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Hydrophobic Polymers Flooding

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Additional information is available at the end of the chapter

Abstract

Crude oil and other petroleum products are crucial to the global economy today due to increasing energy demand approximately (~1.5%) per year and significant oil remaining after primary and secondary oil recovery (~45-55% of original oil in place, OOIP), which accelerates the development of enhanced oil recovery (EOR) technologies. Polymer flooding through hydrophobically associated polyacrylamides (HAPAM) is a widely implemented EOR-technique, so they attracted much attention on both academic and industrial scales. Hydrophobically associating polyacrylamide (HAPAM) prepared by free radical emulsion polymerization of acrylamide (AM) monomer, divinyl sulfone as hydrophobic crosslinked moiety and surfmers, to chemically anchor a surfmer and hydrophobic crosslinker moiety onto the back bone of acrylamide chain. After that, polymeric nanocomposite was prepared through copolymerization of prepared HAPAM with different molar ratios of silica nanoparticles through one shot synthesis. Rheological properties for the prepared composites were evaluated. Wettability evaluation carried through quantitative and qualitative techniques where the results indicate novel polymers ability to alter rock wettability from oil-wet to water- wet.

Keywords: hydrophobic polymers, wettability alteration, enhanced oil recovery, polymerization, surfmers

1. Introduction

Crude oil is the most critical energy source in the world, especially for transportation, provision of heat and light as there has not been a sufficient energy source to replace crude oil has broadly integrated (i.e., today's energy needs are met in large part by crude oil). Petroleum products are crucial to the global economy today due to increasing energy demand approximately 1.5% per year [1] associated with population growth and improving life styles, limited proven oil reserves (i.e., shortage of current oil resources), declining oil production since 1995, difficulties in finding a new oil field, nonproductive primary and secondary recovery, significant oil remaining after secondary recovery (~45–55% of original oil in place, OOIP), and forecasts for tightening oil supply which driving the need to maximize the extraction of the original oil in place for every reservoir, and accelerating the development of enhanced oil recovery (EOR) technologies. EOR can be defined as any processes that increase oil recovery by reduction of the residual oil saturation (S_{or}) after primary and secondary production. Indeed, EOR techniques refer to any process that involves the injection of a fluid not normally present in the reservoir (e.g., polymers, foams, and surfactants) where the injected fluids interact with a crude oil/brine/rock (COBR) system to create favorable conditions, which maximize oil recovery [2]. Tertiary or enhanced oil recovery techniques include chemical, thermal, and miscible flooding [3] for recovering up to 40% of the OOIP. Thermal EOR involves injection of steam or hot water to reduce heavy oils viscosity, thus improving its flow. Miscible methods employ hydrocarbon gases (natural gas and flue gas) nitrogen, supercritical CO_2 to displace oil from a depleted oil reservoir. Gas flooding improves oil recovery by dissolving in, swelling, and reducing the viscosity of oil. Chemical flooding was, up to 2000s, less common EOR method than thermal and gas flooding but now, huge projects are initiated or revisited. In chemical EOR methods, an agent that is not normally present in the reservoir is injected to enhance the oil displacement. The chemical flooding processes involve injection of three kinds of chemicals: alkaline, surfactant, and polymer (soluble and cross-linked polymers), in addition to other chemicals such as foaming agents, acids, and solvents [4] and/or combination of alkaline-surfactant-polymer (ASP) flooding, and surely the most important substance in these methods is polymer flooding [5]. In the polymer flooding method, water-soluble polymers aimed to reduce mobility of displacing fluid leading to a more efficient displacement of moderately viscous oils. Addition of surfactant to the polymer formulation may, under very specific circumstances, reduce oil-water interfacial tension (IFT) and hence remobilizing the trapped oil [6], changing the wettability of the surface, forming emulsions, so enhance the oil production. For all chemical flooding processes, inclusion of a viscosifier (usually a water-soluble polymer) is required to provide an efficient sweep of the expensive chemicals through the reservoir. To increase the oil recovery efficiency in oil-wet reservoirs (unswept regions), different techniques have to be pursued [7].

(1) Improving volumetric sweeping efficiency by adjusting the oil/water mobility ratio through polymer flooding agents, which increase displacing fluid viscosity in order to modify the viscous forces being applied to drive oil out of the pores [8], thus increasing the produced crude oil amount. A polymer solution has increased viscosity and decreased

relative permeability so it is an attractive option to decrease the mobility ratio and increase the volumetric sweep efficiency of the injection [9].

(2) Altering the wettability of porous reservoir rock surfaces to more water-wet (i.e., by letting the value of contact angle $\theta \leq 90°$) [10]. The success of wettability alteration is seen as the increment in percentage of recovered oil, depending on natural wettability [11].

(3) Increase the oil displacement effectiveness by overcoming the capillary barrier through viscous and gravitational forces, so water can invade the rock matrix (i.e., modifying permeability) and displace the oil. Reduction of capillary pressure forces can be achieved by surfactants flooding to lower the oil-water interfacial tension (IFT) to ultralow values ~10^{-3} dyne cm^{-1} [12] which allow spontaneous or nearly spontaneous emulsification and displacement of the oil [13, 14].

2. Surfactants nature and applications in EOR

Surfactants are surface-active components, low to moderate molecular weight polar compound, consisting of an amphiphilic molecule, with a water soluble hydrophilic part called "head" (anionic, cationic, amphoteric, or nonionic) and a water insoluble hydrophobic part called "tail" [15] as shown in **Figure 1**. Surfactants used in EOR applications in order to [16]:

(1) Reduce interfacial tension between the trapped oil and injected aqueous phase to ultralow values (0.001 mN M−1) thereby increasing the capillary number (N_c) by a factor of at least three order of magnitude and reduce capillary force, which decrease the oil contact angle so alters wettability [17] consequently, trapped oil solubilization and mobilization increase.

(2) Alteration of matrix rock wettability toward more water-wet conditions, which would increase the brine-imbibition rates.

(3) Modify the properties of polymeric systems for a variety of applications [18].

(4) Surfactants are widely used in oil recovery for particle dispersion, emulsion stabilization, foam generation, reservoir wetting, and many other applications [19, 20].

