Characterization of Hydrophobically Modified Polyacrylamide in Mixed Polymer-Gemini Surfactant Systems for Enhanced Oil Recovery Application

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ABSTRACT: The study deals with the synthesis and characterization of the hydrophobically modified polyacrylamide (HMPA) copolymer and its functional property evaluation in mixed polymer-gemini surfactant systems for application in enhanced oil recovery (EOR). The copolymer was initially prepared in the laboratory using acrylamide and N-phenylacrylamide monomer units via an addition polymerization route. The synthesized copolymer was characterized by Fourier transform infrared and proton nuclear magnetic resonance to identify suitable functional groups in the compound. Gel permeation chromatography tests showed that the polymer has a molecular weight of 2.098 × 10^5 Da. Copolymer solution showed favorable tolerance to variations in temperature and salinity. Salt precipitation studies identified tolerance limit up to 25% NaCl at a temperature of 343 K. Viscosity of HMPA fluids showed an increase with increasing concentration. Interestingly, salt addition until 1.0% NaCl showed an increase in solution viscosity owing to the electrostatic shielding of the HMPA polymer and strengthened intermolecular association of the hydrophobic groups. This behavior is against physicochemical properties observed in the case of conventional polymers but exhibits promising functionality in EOR processes wherein better oil mobility control is desired under subsurface conditions. Gemini surfactants accommodate onto “vacant adsorption” sites onto the liquid surface, improving the interfacial adsorption property and reducing surface tension. In the presence of gemini surfactant polymers forming mixed nanoemulsion fluid systems with favorable pseudoplastic character, their viscosities initially increase with surfactant concentration due to binding of surfactant molecules to hydrophobic junctions of polymer chains to form mixed micelles. Eventually, polymer hydrophobes get saturated with surfactant micelles, and viscosity decreases due to electrostatic repulsion among surfactant micelles. Dynamic light scattering analyses confirmed the formation of nanoemulsion droplets with sizes of <310 nm in the case of (surfactant + copolymer) encapsulation. Zeta potential measurements showed that an increase in 14-6-14 gemini surfactant concentration enhanced the stability of nanoemulsion fluid due to increasing zeta potential values. However, the nonionic SP-6-SF surfactant does not affect the zeta potential of nanoemulsions. Surfactant addition reduced the oil-aqueous interfacial tension of polymer solutions to several magnitudes of an order of 10^{-1} to 10^{-2} mN/m. Contact angle studies identified the ability of the polymer as well as polymer-surfactant nanoemulsions to alter the wettability of the reservoir rock from the intermediate-wet (90°−120°) to strongly water-wet state (<20°) at different temperatures. Analyzed formulations showed favorable miscibility with crude oil at 343 K. In summary, HMPA/gemini surfactant-based emulsions possess promising physicochemical and stabilization attributes for application in EOR.

INTRODUCTION

Polymer flooding is a promising enhanced oil recovery (EOR) technique involving the use of water-soluble polymeric compounds to mobilize and extract in situ crude oil from petroleum reservoir. Addition of the polymer increases the viscosity of the injected fluid, thus reducing the water/oil mobility ratio. This allows better sweep of crude oil trapped within reservoir pores by capillary and viscous forces and is beneficial in controlling the crude oil mobility. This encompasses the “primary conformance-improvement benefit of polymer waterflooding” as per Sydansk’s theory. Due to this, the development and optimization of novel polymeric systems have become an important field of study among petroleum engineers and researchers alike. However, the effectiveness of polymer injection depends on a number of factors, namely, flow behavior of solution, area of injection, permeability variations, and the area of the front surface of reservoir. Furthermore, drawbacks faced during polymer flood EOR comprise low stability to high temperature and salinity conditions. Acrylamide-based synthetic polymers are com-
monly employed in the oil production sector due to favorable rheological attributes. It is necessary to improve the physicochemical attributes of polyacrylamide polymers by resistance to dynamic changes in an external environment, by synthesizing copolymer systems for extracting oil under harsh reservoir conditions. Acrylamide polymers structurally modified with a hydrophobic monomer have recently become the subject of extensive research. Above a certain polymer aggregate concentration, the polymer chain forms intermolecular hydrophobic association, which leads to the strengthening of polymolecular interactions and formation of the network structure. The synthesized block copolymers exhibit favorable viscosity properties. Therefore, hydrophobically modified copolymers achieve oil displacement and mobilization, preventing backflow and retraction of oil within pore spaces.

