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EFFICACY OF SYNTHETIC HYDROPHOBIC ASSOCIATIVE TETRAPOLYMERS FOR IMPROVED RECOVERY OF VISCOUS OIL IN SANDPACK MODEL

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Abstract.[1] This study examined the suitability of hydrophobic associative tetrapolymers (HATs) for enhanced oil recovery through sandpack flooding. Two novel hydrophobic associative tetrapolymers, herein designated as HAT-1 and HAT-2 were synthesised *via* free radical polymerisation and the structures were confirmed by Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (^{1}H NMR). HAT-1 composed of acrylamide - hydroxyethyl methacrylate - N-vinyl pyrrolidone - N,N-dimethyl acrylamide and HAT-2 consisted of acrylamide - sodium 2-acrylamido-2-methyl propane sulphonate - diallyldimethylammonium chloride - lauryl methacrylate. Comparative tests were carried out under laboratory conditions on the oil displacement efficiencies of the two HAT polymers. The incremental oil recovered using polymer HAT-1 and HAT-2 injection after water flooding were 33.7% and 36.2%, respectively. Combining the oil recovered from water flooding followed by polymer flooding for both scenarios, the cumulative recovered using HAT-2, 83.3 % was relatively higher than that of HAT-1, 74.4%. These values are relatively high from the economic perspective. Based on brine viscosity enhancement, mobility ratio reduction and additional oil recovery, HAT-2 polymer exhibited a relatively higher potential to improve oil recovery for reservoirs with characteristics similar to the experimental conditions for this work.

Keywords: hydrophobic associative tetrapolymers, polymer flooding, viscous oil, sandpack model, incremental oil recovery.

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1. Introduction

Petroleum crude oil is a non-renewable natural resource, comprising mainly a mixture of hydrocarbons, that exists in a liquid phase in the reservoirs and remains wholly or partially liquid at atmospheric conditions after separation through surface facilities. Crude oils usually occur in permeable and porous reservoir rocks deep underground and are produced through conventional recoverable methods. The rapid depletion in conventional oil reserves however, triggers increasing development of heavy oil resources.[1] Much commercial quantities of the oils remain in the reservoir after primary and secondary conventional methods are exhausted,[2,3] attributable mainly to viscous forces, interfacial forces, capillary forces, and reservoir heterogeneities which result in poor displacement efficiency.[4] The natural energies or forces in the reservoir are the drive mechanisms during the primary stage of hydrocarbons production. Secondary production is achieved by augmenting or maintaining the reservoir pressure through injection of water or gas. Water flooding is prone to low oil recovery with time because of poor sweep efficiency arising from bypassed or unswept oil.[5,6] Water flooding is generally less effective for reservoirs with high oil viscosity.[7,8] Heavy oils refer to a category of crude oils with viscosity in the range of 50 – 50,000 cP (mPa·s).[9] For heavy oil reservoirs with thicknesses less than ten metres (10 m) or at depths greater than one thousand metres (1000 m) or where bottom water exists, thermal recovery technology is not economically appropriate and thus, chemical flooding becomes very promising for improving oil recovery.[10] The progressive poor performance of secondary recovery necessitates the implementation of improved oil recovery techniques as a remedy to beef up oil production and to meet the global demands.[11]

For poor oil recovery based on water injection, polymer flooding (polymer augmented waterflooding) provides an antidote for improving oil recovery. Polymer flooding entails the addition of polymers to the water or brine before injecting the fluid into the reservoir. The flooding enhances oil recovery based on improved sweep efficiency because of increase in viscosity of injected

fluid, favourable mobility ratio and reduction of the rock permeability.[2,3] Furthermore, polymers are not corrosive, and their application can reduce water/oil ratio of production. This decreases the operational costs and consequently generates higher economic return.[12]

Polymer flooding, although, longstanding and well promising as a sustainable method for petroleum recovery, still faces some challenges to its wider application.[13] Polymer applications are adversely affected by high temperature, high salinity, high shear, high viscosity of oils, among others.[14] Synthetic polymers, particularly, derivatives of polyacrylamide, aimed at improving polymer performance under unfavourably conditions have been considered the subject of many scientific investigations.[15-17] This work focuses on the design of polymers with the capacity for salt tolerance and ability to enhance the recovery of viscous oils. Polymers are usually dissolved in seawater, an injection fluid in offshore fields, since environmental regulations restrict the use of freshwater. Furthermore, most reservoir water contains salts which interact with the polymers during polymer flooding. Partially hydrolysed polyacrylamide, a conventional polymer used in the oil fields, is prone to viscosity loss at high salinities. Associative polymers, by virtue of the hydrophobic content, are considered to exhibit good salt-tolerance because of the salt screening effect in aqueous brine media. This work deals with the synthesis of novel hydrophobically associative tetrapolymers (HATs) and their efficacy for improved recovery of viscous oil in sandpack model.

Mechanisms of Polymer Flooding

Polymers drive mechanisms for enhancing oil production are basically: (i) augmentation of the driving fluid (water or brine) viscosity, (ii) reducing the driving fluid mobility, and (iii) sweeping (contacting) a larger volume of the reservoir. Optimum polymer concentrations in brine or water for flooding should range from 750ppm to 2500ppm.[18,19] During flooding, the bank of polymer-viscosified solution moves through the injection well toward the production wells. Physical and chemical interactions occur between the polymer solution, the reservoir rock and reservoir fluids. For ideal situations, the polymer solution should travel through the rock formation sweeping the oil toward the production wells. However, when a fluid is injected into a reservoir, it follows a path of least resistance (usually the layers of highest permeability) to a region of lower pressure around the producing wells. If the oil in place has a higher viscosity than the injected fluid the displacing fluid will finger through the oil resulting in low sweep efficiency, or substantial bypassed of residual oil.[6] To improve sweep efficiency and avoid fingering or bypass, the polymer solution should act primarily as a thickener, by increasing the viscosity of the injected water (displacement phase) and can also decrease the permeability of the reservoir, thus improving the vertical and lateral sweep efficiency and ultimately improving oil recovery efficiency.[20,2]

