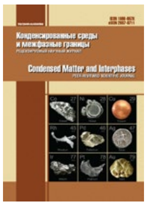

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Review

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The role of polymeric surfactants in enhanced oil recovery: a review

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Abstract

Objective of the article: The continuously increasing demand for oil and petroleum products necessitates the further development of enhanced oil recovery (EOR) methods, including physicochemical techniques such as polymer flooding. Currently, billions of tons of oil remain dispersed and scattered within water-flooded reservoirs. This article provides a review of the literature on the synthesis and application of surfactant solutions and their mixtures with various components (polymers, salts, acids, etc.) in EOR processes.

Experimental section: The use of surfactants contributes to reducing interfacial tension and increasing wettability. Polymeric surfactants represent a promising alternative to modern systems employed in chemical EOR. They can combine the necessary rheological and interfacial properties in a single component, whereas typically, this requires mixtures of several chemical substances. Improved flooding properties using polymeric surfactants are essential for recovering residual oil. In addition to their unique characteristics, it is important to ensure synergy between the surfactant or polymer and other components that meet strict technical requirements. Furthermore, EOR based on polymeric surfactant systems is technologically compatible with conventional water flooding and does not require significant capital investment.

Conclusions: It should be noted that numerous studies have been devoted to the processes of EOR. The presented article emphasizes the efficiency and feasibility of using surfactants based on the results of tests studying the physicochem.

Keywords: Enhanced oil recovery; Polymer surfactant; Ionic liquid; Surface tension; Wettability

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The importance of oil in the global economy is well known. Its consumption by various sectors of the economy has reached colossal proportions, and further growth is expected in the near future. Currently, primary and secondary oil recovery methods account for the extraction of roughly half of the oil reserves in reservoirs [1–6]. Under unfavorable reservoir conditions (such as high heterogeneity of the formation, presence of clay impurities, high oil viscosity, low rock permeability, etc.), the oil displacement coefficient rarely exceeds 30–35 %. The depletion of total oil resources necessitates the improvement of secondary and tertiary oil recovery methods [7–9]. These methods are divided into several groups, including physicochemical ones, which encompass techniques involving surfactants, water-soluble polymers, acids, micellar solutions, as well as micellar-polymer flooding [10–13].

Physicochemical methods for increasing oil recovery are highly promising and exceptionally effective, as they can significantly raise both the oil displacement coefficient and the sweep efficiency of the reservoir by the flooding solution. It is necessary to emphasize the high efficiency of these methods in the extraction of relatively hard-to-recover heavy oils, whose share in global production continues to grow [14–16]. In addition, recent scientific and technical literature highlights studies focused on developing and applying technologies to enhance oil recovery using nanofluids and nanogels [17–21]. Researchers have found that the use of nanoparticles can alter the wettability of reservoir rocks, reduce interfacial tension, lower oil viscosity, and increase disjoining pressure.

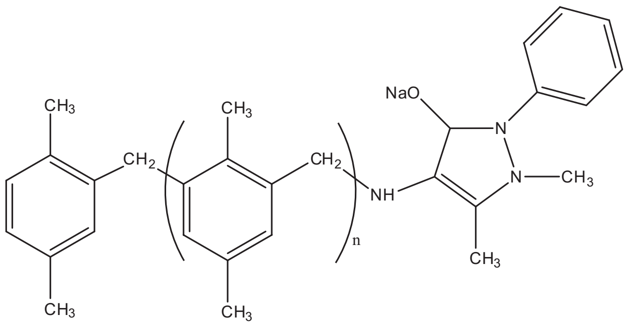
Oil recovery from reservoirs largely depends on the properties of the interfaces between oil, water, gas, and rock. High extraction rates can be achieved by increasing the capillary number, which is defined as the ratio of viscous forces to surface tension [22–25]. To achieve a sufficiently high capillary number effective for displacing oil from the reservoir rock and pore spaces, an ultra-low interfacial tension in the range of 10^{-3} mN/m is required [26–34]. Such low interfacial tension can be achieved through the use of surfactants and/or combinations of surfactants [35–38]. The use of surfactants in tertiary oil recovery represents a promising direction that requires detailed investigation not only of the surfactants themselves but also of their mixed solutions with polymers, salts, acids, and other components capable of enhancing their performance.

The purpose of this review is to provide a concise analysis of studies on the synthesis and properties of reagents used for tertiary oil recovery.

Polymers employed to enhance oil production should dissolve well in saline water and possess the ability to reduce surface tension. For this purpose, polymers containing functional groups, surface-active polymers, surfactant–polymer complexes, surfactant–polymer mixtures, and surface-active oligomers are used [39–48].