Hydrophobically connecting polymers/polymeric materials can demonstrate intriguing physicochemical traits under dynamic conditions. Thus, it is conceivable to dodge the irreversible mechanical dissociation among interacting molecules, which happens to high molecular weight polymers under high shear. Polymers with the amphiphilic structure of hydrophobically associative polymers exhibit synergistic interfacial and rheological properties in diverse systems. Synthesis techniques have been developed to achieve high-molecular-weight block copolymers with enhanced rheological attributes. The functionality of hydrophobically modified copolymer systems comprises a wide array of enhanced physicochemical attributes and diverse research areas. In the past few years, several types of associative copolymers have been developed, depending on the synthesis technique, nature of interacting monomers, mode of structural attachment of hydrophobes as end attachment (telechelic polymers) or distribution as small blocks in the hydrophilic polymeric backbone (multisticker polymers). Such systems have found application in cosmetics, drilling fluids, preparative chemistry, and as materials/coatings for food, fiber, and leather. However, their application in the field of enhanced oil recovery (EOR) is relatively new and further needs to be optimized/designed as a chemical injection fluid in petroleum industry. Van Doren et al. studied the optimization of polymer flooding to increase NPV of the field and they also demonstrated by full field scale reservoir simulation of polymer flooding. This laid the groundwork for formulation of different pure and mixed polymer systems for oil extraction processes. Caulfield and co-workers studied the degradation of polyacrylamide under different conditions and proved that copolymer synthesis is vital for further advancement. Wei et al. discussed the mechanistic processes responsible for favorable rheological attributes of polymer and copolymer fluids. Dai et al. synthesized the polyacrylamide-based polymer and showed the effect of salinity and temperature on stability. Kopperud and others showed the interaction of polyacrylamide and hydrophobically modified polyacrylamide with surfactant SDS. They showed non-Newtonian shear thinning as well as thixotropic behavior under surfactant concentration, which are considered desirable for EOR processes. Magny et al. showed the rheological behavior between the hydrophobic polymer and anionic/nonionic/cationic surfactant and identified favorable systems for petroleum recovery function. Synthesized polymer interaction with a surfactant and its emulsification properties are essential for their potential application for enhanced oil recovery. Wang and Tam studied the interaction between the charged polymer and surfactant molecules and found that electrostatic interactions influence their stabilization and flow behavior. This mechanism was further improved in 2018 by Wang et al. during which hydrophobic interactions and hydrogen bonding were identified as primary interactive forces, which affect physicochemical properties of monomeric surfactant-polymer fluids in terms of interfacial activity and rheology. Kothenez et al. and others and Al-Sabagh et al. also studied the interaction between polymer chains and surfactant micelles/molecules and optimized fluid compositions to control their relative effects on mixed polymer-surfactant systems. Surfactant-polymer systems are functional in situations wherein high tolerance to salt is necessary. The synergistic interactions between the polymer and surfactant play a pivotal role in understanding mechanistic interactions, as well as devising/optimizing novel chemical displacing fluids. Our current article deals with the interaction between novel synthesized HMPA and cationic/nonionic gemini surfactant systems that has not yet been investigated for EOR previously.

This paper deals with the synthesis and functional application of a hydrophobically modified copolymer (acrylamide + N-phenylacrylamide) in EOR processes. Characterization studies were performed by Fourier transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC), salt tolerance test, and viscosity measurements. Polymer interactions with gemini surfactants (14-6-14 GS and SF-6-SF GS) were studied in an aqueous solution phase and their physicochemical properties were studied. The viscosity and viscoelastic behavior of surfactant-copolymer mixtures were studied under dynamic shear conditions. A mechanistic approach illustrating gemini surfactant-polymer interactions was also discussed in this study. Surface properties of the polymer and polymer/surfactant solution were studied using dynamic interfacial tension (IFT) measurements. Thereafter, emulsification behavior of surfactant-polymer formulations was studied by a dynamic light scattering (DLS) technique. Rock-wettability alteration and crude oil miscibility investigations were investigated with an elapsed time. In summary, novel chemical fluid systems (HMPA + gemini surfactant) were optimized and developed to prove their efficacy as a suitable EOR chemical fluids.

RESULTS AND DISCUSSION

HMPA Copolymer Characterization. FTIR and 1H NMR Analyses. The FTIR spectrum of the synthesized HMPA copolymer is depicted in Figure 1. The peaks at 1632 and 3430 cm$^{-1}$ are assigned to C==O and N--H stretching vibrations of the $\text{C}[-\text{CONH}_2$ group, respectively. These peak characteristics established the presence of the acrylamide group in synthesized polymer. Adsorption bands at 2963 and 2925 cm$^{-1}$ relate to the stretching vibrations of $\text{C}_2\text{H}_4$. Adsorption bands at 2853 and 1457 cm$^{-1}$ correspond to the $\text{C}_2\text{H}_4$ bonding on the polymer chain. Peaks showing C==C bonding on an aromatic ring appear at 1500 and 1457 cm$^{-1}$. Adsorption bands at 1116 cm$^{-1}$ show the existence of $\text{C}--\text{N}$ stretching. The presence of spectral peak at 616 cm$^{-1}$ is characteristic of aromatic rings in a compound. FTIR peaks suggest successful copolymerization of acrylamide and N-phenylacrylamide to form the HMPA copolymer.

Figure 2 shows the 1H NMR spectral data for hydrophobically modified polyacrylamide (HMPA). The compound was dissolved in dimethyl sulfoxide in deuterated form (DMSO-$d_4$)
as a lock solvent and its spectral data was recorded in the solution state to identify NMR peaks. The existence of characteristic signals at chemical shift ($\delta$) values of 0.81–1.63 ppm relates to methyl $-CH_2$ groups. Peaks located in the NMR region at ($\delta$) 2.06–2.48 ppm are attributed to $-CH$ of acrylamide units present within a copolymer structure. Evidence showing the carbon–nitrogen (C–N) bond of an acrylamide functional group is obtained as a multiplet signal at ($\delta$) 3.00 ppm. It is pertinent to note that this NMR peak is stronger as compared to the chemical shift of $\alpha$H of the CH$_2$–NH$_2$ group, showing that the carbonyl group acts an electron-withdrawing group (EWG), that is, it draws the electron away from the reaction center, with decreased shielding effect. The presence of the phenyl group within the HMPA molecule is confirmed due to the resonance peak at 7.30 ppm ($\delta$). Therefore, these results corroborate the formation of the multiblock copolymer (HMPA) containing long acrylamide chains and a short sequence of hydrophobic acrylamide/N-phenyl acrylamide monomeric components.