One of the most important screening parameters for oil displacement efficiency is the mobility ratio (Eq. 1). Mobility is a measure of how easily a fluid moves through porous media. Oil displacement is most efficient when the mobility of the drive fluid is less than that of the oil. Optimum displacement requires a low mobility drive fluid in a cost-effective manner.[2] The mobility ratio is reduced by lowering the viscosity of the displaced fluid (oil), increasing the viscosity of drive fluid (water/brine), increasing the effective permeability to oil, or decreasing the effective permeability to the displacing fluid. Polymer flooding improves the efficiency of oil recovery through a favourable adjustment of fractional flow, by decreasing the water/oil mobility ratio and by diverting injected water from zones that have been swept. Mathematically expressed:
the mobility of oil (displaced fluid), [λ_o], in the reservoir is

$$\lambda_o = \frac{k_o}{\mu_o} \tag{1}$$

the mobility of the injected fluid, [λ_w]

$$\lambda_w = \frac{k_w}{\mu_w} \tag{2}$$

the mobility ratio, [M]

$$M = \frac{\lambda_w}{\lambda_o} = \frac{\mu_o k_w}{\mu_w k_o} \tag{3}$$

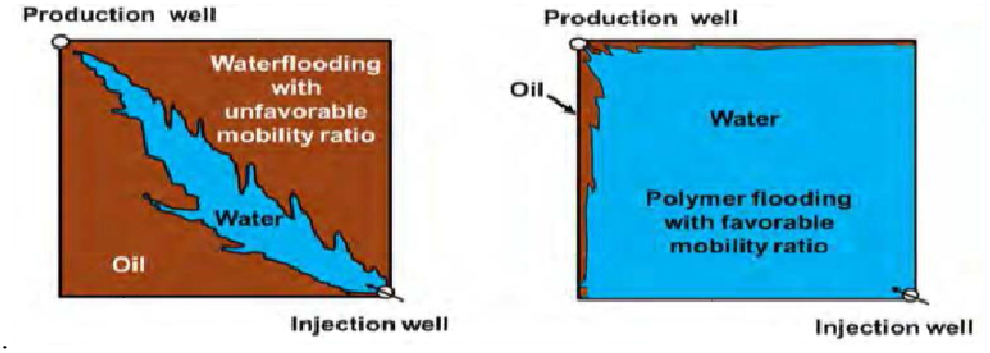
Furthermore, the combined effects of relative permeability and viscosity of water and oil can be expressed as a function of fractional flow using Darcy's law as stated below.[6]

$$f_o = \frac{1}{[1+M]} = \frac{1}{\left[1+\frac{(\mu_o k_w)}{(\mu_w k_o)}\right]} \tag{4}$$

$$f_w = \frac{M}{[1+M]} = \frac{1}{\left[1+\frac{(\mu_w k_o)}{(\mu_o k_w)}\right]} \tag{5}$$

f_o and f_w are fractional flows of oil and water, respectively.

A diagrammatical illustration of waterflooding with unfavourable mobility ratio (M>1) and polymer augmented waterflooding with favourable mobility ratio ($M \leq 1$) is shown in Fig. 1a,b. Any change that reduces the mobility ratio will improve the rate of oil recovery by increasing the fractional flow of oil. This is achieved by polymers injection through the increase in the viscosity of water and reduction of the relative permeability to water. A mobility ratio of one or slightly less effected by the polymer will achieve an efficient and piston-like displacement of the oil,[21] resulting in an increase in production.[6] Even when the mobility ratio is favourable, reservoir heterogeneity primarily in the vertical direction can still cause poor volumetric sweep. This calls for polymer-augmented waterflooding to reduce the water mobility in the high-permeability layers, in order to displace oil from lower-permeability layers.



a) b)

Fig.1. (a) Waterflooding with unfavourable mobility ratio (M> 1), (b) Polymer augmented waterflooding with favourable mobility ratio (M ≤ 1) [22]

High mobility ratio promotes poor displacement and sweep efficiencies due to the large viscosity difference between the displacing fluid and the oil, or due to the presence of high permeability flow channels that result in early breakthrough (viscous fingering) of the displacing fluid toward the producer well.[23]

2. Experimental

2.1. Materials

Homopolymers, in general, do not exhibit a wide range of vital properties for many applications in oil recovery. This calls for heteropolymer syntheses, which provide the ability to combine the properties of homopolymers by polymerising two or more functional monomers to realise a single copolymer with attractive functionalities. This section focuses on the syntheses of two tetrapolymers by combining four monomers in each process. HAT-1 consists of acrylamide, hydroxyethyl methacrylate, N-vinyl pyrrolidone, and N,N-dimethyl acrylamide while HAT-2 was formed using acrylamide, 2-acrylamido-2-methyl-1-propane sulphonic acid, lauryl methacrylate, and diallyldimethylammonium chloride.

2.2. Methods

2.2.1. Synthesis of HAT-1 Polymer

HAT-2 was synthesised in a three-neck flask equipped with a magnetic stirrer, nitrogen gas delivery tube and a thermostatic water bath by a free radical polymerisation in deionised water under nitrogen sparging using 2-2'-azobisisobutyronitrile as an initiator. Detailed procedure for synthesis (Scheme 1) and structural analyses of the HAT-1 polymer by FTIR and proton nuclear magnetic resonance (^{1}H NMR) spectral analyses were previously reported.[24]

2.2.2. Synthesis of HAT-2 Polymer

HAT-2 comprising acrylamide (AM) - sodium 2-acrylamido-2-methyl propane sulphonate (NaAMPS) - diallyldimethylammonium chloride (DADMACL) - lauryl methacrylate (LMA) was synthesised by free radical micellar polymerisation using monomer feed mole ratios of 69%AM/27% AMPS/2.7%DADMACL/1.3%LMA, total monomer concentration of 21.8 wt./vol. %, pH of 8.0, 50^{o}C and initiator dosage of 0.5 wt. %, 2.0 wt. % of sodium dodecylbenzene sulphonate (surfactant) and reaction time of 1.0 h. Specified quantities of AMPS were first dissolved in a separate volume of sufficiently low quantity of deionised water; pH was then adjusted to the desired value using 2 M NaOH. Acrylamide was dissolved in a separate low volume of deionised water before being added to AMPS solution, the mixture was introduced into the three-neck flask and purged with nitrogen for at least 20 minutes. While stirring the mixture in the flask with the temperature adjusted to 50^{o}C, lauryl methacrylate, diallyldimethylammonium chloride, $K_2S_2O_8$, and sodium dodecylbenzene sulphonate (SDBS) were mixed in the right proportion and gradually dispensed into the flask. After polymerisation, the tetrapolymer was isolated from highly viscous mass using excess of 50:50 vol./vol. acetone-ethanol mixed solvent and finally, dried at 60^{o}C. Reaction is shown in Scheme 2.

