FULL LENGTH ARTICLE

Evaluation of solution and rheological properties for hydrophobically associated polyacrylamide copolymer as a promised enhanced oil recovery candidate

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Abstract  Crude oil is the most critical energy source in the world, especially for transportation, provision of heat and light as there has not been a sufficient energy source to replace crude oil has broadly integrated, so there is an urgent need to maximize the extraction of the original oil in-place for every reservoir, and accelerating the development of enhanced oil recovery (EOR) technologies. Polymer flooding by hydrophobically associated polyacrylamides (HAPAM) is a widely used technique through EOR technology. For successful application of these polymers, one should evaluate rheological and solution properties at simulated reservoir conditions as a function of polymer concentration, salinity, temperature and shear rate. The results showed that these copolymers exhibit favorable salt tolerance, temperature resistance, and recoverable viscosity after shearing, reasonable thickening behavior and improved viscosity enhancement properties due to presence of hydrophobic association in the copolymer main chains. Moreover, its capacity for oil production improvement was evaluated during flooding experiments through one dimensional sandstone model at simulated reservoir conditions.

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1. Introduction

Petroleum products are crucial to the global economy today due to increasing energy demand approximately 1.5% per year [1] associated with population growth and improving life styles, so there is a dire need to produce more unrecoverable crude oil through different enhanced oil recovery (EOR) techniques. Polymer flooding through hydrophobically associated
polyacrylamide polymers (HAPAMs) have attracted much attention in oil industry [2,3] because of their unique structures and properties, including their thickening properties, shear thinning, anti polyelectrolyte behavior as a mobility control agents and rheology modifiers [4]. These polymers synthesized by free radical emulsion copolymerization are processed through grafting or incorporating hydrophilic chain cross-linking segments onto their hydrophobic main chain [5,6] or by copolymerization of hydrophilic and hydrophobic monomers [7]. Polymer flooding aims to increase viscosity of aqueous phase, so decreases water/oil mobility ratio to less than unity ($M < 1$), which in turn improves sweeping efficiency [8]. One of the routine screening parameters used for a preliminary analysis of a reservoir is the mobility ratio that represents effects of relative permeability and viscosity of water and oil on mobility based on Darcy’s Law (Eq. (1)) [9].

\[ M = \frac{\mu_O}{\mu_W} \left( \frac{K_W}{K_O} \right) \]

where, ($M$) mobility ratio; ($\mu W$) water phase mobility; ($\mu O$) oil phase mobility; ($K W$) relative permeability of water phase, mD; ($K O$) relative permeability of oil phase, mD; ($\mu W$) water phase viscosity, cp; ($\mu O$) oil phase viscosity, cp. Consequently, we can conclude that; by increasing of aqueous phase viscosity, mobility ratio decrease, so enhance sweeping efficiency which in turn increases recovered oil amount [10]. Several polymer field projects have been referenced or reported in the literature. Vossoughi and Buller [11]; and Manrique et al., [12] reported some advantages in using anionic polyacrylamide/acrylic acid (PAM/AA) in tests carried out on sandpacs and native cores from the Richfield East Dome Unit (REDU) in California. Platt and James [13] prepared poly (alpha-alkoxy) acrylamides and claimed improved stability in brine solutions. Similar claims were made by Hunter [14] and Cao et al. [15] who prepared N-substituted PAM/AA via ethoxylation. Murdachowitz [16] disclosed terpolymers of acrylamide, acrylonitrile and acrylic acid [17]. McCormick et al. [18] copolymerized sulfonated monomers such as 2-acrylamido-2-methylpropan sulfonic acid (AMPS) with acrylamide monomers, which provide a somewhat improved calcium ion tolerance. HAPAMs possess unique solution and rheological characteristics even at high temperatures and high ionic strength [19] which can be summarized as follows; (1) in aqueous solutions, above a critical association concentration ($C^*$), their hydrophobic groups develop intermolecular hydrophobic associations in nanodomains, leading to building up of a 3D-transient network structure [20] in high ionic strength medium [21] so, providing excellent viscosity building capacity [6,3,22], remarkable rheological properties and better stability with respect to salts than the unmodified hydrolyzed polyacrylamides (HPAM) precursors [23], (2) reduce interfacial tension at solid/liquid interface, since hydrophobic moieties associates forming aggregates or micelles, (3) shows an unusual adsorption isotherm [24] so, can be considered as a wettability modifier, (4) does not undergo mechanical degradation under high shear stress, since the physical links between chains are disrupted before any irreversible degradation occurs, also they reform and retain their viscosity upon shear decreasing [25], (5) high resistance to physicochemical conditions (temperature, pH, and ion content) prevailing around the wells, so considered a prospective EOR candidate as thickeners or rheology modifiers in high temperature, high pressure reservoirs [26–28] and tertiary oil recovery [29]. In this research, the authors reported about evaluation of solution and rheological properties of a novel copolymer poly (4-Dodecyl-benzenesulfonate-3-[5-(butane-2-sulfonyl)-3-carbamoyl-1-methylheptyl] imidazol-3-ium) previously reported in our previous literature [30]. Flooding experiments were carried out through one dimensional sandstone model to calculate recovery factor at simulated reservoir conditions, moreover the prepared copolymer ability to alter wettability of sandstone rock from oil-wet to water-wet was evaluated by static sessile drop method as had been previously reported in our previous literature [30,31]. To the best of our knowledge, the novel copolymer hadn’t been previously reported in enhanced oil recovery applications as a wettability modifying agents, also it reduces oil-water interfacial tension (IFT), to ultra low values, so improves oil displacement efficiency. Also, there is a difference in rheological behavior between this polymer and the one that had been previously reported in our literature [31].