**Gel Permeation Chromatography.** The molecular weight of the HMPA polymer was analyzed by gel permeation chromatography (GPC) using universal calibration and HPLC water as an effluent. The polymer has an average molecular weight ($M_w$) of $2.098 \times 10^5$ Da and polydispersity index (PDI) of 1.643. Figure 3 shows molecular weight distribution for the HMPA copolymer.

**Salt Tolerance.** The salt tolerance values of synthesized copolymer solution at 5000 ppm copolymer concentration at 303 and 343 K are 20 and 25%, respectively. This is performed by gradually increasing the percentage of salt (NaCl) in aqueous copolymer solution until precipitation is observed. Salt tolerance is observed to increase with temperature. This behavior is relevant to many polymer solution behavior, as solubility of NaCl tends to increase with increasing temperature.

**Effect of HMPA Concentration on Viscosity.** The synthesized HMPA copolymer shows an increase in viscosity with increasing polymer concentration. Aggregates are formed by strong interchain associations as copolymer concentration increases. The formation of large polymer aggregates is evident from dynamic light scattering (DLS) results of copolymer solutions. With increasing HMPA concentration, the average
size of polymer aggregates is observed to increase due to strong interchain associations. The average aggregate sizes for HMPA copolymer solutions containing 1000, 2000, 3000, 4000, and 5000 ppm HMPA are found to be 410, 558, 725, 898, and 1015 nm, respectively. This confirms the gradual formation of HMPA-stabilized aggregates within a bulk aqueous phase. At low polymer dosages, small aggregates are formed with small hydrodynamic volume due to low extent of intermolecular network structure formation of constituent polymer chains with one other. With increasing HMPA concentration in aqueous solution, the hydrophobic intermolecular associations are more dominated and formed a physical network structure with large polymer chain aggregates and, subsequently, higher solution viscosities are achieved.28

Figure 4 shows the effect of copolymer concentration and temperature on viscosity with varying shear rates. The solution exhibits decreasing viscosity with increasing shear rates up to 100 s\(^{-1}\). This shear thinning or pseudoplastic character of HMPA solution is because of the minimal effect of colloidal dispersion in the presence of large copolymer chain molecules. Beyond a critical shear rate, viscosity is observed to increase slightly showing dilatant or shear thickening character in an aqueous phase. However, this may be attributed to the effect of turbulence at a high shear rate. This behavior can be explained with the help of different phenomena, namely, the order–disorder transition (ODT) theory, hydrodynamic lubrication theory, and Jamming theory. According to the ODT theory, a viscosity increase is observed due to transition of polymer molecules from the ordered to disordered state with increasing shear rates.29 The theory of hydrodynamic lubrication states that hydroclusters are formed above critical shear rates, resulting increased viscosity of copolymer fluids.30 As per the Jamming theory, frictional contact occurs between entangled polymer chains at a high shear rate, leading to shear thickening behavior.31 However, dynamic shear conditions within reservoir do not exceed 100 s\(^{-1}\) even under variable permeability throat regions and blind ends. Therefore, HMPA copolymer fluids show pseudoplastic behavior, which is considered as a desirable property of EOR injection fluids. With increasing temperature, viscosity of HMPA solution is observed to decrease. This is due to increasing mobility of polymer chains, which decreases their degree of entanglement. This disrupts the hydrophobic interactions among polymer (tail) chains and lesser intermolecular association. This effect is more profound in solutions containing favorably high polymer concentration where intermolecular association is dominated.

**Effect of NaCl Concentration and Temperature on Polymer Viscosity.** To verify the effect of NaCl content on polymer solution of viscosity, copolymer solution was prepared with 5000 ppm concentration in distilled water and then various solutions were prepared at 0, 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, and 15% NaCl concentration. The plots showing solution viscosity versus the shear rate are shown in Figure 5. Viscosity of solution decreased with increasing NaCl concentration up to 1%. This is attributed to the presence of the inefficient (macromolecular) network structure by initial weakening of hydrophobic associations, which reduces the ionic strength of polymer fluids. However, this behavior showed a reverse trend when salinity increased beyond 1% NaCl concentration.
Thereafter, increasing salinities lead to formation of a more pronounced dynamic cross-linking network structure owing to increased solution polarity.\textsuperscript{32,33} In Figure 6, the electrical double layer of the hydration shell around polymer hydrophobic chains is compressed by salt ions, thus improving the degree of mutual attraction among polymer surfaces.\textsuperscript{32-34} Consequently, intermolecular associations among polymer hydrophobes increase, resulting in electrostatic shielding of the HMPA polymer. With increasing temperature, intermolecular association of hydrophobic groups weakens and the degree of entanglement of hydrophobic groups decreases, leading to viscosity reduction in copolymer solution.\textsuperscript{35}