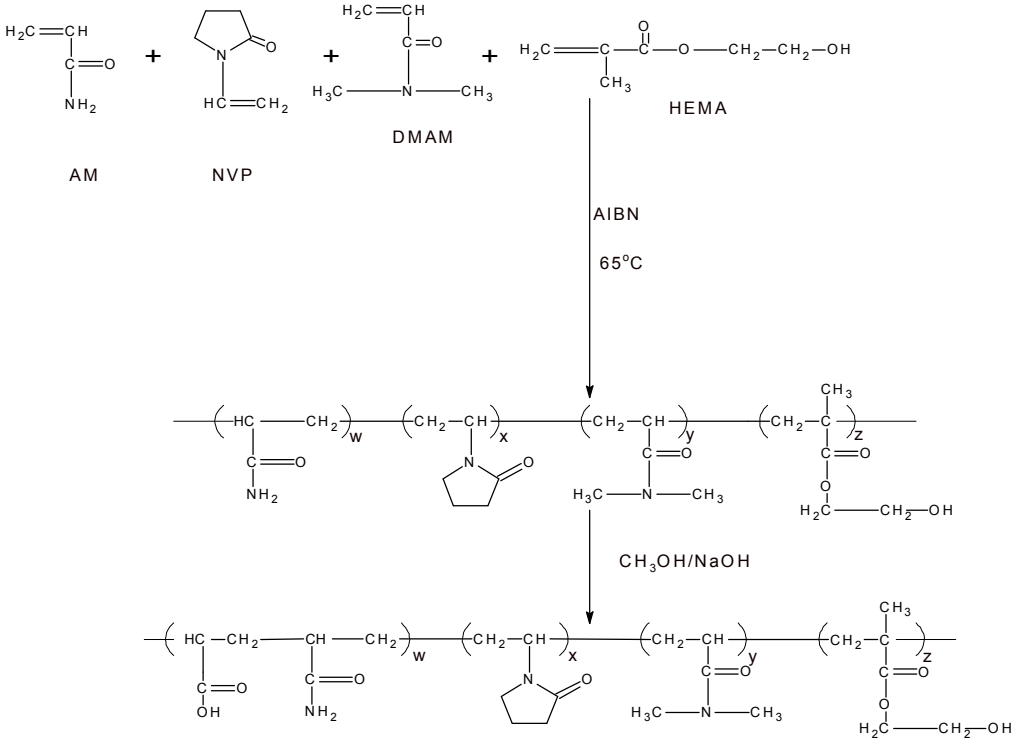
2.2.3. Sandpack Flood Experiment

Laboratory core and sandpack flood experiments are used to validate the performance of candidate polymers for enhanced oil recovery for potential field applications. The effectiveness of polymers for enhanced oil recovery (EOR) can be assessed under simulated reservoir conditions by determining the percentage of crude oil produced from sandpack or core plug containing oil. Residual oil trapped in the core after water flooding is the target of

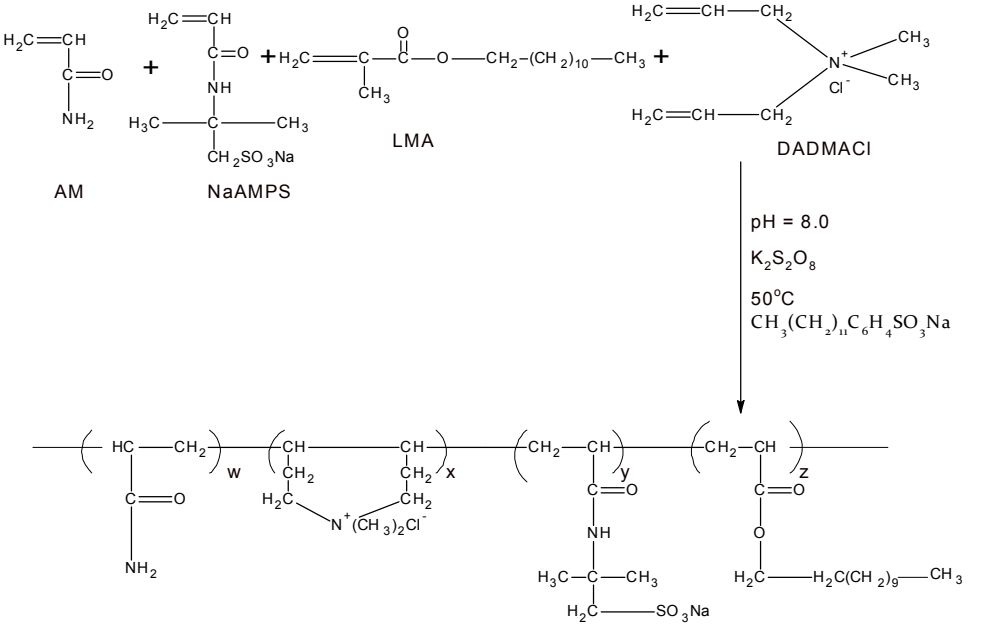
the polymer flooding. The section evaluates the performance of the two HAT polymers in recovering medium oil under saline conditions through polymer flooding using sandpack models.

Bulk Volume, Pore Volume and Porosity of Sandpack

The bulk volume of the sandpack was calculated using the internal diameter and length of the sandpack holder. The pore volume (V_{pore}) was calculated by a mass balance from the mass of saturated brine divided by density of brine. Porosity is one of the most important rock properties in describing porous media. Porosity of the sandpack is the pore volume (V_{pore}) divided by its bulk volume (V_b), and expressed as a percentage using the formula of Table.



Scheme 1. Tetrapolymerisation followed by partial hydrolysis and structure of HAT-1 polymer



Scheme 2. Tetrapolymerisation and structure of HAT-2

Experimental Fluids

A hard synthetic brine typical of a reservoir brine was prepared, consisting of 3% NaCl, 0.15% $CaCl_2$, and 0.15% $MgCl_2$ (3,300 ppm). HAT-1 was dissolved in the brine producing a solution viscosity of 12.9 cP, HAT-2 had a solution viscosity of 15.3 cP, and the oil sample viscosity was 72.0 cP.

Water and Oil Saturations

Liquid saturation refers to the fraction of the pore space occupied by the liquid. It is the volume of the liquid expressed as a percentage or fraction of the pore volume. In the reservoir, the pore volume (V_{pore}) is occupied by water or brine of volume (V_w), initial oil volume (V_o), gas volume (V_g) and can be expressed as:

$$V_{pore} = V_w + V_o + V_g \tag{6}$$

Therefore, neglecting the gas volume,

$$Initial\ Oil\ saturation, S_{oi} = \frac{V_o}{V_{pore}} \tag{7}$$

and

$$Initial\ Oil\ saturation, S_{wi} = \frac{V_w}{V_{pore}} \tag{8}$$

Brine Permeability

After injecting brine into the sandpack to saturate it, the stabilised pressure drop and constant flow rate after saturation of the sandpack were noted and recorded. The absolute brine permeability (K_b) was calculated using the Darcy's law (Table).