(5) Favorable surfactant should characterized by low adsorption on reservoir rocks and, long-term surfactant stability under reservoir conditions (temperature, brine salinity, and hardness) and appropriate compatibility with reservoir fluids, especially tolerance to divalent cations such as Ca^{2+} and Mg^{2+}.

Depending upon the nature of the hydrophilic head group, the surfactants are classified, as shown in **Figure 2**, into the following:

(1) **Anionic**: the surface-active portion of the molecule (hydrophilic group) bears a negative charge such as carboxyl ($RCOO^-M^+$), sulfonate ($RSO_3^-M^+$), sulfate ($ROSO_3^-M^+$), or phosphate ($ROPO_3^-M^+$) (e.g., $RC_6H_4SO_3^-Na^+$, alkyl benzene sulfonates).

(2) **Cationic**: the surface-active portion bears a positive charge such as the quaternary ammonium halides ($R_4N^+X^-$) (e.g., $RNH_3^+Cl^-$, salt of a long chain amine).

(3) **Amphoteric (zwitterionic)**: where the molecule contains both a negative and a positive charge on the principal chain (surface-active portion) such as the sulfobetaines, $RN^+(CH3)_2CH_2CH_2SO_3^-$ (e.g., $RN^+H_2CH_2COO^-$, long chain amino acid).

(4) **Nonionic**: where the surface-active portion (hydrophilic group) bears no apparent ionic charge (has no net charge) but gets its water solubility from highly polar groups such as polyoxyethylene (POE or $ROCH_2CH_2O^-$), sugars, or similar groups (e.g., $RCOOCH_2CHOHCH_2OH$, monoglyceride of long chain fatty acid).

Surfactant flooding in enhanced oil recovery processes is considered uneconomical and remains challenging, especially in a high-salinity, high-temperature environment due to the following drawbacks:

(1) Loss of chemicals by adsorption in porous media [21], which dictate, the economics of an oil recovery or remediation process.

(2) Surfactant aggregates exhibit relatively low tolerance to divalent ions, salinity, and high-temperature condition $\geq 90^\circ C$ [22].

(3) As described by Austad and Taugbøl [23] and Berger et al. [24], high performance surfactants, greatly lower oil/water IFT, but do not favor capillary-driven imbibition during water flooding [25, 26].

These previously reported shortages made the one think in an alternative when speak about EOR project [27].
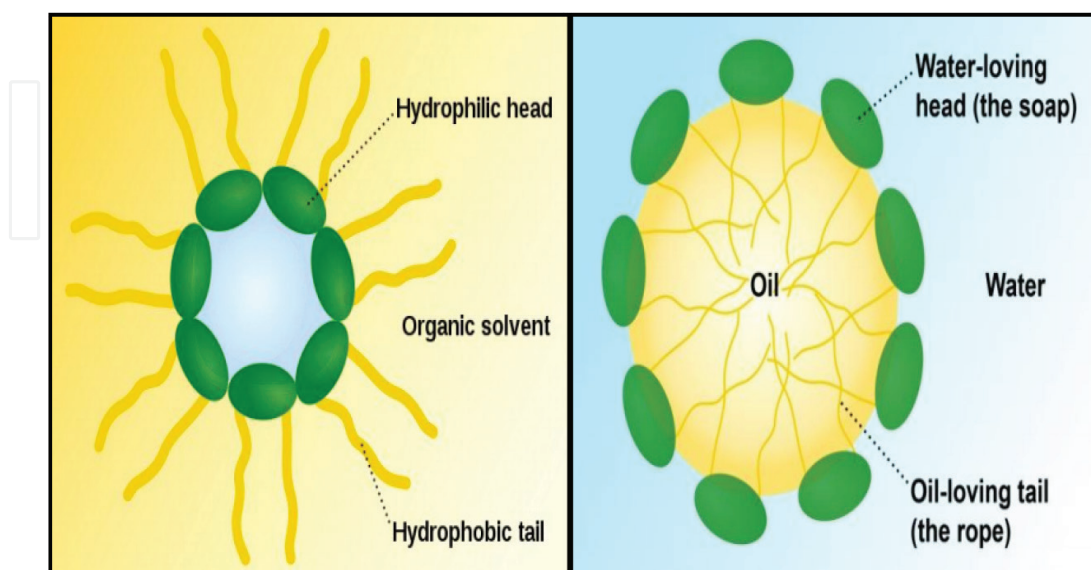
Figure 1. Surfactant skeletal structure (http://conf.sej.org/pollution-environmental-health/, 2011).
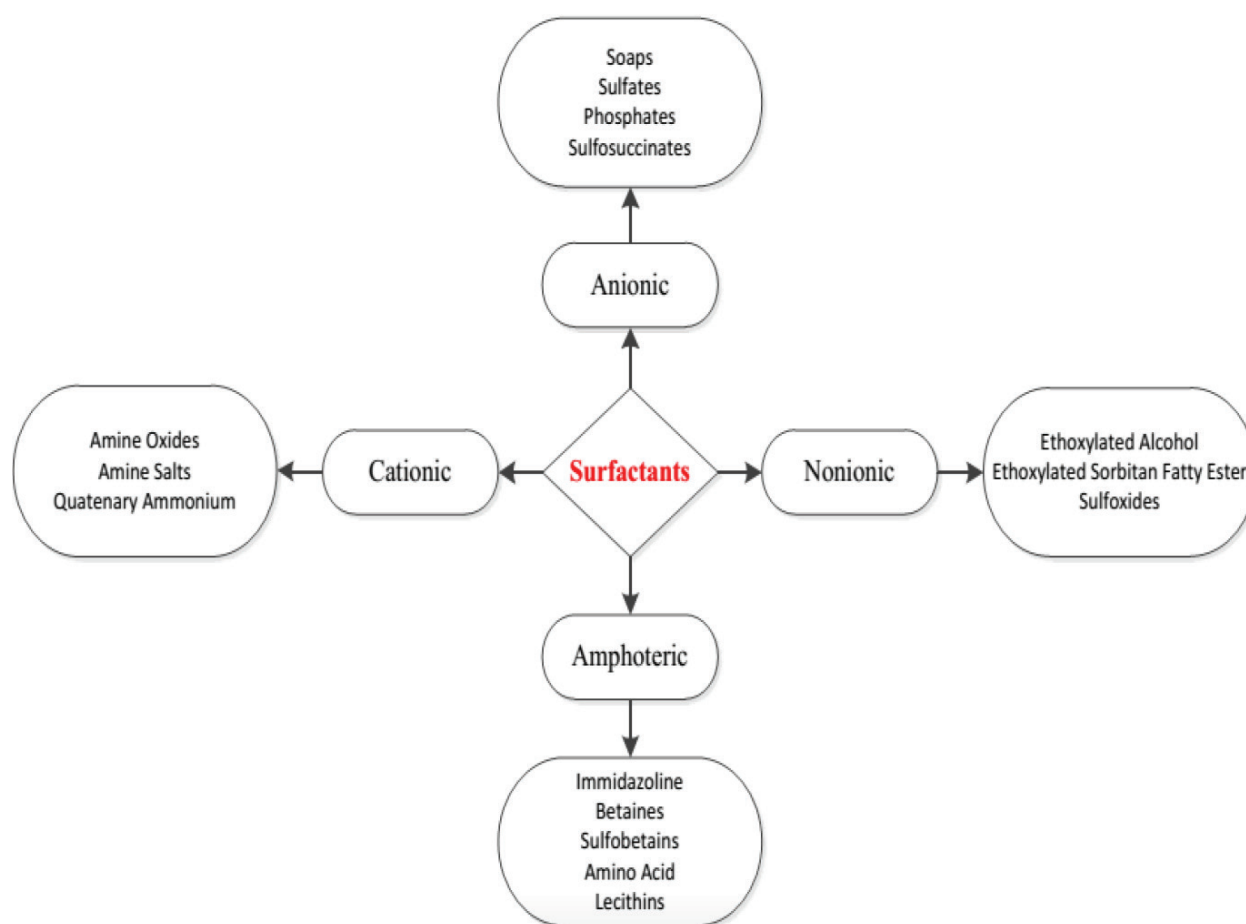
Figure 2. Classification of surfactants depending upon hydrophilic group nature.