**Interfacial and Rheological Behavior of HMPA/Gemini Surfactant Systems.** *Surface Tension of Aqueous Solution.* Figure 7 shows the surface tension of HMPA solutions and HMPA/gemini surfactant solutions at 303 K. From Figure 7a, it is observed that the surface tension of HMPA solution increases with increasing polymer concentration. This is due to adsorption of polymer molecules onto air-aqueous interfaces. The hydrophobic tail component in polymer molecules entangles with one another to form a chain network structure in the bulk phase as well as adsorb onto air-aqueous interfaces. When the interface becomes saturated with polymer molecules, the surface tension is observed to increase.\textsuperscript{17,18} Surface tension measurements were conducted to identify the point of critical micelle concentration (CMC) for the HMPA copolymer system in an aqueous phase. At 750 ppm, the lowest value of surface tension was obtained due to complete adsorption of air-aqueous interfaces with polymer molecules. This concentration limit marks the beginning of the hydrophobic interactions’ effect among polymer chains in the bulk phase due to unavailability of “vacant sites” for HMPA adsorption. Beyond CMC, hydrodynamic interaction dominates significantly as a function of copolymer concentration owing to polymer chain entanglement and subsequent formation of the network structure.\textsuperscript{36} Surface tension values at 303 K were found to be 39.5, 40.9, 42.3, 43.2, and 43.6 mN/m at varying polymer concentration values of 1000, 2000, 3000, 4000, and 5000 ppm, respectively. Addition of the gemini surfactant in 5000 ppm HMPA solution leads to a marked decrease in surface tension values as described from Figure 7b plots. Gemini surfactants favorably accommodate onto “vacant adsorption” sites onto the liquid surface and improve surfactant adsorption. The lowest surface tension for the HMPA/14-6-14 GS system was observed at 2000 ppm, which is measured as 29.8 mN/m. For the HMPA/SF-6-SF GS system, a minimum tension value of 27.1 mN/m is obtained at 2000 ppm surfactant concentration. The HMPA/SF-6-SF GS surfactant system has lower surface tension due to hydrophobic interaction and the absence of “ionic” repulsion in comparison to HMPA/14-6-14 GS since 14-6-14 GS surfactant molecules have cationic head groups.

In copolymer solutions, hydrophobic interactions among polymer chains dominate owing to intramolecular associations. As concentration of the copolymer is increased, hydrophobic intermolecular associations are more dominated and formed the physical network structure with large polymer chain aggregates.\textsuperscript{28} This increased the hydrodynamic volume of polymers, and subsequently, higher solution viscosities are achieved. The presence of phenyl groups within a copolymer molecular structure induces the van der Waals effect due to its planar, polarizable structure.\textsuperscript{20,37} This, in fact, can improve the stabilization behavior of alkyl chain-involved hydrophobic interactions, thus enhancing the structural rigidity of the polymer (macromolecular) network.\textsuperscript{15} The entanglement of

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polymer tail groups occurs because of combined van der Waals and the hydrophobic association effect among polymer surfaces. Hence, the viscosity behavior of polymer solutions is a function of concentration and nature of interacting monomer species.

**Viscosity Measurements.** In HMPA copolymer solution, thickening behavior is observed with increasing cationic surfactant (14-6-14 GS) due to a shear-induced structure in the form of worm-like micelle structures. Viscosity of HMPA/14-6-14 GS solution increases up to a certain concentration of the copolymer (1500 ppm) in an aqueous phase. This is due to the binding of surfactant molecules to the hydrophobic junction of HMPA chains to form mixed micelles. Hydrophobes of HMPA polymer chains are saturated with individual surfactant micelles, and viscosity begins to decrease due to electrostatic/steric effects among surfactant micelles. Polymer-surfactant interactions in aqueous media (displacing phase) are mainly dominated by hydrophobic interactions, electrostatic repulsion/attraction, and steric effects. Above 1500 ppm, viscosity of the mixed solution system decreases with 14-6-14 GS concentration, indicating one hydrophobe per micelle and a resulting decrease in interchain interaction due to repulsion among micelles encapsulated by cationic polar head groups. In the case of HMPA + SF-6-SF systems, increasing surfactant concentrations to 500 ppm increased solution viscosity due to interchain cross-linking phenomena as above. However, a further increase in SF-6-SF concentration showed a decrease in viscosity. Again, this effect indicates micellar repulsion due to the steric effect. Figure 8 shows the variation of solution viscosity with increasing shear rates shown for HMPA + gemini surfactant fluid systems.

**Viscoelastic Behavior.** Dynamic moduli are plotted as a function of angular frequency ($\omega$) in Figure 9 for chemical solutions containing 5000 ppm HMPA copolymer and 5000 ppm HMPA copolymer + SF-6-SF/14-6-14 surfactants. Crossover frequency is identified at ~2 rad/s for both HMPA and HMPA/gemini surfactant systems. Below crossover frequency, $G''$ is found to be greater than $G'$. At angular frequencies above 2 rad/s, both HMPA and HMPA/gemini surfactant systems showed dominant elastic behavior as $G' > G''$. In micro/nanoscale reservoirs wherein polymer and polymer/gemini surfactant solution are injected, some pores are blocked due to the large size of molecules or micelles compared to pores. This leads to trapping of residual oil within rock pores. This shows that they are able to displace oil from...
small size pore throats. High viscoelastic behavior shows lesser residual oil saturation for the synthesized polymer and polymer/surfactant solutions. Oil displacement from pores may be higher in this type of polymer and polymer/gemini surfactant system. Further studies were performed for 5000 ppm HMPA, {5000 ppm HMPA + 2000 ppm 14-6-14 GS}, and {5000 ppm HMPA + 2000 ppm SF-6-SF GS} solutions because these solutions showed desirable physicochemical properties needed for enhanced oil recovery.