Effective Oil, Water, and Polymer Permeability

The effective oil permeability (k_o) is the oil permeability at the end of oil injection under stabilised oil flow conditions. It was calculated based on the Darcy's law using the oil flow rate, oil viscosity, and the overall pressure drop (ΔP_o) exerted. Similarly, the effective water permeability (k_w) and effective polymer permeability (k_p) were estimated using the water/polymer flow rate, water/polymer viscosity and overall water pressure (ΔP_w) or polymer pressure drop (ΔP_p) at the end of the water flooding and polymer flooding, respectively (Table).

Sandpack Flooding Procedure

Sandpack Modeling

The internal dimensions, length (L) and diameter (D) of the cylindrical sandpack holder, were measured and its volume (AxL) calculated, which represents the bulk volume of the sandpack. With one end closed, the holder was then filled with dry sand under a pressure of about 17.5 MPa. The opposite end was then closed and its weight was measured. After setting up the sandpack model, the test procedures began with brine flooding, then oil flooding, followed by water flooding, and finally polymer flooding, as briefly described below. During each stage, pressure drops were noted and effluent flow data was collected.

Saturation of Sandpack with Brine

The holder was then mounted horizontally and the sandpack saturated with synthetic brine solution. The brine composition was the same as the brine solvent used for preparing the polymer solutions. The synthetic brine was then injected through the sample at linear velocities of 0.5mL/min. The flow rates and pressures were monitored until steady-state conditions were reached (a constant flow rate was attained at a constant pressure differential), the flow rates and pressure differentials were noted. The permeability was then calculated using the Darcy's equation for horizontal flow of incompressible fluids. After saturation, the system was disassembled and the weight (wet) of the sandpack and holder obtained. The weight of the brine (wet weight- dry weight of sand) and brine density were then used to calculate the pore volume and hence the sample porosity. The core holder was designed so that when the sample was properly mounted the entire unit was leak-proof and fluid flow occurred through the sample only. The experiments were conducted at an average room temperature of 25 ^{o}C.

Oil Flooding

The objective of oil flooding was to establish the initial oil saturation and condition of the sandpack to reflect exhaustion of primary production prior to water flooding. The test oil was flooded horizontally through the sandpacks to displace the brine until reaching an irreducible water condition, as indicated by no further brine production in the outlet, constant volume of oil collected and reproducible permeabilities had been established. The volume of oil injected into the sandpack was deduced from the volume of brine displaced from the sandpack.

Water Flooding

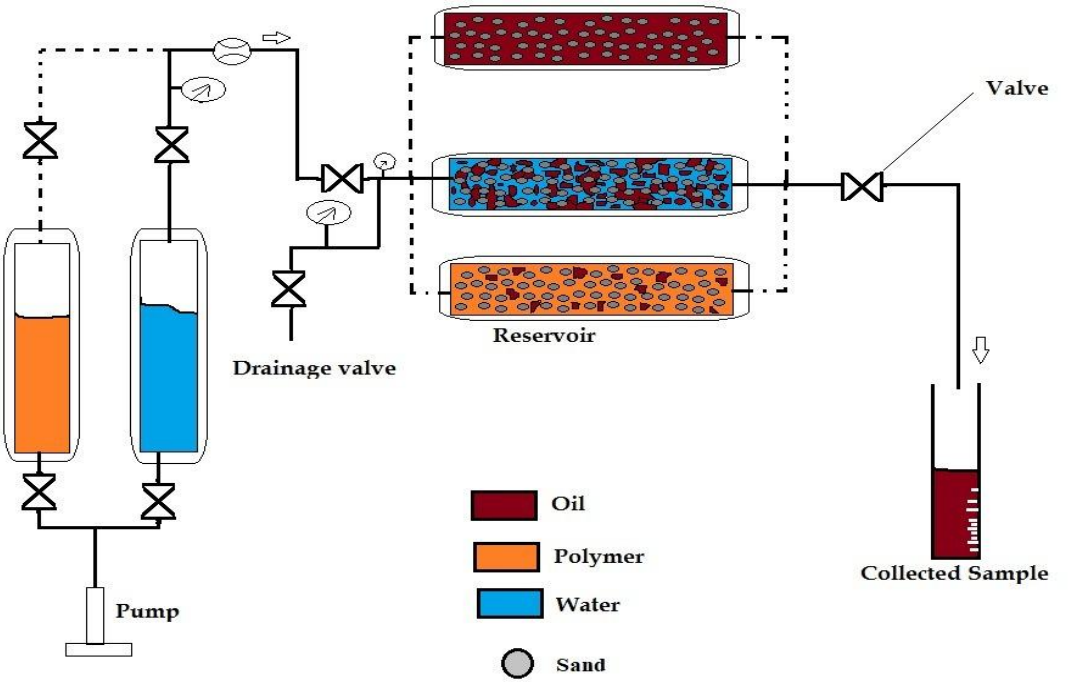
Water flooding was then conducted as a secondary production with the brine until the system attained residual oil saturation. Brine injection flow rates of 0.3 mL/min were used to mimic an actual reservoir water flood situation. Incremental oil recoveries were measured against time and recorded in the time intervals of 5.0 -10.0 minutes until about $1.5V_{pore}$ water injection when oil cuts were generally decreased to less than 1% and pressures stabilised. All steps were conducted at room temperature. The volume of brine injected into the sandpack was essentially equal to the volume of crude oil displaced at room temperature, taking into account the dead tubing/valve volume. Residual oil/water saturations were calculated.

