/cm); however, using only one additive to the traditional polymer flooding yields the simplicity of the method implementation. In general, ASP flooding requires various types of chemicals: alkali, polymer, surfactant, cosurfactant, and cosolvent. The design and implementation become inevitably more complicated as the number of additives increases.

Also, the ultrashort hydrophobe surfactants are relatively less expensive than conventional surfactants; for example, the cost is expected to be about 1.25 USD/lb (100% active basis) because of the base solvent (e.g., phenol in this paper) is not expensive and because they are nonionic surfactants. Furthermore, the nonionic ultrashort hydrophobe surfactants

are expected to be less affected by surfactant loss due to the adsorption on rock surfaces.^{31,33} This would also contribute to simpler and less expensive implementation.

6. CONCLUSIONS

This paper presented an experimental study of the phenol- x EO- y PO surfactant as a sole additive to conventional polymer flooding for heavy oil recovery. The optimal EO and PO numbers were found in terms of emulsion phase behavior and aqueous stability at 368 K. Displacements of heavy oil (276 cp at 368 K) through a glass-bead pack were conducted by water flooding, polymer flooding, and surfactant-improved polymer flooding. These oil displacements were compared to quantify the effect of the simple nonionic surfactant with the cosolvent character on heavy oil displacement efficiency by the polymer. Key conclusions are as follows:

1. Phenol-4PO-20EO was selected as an optimal surfactant for improved polymer flooding at 368 K for the heavy oil studied in this research. The IFT between the selected surfactant solution and heavy oil was measured to be 0.39 dyn/cm at 368 K. This is substantially lower than the value, 11 dyn/cm, for oil and 0.1 wt % NaCl brine at 368 K.
2. The selection of an optimal surfactant can be performed in a systematic manner as demonstrated with phenol- x PO- y EO in this research. This nonionic surfactant was made by the alkoxylation of phenol, a cosolvent that shows a high level of affinity for the heavy oil studied in this research. Then, the optimal ranges of EO and PO numbers were found at reservoir conditions in terms of temperature and brine salinity.

- The improved polymer flooding resulted in 79% oil recovery after 1.0 PVI. It was 52% more recovery than water flooding and 29% more recovery than polymer flooding. The polymer flooding improved the oil recovery efficiency by increasing the water viscosity. The polymer flooding was improved by the addition of 2 wt % phenol-4PO-20EO, which reduced the IFT between the displacing and the displaced phases. Fractional flow theory along with the experimental results indicated that the lowered IFT resulted in the significant reduction of residual oil saturation during the improved polymer flooding.
- The results suggest a new opportunity of enhanced heavy oil recovery by adding a slug of one multifunctional surfactant with the cosolvent character to conventional polymer flooding. The injection solution was composed of one nonionic ultrashort hydrophobe surfactant and one polymer without any alkali, cosurfactants, and cosolvents. Depending on the cost of the base solvent (e.g., phenol in this research), the cost of the ultrashort hydrophobe surfactant can be lower than conventionally used surfactants for ASP and SP. Future research tasks include the investigation of ultrashort hydrophobe surfactants as an additive that improves water flooding in low-permeability reservoirs.

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Notes

The authors declare no competing financial interest.

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