**Interaction Mechanism of (HMPA + Gemini Surfactant)-Based Aqueous Systems.** The primary interactions existing between the Gemini surfactant and polymer molecules comprise electrostatic attraction, hydrophobic forces, and hydrogen bonding. Surfactant addition improves the adsorption ability of polymer fluids, resulting in an improved electrostatic effect (in the case of cationic 14-6-14 GS) and multiple interactions and hydrogen bonding interactions (in the case of nonionic SF-6-SF GS). Figure 10 shows the interaction mechanisms between HMPA polymer and Gemini surfactant.
surfactant molecules in aqueous solution. It is observed that viscosity of copolymer solutions increases with increasing concentration. This suggests the formation of interchain and intrachain aggregates caused by entanglement of HMPA hydrophobe chains. However, in gemini surfactant + copolymer-based systems, surfactant micelles associate with polymer chains described as a “string of beads model” owing to the improved hydrophobic interaction effect. In the presence of 14-6-14 GS, cationic head groups enhanced the electrostatic forces existing among the polymer-surfactant molecule. On the contrary, strong hydrogen bonding exists between polymer and nonionic SF-6-SF GS molecules. As a result, the number of charges for polymer chain increases, causing the polymer chain to further extend and the structure viscosity to increase. This is corroborated by analysis of viscosity profiles of different polymer solutions in the presence of the gemini surfactant discussed in Figure 8. A spatial network structure formed by interaction between GS micelles and polymer chain groups, which is corroborated by a viscosity increase until a concentration of 2000 ppm 14-6-14 GS or 750 ppm SF-6-SF in solution is reached. This marks that the adsorption limit of surfactants reaches their saturation and the viscosity of surfactant-polymer fluids increases to a maximum value. Higher concentration of gemini surfactants (above adsorption limit) causes HMPA chains to lose their associative properties and partially curl within the bulk phase, which is clear from a viscosity decrease in polymer solution.

**Nanoemulsion Characterization. Particle Size Distribution Studies.** Figure 11 shows the intensity-weighted particle size distribution profile for the nanoemulsion system in the presence of the polymer, {HMPA +14–6–14}, and {HMPA + SF-6-SF}. For polymer-stabilized nanoemulsions, large droplet sizes are observed because of oil droplet coalescing ability. Hydrodynamic diameter values vary in a range of 10.5–2780.0 nm and the average droplet diameter is measured as 365.4 nm. For the {HMPA +14–6–14}-based nanoemulsion system, hydrodynamic diameter varies from 3.77 to 307.6 nm, with an average value of 144.3 nm. An average droplet diameter of 137.3 nm was obtained for {HMPA + SF-6-SF} nanoemulsion, wherein hydrodynamic diameter of dispersed oil droplets varies in a range of 29.4–278.0 nm. This shows that the addition of the gemini surfactant into HMPA solution reduces the average oil droplet diameter. In summary, surfactant molecules adsorb onto oil-aqueous interfaces, thus reducing droplet (dispersion) size in polymer containing fluids.

**Zeta Potential Results.** In oil-in-water nanoemulsion systems, oil phases remain dispersed within a continuous aqueous phase. The stability of oil droplets is mainly dependent on two main influences. The first effect comprises the steric stabilization effect, wherein the hydrophilic polymer and/or other emulsifier molecules encapsulate oil droplets, in such a way that their long chains reach out into solution. Another influence is electrical repulsive interactions among surfactant head groups (adsorbed onto droplet surfaces). The zeta potential versus surfactant concentration plots is depicted in Figure 12. In HMPA solutions, steric interactions among polymer chains dominate over electrical forces and zeta potential values are found to be about −2.5 mV. In the presence of SF-6-S GS, potential between oil droplets does not show a considerable change due to the nonionic nature of surfactant head groups. However, addition of cationic 14-6-14 GS surfactant molecules into HMPA polymer-based nanoemulsion systems shows a considerable increase in surface charge magnitudes in a positive direction. Zeta potential values are observed to increase to +4.7, +9.4, and +14.6 mV in surfactant-polymer mixtures with 1000, 1500, and 2000 ppm 14-6-14 GS concentrations, respectively. This is attributed to the dominance of electrostatic repulsion among head groups of surfactants constituting the electrical double layer (EDL) surrounding dispersed oil droplets. Increasing temperature showed a slight change in zeta potential readings, confirming that HMPA solution and HMPA + GS fluids retain their stability under high-temperature conditions. The introduction of gemini surfactant + polymer molecules creates a mechanical barrier (steric + electrical repulsion) effect around dispersed oil droplets and consequently slows the rate of oil coalescence. Therefore, {14-6-14 GS + HMPA polymer} systems exhibit better droplet stabilization behavior in comparison to {SF-6-SF + HMPA} and pure HMPA-stabilized emulsions.