2. Experimental setup

Preparation of surfmer (4-Dodecyl-benzenesulfonate-1-vinylmidazol-3-ium; DBSV) and HAPAM copolymer “Poly(4-Decyl-benzenesulfonate-3-[5-(butane-2-sulfonyl)-3-carbamoyl-1-methylheptyl] imidazol-3-ium)” as well as characterization and structure determination had been previously reported in our previous literature [30]. Rheological measurements were performed on Brookfield programmable DV-II+ viscometer, equipped with LV (SC4-25) adapter spindle cone/plate geometry (diameter = 60 mm, angle = 1°, plate-to-plate gap = 0.104 mm). Viscosity of aqueous polymer solutions was investigated with respect to the polymer concentration, shear rate, salinity and temperature. The salt tolerance experiments were made in salty solutions simulating injection sea water in the field with different salinity concentrations (1, 40, 80 and 100 g L\(^{-1}\)). Then, the polymer samples were added to such salty solution for the apparent viscosity measurement at shear rate of 7.3 s\(^{-1}\) and temperature of 25.0 ± 0.1 °C [31]. We call the attention to the viscosity at this shear rate because
there is a consensus in the petroleum industry that the shear rate of 7.3 s\(^{-1}\) is similar to the shear rate which the fluids are subjected when injected in an oil or gas reservoir [19]. Interfacial tensions between oil and brine and between oil, brine and polymer with different concentrations of (1, 2, 3 and 4 g L\(^{-1}\)) at salinity of 40 g L\(^{-1}\) were determined from surface tension measurements by Du Noüy Ring Tensiometer. Flooding tests were carried out on one-dimensional sandstone model developed by our PVT-lab to simulate flooding process on reservoir scale as had been previously reported in our literature [31]. The sand was firstly cleaned and evacuated [32] then saturated by brine for 14 days followed by oil flooding, then brine flooded until oil cut ceased (i.e. oil cut <1%). After that, copolymer solution with different concentrations was flooded to determine recovery factor based on volumetric basis.

3. Results and discussions

3.1. Rheological and solution characteristics

A series of experiments were carried out to test polymer rheological properties. Moreover, a comparative study with respect to solution and rheological criteria was done between, the novel prepared copolymer and a commercial polyacrylamide (PAM) polymer already used in polymer flooding projects. The following discussions detail these experiments [31].