In recent years, to avoid side effects associated with alkali–surfactant–polymer flooding (caused by the use of caustic alkalis), greater attention has been given to alkali-free surfactant–polymer flooding [49]. This approach makes surfactants more hydrophobic. Researchers have synthesized a new type of carboxybetaine surfactant – didodecyl polyoxyethylene (n) ether methylcarboxylbetaine ($diC_{12}E_nB$, n = 2, 3, 4) – in the form of homogeneous compounds, as well as dicocosyl alcohol polyoxyethylene ether methylcarboxylbetaine, and evaluated their properties as surfactants for alkali-free surfactant–polymer flooding. With an increase in the number of ethylene oxide groups, the solubility of surfactants increases, while their adsorption capacity decreases, resulting in enhanced hydrophilicity of the surfactant molecules. The use of these surfactants enables the achievement of ultra-low interfacial tension values on the order of 10^{-2} mN/m between crude oil and water.

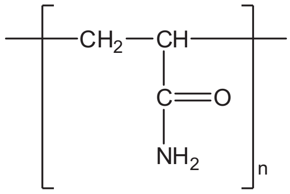
N. V. Klyuchnikova and co-authors [50] developed a formulation for the production a polymeric surfactant based on xylene–formaldehyde resin and 4-aminoantipyrine. FTIR spectroscopic studies confirmed the proposed structure of the synthesized compound.



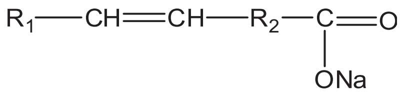
The technological characteristics of the obtained product were studied. The investigation of the wettability intensity of a solid surface by the synthesized polymeric surfactant showed that at a surfactant concentration of 0.05 %, instantaneous absorption into the surface occurs. The surface tension of the synthesized polymeric surfactant solution at the air interface was also examined. At a concentration of 1.2 %, the surface tension decreased to 38.7 mN/m. The hydrophilic–lipophilic balance was calculated using the Davies method, yielding a value of 8.33. These studies indicate the potential applicability of the synthesized polymeric surfactant as a wetting additive.

M. Madani [51] and co-authors conducted fundamental research on an environmentally friendly surfactant as a chemical agent for EOR. Surfactant injection is a key chemical EOR method that enhances oil production from underground reservoirs by reducing interfacial tension and altering wettability. However, most available or proposed synthetic surfactants have negative environmental impacts. In this study, a new synthesis procedure was described for a surfactant based on amino acids, which is non-toxic, biocompatible, and easily biodegradable. The interfacial tension (measured using the pendant drop method) at the kerosene–water interface and the wettability of the surfactant solution (measured by the contact angle method) were determined in the presence of both oil phase and characteristic rock types (carbonate and sandstone). By evaluating the critical micelle concentration (CMC), the optimal surfactant concentration was determined (under typical salinity conditions) for conducting dynamic secondary and tertiary core flooding tests. A comparison of secondary and tertiary flooding schemes using the surfactant suggests that it is potentially more effective when introduced as a secondary recovery agent.

Researchers from Bashkortostan [52] investigated the physicochemical properties of a surfactant–polymer system for EOR. As the base components, polyacrylamide



and a micelle-forming anionic surfactant (brand A) derived from plant-based raw materials were used,



where R_1, R_2 – C_6–C_9.

Based on them, two surfactant–polymer systems were prepared. In the first case, the reagent containing a water-soluble polymer was designated as the basic formulation (grade B), while in the second case, the reagent containing both a water-soluble polymer and modifying additives was designated as the optimized formulation (also grade B). Both systems belong to the category of “green chemistry” reagents. The dependence of dynamic viscosity of the tested solutions on concentration at different temperatures was investigated. At a polyacrylamide solution concentration of 0.11 wt. %, increasing the temperature from 10 to 60 °C reduced the viscosity from 22.6 mPa·s to 7.7 mPa·s. For grade A, increasing the temperature and concentration did not cause significant changes. The grade B reagents behaved similarly to polyacrylamide solutions – that is, as temperature increased, viscosity decreased, while increasing concentration led to further rise in viscosity. The surface activity of aqueous reagent solutions at the kerosene–water interface was also examined. It was found that reagent grade A exhibited the highest surface activity: at a concentration of 0.3 %, the interfacial tension was 2.5 mN/m. Based on the experimental data, graphs were constructed showing the dependence of interfacial tension on reagent concentration at the kerosene interface (Fig. 1).