**Crude Oil Miscibility.** Miscibility is the property of two liquids to mix or fully dissolve to form homogeneous solution. To solubilize trapped oil, a large amount of polymer, polymer/surfactant slug, and turbulent flow are needed to form in situ emulsion during surfactant injection. The properties of these
emulsion phases are inexact in terms of miscibility and droplet stability with crude oil, which are reliant on the salinity and formation fluid conditions. Thus, to replace the polymer and polymer/surfactant slug with emulsion slug, it is desirable to optimize emulsion properties for EOR. It helps to predict the behavior and viability of emulsion in the reservoir. Crude oil, being an immiscible liquid, is separated from emulsion after a certain period. The gemini surfactant improves the oil miscibility of copolymer solutions since it decreases the oil-aqueous IFT. Figure 13 show the miscibility of crude oil in emulsion with time, after 12 h. The crude oil separated from the emulsion phase after 18 h for 5000 ppm HMPA solution, {5000 ppm HMPA + 2000 ppm 14-6-14} solution, and {5000 ppm HMPA +2000 ppm SF-6-SF}. Therefore, analyzed polymer-surfactant systems exhibit favorable crude oil miscibility with prepared emulsion slug formulations. Interfacial Tension between Oil-Aqueous Solution. IFT studies are important for assessing the oil recovery ability of chemical fluids during EOR processes. Figure 14 shows the variation of IFT with an elapse of time. It is observed that IFT values continuously decrease with time and gradually achieve a plateau region. The equilibrium values of oil-aqueous IFT for HMPA, HMPA +14-6-14 GS, and HMPA + SF-6-SF GS solutions are 0.854, 0.148, and 0.034 mN/m, respectively. As compared to HMPA solution, HMPA/GS systems achieve an early plateau in IFT plots. Interactions between the hydrophobic group of the HMPA polymer chain and GS molecules increase with surfactant addition. HMPA + 14-6-14 possesses the cationic group due to which electrostatic repulsion between polar groups dominates between molecules at oil-aqueous interfaces. This observation indicates that surfactant-polymer mixtures exhibit better oil displacement ability as compared to polymer fluids owing to improved interfacial activity at oil-aqueous interfaces. Dynamic Contact Angle Investigations. Wettability characteristic studies using sessile drop analysis were performed onto quartz and carbonate rock surfaces at different temperature conditions to study the oil displacement efficacy. During the oil ageing process, the rock sample(s) were permitted to saturate with crude oil in a closed (sealed) environment to simulate oil-saturated reservoir. Using sessile drop analysis, the contact angle was measured with respect to time onto a rock surface. Initially, the reservoir rock surface revealed the intermediate-wet state. From Figure 15, the contact angle gradually decreased with elapse of time at different rates, depending on the nature of fluid and rock specimen. The solutions possess the ability to alter rock wettability to the favorable water-wet state. Wettability alteration characteristics improve with increasing temperature, as evident from less time required to reach strongly water-wetting behavior. This is attributed to greater availability adsorption sites at the oil-aqueous interface and more effective oil displacing behavior of chemical fluids onto the oil-saturated rock surface. CONCLUSIONS The synthesis and physicochemical properties of the hydrophobically modified water-soluble acrylamide/N-phenylacrylame copolymer (HMPA) were studied for application as chemical displacing fluid in EOR processes. FTIR and $^1$H NMR spectra of the synthesized polymer showed the incorporation of N-phenylacrylamide monomer (repeating) units in addition to repeating acrylamide polymer chains. Molecular weight determined by the gel permeation chromatography (GPC) method was found to be 2.098 × 10^7 g/mol. The synthesized copolymer demonstrated relatively high salt tolerance, which is typical for the nonionic polymers. The copolymer showed favorable pseudoplastic or shear-thinning behavior. Addition of the gemini surfactant into polymer solution showed an initial increase in solution viscosity due to the binding of cross-linking polymer chains with surfactant molecules to form mixed micelles. After a certain concentration limit is reached, the electrostatic/steric effects among surfactant micelles dominate and the degree of the cross-linking network starts decreasing, leading to reduced viscosity of polymer-surfactant fluids. These observed properties of pseudoplasticity, salt tolerance, encouraging viscosity/viscoelasticity, and temperature profiles are attractive features of the hydrophobic copolymer, which show potential in EOR processes. Surface tensions of HMPA, HMPA + 2000 ppm 14-6-14 GS, and HMPA + SF-6-SF GS were found to be 43.6, 29.8, and 27.1 mN/m, respectively. Oil-aqueous IFT values for HMPA polymer solution were measured as 0.854 mN/m, which decrease to 0.148 mN/m with 14-6-14 GS addition and 0.034 mN/m in the presence of SF-6-SF GS. Dynamic light
scattering results showed the formation of small oil droplets with average size in a range of 100–200 nm. Zeta potential studies showed that 14-6-14 GS + HMPA emulsions exhibit enhanced stability as compared to other analyzed systems. HMPA + gemini surfactant fluids also exhibited favorable emulsification behavior in the presence of crude oil. Reduction in interfacial tension values of HMPA polymer solution was achieved by addition of the gemini surfactant due to increased hydrophobic interactions between polymer and gemini surfactant molecules. Surfactant-polymer combinations showed rock-wetting characteristics, showing their abilities to displace residual oil deposited onto reservoir rock surfaces. In summary, both HMPA copolymer and HMPA + gemini surfactant mixtures revealed favorable physicochemical traits as potential oil recovery agents.

■ EXPERIMENTAL SECTION

Materials. Acrylamide (≥98.5%) was used as supplied by Avantor Performance Materials India Ltd. N-Phenylacrylamide (99%) was obtained by Sigma-Aldrich. Potassium persulfate (≥99%) and n-hexane CTAB (hexadecyltrimethyl ammonium bromide) (≥99%) were purchased by Sigma-Aldrich. Cationic gemini surfactant N,N'-bis(dimethyldodecyl)-1,6-hexanediynammonium bromide (14-6-14 GS) and nonionic gemini surfactant bis(monoglyceride-1-hydroxymethyl-2-fattyacidenter)-1,6-hexanediether (SF-6-SF GS) were synthesized in the laboratory as per the previously reported method. Distilled water was obtained from a double distillation apparatus. Crude oil (API gravity of 23.55°) was obtained from ONGC field, Ahmedabad Asset, India.