3. Polymeric surfactants (surfmers)

Polymeric surfactants (surface-active monomers) are one kind of functional surfactants, which not only have amphiphilic structure composed of hydrophobic tail and hydrophilic head group [28], but also contain polymerizable vinyl double bonds [29] in their molecular architecture, resulting in novel physicochemical properties distinct from conventional surfactants [30] as follows:

(1) Analogous to common surfactants, they have surface activity and similar to vinyl monomers, they can be initiated and polymerized.

(2) Due to amphipathic property and polymerizability of surfmers, they can be used to synthesize inorganic/organic nanocomposite, can be applied to emulsion polymerization as polymerizable emulsifiers, to surface modification of solid substances, to synthesis of novel water-soluble hydrophobically associating polymers with strong thickening properties [31] so, they have great significance in enhanced oil recovery [32].

(3) Offer potential for developing hybrid-nanosized reaction and templating media with constrained geometries. Moreover, surfmer can be directly used as a hydrophobic monomer

to copolymerize with acrylamide (AM) forming hydrophobically associating polyacrylamide (HAPAM), which has been widely used in enhanced oil recovery, drilling fluids, coats, and paintings [33].

Freedman et al. [34] reported the first synthesis of vinyl monomers [35], which also functioned as emulsifying agents [36, 31]. Typical polymerizable groups that have been exploited are vinyl, allyl, acrylate, methacrylate, styryl, and acrylamide [37]. The position of the polymerizable group either "H-type" where the polymerizable group located in the hydrophilic head group, or "T-type" where the polymerizable group located in the hydrophobic tail have a profound effect on the surfactant self-assembly and properties [38, 39].

4. Wettability of porous media

Wettability defined as the preferential affinity of the solid matrix for either the aqueous phase or the oil phase "the tendency of one fluid (wetting fluid) to spread on or adhere to a solid surface in the presence of another immiscible fluid (nonwetting fluid)" [40]. Reservoir wettability is an important and elusive petrophysical parameter in all types of core analyses, which affect saturation and enhanced oil recovery processes [41]. There is a consensus in petroleum engineering that preferentially water-wet cores flood more efficiently than oil-wet cores; since, more oil is recovered from water-wet cores in the early flooding stages than from oil-wet cores [42]. This can be attained due to the strong wetting preference of the rock for water yields the most efficient oil displacement and due to imbibition phenomenon and other complex interactions occurring in the reservoir during production [43]. Modified polymers can affect markedly mineral wettability. The copolymer of acrylamide-methacrylamido propyl trimethyl-ammonium chloride can alter surface of oil-wet quartz with adsorbed dodecyl amine into water-wet one. Where the polymer masking the surfactant layer on the quartz particle accounts for the water wettability [44]. Consequently, in the present study, the authors try to prepare a copolymer and a nanocomposite modified by silica addition to alter wettability of sandstone rock from oil-wet to water-wet.

5. Principle and mechanism of polymer flooding for enhanced oil recovery

The polymer flooding process involves injection of polymer "slug" followed by continued long-term water flooding to drive the polymer slug and the oil bank in front of it toward the production wells, as shown in **Figure 3**. By water injection, it seeks layers of high permeability and since the oil is highly viscous as compared with injected water so, water will finger through oil resulting in decreased sweeping efficiency [5].