Polymer Flooding

Polymer injection was then pursued immediately after water flooding aimed at recovering additional residual oil in the sandpack. The polymer injection was performed under similar ambient conditions to the waterflooding at a constant flow rate of 0.3 mL/min until incremental oil production was almost zero. The percent

cumulative oil recovery was calculated in terms of the original oil in place (OOIP). Experimental set up of the sandpack flood test is presented in Figs. 2a and 2b. After the sandpack experiment (sandpack-1) using HAT-1was completed, the content of the sandpack holder was discarded. The cylinder was properly cleaned, refilled under the same pressure (sandpack-2) and the experiment repeated under similar conditions using HAT-2 polymer.

a)



b)

Fig. 2. Experimental set up of sandpack polymer flooding

3. Results and Discussion

3.1. FTIR and Proton Nuclear Magnetic Resonance (^{1}H NMR) Spectral Analyses

The structure HAT-2 was confirmed based on the following FTIR spectral analysis. As shown in Fig. 3a, absorptions at 3434.67 cm^{-1} emanated from –NH stretching and 2934.52 cm^{-1} from $–CH_2$ stretching vibration, 1661.56 cm^{-1} from C=O stretching vibration, and 1543.56 cm^{-1} (C–N stretching vibration and –NH bending vibration). The -N-C symmetrical stretch of DADMACl occurred at 1116.67 cm^{-1}-1189.14 cm^{-1} and overlapped with asymmetric stretching of the sulphonate group at 1189.14 cm^{-1}. A strong sharp signal recorded at 1042.00 cm^{-1} reflects

symmetric stretching of sulphonate group of AMPS. The C-H bonds of methyl group rocking occur at 1390.86 cm^{-1}. Furthermore, peaks at 1455.06 cm^{-1} were probably from methyl or methylene bending while 813.00 cm^{-1} and 688.73 cm^{-1} confirmed the alkane backbone of the tetrapolymer. As expected, the FTIR spectrum has established the polymerisation of the four monomers to form HAT-2. Fig. 3b shows the ^{1}H NMR spectrum of HAT-2, proton signals that resonate at chemical shifts of 1.2, 1.5 ppm indicated methylene ($-CH_2$) on the tetrapolymer backbone chain, and $-CH_2$ protons on the ring of DADMACl and along the side chain of LMA, in addition to methyl ($-CH_3$) on the AMPS and LMA. The methine proton (-CH) of the backbone chain of HAT-2 appeared at δ = 2.1. The hydrogens of the CH_2 group bonded to $-SO_3Na$ were detected at 3.4 ppm. The chemical shift at δ = 3.6 ppm reflected hydrogens in $-CH_2-N(CH_3)_2Cl-CH_2-$ of DADMACl and the methoxy ($-CH_2O-$) of LMA. The signal at 4.7 ppm was attributed to the hydrogens of the -NH and $-NH_2$ groups and D_2O.