Characterization of Gemini Surfactants. The infrared spectra of gemini surfactants were studied with a Perkin-Elmer Spectrum 2 IR spectrometer. The synthesized gemini surfactants were milled in KBr in a concentration range of ≤2.0% to obtain a fine powder. This powder is then compressed to form a thin pellet that is used for FTIR analysis. TGA of the synthesized gemini was studied with the help of Diamond thermogravimetric/differential analyzer (Perkin-Elmer, USA) in an argon (Ar) atmosphere at a heating rate of 5 K/min.

Cationic Gemini Surfactant, N,N'-Bis(dimethyldodecyl)-1,6-hexanediynammonium Bromide (14-6-14 GS). The characteristic infrared bands showing the presence of different functional groups are depicted in Figure 16a. Adsorption peaks at 2920 and 2852 cm⁻¹ show the presence of symmetrical and asymmetrical stretching vibrations of alkanes at terminal –CH₃ groups. Asymmetrical bending vibrations of the –CH₂– group are displayed by bands at 1470 cm⁻¹. The existence of peaks at

Figure 15. Contact angle of 5000 ppm HMPA, 5000 ppm HMPA + 2000 ppm 14-6-14 GS, 5000 ppm HMPA + 2000 ppm SF-6-SF GS emulsions on rock surface of (a) quartz at 303 K, (b) quartz at 343 K, (c) carbonate at 303 K, and (d) carbonate at 343 K.
1270 and 1179 cm\(^{-1}\) confirms C−N stretching from the polar head groups. \(R_4N^+\) stretching vibrations, which exhibit the presence of quaternary amine groups, are identified from peaks at 1081 cm\(^{-1}\). The peak at 721 cm\(^{-1}\) corresponds to the weak intensity of (CH\(_2\))\(_6\) rocking vibrations in the spacer. Therefore, FTIR analysis show that the chemical compounds under analysis consist of two hydrophobic tail groups and two head groups connected by a spacer chain, that is, a gemini surfactant.

Thermal degradation zones are identified in Figure 16b to investigate weight losses occurring with increasing temperature. The first stage of thermal degradation (\(\sim\)0.35%) is due to breakdown of weakly bonded water molecules, resulting in the removal of moisture in the specimens. Thereafter, the second weight loss (additional 30.78%) occurs at a higher temperature range (448−523 K), indicating complex thermal decomposition of surfactant molecules, beginning from alkyl tail chains. Thus, 14-6-14 GS has the ability to retain its structural integrity under subsurface conditions.

Nonionic Gemini Surfactant, Bis(monoxyethylene-1-hydroxymethyl-2-fattyacidester)-\(\alpha,\omega\)-alkanediether (SF-6-SF GS). Analysis of infrared spectra of the nonionic SF-6-SF GS was performed to identify peak regions corresponding to various functional groups, as depicted in Figure 17a. Two sharp adsorption bands were obtained at 3420 and 3386 cm\(^{-1}\), showing the existence of −OH bonds. Peaks at 2918 and 2851 cm\(^{-1}\) account for the symmetric and asymmetric C−H stretching vibrations, respectively. The existence of O−C=O and C=O bonds in ester groups in the compound is evident from stretching vibrations identified by the presence of peaks near 1659 and 1731 cm\(^{-1}\). A single peak near 1462 cm\(^{-1}\) is indicative of alkane C−H bending vibrations. A single peak located at 719 cm\(^{-1}\) shows the rocking vibrations of the (CH\(_2\))\(_6\) spacer present in the ester compound. In addition, peaks in the region of 1145 and 1075 cm\(^{-1}\) correspond to C−O stretching vibrations of ether groups attached to either sides of the aliphatic spacer chain. Thus, it is confirmed that the synthesized compound is a gemini surfactant consisting of two alkyl chains (tails) with ester and ether groups, which are connected by an aliphatic spacer.

Figure 17b shows the thermal loss curves of the SF-6-SF-based gemini surfactant. The first stage of degradation starts at 373 K, showing the loss of intramolecular hydroxyl (−OH) groups with a weight loss of \(\sim\)3.37%. The second degradation stage (additional 13.38%) is observed at a temperature of 448 K due to the initial decomposition of ester groups and subsequent destruction of fatty acid chain groups until 518 K. Hence, SF-6-SF GS is capable of maintaining its stability within the temperature range of petroleum reservoir.

The above discussions comprise the chemical and thermal characterization properties of cationic gemini surfactant (14-6-14 GS) and nonionic gemini surfactant (SF-6-SF GS). The
data have already been reported and discussed in our previous articles. Their CMC values are very low, confirming their self-aggregation ability at low temperatures. The CMC value of 14-6-14 GS (cationic surfactant) is 160 ppm (0.22 mmol/L), whereas the CMC of the SF-6-SF surfactant is 200 ppm (0.24 mmol/L) in aqueous solution. In this article, surfactant concentrations in a range of 500−3000 ppm are selected in mixed polymer-surfactant systems in this study to ensure the formation of surfactant micelles in the bulk phase and optimize interfacial and rheological properties for EOR application.