Mobility ratio (M) is defined as mobility of the displacing phase divided by the mobility of the displaced phase. Based on the principle of mobility ratio, water-soluble polymers reduce water mobility by two mechanisms: (1) increase the viscosity of the water phase and (2) reduce
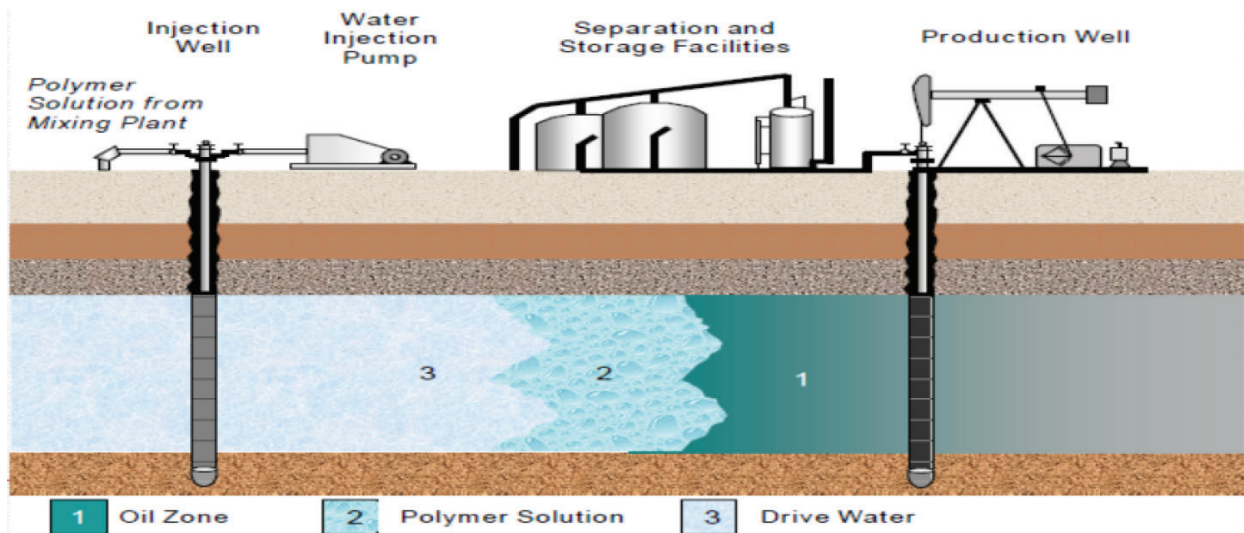
Figure 3. Polymer flooding mechanism.

the relative permeability of water to the porous rock by adsorption/retention of the polymer in the rock pore throats [45], and thereby creating a more efficient and uniform front to displace unswept oil from the reservoir (i.e., the mobility ratio (M) is inversely proportional to the water viscosity. With a reduced mobility ratio, the sweep efficiency is increased and, as a consequence, oil recovery is enhanced [46].

6. Hydrophobically associating polyacrylamide polymers (HAPAMs)

Hydrophobically associating polyacrylamide are prepared conveniently by micellar copolymerization of hydrophilic and hydrophobic monomers [47], or through grafting or incorporating hydrophobic chain cross-linking segments onto main chain of partially hydrolyzed polyacrylamide (HPAM). A lot of small molecule surfactants need to be added in order to enable the hydrophobic monomer to be solubilized into micelles, and the addition of small molecule surfactants brings many negative influences [30]. During HAPAM polymerization, hydrophilic surfmers dissolve in an aqueous phase resulting in homogeneous phase copolymerization of hydrophilic surfmers and acrylamide [48], which avoid drawbacks of surfactant addition. Moreover, above the critical micellar concentration (CMC) of surfmer, a microblock copolymerization mechanism carried out which means that a surfmer will be inserted into the backbone structure of acrylamide main chain, which gives rise to enhanced hydrophobic properties [49], stronger thickening property of HAPAM [50], and improved salinity resistance of HAPAM. As surfmer copolymerized with monomer and inserted in its main chain so surfmer separation from the polymer chain is prohibited [51]. These enhanced stability properties of polymers [52] have been reported for mechanical stability [53], electrolyte stability of the latex [54], a decrease of surfactant migration [51], and control of surface charge density [55]. Since surfactants are simply adsorbed onto the surface of particles in conventional emulsion polymerization, consequently increase emulsion stability by permanently fixing of the

head groups. It has been long desired to obtain nanosized latexes containing higher polymer contents at lower surfactant concentrations [56]. Moreover, it was realized many years ago that polymerization of surfactants can lead to well-defined polymeric surfactants and potentially to polymerized micelles [57]. Recently, monomers composed of hydrophobic tail groups and hydrophilic head groups as well as a polymerizable group have been investigated [58]. Introduction of ionic groups contained in surfmer into polymer chains will improve the water solubility accompanying with perturbation of the hydrophobic association resulting in lowering the thickening effect [59]. The presence of phenyl group in the surfmer structure is well known to induce stronger van der Waals interactions than typical aliphatic groups due to their planar and polarizable structure, so the incorporation of one or more aromatic group(s) can stabilize hydrophobic associations involving the alkyl chain. Furthermore, the benzene rings can act as spacers, increasing the rigidity of polymer chains [60]. Consequently, incorporation of phenyl rings into the polyacrylamide (PAM) backbone through surfmer will improve its flooding characteristics in EOR applications. In addition, introduction of cationic groups into the PAM structure increases water solubility [61, 62] and decreases the water phase permeability (K_w) as it flows through porous media, which improve oil recovery in oil-displacing applications [63]. Hydrophobic polymers have attracted much attention on both academic and industrial laboratories for polymer flooding in enhanced oil recovery [64, 65] owing to their unique characteristics [66] which can be summarized as follow;

(1) In aqueous solutions, above a critical association concentration (C*), their hydrophobic groups develop intermolecular hydrophobic associations in nanodomains, leading to building up of a 3D-transient network structure [67] in high ionic strength medium, so providing excellent viscosity building capacity [68, 69], remarkable rheological properties, and better stability with respect to salts than the unmodified HPAM precursors [70].

(2) Reduce interfacial tension at the solid/liquid interface, since hydrophobic moiety associates forming aggregates or micelles.

(3) Shows an unusual adsorption isotherm [71] so can be considered as a wettability modifier.

(4) Does not undergo mechanical degradation under high shear stress such as those encountered in pumps and near the well bore area, since the physical links between chains are disrupted before any irreversible degradation occurs, also they reform and retain their viscosity upon shear decreasing [72].

(5) High resistance to physicochemical conditions (temperature, pH, and ion content) prevailing around the wells, so considered a prospective EOR candidate as thickeners or rheology modifiers in high-temperature, high-pressure reservoirs [73–75], reservoir stimulation [76], and tertiary oil recovery [77].