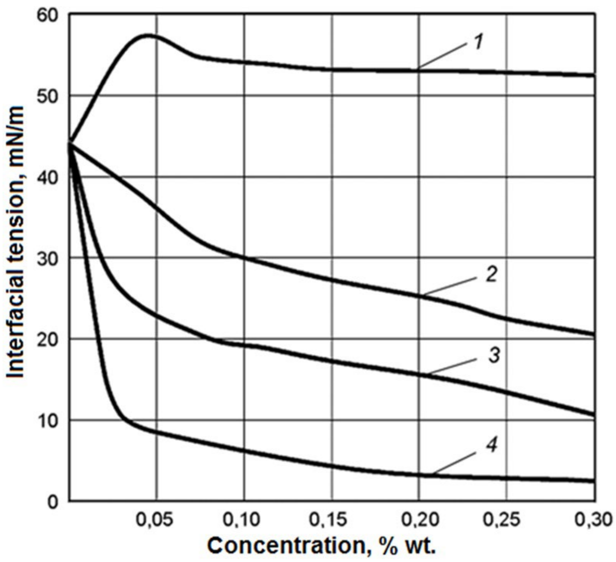


Fig. 1. Graph of the dependence of surface tension on the concentration of the reagent solution at the interface with kerosene [52]: *1* – polyacrylamide; *2* – basic (grade B); *3* – optimized (grade B); *4* – (grade A)

Analysis of these results suggests a positive influence of the developed systems on EOR processes.

Surfactants of polymeric and oligomeric nature synthesized by the authors [53–54] were tested for oil-displacing capability with the aim of using them to increase oil recovery from reservoirs [55–61]. Laboratory experiments involved propoxylated polymethacrylic acid (PPMAA) neutralized with 50 % sodium hydroxide, and propoxylated polyacrylic acid (PPAA-50). Samples of partially neutralized polyacrylic acid (using different bases) were also propoxylated, as well as propoxylated copolymers of quaternary 4-vinylpyridine salts with acrylic acid and copolymers of hydroxypropyl acrylate with acrylate salts. Bench tests demonstrated that PPMAA and PPAA-50 not only match but outperform polyacrylamide (the widely used polymer for EOR worldwide) in terms of efficiency and dosage. According to the test results, PPAA-50, in both sodium and potassium modifications, displayed the dual characteristics of a surfactant and a polymer during the oil displacement process in porous media.

Russian researchers [62] conducted laboratory tests to identify the optimal surfactant–polymer mixture composition, evaluating interfacial tension, thermal stability, phase behavior, and rheological properties. After laboratory trials, field tests were performed on two wells of the Kholmogorsk oilfield, using separating chemical tracers. Field results for the selected surfactant correlated well with laboratory findings. The tests revealed that residual oil saturation within the treated zone decreased by approximately 11 %, equivalent to about one-third of the residual oil remaining after water flooding – a strong indication of the surfactant–polymer system's effectiveness.

German scientists [63] explored a process involving grafting sulfo groups from a solvent into the polymer chain. The methyl ether sulfonate, an anionic surfactant derived from palm oil, was used as the reactive species. The optimal polymerization results were achieved at a molar ratio of methyl ether sulfonate : acrylamide = 1 : 0.3. When the polymeric surfactant was added, the interfacial tension decreased from 8.6 to 2.3 mN/m. Thermogravimetric analysis confirmed that this polymeric surfactant is thermally stable under reservoir conditions and capable of emulsifying crude oil. Adsorption studies showed that the adsorption on rock surfaces increased with surfactant concentration, and core flooding experiments demonstrated improved oil recovery across various surfactant concentrations. Despite not achieving extremely low interfacial tension, this polymeric surfactant is considered a viable alternative for EOR applications.

In [64], attention was given to the synthesis of an anionic polymeric surfactant derived from non-edible Jatropha oil for EOR applications. The surfactant was produced by reacting monomeric acrylamide with methyl ether sulfonate derived from Jatropha oil via free-radical polymerization. The synthesized surfactant was characterized using FTIR, ^{1}H NMR, FE-SEM, EDX, TGA, and DLS analyses. The polymeric surfactant exhibited properties of both surfactant and polymer components. Physicochemical testing of the aqueous solutions showed effective reduction of interfacial tension, alteration of wettability, and favorable rheological behavior. The interfacial tension between crude oil and the polymeric surfactant solution at CMC was 2.74 mN/m, which decreased to 0.37 mN/m upon addition of 2.5 wt. % NaCl. The product remained thermally stable under reservoir conditions (80–120 °C) and enhanced oil recovery by more than 26 % after conventional water flooding, with even greater improvement at elevated temperatures.

Researchers [65] synthesized a polymeric surfactant from castor oil for chemical EOR applications. Formulations were prepared with varying mass ratios of surfactant to acrylamide, and the final products were characterized using FTIR, FE-SEM, EDX, TGA, and DLS. The performance of these polymeric surfactants was evaluated by measuring interfacial tension, rheological behavior, and contact angle with sandstone surfaces. Adding NaCl to the surfactant solution reduced the interfacial tension to an ultra-low value of $2.0\cdot10^{-3}$ mN/m. Core flooding experiments demonstrated additional oil recovery of 26.5, 27.8, and 29.1 % with 0.5, 0.6, and 0.7 wt.% polymeric surfactant solutions, respectively, after conventional water flooding.