**Synthesis of HMPA Copolymer.** The acrylamide/N-phenylacrylamide-based copolymer was prepared in the laboratory. Initially, aqueous solution containing 20 wt % acrylamide monomer was mixed in an R.B. three-neck flask. After solubilization of acrylamide in water, CTAB (8 g) was added into the solution, followed by 0.423 g of N-phenylacrylamide (2 mol %). Then, it was allowed to stir until a clear solution was achieved. Thereafter, potassium persulfate (0.0036 g) was added into the mixture and the temperature was increased to 323 K for polymerization to occur for 8 h. The reaction was performed under a nitrogen (N₂) environment. The obtained liquid was allowed to cool at room temperature and then extracted by precipitation onto continuously stirred methanol (1 L). The precipitated polymer was filtered out, dissolved in water, and again reprecipitated in methanol (1 L). This process was performed four times to remove CTAB from the final product. Then, the polymer was dried under vacuum at 328−338 K to obtain the HMPA copolymer. Figure 18 shows the chemical reaction for the synthesis of acrylamide/N-phenylacrylamide to form the hydrophobically modified polyacrylamide (HMPA) copolymer.

![Figure 18. Reaction scheme for synthesis of HMPA copolymer.](image)

**HMPA Characterization.** **Chemical Analysis.** FTIR of the polymer compound was performed using a Perkin-Elmer Spectrum 2 spectrophotometer using potassium bromide (KBr) pellet in a wavenumber range of 4000−400 cm⁻¹. Chemical characterization by proton nuclear magnetic resonance of the synthesized HMPA copolymer was performed with the help of a Bruker Ascend 400 MHz NMR spectrometer. Polymer molecular weight was studied by a multiangle light scattering spectrophotometer by BI-MwA, Brookhaven Instruments. Polymer solution was prepared in HPLC grade water using 3020 ppm polymer concentration. Aqueous copolymer solution was tested to check its tolerance in the presence of salt ions. Salt tolerance studies were carried out at 303 and 343 K and solution was visually inspected for formation of precipitates. The viscosity of the polymer solution is measured at different shear rates using a Bohlin Gemini rheometer (Malvern Instruments Ltd., U.K.) under influences of temperature and salinity.

**Physicochemical Evaluation of HMPA + Gemini Surfactant Fluids.** **Surface Tension Measurement.** The Du Noüy ring method employed in a tensiometer to measure surface tension at the air-aqueous interface at 303 K. Initially, experiments were conducted with varying polymer concentrations. Thereafter, polymer-gemini surfactant mixtures were prepared with varying 14-6-14 GS concentrations at constant polymer concentration (5000 ppm).

**Rheological Studies.** Viscosity of copolymer nanoemulsion fluids was studied as a function of varying shear rates using a cup and bob measuring system using a Bohlin Gemini rheometer. The viscoelastic properties of copolymer solutions (containing 5000 ppm HMPA) with varying NaCl concentrations were determined at 343 K using the same instrument. At first, to find the strain value, the amplitude sweep was performed on solution and then at constant strain value, frequency sweep tests were performed. G' (elastic modulus) and G" (viscous modulus) indicate elastic energy stored within the fluid and energy required to initiate the flow, respectively.

**Nanoemulsion Preparation and Characterization.** **High-Energy Synthesis.** Nanoemulsion consists of n-heptane (oil) cores, stabilized by the {polymer (HMPA) + gemini surfactant (14-6-14 GS/SF-6-SF GS)} shell and dispersed in an aqueous phase. The high-energy method was used to prepare emulsion. Emulsion was prepared by mixing a solution containing 90% (v/v) aqueous solution and 10% (v/v) n-heptane (oil) using a magnetic stir bar for 10 min at 1000 rpm. Afterward, a Hielshers UP200HT ultrasonic homogenizer (200 W, 26 kHz) was used to prepare emulsion by ultrasonication. The stability of formed emulsions was observed as a function of polymer/surfactant composition and time.

**Nanoemulsion (Oil) Droplet Analyses: DLS and Zeta Potential.** Emulsions were characterized using a Malvern Zetasizer Nano S90 instrument at 303 K. Refractive indices and absorbance were determined by a Refracto 30PX meter and UV-1800 spectrophotometer for dynamic light scattering (DLS) input data, respectively. Emulsion samples were analyzed in an Omega cuvette to determine zeta potential among dispersed oil droplets in an Anton Paar LiteSizer 500 instrument.

**Miscibility Experiments.** To test crude oil miscibility of copolymer and copolymer/gemini surfactant solution, crude oil and prepared polymer or polymer/gemini surfactant solution (1:1 ratio) were poured into test tubes and mixed for a period of 12 h. The total mixture volume was 20 mL. The two liquid mixed by a Rivotek horizontal shaker. The miscibility time of crude oil in solution signifies a relative measure of the fluid’s enhanced oil extraction ability. The miscibility of liquids was determined optically (visual observation).

**IFT Measurement.** Interfacial tension between crude oil and aqueous solution of polymer or polymer-surfactant solutions was measured by a spinning drop SVT 20 tensiometer. To measure IFT, prepared solution was loaded into a glass tube followed by injection of crude oil. After that, the glass tube was placed in a tensiometer and rotated at 3500 rpm. The IFT value was measured by profile fitting of oil drop within a continuous aqueous solution phase.

**Contact Angle Measurements.** The drop shape analyzer (DSA25, Kruss, Germany) was used to measure the dynamic contact angle between polymer, polymer/gemini surfactant solutions, and quartz and carbonate rock surfaces to evaluate their wettability alteration characteristics. In this experiment, precisely measured 10 μL solution was dropped onto the top of quartz and carbonate rock surfaces. After that, variation in the contact angle was recorded by a video/photographic zoom.
camera. Then, in-built KRUSS software was used to perform further analyses.

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**Notes**
The authors declare no competing financial interest.

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