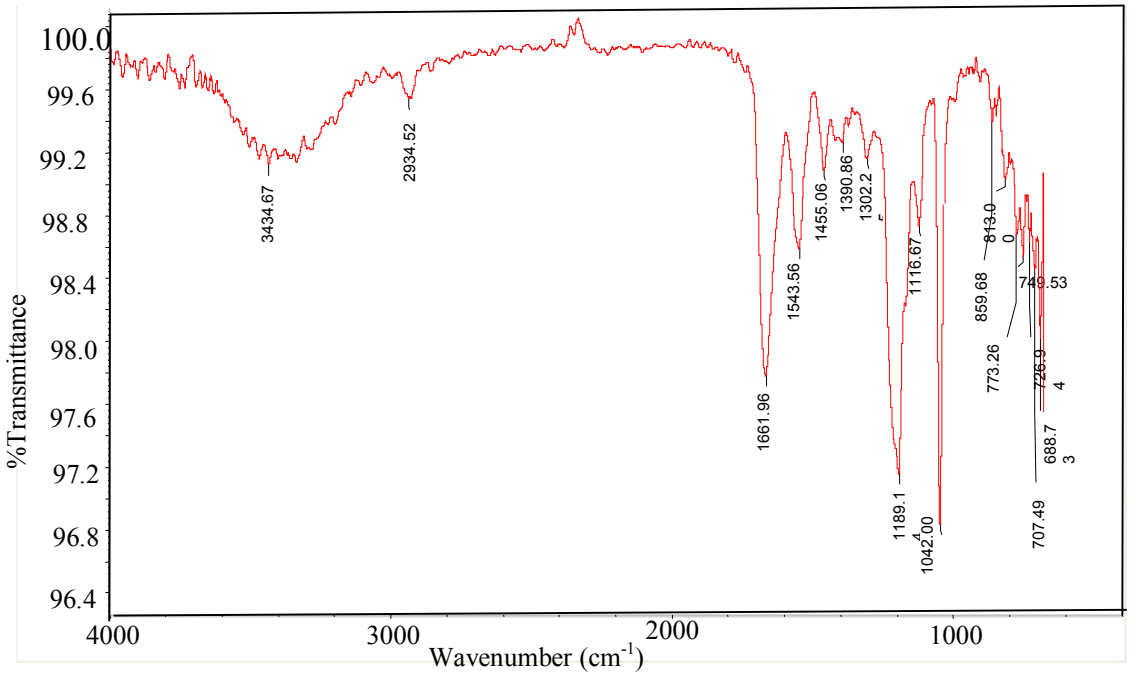


Fig. 3a. FTIR spectrum of HAT-2

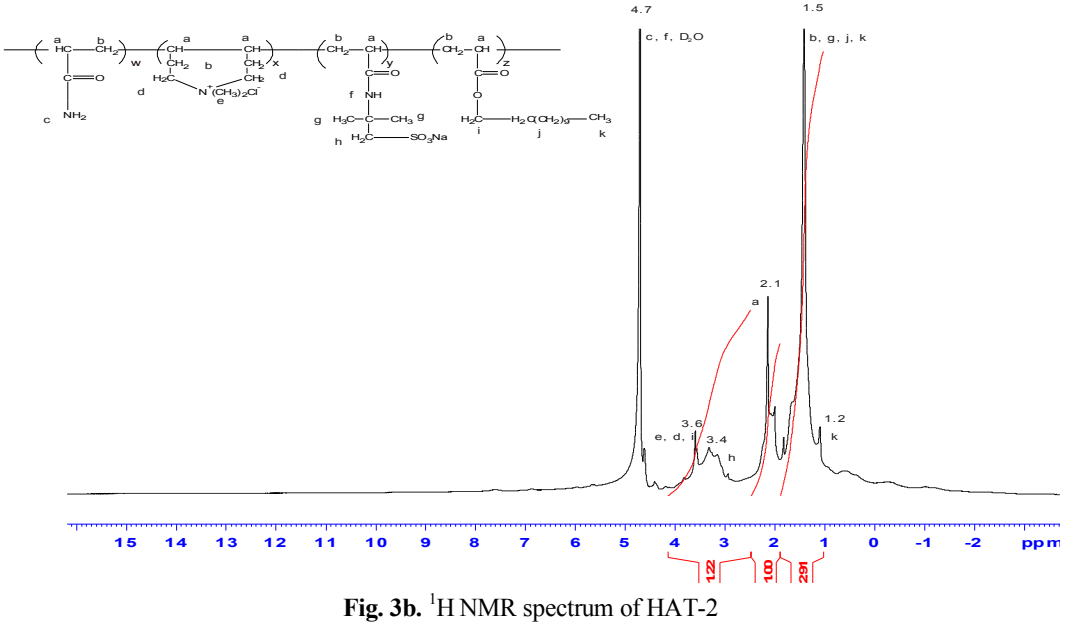


Fig. 3b. ^{1}H NMR spectrum of HAT-2

3.2. Solubility and Mechanisms of Viscosity Enhancement of the HAT Polymers in Aqueous Media

Viscosity enhancement of the driving fluid is the key reason for which the polymers are added during polymer enhanced oil recovery. Solubility in aqueous media is thus a mandatory requirement and the first selection criterion for polymers earmarked for enhanced oil recovery.[25,26] pH affects solubility of acrylamide-based polymers in brine[27] and since some oil reservoirs contain acid gases (CO_2 and H_2S) and naphthenic acids and therefore, most likely acidic,[28] the effect of pH on the solubility and viscosity of the polymers was examined and presented in Fig. 4. The pH range of 4.0 to 11.0 was selected mainly to avoid possible damage to the viscometer. As observed, HAT-2 exhibited stable solution viscosity within the measured pH range whereas HAT-1 achieved a fairly stable solution viscosity within pH 6.0-11.0. The solubilities of the HAT polymers in alkaline, acidic and brine media were mainly attributed to their strong ionic, hydrophilic or polyelectrolytic character.

The HAT-1 and HAT-2 polymers also readily dissolved in brine containing 3000 ppm NaCl and 300 ppm $CaCl_2/MgCl_2$ (1:1) without precipitation or flocculation. The viscosity of polymer-free brine viscosity was 1.20 cP. However, when 0.3 wt. % HAT-1 polymer was added to the brine, the viscosity increased to 12.9 cP (representing about eleven-fold increase) whereas the same amount of HAT-2 in the brine produced a solution viscosity of 15.3 cP (about thirteen fold increase). The ionic (hydrophilic) groups ($-CO_2^-$ and -OH) of HAT-1 and ($-SO_3^{2-}$ and $-CO_2^-$ groups) of HAT-2 polymers have the capacity to hydrate water molecules into the polymer matrix to form a gel, as the gel breaks up, the molecules are dispersed into the solution creating a large hydrodynamic volume along with an increase in viscosity.[25]

HAT-1 polymer, comprising acrylamide, hydroxyethyl methacrylate, N-vinyl pyrrolidone, and N,N-dimethyl acrylamide was partially hydrolysed to make it completely soluble in aqueous medium. HAT-1 is a polyelectrolyte because of carboxylate group $-CO_2^-$ on the partially hydrolysed acrylamide. In aqueous medium, the anionic groups repel each other and cause the polymer chains to adopt more expanded and rigid-rod-like conformations and create an increase in hydrodynamic volume, coupled with the amide-water hydrogen bonding, resulting in viscosity enhancement.[29] The vinyl pyrrolidone is relatively inert toward salt and, coupled with the inelastic structure of the pyrrole ring, can provide rigidity to mitigate polymer molecular chains folding or collapse. The dimethyl group offers hydrophobic associations which mitigate salt screening effect to prevent chain coiling of the polymers.

HAT-2 is hydrophobically modified associative polymer comprising acrylamide and sodium 2-acrylamido-2-methyl propane sulphonate. The presence of the $-SO_3^-$ group imparts a high degree of hydrophilic and anionic character over a wide range of pH coupled with the strong secondary attractive forces of amides contributes significantly to the polymer solubility and viscosity enhancing properties of HAT-2. The hydrophobic monomer (lauryl methacrylate) will impart hydrophobic associations in saline environment to retain the HAT-2 viscosity. The cationic divinyl monomer (diallyldimethylammonium chloride) could enrich polyelectrolytic function and introduce cyclic structures during polymerisation. The cyclic structures potentially provide rigidity and steric hindrance against thermal degradation and viscosity loss in saline medium.[24]

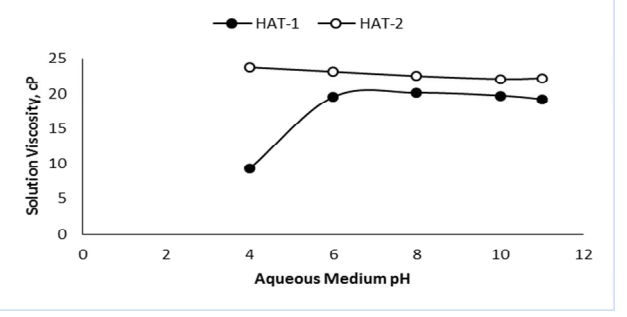


Fig. 4. Effect of pH on solubility and viscosity of tetrapolymers

3.3. Sandpack Flooding

3.3.1. Oil Saturations and Incremental Oil Recoveries

The flooding experiments were performed in high permeability sandpacks, separately with HAT-1 and HAT-2 polymer as samples. Experimental results are presented in Table and Figs. 4, 5. Porosities and brine permeabilities of the sandpacks were observed as exceptionally good in respect of oil reservoir characteristics. Initial oil saturations (S_{oi}) were 87.7% and 90.3% for HAT-1 sandpack and HAT-2 sandpack, respectively but reduced to 52.3% and 48.3% after water flooding; then further decreased to 22.5% and 15.2% following the injections of HAT-1 and HAT-2 polymers. HAT-2 polymer flooding produced higher 36.2% incremental oil recovered than HAT-1 with 33.7%. When compared to the results of previous researchers, these values are relatively higher than previous results of 4–19%,[30] 20%,[31] ~13%,[32] 8–21%,[33] and 6.4–14.7%[10] obtained in sandpack media using polymer floodings. The significant differences in results are largely attributed to relatively higher viscosity test oils examined by these authors, in addition to disparities in experimental conditions. Significantly high incremental or mobilization

of oil from the polymer injections reflected an increase in volumetric sweep efficiency of the sandpack reservoir.