Recently, ionic liquids (ILs) have been investigated as alternatives to traditional surfactants due to their tunable surface-active properties. A review by Spanish researchers [66] highlighted the advantages of ionic-liquid-based surfactants for EOR, particularly their stability under harsh conditions (high salinity and/or temperature). However, the number of core flooding experiments with ILs remains limited. After secondary flooding, oil recovery reached 32 % of the original oil in place. Most IL formulations were developed for sandstone reservoirs, with few studies involving carbonate cores. The authors proposed and analyzed 1-decyl-3-methylimidazolium triflate ([C_{10}mim][OTf]), which significantly reduced interfacial tension at the oil–water interface. The effect improved with increasing NaCl concentration and decreasing NaOH concentration. An optimized formulation containing 4000 ppm [C_{10}mim][OTf] + 1 wt. % NaOH + 2 wt. % NaCl was suggested. High adsorption in sandstone limited efficiency, but in carbonate cores, an additional 10.5 % oil recovery was achieved at room temperature. When followed by polyacrylamide polymer flooding, the process remained cost-effective. The main EOR mechanism was attributed to interfacial tension reduction, with viscosity effects playing a secondary role.

Indian scientists [67] studied the interfacial properties of imidazolium ionic liquid surfactants and their application for enhanced oil recovery. The advantage of 1-hexadecyl-3-methylimidazolium bromide (C_{16}mimBr) over the traditional cationic surfactant, cetyltrimethylammonium bromide (CTAB), was highlighted. The effectiveness of both (C_{16}mimBr and CTAB) in recovering additional oil was established by conducting laboratory core flooding experiments. The experiments showed that C_{16}mimBr more effectively reduces the interfacial tension between the water-oil system and, thus, recovers more additional oil than the traditional cationic surfactant, CTAB. The obtained results reflect the high interfacial activity, high oil solubility (due to emulsion formation), and stability of C_{16}mimBr during the EOR process under harsh reservoir conditions.

In [68], synthesized ionic liquids (C_8mimBF_4, C_{10}mimBF_4, and C_{12}mimBF_4) were analyzed for their potential application in EOR. Reactions between 1-methylimidazole and alkyl bromide (1-bromooctane for [C_8mimBF_4], 1-bromodecane for [C_{10}mimBF_4], and 1-bromododecane for [C_{12}mimBF_4]) were carried out at a 1:1 molar ratio at 70°C for 48 hours. The resulting ionic liquids were investigated in terms of surface activity, interfacial tension reduction, wettability alteration, adsorption properties, emulsification, and oil recovery. It was observed that surface activity increases with an increase in alkyl chain length. The results of studying interfacial activity as a function of the concentration of ionic liquid, salt (NaCl), and alkali (triethylamine) showed that the synthesized ionic liquids effectively reduce interfacial tension. It was found that with increasing alkyl chain length, the CMC values and interfacial tension (0.041 mN/m) decrease. The synthesized ionic liquids are capable of altering the reservoir rock wettability towards more water-wet (hydrophilic) conditions, leading to greater oil recovery efficiency. Comparative flooding tests were conducted: polymer (partially hydrolyzed polyacrylamide), ionic liquid+polymer, and ionic liquid+polymer+alkali. In terms of interfacial tension reduction, wettability alteration, and additional oil recovery (32.28%), the ionic liquid+polymer+alkali flooding stood out. The authors concluded that ionic liquids can be considered as a new generation of surfactants in chemical EOR processes for reservoirs with harsh conditions.

Scientists from Saudi Arabia [69] conducted comparative studies to investigate the efficiency of four environmentally friendly, low-cost, and commercially available imidazolium-based ionic liquids (1-butyl-3-methylimidazolium chloride $[C_4mim]^+[Cl]^-$, 1-hexyl-3-methylimidazolium chloride $[C_6mim]^+[Cl]^-$, 1-octyl-3-methylimidazolium chloride $[C_8mim]^+[Cl]^-$, and 1-dodecyl-3-methylimidazolium chloride $[C_{12}mim]^+[Cl]^-$) with two conventionally used surfactants (CTAB and SDS) for EOR from a hydrophobic carbonate sample. The effects of various factors were studied, including ionic liquid concentration (0; 50; 100; 250; and 500 ppm), aging time (0; 2; and 8 weeks), and permeability contrast (50 and 250 mD). The experiments were conducted using Saudi Arabian crude oil at high temperature (100 °C) and high salinity (total dissolved solids (TDS) = 240,000 ppm), simulating harsh reservoir conditions. The rock samples were subjected to NMR analysis to determine the imbibition rate and evaluate the oil and water phase distribution during the process. Overall, the ionic liquids had a positive effect on EOR from the carbonate reservoir. The maximum oil recovery using the ionic liquid is 64.6%, which is almost double the performance of seawater (31.3%), while conventional surfactants SDS and CTAB only reached 40.3% and 42.8%, respectively. Furthermore, as the alkyl chain length increases, the oil recovery efficiency grows. Thus, $[C_{12}mim]^+[Cl]^-$ demonstrates the maximum efficiency. Achieving a 15–35% increase in oil production using this ionic liquid-based technology could lead to economic profit in the oil industry. Additionally, these ionic liquids demonstrate good colloidal stability under high temperature and high salinity conditions.