3.1.1. Shear behavior and stress scanning [33]

Shear behavior of the aqueous copolymer solution with concentration of 2 g L\(^{-1}\) were measured at shear rates from (2.42–55.0 s\(^{-1}\)) at 25 °C, and the results are presented in Fig. 1. It is observed that viscosity decreases sharply with increasing shear rate. But, the viscosity curve and viscosity-constant values of HAPAM were above those of PAM. Meanwhile, the shear resistance properties were investigated by letting the sample rest for 10 h and then remeasure the viscosity under the same conditions. The results show that the viscosity of HAPAM recovered to the original one (i.e. retain its viscosity even at higher shear rates and exhibit pseudoplastic behavior), which indicates a dynamic equilibrium between intermolecular association and dissociation, while the viscosity of PAM is not restored after shearing because there may be mechanical degradation at high shear rates (i.e. chain scission) occurring during the shearing process. This excellent performance of HAPAM could be attributed to; (1) intermolecular/intramolecular hydrogen bonding and/or the hydrophobically associating interactions between the intra/intermolecular associations, (2) introducing the long hydrophobic dodecyl chain (C\(_{12}\)) of surfmer and hydrophobic crosslinker moiety into the macromolecular backbone structure of polyacrylamide enhancing its rheological properties [31]. From Fig. 2, it is clear that the HAPAM polymer exhibit a pseudoplastic behavior that belonged to a non-Newtonian fluid; which is often used by chemical flooding agents [34], where shear stress (\(\Gamma;\) Pa) related to shear rate (\(\gamma;\) s\(^{-1}\)) through the formula known as the power law model [35] “Eq. (2)”

\[
\Gamma = K\gamma^n
\]

where, (k) is the flow consistency coefficient (Pa s\(^{-1}\)) and (n) is the flow behavior index. In the pseudoplastic regime (n \(\leq 1\)) typically (n = 0.4-0.7). After linear fitting of the graph processing, (n) and (k) values found to be in a great compliance with results of Gou et al., [33] since \(n = 0.681\). This suggested that HAPAM had the perfect property of retaining the viscosity and strong non-Newtonian (pseudo plastic) fluids, so they can be considered as EOR candidates for polymer flooding projects.

3.1.2. Effect of concentration

Apparent viscosity (\(\eta_{app}\)) measured as a function of different polymer concentrations (1, 2, 3 and 4 g L\(^{-1}\)). It is observed from Fig. 3 that viscosity of PAM-polymer increases with polymer concentration increase (i.e. linear relationship) while viscosity of HAPAM increases to a certain limit 2 g L\(^{-1}\) polymer concentration increase (i.e. linear relationship) while viscosity of HAPAM increases to a certain limit 2 g L\(^{-1}\) (i.e. linear relationship) while viscosity of HAPAM increases to a certain limit 2 g L\(^{-1}\) than that of PAM at concentration of 4 g L\(^{-1}\). This indicates that novel polymer has good viscosifying properties as compared to high molecular weight PAM under the same experimental conditions. Also, it is assumed that concentration of 2 g L\(^{-1}\) is the optimum concentration. The behavior of viscosity decreases by concentration increase in case of HAPAM can be resorted to increasing of surface active properties of the polymer solution which in turn decrease compactness of macromolecular chains so, viscosity decreases.

3.1.3. Effect of salinity on the viscosity (salt resistance)

The aqueous saline solutions of (PAM and HAPAM) polymers with different salinities (10, 40, 80, and 100 g L\(^{-1}\)) were prepared with NaCl, CaCl\(_2\), and MgCl\(_2\), 6H\(_2\)O. The concentra-
tion of the polymer solutions was 2 g L⁻¹. The viscosities of the mixture were measured at shear rate of 7.34 s⁻¹ and concentrations of 2 g L⁻¹ and 25 °C. Experimental results are summarized in Fig. 4 which reveal that, the viscosity of the PAM decreased with increasing salinity; this can be attributed to; (1) decreasing the intramolecular/intermolecular bindings (hydrogen and vander Waal’s) bonding by electrolyte addition which results in compressing the thicknesses of the electric double layer and hydration layer of the ionic groups, so shields ionic repulsion and causes macromolecular chain contraction with small hydrodynamic volumes, resulting in apparent viscosity reduction, (2) by salinity increase, the solution charge is neutralized, so polymer chain condenses, and viscosity reduction occurs [36]. On the other hand, the viscosities of HAPAM initially decrease then increase by salt addition. This can be resorted to; (1) by increasing solvent’s polarity the tendency for forming intramolecular or/and intermolecular hydrophobic association increase and forming a dimensional crosslinked network which in turn strengthened the rigidity of macromolecule chains and prevented chains curling under the high salinity conditions, (2) addition of salt to the polymer solution is known to lower the solubility of the hydrophobic moieties and enhance the degree of association [37] promoting the formation of intermolecular aggregates with large hydrodynamic volumes in water (i.e. enhances the hydrophobicity and prevents the chain from being compressed, so viscosity increases), (3) presence of sulfonate (SO₃H⁻) group improves ionic exchange capability, electric conductivity, and reduces precipitation with bivalent Ca²⁺ and Mg²⁺ ions; improves resistance to salinity in general [38,39].