In the present chapter, the authors try to overcome the shortage in chemical EOR candidates through synthesis of a novel surfmers (H-type) by the reaction of a 1-vinyl imidazole as a polymeric moiety containing double bond and 4-dodecyl benzene sulfonic acid surfactant, then hydrophobically associating polyacrylamide (HAPAM) prepared by free radical emulsion polymerization of acrylamide (AM) monomer, divinyl sulfone as a hydrophobic cross-linked

moiety and surfmers, to chemically anchor a surfmer and hydrophobic cross-linker moiety onto the hydrophilic backbone of acrylamide chain. After that a hydrophobically associating polyacrylamides-SiO$_2$ (HAPAM-SiO$_2$) nanocomposite was prepared through copolymerization of acrylamide monomer with silica nanoparticles through one-shot synthesis. The rheological properties of copolymer solutions were investigated with respect to the polymer concentration, shear rate, shear stress, temperature, and salinity. Moreover, evaluation of behavioral characteristics and performance of these copolymers solution on wettability alteration, mobility ratio reduction, interfacial tension (IFT) reduction, and recovered oil amount under harsh reservoir are also reported [78, 79].

7. Experimental design and procedure

7.1. PROTOCOL 1: synthesis of polymeric surfactant (surfmer)

The addition reaction was carried out in a 250 ml three-necked Erlenmeyer flask equipped with a reflux condenser, mechanical stirrer, and nitrogen inlet/outlet. Note that 0.106 mol of 1-vinylimidazole was added dropwise to 0.106 mol of 4-dodecyl benzene sulfonic acid in ethyl acetate (150 ml) in an ice bath under a N$_2$ atmosphere. The reaction mixture maintained at 0°C for 2 h and then stirred for 12 h at 45°C. The white product was precipitated and recrystallized in 50 ml ethyl acetate upon cooling [78]. The yield was about 73%. The proposed structure is shown in **Scheme 1**.

7.2. PROTOCOL 2: synthesis of HAPAM copolymer

An aqueous solution of acrylamide in distilled water was gently bubbled with nitrogen gas for 30 min. The emulsion polymerization was carried out as previously reported in our literature [78] where designated reactants as listed in **Table 1** were added in a jacketed autoclave under an inert nitrogen environment for 12 h at 60°C. After reaction completion, viscous polymer gel was precipitated by acetone, redissolved in water, and reprecipitated in acetone then subjected to Soxhlet extraction with methanol for 24 h until a white solid obtained. The proposed structure is shown in **Scheme 2**.
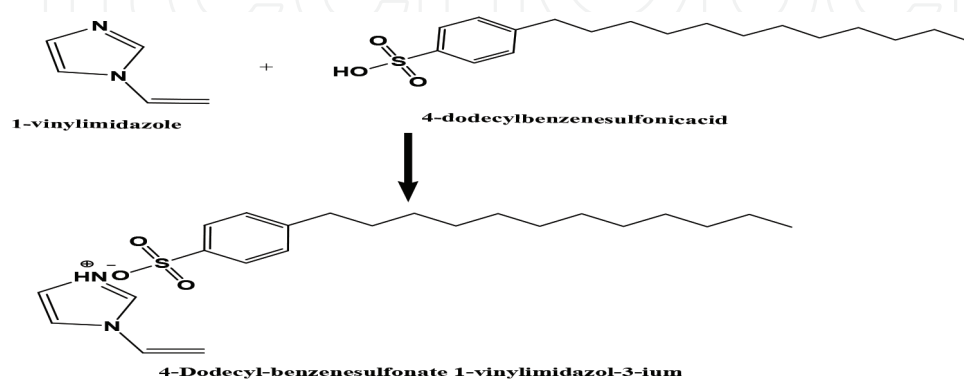


Scheme 1. Structure of surfmer.

Run #	A	×B	C	D	E	F	G	H
1	4.22×10^{-1}	8.44×10^{-3}	1.52×10^{-3}	2.84×10^{-3}	40	5.4	12	260
2	8.44×10^{-1}	1.69×10^{-2}	3.03×10^{-3}	5.68×10^{-3}	50			
3	1.69	3.38×10^{-2}	6.07×10^{-3}	1.14×10^{-2}	60			
4	3.38	6.75×10^{-2}	1.21×10^{-2}	2.27×10^{-2}	65			
5	6.75	1.35×10^{-1}	2.43×10^{-2}	4.54×10^{-2}	70			

Notes: × Surfmer concentration is (3–45) times its CMC value. A; monomer (acrylamide) concentration, mol L^{-1}. B; surfmer concentration, mol L^{-1}. C; initiator (KPS) concentration, mol L^{-1}. D; cross-linker (DVS) concentration, mol L^{-1}. E; temperature, °C. F; pH-value. G; reaction time, h. H; deionized water, g.

Table 1. Reactants concentration and reaction conditions in the case of HAPAM.