M. S. Benzagouta et al. [70] investigated 6 "Ammoeng" type ionic liquids as surfactants for EOR. The interfacial tension at the interface between oil and solutions of the aforementioned ionic liquids at various concentrations in a 10% wt. aqueous NaCl solution was measured as a function of temperature. The interfacial tension value increases with increasing temperature. In all cases, as the ionic liquid concentration increases, the interfacial tension value decreases. Ammoeng 102 showed the lowest surface tension value, which decreased with increasing temperature. The obtained values were compared with those of commercially available surfactants, namely Triton X-100, measured under similar conditions. The comparison showed that the surface tension values using ionic liquids are much lower. Furthermore, the interfacial tension values for all reagents used in the 10% wt. aqueous NaCl solution were lower than in deionized water under the same conditions. The possibilities of a synergistic effect when using a mixture of Ammoeng 102 and Triton X-100 were also investigated. Experiments showed that the interfacial tension value depends on the total concentration, the mass ratio of the surfactant to the ionic liquid, and the temperature. The saline solution of Ammoeng 102 showed the best results. The study of the effect of these reagents on oil recovery showed that this ability depends on the three-phase contact, namely oil, aqueous solution, and rock.

Iranian scientists [71] conducted research on well stimulation using surfactants as a practical method for EOR. Three different surfactant samples were selected: newly developed commercial (AN-120, NX-610, NX-1510, NX-2760, and TR-880), traditional (sodium dodecylbenzene sulfonate (SDBS) and SDS), and ionic liquid-based surfactants ($[C_{12}mim]^+[Cl]^-$ and $[C_{18}mim]^+[Cl]^-$). Aqueous solutions were prepared in distilled, formation, and seawater. All samples were highly compatible with distilled water. The commercial and ionic liquid-based surfactants were compatible with formation and seawater, while traditional surfactants experienced a loss of functionality as salinity increased. It was found that the commercial and ionic liquid-based surfactants tolerated harsh salinity conditions well and possessed the ability to reduce interfacial tension down to 0.07 mN/m. Contact angle measurements showed that among the investigated surfactants, $[C_{12}mim]^+[Cl]^-$, AN-120, and NX-2760 shifted the rock wettability towards more water-wet conditions, while other surfactants showed no significant effect on altering rock wettability. To study the effect of wettability during the injection of $[C_{12}mim]^{+}[Cl]^{-}$, an imbibition process (duration 21 days) was conducted on a water-flooded core, which revealed that the tertiary oil recovery efficiency was critically increased to 12.7% of the original oil in place.

To clarify the details of the EOR process through surfactant solution flooding, the authors [72] studied the behavior of model systems consisting of a packed column of calcium carbonate (as the porous rock), n-decane (as the oil), and aqueous solutions of the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT). Figure 2 shows a schematic of the setup for packing the powder column.

The AOT concentration was varied from zero to above the critical aggregation concentration (CAC). The salt content in the aqueous solutions was varied to obtain systems with a wide range of interfacial tension values at the oil-water interface. It was shown that the change in contact angle with the change in surfactant concentration is related to surface tension measurements and adsorption isotherms. The adsorption isotherms allow for estimating the concentration of non-adsorbed surfactant in the packed column, which, in turn, permits a detailed analysis of the change in percentage oil recovery as a function of surfactant concentration. At surfactant concentrations below the CAC, the percentage oil recovery is determined by the contact angle. In the case of concentrations above the CAC, additional oil recovery occurs due to solubilization and an emulsification mechanism.

Study [73] primarily focuses on a review of the application of the alkali-surfactant-polymer (ASP) flooding process in oil production and its limitations in onshore and offshore oil recovery. The ASP EOR technology is a versatile method of tertiary oil recovery. Alkali-surfactant-polymer flooding is a combined process in which all three components—alkali, surfactant, and polymer—are injected in a single slug. Thanks to the synergy of these three components, ASP is widely applied in both pilot and field operations with the aim of achieving optimal results at minimal cost. To take this technology to the next level, it is necessary to develop more advanced ASP systems with more cost-effective surfactants in low-alkali systems and with pH-resistant polymers. The article discusses technical solutions for some of these challenges.