### 3.1.4. Effect of temperature on the viscosity (temperature tolerance)

Effect of the temperature on aqueous polymer solutions was studied at polymer concentrations of 2 g L⁻¹ and shear rate of 7.34 s⁻¹ at different temperatures (25, 50, 75, 100 °C). Experimental results are summarized in Fig. 5 which reveal that apparent viscosity for PAM decreases monotonically with increasing temperature, this can be attributed to enhancement of intermolecular hydrophobic association with increase of temperature, at least to an extent because hydrophobic association is an endothermic process accompanied by an entropy increase [33].

### 3.1.5. Interfacial tension reduction

Different polymer concentrations in brine solution of 40 g L⁻¹ salinity were tested for its effects on reducing interfacial tension between crude oil and brine solution at room temperature. The results are shown in Fig. 6. It is obvious that, HAPAM copolymer has the ability to decrease interfacial tension to lower values than those between oil and brine solution. This interfacial tension reduction may be explained on basis of; (1) their amphiphilic structure (contain both hydrophilic and hydrophobic groups) which promote intermolecular hydrophobic associations and formation polymolecular micelles, so reduce interfacial tension, (2) presence of hydrophobic groups in backbone structure of copolymer which are insoluble in water and associate by making aggregates or micelles to minimize their exposure to water. They also have the ability to insert themselves into interfaces and to reduce interfacial tension [23]. Hence, this copolymer may be included in an EOR design as interfacial tension reducing agents for improving displacement efficiency in high saline reservoirs.

### 3.1.6. Permeability reduction and mobility ratio

Permeability reduction was determined by measuring the pressure drop during the core flood experiments which used to calculate the resistance factor (RF) and residual resistance factor (RRF). In flooding experiments, the HAPAM solutions gave higher resistance factor and residual resistance factor as illustrated in Table 1, as compared with values reported by Chuan et al. [40] of 9.38 and 3.39, respectively. Such improved prop-

![Figure 3](image3.png)  
Figure 3 Effect of polymer concentration at temperature 25 °C and shear rate of 7.34 s⁻¹.

![Figure 4](image4.png)  
Figure 4 Effect of salinity at temperature 25 °C and shear rate of 7.34 s⁻¹.

![Figure 5](image5.png)  
Figure 5 Effect of temperature at shear rate of 7.34 s⁻¹ and concentration of 2 g L⁻¹.
Oil drops are found in the large pores [23] but the possibility of preferentially the permeability of the small pores, whereas the polymer injection is minimal, as shown by Grattoni et al. [31]. The risk of decreased oil permeability with copolymer [31]. The efficiency of water injection would be improved with such novel low porosity. Consequently, it is expected that the low efficiency of oil recovery in the rock reservoir from middle to low permeability. The adsorbed polymer layer thickness ($e$) was determined using equation 3 [42,43].

$$e = r(1 - RRF^{-1/4})$$  \( (3) \)

where $r$, is the average pore radius, $\mu$m. It is observed that, adsorbed polymer layer thickness ($e$), are 1.4 $\mu$m, which are thin layers and will not cause pore plugging. Mobility ratio reaches to 0.793 which indicates high sweeping efficiency (i.e. piston like motion) during flooding processes since ($M \leq 1$).