3.3.2. Mobility Control

As noted in the previous sections, the viscosities of the oil, brine, HAT-1 and HAT-2 in brine were 72 cP, 1.20 cP, 12.9 cP, and 15.3 cP, respectively. With reference to viscosity values and permeability data in Table, the mobilities of the viscosified brine (polymer solutions) ($\lambda_p = k_{rp}/\mu_p$= 0.33 for HAT-1 and 0.27 for HAT-2) decreased significantly during HAT polymer flooding compared to the mobilities of brine ($\lambda_b = k_b/\mu_b$ =19.92 for sankpack-1 and 19.08 for sandpack-2) during water flooding. Meanwhile, the oil mobility (displaced fluid), $\lambda_o = k_o/\mu_o$ = 0.29 (sandpack-1) and 0.3 (sandpack-2) was fairly constant since the viscosity of oil was essentially unaffected for both water and polymer flooding. The manifold increase in brine viscosity, about eleven fold by HAT-1 and thirteen fold by HAT-2 results in the lowering of mobility ratios ($M = \lambda_p/\lambda_o$ = 1.10 for HAT-1 and 0.93 for HAT-2) between the displacing fluid (polymer solution or viscosified brine) and oil (displaced fluid). The increase in polymer viscosity, the reduction drive water (brine) mobility and, thus, the reduction in mobility ratio leads to an increase in volumetric sweep efficiency and therefore a favourable displacement of more oil through the sandpack.[34-36] Considering the brine viscosity improvement by the polymers, their solubility over a wider pH range as well as the reduction of mobility ratio coupled with relatively high oil recovery efficiencies (74.4% for HAT-1 and 83.3% for HAT-2), both HAT polymers reflected potential characteristics as candidates for improving oil recovery in reservoir environment similar to the experimental conditions. However, HAT-2 demonstrated superior efficacy compared to HAT-1. HAT-2 possessed a much longer hydrophobic monomer (lauryl methacrylate) compared to a smaller hydrophobic monomer (N,N-dimethyl acrylamide) in HAT-1. Therefore, the hydrophobic associating effect of HAT-2 in brine was better than of HAT-1, implying that HAT-2 exhibited a relatively higher salt-tolerant and experienced weaker salt screening in the aqueous media than HAT-1.

Table. Sandpack Flood Experimental Values

Parameter	Formula	HAT-1	HAT-2
Bulk volume of sandpack, V_b (cm^3)	$V_b = \frac{\pi D^2 L}{4} = \frac{\pi x 2.5^2 x\, 30}{4}$ Diameter of sandpack holder, D = 2.5cm. Length of sandpack holder, L= 30.0cm	147.3	147.3
Pore volume, V_{pore}(cm^3)	$V_{pore} = \frac{W_{sws} - W_{ds}}{\rho_{brine}}$ W_{sws}= saturated wet sandpack, W_{ds} = dry sandpack, ρ_{brine} = *density of brine*	51.1	46.6
Porosity, Φ (%)	$\phi = (100 V_{pore})/V_b$	34.7	31.6
Initial oil volume injected, V_o (cm^3)	Determined based on total measured volume of brine displaced by oil	44.5	42.1
Absolute Brine permeability, K_b, (D) Note: 1 D = $0.9869'10^{-12}$ m^2	$K_b = Q\mu L / A\Delta P$ Where K_b :absolute brine permeability, mD; Q :flow rate,cm^3/min; ΔP ;overall pressure drop in atm across the sandpack; μ :the brine viscosity, cP; L :the length of sandpack, cm; and A :the cross-sectional area of sandpack, cm^2.	23.9	22.9
Oil permeability, K_{ro}, (D)	$K_{ro} = Q\mu_o L / A\Delta P_o$ Where, k_o :oil permeability, μ_o :oil viscosity;	21.6	20.7
Effective brine permeability, K_{rb} (D)	$K_{rb} = Q\mu_w L / A\Delta P_w$ Where, k_{rb} :effective water permeability, μ_w :water viscosity	5.81	6.00
Effective polymer permeability, K_{rp} (D)	$K_{rp} = Q\mu_p L / A\Delta P_p$ K_{rp} is effective polymer permeability and μ_p is water viscosity.	4.33	4.08
Estimated Mobility Ratio, M	$M = \frac{\lambda_p}{\lambda_o} = \frac{\mu_o k_{rp}}{\mu_p k_{ro}}$ Symbols have their usual notations as defined in this work	1.10	0.93
Polymer resistance factor, R_f	$R_f = (k_{rb}/\mu_b)/(k_{rp}/\mu_p) = (k_{rb}\mu_p)/(k_{rp}\mu_b)$ Symbols have usual their notations as defined in this work	14.4	18.8
Oil saturation after waterflooding, S_{orw} (%)	$S_{or} = V_{or}/V_{pore} = \left[(V_o - (V_{(oil\ displaced)} - V_{dead})\right]/V_{pore}$ S_{or} :residual oil saturation, $V_{oil\ displaced}$:volume of oil displaced, V_{dead} :dead volume	52.3	48.3

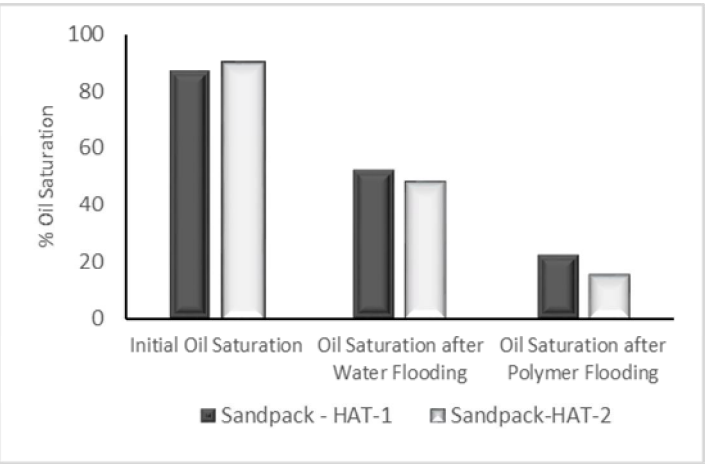


Fig. 4. Initial oil saturation and post-flooding oil saturations

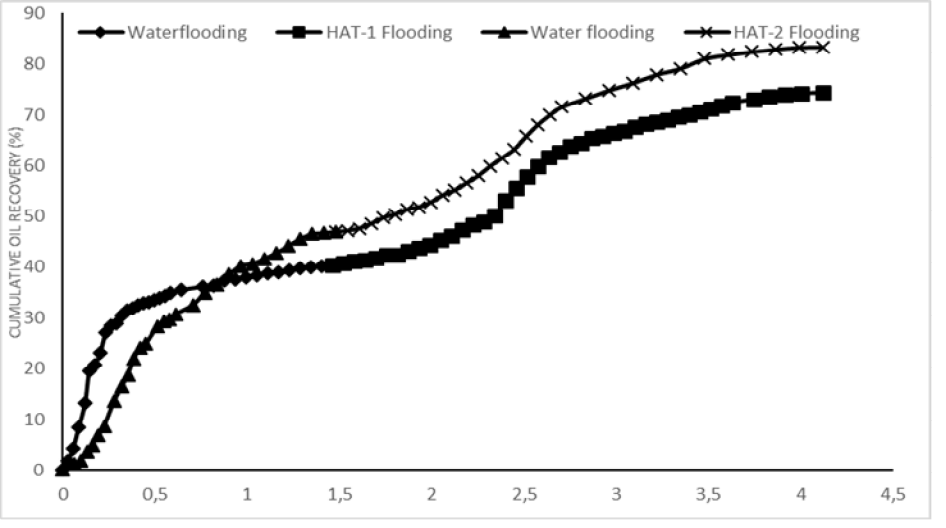


Fig. 5a. Percent cumulative oil recovery with water flooding followed by HAT-1 or HAT-2 polymer flooding