The authors of [74] conducted a review of research papers on alternative alkalis, surfactants, and polymer chemical agents for EOR. Based on these works, organic alkalis have been proposed as an alternative to inorganic alkalis to address problems of incompatibility with seawater and formation brine, scaling issues, and the detrimental effect of alkali on polymer thickening. Among the organic alkalis, ethanolamine was found to be the most effective and has therefore been the most widely studied as a potential alkali for field applications. Fig. 3 provides micrographs of "oil-in-water" emulsions with different chemical solutions: surfactant, ethanolamine, and surfactant+ethanolamine.

Its performance is comparable to conventional inorganic alkalis, and in some aspects, surpasses them. Based on various studies, bio-based surfactants have been proposed as an environmentally friendly and cost-effective alternative to synthetic surfactants. Plant-oil-based surfactants have been proven to be superior to synthetic surfactants and are also

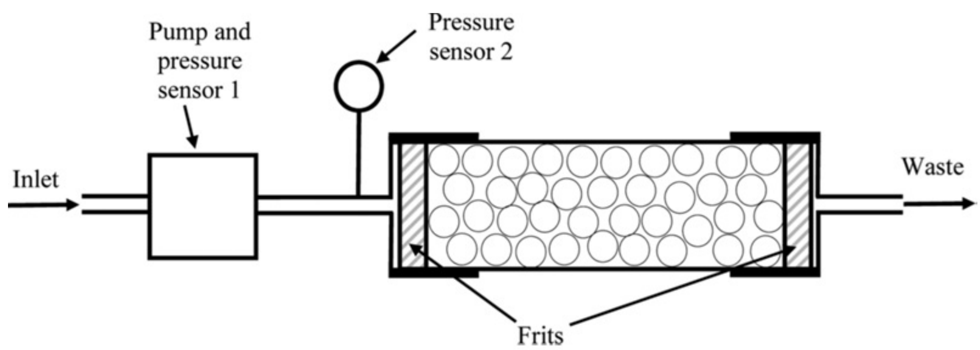


Fig. 2. Diagram of the installation for filling a column with packed powder [72]

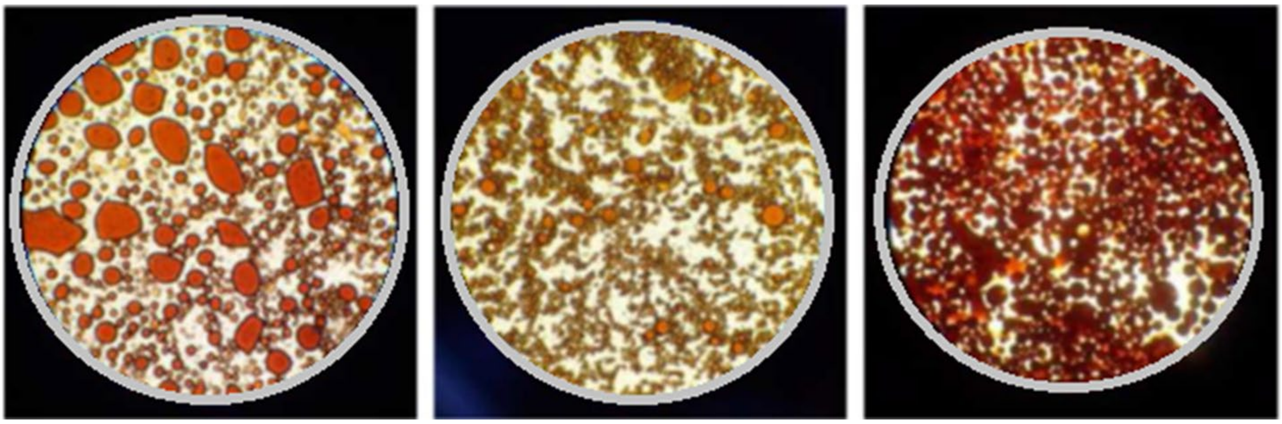


Fig. 3. Microphotographs of oil-water emulsions with various chemical solutions [74]: surfactant (left), ethanolamine (center), as well as surfactant and ethanolamine (right) [74]

environmentally safe. Ionic liquids have been proposed as alternative surfactants for harsh temperatures and high-salinity reservoirs.

However, further research is needed to improve their performance in achieving ultra-low interfacial tension. Biopolymers have been recommended as a stable alternative to synthetic polymers under harsh temperature conditions in high-salinity reservoirs.