### Table 1 Resistance factor ($R_F$), residual resistance factor ($RR_F$) and mobility ratio of HAPAM copolymer.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>HAPAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brine viscosity at flooding conditions, cp</td>
<td>1.2</td>
</tr>
<tr>
<td>Oil viscosity at flooding conditions, cp</td>
<td>9.28</td>
</tr>
<tr>
<td>Water permeability $K_w$ (mD)</td>
<td>45.39</td>
</tr>
<tr>
<td>Oil permeability $K_o$ (mD)</td>
<td>37.30</td>
</tr>
<tr>
<td>Water-polymer permeability $K_{w-p}$ (mD)</td>
<td>3.82</td>
</tr>
<tr>
<td>$(AP)_{lbs}$, psi</td>
<td>42.5</td>
</tr>
<tr>
<td>$(AP)_{lbs}$, psi</td>
<td>3.0</td>
</tr>
<tr>
<td>$(AP)_{lbs}$ (Before Polymer), psi</td>
<td>3.0</td>
</tr>
<tr>
<td>$(AP)_{lbs}$ (After Polymer), psi</td>
<td>18.5</td>
</tr>
<tr>
<td>$R_F$</td>
<td>14.2</td>
</tr>
<tr>
<td>$RR_F$</td>
<td>6.2</td>
</tr>
<tr>
<td>Mobility ratio</td>
<td>0.793</td>
</tr>
<tr>
<td>Adsorbed polymer layer thickness ($e$), $\mu$m</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Flooding experiments were carried out on one-dimensional sandstone packed model as previously reported [31]. Different concentrations (1, 2, 3 and 4 g L$^{-1}$) of HAPAM copolymer solutions were used in the core flood tests. Recovered oil and cumulative oil recovery%$S_o$, as a function of injected pore volumes are shown in Figs. 7 and 8 respectively. It is observed that, maximum recovery occurs after injection of (2.0 PV) at all concentrations. Also, its observed that, maximum oil recovery occurs at a concentration of 2 g L$^{-1}$ which reaches to nearly 48% of residual oil saturation ($S_{Or}$). As original oil in place (OOIP = 420 cc), the tertiary oil recovery was approximately 20.8% OOIP at a concentration of 2 g L$^{-1}$, so it is the optimum concentration to be applied during flooding process as it achieves the maximum slug efficiency. The results were obviously superior to those of PAM [44]. By increasing slug concentration above 2 g L$^{-1}$, recovered oil amount decreases especially at a concentration of 4 g L$^{-1}$. This may be attributed to the formation of emulsion which hindered free flow of fluids and caused high pressure drops across the model assembly resulting in low end-point oil permeabilities and thus, oil recovery decreases. Table 2 summarizes porous media properties and oil recovery by polymer flooding. Chang et al. [45] reported that incremental oil recovery factors of up to 14% of the OOIP have been obtained in polymer flooding good quality reservoirs. A comparison of the incremental oil recov-
Rheological and solution properties of a novel high molecular weight hydrophobically associated polyacrylamide copolymer were investigated under various conditions such as polymer concentration, salinity, temperature and shear rate at simulated severe reservoir conditions of high temperature and high ionic strength to test its compatibility for enhanced oil recovery (EOR) applications. Flooding experiments were carried out through one-dimensional sandstone packed semi-pilot model at simulated reservoir conditions. Based on the experimental results, the following conclusions can be drawn;

1. HAPAM copolymer had the perfect property of retaining the viscosity and strong non-Newtonian behaviors (i.e. exhibit shear thinning behavior).
2. Response to in situ reservoir stimuli (temperature, ionic strength, pH, and shear stress) also, shows good thermal, rheological and salt resistant properties even at reservoir conditions, and consequently improves sweeping efficiency.
3. Exhibits resistance factor \( R_F \) of 14.2, so produces improved shearing behavior and sweeping volume in EOR applications. Also, it is observed that, adsorbed polymer layer thickness \( (e) \), are 1.4 µm, which are thin layers so, there is low slug loss by stratum adsorption and will not cause pores plugging.
4. Effectively reduces interfacial tension to ultra low values, so increases mobilization of residual crude oil which resembles the behavior of interfacial tension agents.
5. In the core flood test, the recovered oil amount reaches to nearly 48% of residual oil saturation \( (% S_{Or}) \) at a concentration of 2000 mg L\(^{-1}\) and salinity of 40,000 ppm NaCl equivalent at a flooding temperature of 90 °C.

Finally, its ability for wettability alteration was evaluated in relevance to sandstone reservoirs and shows promising results to alter oil-wet rock to water-wet, so increases recovered oil amount as had been previously reported in our literature [30]. To the best of our knowledge, there is no previously reported HAPAM copolymer for wettability alteration, so this polymer is highly recommended for enhanced oil recovery applications in high pressure-high temperature offshore sandstone reservoirs.

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