7.3. PROTOCOL 3: preparation of HAPAM-SiO$_2$ nanocomposite

After determination of optimum polymerization conditions and optimum reactants concentration, (3-aminopropyl) triethoxy silane was added in different molar ratios, as shown in **Table 2**. The polymerization procedure was carried out typically as shown previously in **PROTOCOL 2** with regarding addition of 3-aminopropyl triethoxy silane and KPS-initiator at the same time individually at reaction temperature of 60°C. The proposed structure is shown in **Scheme 3**.
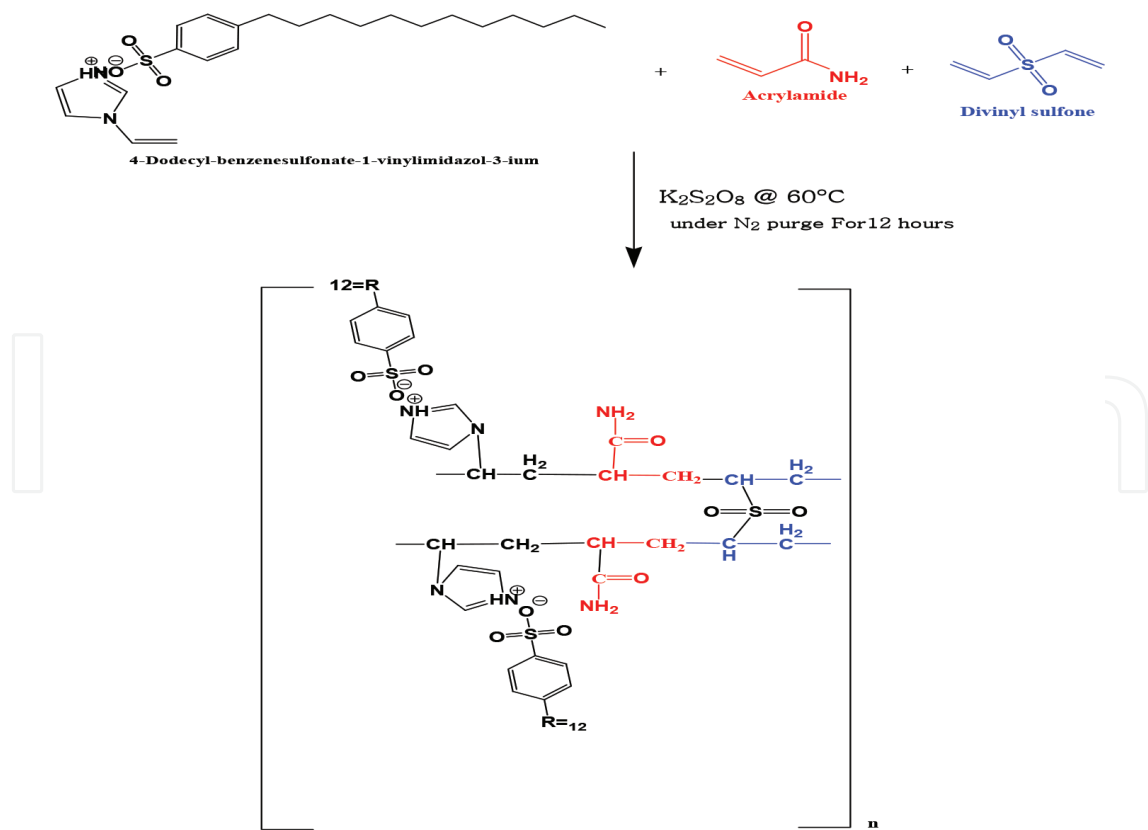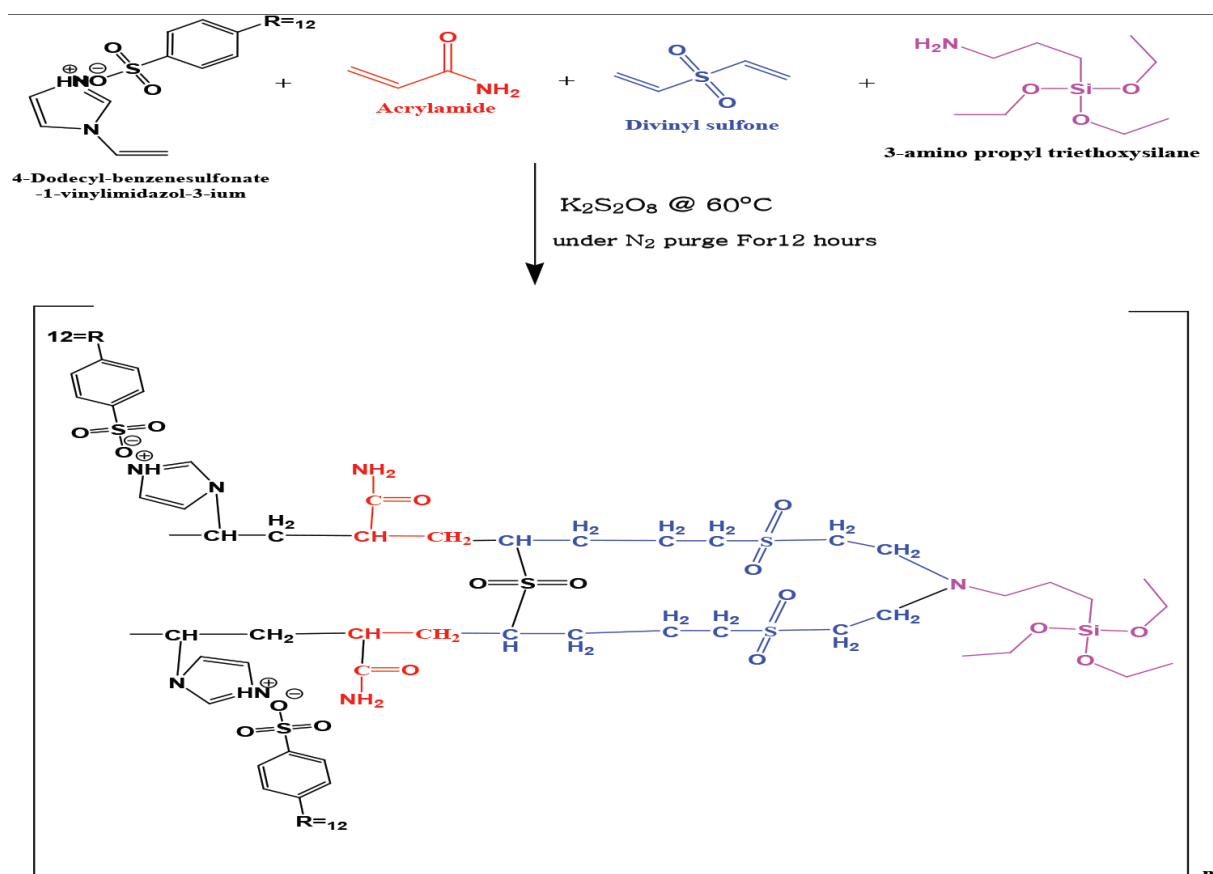

Scheme 2. Structure of HAPAM copolymer.