Study [75] reported the development and testing of enzyme-based biochemical complexes in Vietnam's oil industry. Studies showed that to avoid a decrease in enzyme activity in reservoir conditions (due to high temperature and salinity), the use of a chelating agent is required to limit the influence of metal ions. To improve the properties of the enzymes, they were combined with a surfactant, for which alpha-olefin sulfonate was selected. The surface tension of the solution decreased to 2.7 mN/m. The surface tension of the initial enzyme solution increases during thermal stabilization, whereas in the enzyme-surfactant solution, the surface tension changes insignificantly. This means the added surfactant helps to increase the surface activity and thermal stability of the initial enzyme solution. Using the Modde 5.0 (Modeling and Design) program, the optimal concentration of the enzyme solution and surfactant was determined for the minimum surface tension value of the enzyme solutions. Based on the results, the following component composition was determined, %: enzyme - 50.0; surfactant - 30.0; stabilizer - 1.0; microorganism inhibitor - 0.5.

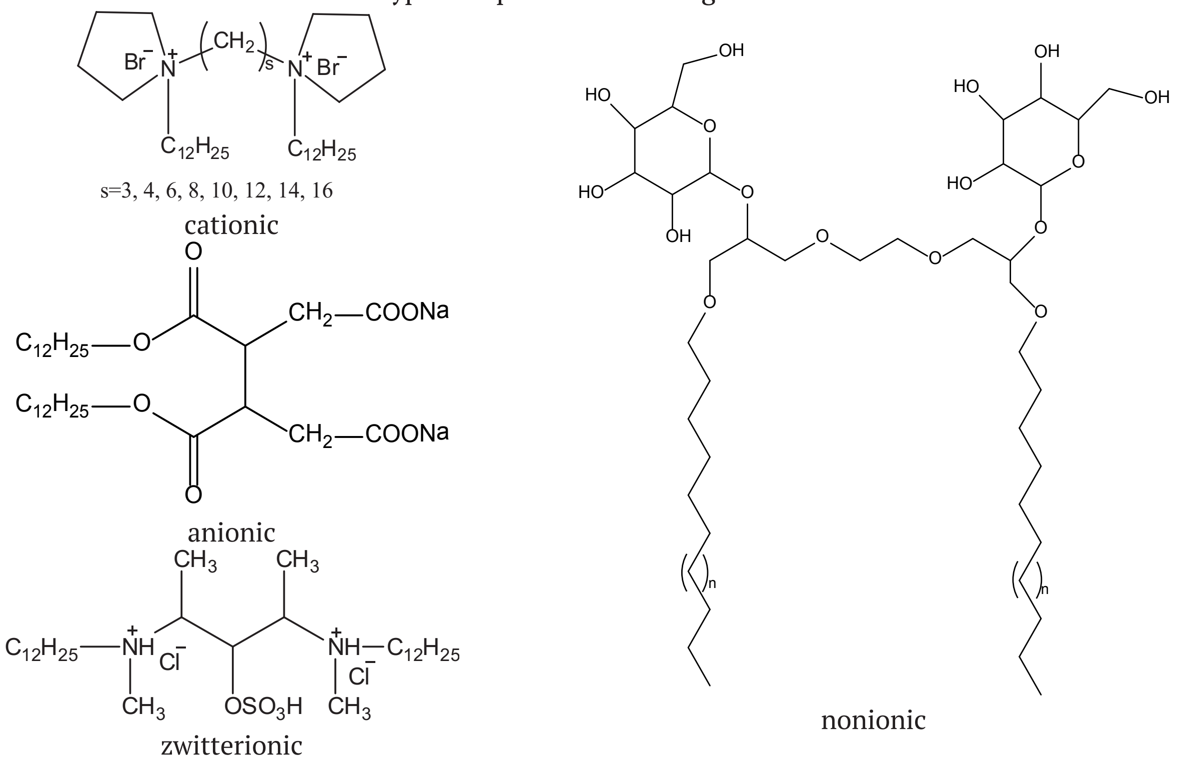
In [76], four different types of surfactants from a new class were investigated for their effectiveness in tertiary oil recovery: ditridecyl sulfosuccinate ester; coconut diethanolamide; alkyl polyglycosides (APG); and sodium salts of alkyl propoxy sulfate. The tested formulations were selected after extensive research, including measurements of interfacial tension and adsorption behaviour on kaolinite clay. The main results of this study include: ditridecyl sulfosuccinate ester showed only low (15%) tertiary oil recovery; coconut diethanolamide demonstrated high TOR (75%); APG showed good tertiary oil recovery, from 40% to 55%; sodium salts of alkyl propoxy sulfate were also effective in terms of tertiary oil recovery (recovering 35% to 50% additional oil); coconut diethanolamide and sodium salts of alkyl propoxy sulfate were effective even at high salinity (4–10 wt% NaCl). The adsorption of APG surfactants onto the solid state depended on the alkyl chain length of the APG. A longer chain length resulted in greater adsorption. All surfactant formulations were suitable in terms of EOR (after waterflooding). The observed tertiary oil recovery was in the range of 15–75% for consolidated sandstone cores. 94% recovery of the original oil in place from the reservoir was reported in the case of sandstone. The results indicate that a wide range of surfactants can meet the technical requirements for EOR agents.