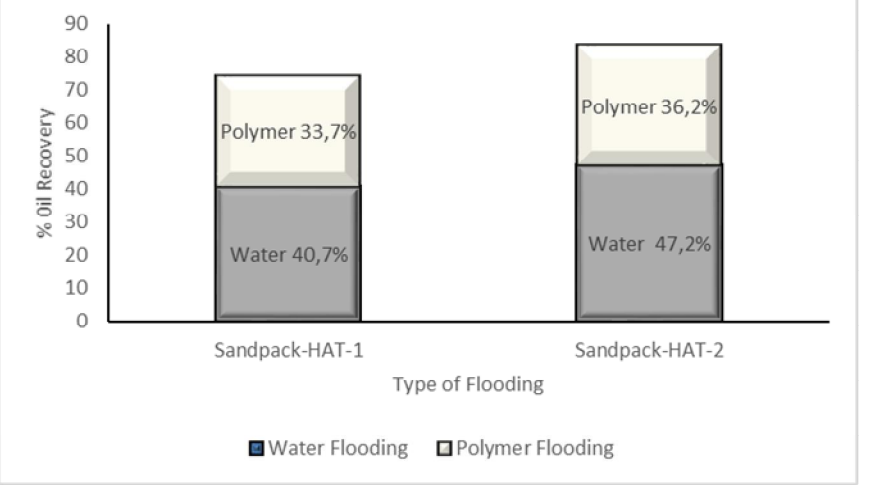


Fig. 5b. Percent cumulative oil recovery with water flooding followed by HAT-1 and HAT-2 polymer flooding

Thus, there was, comparatively, a higher chain elongation or unfolding, inter-polymer-chains associations, and hydrodynamic volume of HAT-2 molecules in aqueous brine medium than that of HAT-1, resulting in a higher viscosifying power of HAT-2 in brine solution than HAT-1.

4. Conclusions

In this work, a synthetic brine mimicking a reservoir brine was prepared, consisting of 3% NaCl, 0.15% $CaCl_2$, and 0.15% $MgCl_2$ (3,300 ppm). HAT-1 polymer (0.3 wt./vol. %) dissolved in the brine achieved a solution viscosity of 12.9 cP while the same concentration of HAT-2 recorded a solution viscosity of 15.3 cP. Both polymer solutions exhibited the capacity to separately displace oil sample with viscosity of 72.0 cP through the sandpack, thus establishing the efficacy of the HAT-polymers to improve recovery of viscous oils with viscosity of at least four fold more than that of the drive fluids.

Hydrophobic associative polymers developed in this work can retain substantial viscosity in saline aqueous media and effect favourable brine/oil mobility ratio during polymer flooding.

The incremental oil recovered using HAT-1 and HAT-2 injections after water flooding were 33.7% and 36.2%, respectively. These translate into the respective cumulative oil recovery efficiencies of 74.4% and 83.3 % from the water flooding followed by HAT-1 and HAT-2 polymers.

These values are relatively high from the economic perspective and therefore project both HAT-polymers as potential agents for oil recovery in reservoirs with characteristics similar to the experimental conditions for this work. However, based on the brine viscosity enhancement, mobility ratio reduction and oil displacement efficiency, HAT-2 appears more favourable compared to HAT-1.

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Abbreviations

AM: Acrylamide
AMPS: 2-acrylamido-2-methyl propane sulphonic acid
DADMACL: Diallyldimethylammonium chloride
LMA: Lauryl methacrylate
HAT-1: Hydrophobic associative tetrapolymer consisting of acrylamide, hydroxyethyl methacrylate, N- vinyl pyrrolidone and N,N-dimethyl acrylamide
HAT-2: Hydrophobic associative tetrapolymer comprising acrylamide, sodium 2-acrylamido-2-methyl propane sulphonate, diallyldimethylammonium chloride and lauryl methacrylate

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ЕФЕКТИВНІСТЬ СИНТЕТИЧНИХ ГІДРОФОБНИХ АСОЦІАТИВНИХ ТЕТРАПОЛІМЕРІВ ДЛЯ ПОКРАЩЕНОГО ВИДОБУТКУ В'ЯЗКОЇ НАФТИ З МОДЕЛІ ПІЩАНОГО ШАРУ

Анотація. *У цьому дослідженні вивчено придатність гідрофобних асоціативних тетраполімерів (HAT) для покращеного видобутку нафти за допомогою затоплення піщаного шару. Два нові гідрофобні асоціативні тетраполімери (HAT-1 і HAT-2) були синтезовані вільнорадикальною полімеризацією, а їхня будова підтверджена за допомогою інфрачервоної спектроскопії з перетворенням Фур'є (FTIR) і протонного ядерного магнітного резонансу (^{1}H NMR). HAT-1 складається з ланок акриламіду - гідроксіетилметакрилату - N-вінілпіролідону - N,N-диметилакриламіду, а HAT-2 – акриламіду - 2-акриламідо-2-метилпропансульфонату натрію – діалілдиметиламонійхлориду - лаурилметакрилату. У лабораторних умовах були проведені порівняльні випробування ефективності видобутку нафти обома полімерами HAT. Приріст нафти, видобутої за допомогою закачування полімерів HAT-1 і HAT-2 після заводнення, склав 33,7% і 36,2%, відповідно. Якщо об'єднати нафту, видобуту в результаті заводнення водою з подальшим закачуванням полімеру в обох сценаріях, то кумулятивний видобуток нафти з використанням HAT-2 (83,3 %) виявився відносно вищим, ніж з використанням HAT-1 (74,4 %). Ці значення є відносно високими з економічної точки зору. На основі підвищення в'язкості розсолу, зниження коефіцієнта рухливості та додаткового нафтовидобутку полімер HAT-2 продемонстрував відносно вищий потенціал для покращення нафтовидобутку для пластів з характеристиками, подібними до експериментальних умов для цієї роботи.*

Ключові слова: *гідрофобні асоціативні тетраполімери, полімерне заводнення, в'язка нафта, модель піщаного шару, додатковий видобуток нафти.*