Run #	A	B	C	D	E	F	G	H	I
1	1.69	3.38×10^{-2}	6.07×10^{-3}	1.14×10^{-2}	60	5.4	12	260	7.53×10^{-4}
2									1.51×10^{-3}
3									3.01×10^{-3}
4									6.02×10^{-3}
5									1.20×10^{-2}

Note: **I**; silica concentration, mol L^{-1}.

Table 2. Reactants concentration and reaction conditions in the case of HAPAM-SiO$_2$.

Further discussions of chemical synthesis and spectroscopic characterization of surfmer, HAPAM copolymer, and nanocomposite by means of FTIR, ^{1}H-NMR, ^{13}C-NMR, transmission electron microscope (TEM), scanning electron microscope (SEM), X-ray diffraction (XRD), and differential scanning calorimetry (DSC) as well as optimum polymerization conditions are reported in our previous literature [9, 78, 80]. Moreover, critical micelle concentration, surface excess concentration, and surface area of prepared surfmer and original surfactant indicate higher surface activity of prepared surfmer, which increases latex stability [78].


Scheme 3. Structure of HAPAM-SiO$_2$ nanocomposite.

Rheological and solution properties were evaluated under simulated reservoir conditions as a function of polymer concentration and reservoir salinity, temperature, and shear rate. The results show good salt and temperature resistance, interfacial tension reduction and enhanced viscosity characteristics. The capability of polymer and nanocomposite to increase oil recovery was assessed through a linear packed sandstone model, as previously reported [78, 80]. Core flood tests were carried out under simulated reservoir conditions where a sand cleaning procedure, packing, flooding experiments, and recovered oil amount were discussed elsewhere [78, 80].

8. Rock wettability evaluation

8.1. Quantitative assessment

Wettability was evaluated by measuring the contact angle between oil droplet and rock surface at temperature = 90°C and salinity = 40,000 ppm) and polymer solution concentration of 2 g L^{-1}. The contact angles measured through a static sessile drop method for a spherical core plate for a period of 2 days as reported in **Figure 4**. After aging with crude oil for a day at elevated temperature, the plate was found to be oil-wet. The plate is then immersed in polymer/nanocomposite-brine solution under reservoir conditions, where oil droplet hanged on the plate lower surface and photographed for 48 h. Images are analyzed mathematically to calculate the contact angle. It is observed that advancing contact angle decreases with time and stabilizes at a value of about 74 and 68° in the case of HAPAM and HAPAM-SiO$_2$, respectively [78]. Wettability alteration by can be explained on basis of (1) by polymer/nanocomposite adsorption on the rock surface, physicochemical properties altered, where thin wetting water film becomes unstable at the interface [81] and ruptured so, creating a continuous oil path for oil displacement which in turn increases oil recovery, (2) positively charged nitrogen bases adsorb on negatively charged sandstone rock surface at pH = 6, so wettability


(A)   (B)
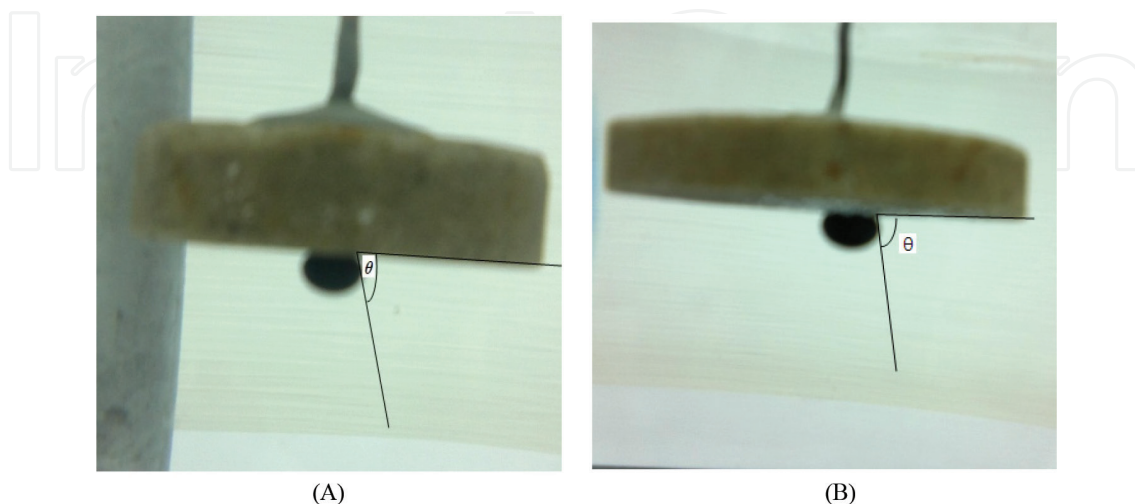
Figure 4. Contact angle photograph after 48 h. (A) HAPAM copolymer and (B) HAPAM-SiO$_2$ nanocomposite.

changed from oil-wet to water-wet, (3) flood detergency improved by SiO_2-nanoparticles addition leading to higher recoveries of residual oil, since associating polymer chain with nanoparticles enables a nanofluid to act as wetting agents, demulsifiers, and surface tension reducers at the very smallest of contact angles, which greatly enhances the removal of "foreign" materials such as oil, paraffin, and polymer residues, leaving the substrate water-wet. This is confirmed by reducing contact angle to nearly 74 and 68° in the case of HAPAM and HAPAM-SiO_2, respectively [78].