Study [77] focused on gemini surfactants, examining their adsorption, rheology, wettability alteration, and interfacial properties, highlighting their potential as next-generation reagents for EOR. The rich variety of anionic, nonionic, cationic and zwitterionic gemini surfactants makes them accessible. The structures of typical representatives of gemini surfactants are shown below.

Low CMC, excellent wetting and foam-forming properties, the ability to reduce surface tension, unique aggregation behavior, and the capacity to achieve ultra-low interfacial tension at low concentrations make gemini surfactants highly suitable for use in EOR processes. Despite the growing number of laboratory studies and promising results obtained for gemini surfactants, core flooding data remain scarce. This is likely due to the fact that gemini surfactants are still a relatively new class of surfactants; however, they are expected to replace conventional monomeric surfactants in the future.

Authors [78] presented a chronological overview of technological developments and physicochemical research related to gemini-type surfactant systems. The paper focuses primarily on cationic, anionic, nonionic, and zwitterionic gemini surfactants. Traditional EOR systems are characterized by the widespread use of monomeric surfactants, which tend to self-aggregate at high concentrations. Consequently, crude oil often remains insufficiently mobile during displacement, necessitating the use of viscous buffers to push oil toward production wells. By contrast, gemini surfactants, due to their unique dimeric molecular structure and superior properties, yield innovative and efficient results in EOR applications. Cationic gemini surfactants are the most extensively studied and have demonstrated excellent performance in thermodynamically stable solutions, microemulsions, and nanofluid-based systems, suitable for both conventional and unconventional reservoirs. Anionic surfactants, particularly sulfonates, form a diverse range of high-quality emulsifying and foaming aqueous solutions, ideal for EOR. Nonionic surfactants, when used in mixtures or formulations, exhibit salt tolerance, favorable rock adsorption, and compatibility with formation fluids. Zwitterionic surfactants, owing to their structural features, offer stability over a wide salinity range, ultra-low interfacial tension, and viscoelastic properties, combined with low binding energy, which enhance their EOR potential. Gemini surfactants are effective in small quantities, and their dimeric structures enable synergistic

The structures of typical representatives of gemini surfactants



interactions with polymers, nanoparticles, and other additives, leading to increased tertiary oil recovery. The authors concluded that it is essential to develop commercially viable strategies for applying gemini surfactants to recover additional crude oil via EOR. The use of gemini surfactants in efficient oil recovery is expected to show stable and dynamic growth in the future.

In [79], four cationic gemini surfactants with different aliphatic spacer lengths were synthesized via the reactions of 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, and 1,6-dibromohexane with N,N-dimethyltetradecylamine. Unlike conventional surfactants, gemini surfactants exhibited very low CMC values (< 200 ppm). It was found that the CMC increases with temperature. These surfactants demonstrated excellent salt resistance and long-term thermal stability. Optimal viscosities were observed in systems where wormlike micelles formed typically in shorter-spacer systems (with longer spacers leading to spherical micelles). Dynamic surface tension measurements showed an initial decrease over time until equilibrium was reached. Ultra-low interfacial tension values, in the range of 10^{-2} mN/m, were observed in crude oil–surfactant systems, further reduced to 10^{-3}mN/m with salt addition. Both salt addition and temperature increase improved wettability. TOR in the range of 24–30% was achieved with gemini surfactants alone and 30–35% for polymer (partially hydrolyzed polyacrylamide)–gemini surfactant systems. The compound 14–6–14 exhibited the best performance for EOR applications.

Conclusions

A concise literature analysis on the study of polymeric surfactants in EOR processes leads to the conclusion that using surfactants either as independent agents or in mixtures with polymers, acids, salts, and other components enhances their properties and represents a promising direction for research and practical application. Therefore, the study of polymeric surfactants as agents for improving oil recovery remains a relevant and significant topic.

Contribution of the authors

G. A. Ahmadova – scientific supervision, research concept, writing, and final conclusions. R. A. Rahimov – scientific supervision, research concept. A. Z. Abilova – experimental research, literature selection, and text editing. Sh. M. Nasibova – formal analysis, data curation. Kh. A. Mammadova – formal analysis, data curation.

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