8.2. Qualitative assessment

Figure 5 shows qualitative evaluation of wettability through a two-phase separation test, it is shown that grinded sandstone grains are oil-wet as it is dispersed in the oil phase in the case of oil and brine solution, as shown in **Figure 5A**. While the sandstone grains sink into the aqueous phase of polymer solution in the case of polymer/nanocomposite, as shown in **Figure 5B** and **C**. This means that sandstone grains become water-wet. So, we can conclude that the polymer/nanocomposite able to alter wettability of the rock from oil-wet to water-wet so, improve recovered oil amount [78].
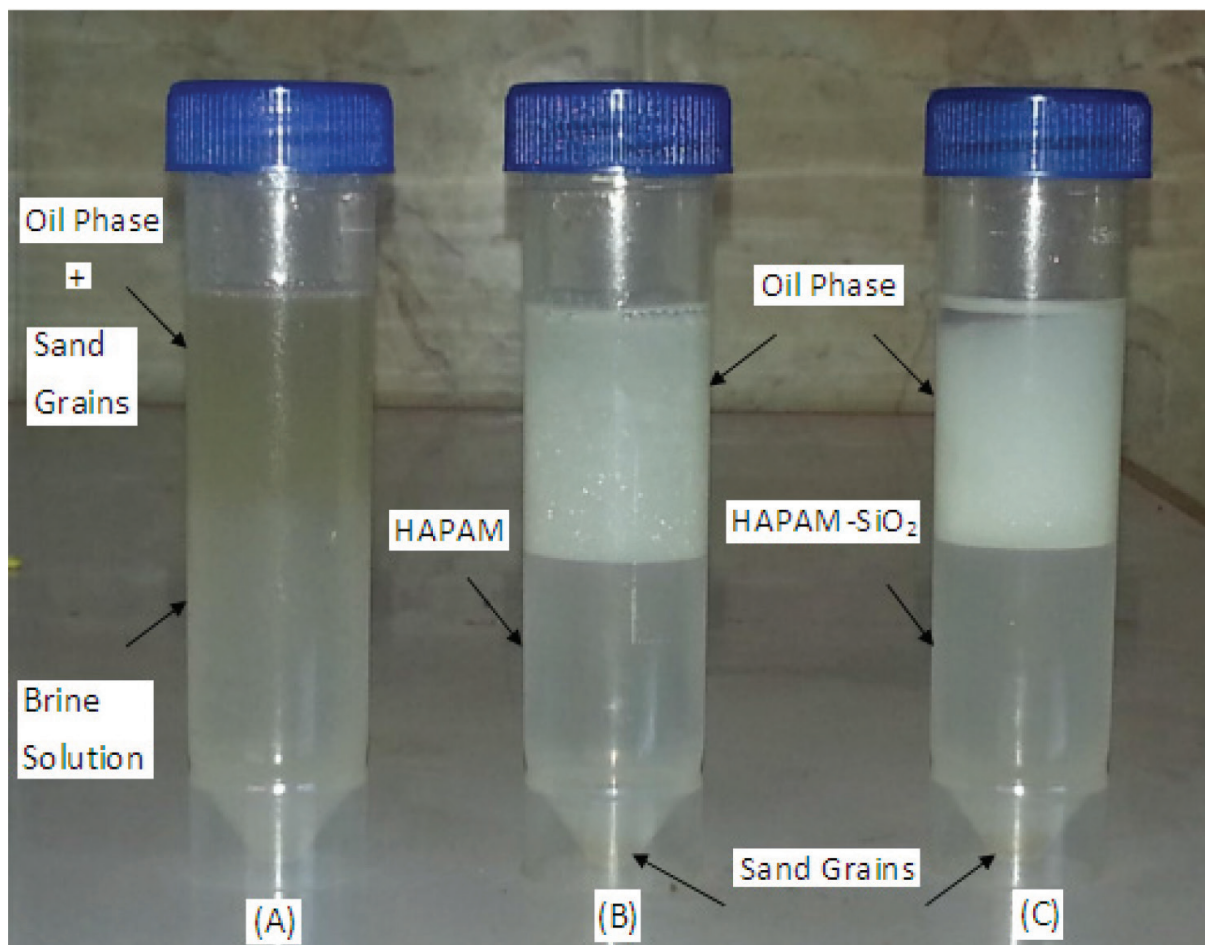
Figure 5. Two-phase separation test.

9. Conclusion

Improved oil recovery by polymer flooding involves injection of a mobility control agent (e.g., polyacrylamide and its hydrophobically associated derivatives) in order to displace the mobilized oil to the producing well, and improve seeping efficiency. In this chapter, the authors reported about synthesis of hydrophobically associating polyacrylamide (HAPAM) prepared by free radical emulsion polymerization and its modified nanocomposite derivative. Chemical structure of the prepared latexes was proven through different techniques such as FTIR, ^{1}H-NMR, ^{13}C-NMR, scanning electron microscope (SEM), transmission electron microscope (TEM), and X-ray diffraction, while particle size and particle size distribution were characterized by dynamic light scattering (DLS) and thermal properties characterized by thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) as reported in our previous literature [78, 80]. Rheological properties were assessed in accordance with salinity and temperature tolerance, polymer concentration, and shear rates. Core flooding carried out via a linear pressurized packed model [9, 78–80]. Based on the experimental results, the following conclusions can be drawn:

(1) HAPAM-SiO$_2$ nanocomposite prepared by introducing silica nanoparticles through one-shot synthesis via Aza-Michael addition reaction, so we can overcome shortages arising from agglomeration and coagulation of modified silica particles during emulsion polymerization reactions.

(2) The prepared HAPAM copolymer and HAPAM-SiO$_2$ nanocomposite had the perfect property of retaining the viscosity and strong non-Newtonian behaviors (i.e., exhibit shear thinning behavior); so they can be considered as a promised EOR candidates for polymer flooding projects.

(3) They respond to *in situ* reservoir stimuli (temperature, ionic strength, pH, and shear stress) also, show good thermal, rheological, and salt resistant properties even under reservoir conditions, and consequently improve sweeping efficiency.

(4) They effectively reduce interfacial tension to ultralow values, so increase mobilization of residual crude oil, which resemble the behavior of interfacial tension agents.

(5) Wettability assessment by a static sessile drop method indicates that the HAPAM copolymer and HAPAM-SiO$_2$ nanocomposite can alter rock wettability from oil-wet to water-wet, which in turn will increase a recovery factor as there is a consensus in petroleum engineering that water-wet reservoirs recover more oil than oil-wet ones.

In addition to the aforementioned aspects, and to the best of our knowledge, no polymers had previously reported to alter sandstone rock wettability, consequently the novel copolymer and nanocomposite considered as a promising candidates for EOR applications as a wettability-modifying agent in high-temperature and high-mineralization oil fields as compared to currently applied commercial polyacrylamides. On an industrial scale, we hope that a novel polymer applied as an EOR candidate to solve some of energy shortages as recovered oil amount reach to 26% from original oil in place (OOIP).

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