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Experimental investigation using an acrylamide-based polymer with emulsifying capability for enhanced oil recovery: A preliminary study

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ABSTRACT

This work presents the synthesis and characterization of a new polymer, named AVS, which not only thickens the displacing fluid at high salinity and/or elevated temperature, but also emulsifies the crude oil. The results demonstrate AVS solution displays 50% higher apparent viscosity than the commonly used hydrolysed polyacrylamide (HPAM) solution in the same testing conditions. Furthermore, compared to HPAM, AVS has greater capacity to resist the shearing stress. Finally, core flooding experiments verify the AVS solution recovers more incremental oil than HPAM solution does, which is mostly attributed to its outstanding ability to simultaneously enhance the sweep efficiency and the displacement efficiency.

Introduction

It is widely acknowledged that, on average, only one third of the original oil in place (OOIP) is recovered through the primary and secondary recovery methods, suggesting the residual oil saturation can be significant even after a substantial volume of brine is injected into the target formation [1–3]. In order to keep pace with the rapidly growing energy demand, various enhanced oil recovery (EOR) technologies have been proposed over the past few decades. Meanwhile, extensive researches of each EOR technology have been performed [4–7].

Pye [8] and Sandiford [9] first pointed out the addition of a water soluble polymer could thicken the formation brine through molecular chain extension. They also stated that the physical entanglement might contribute to the conformance control, in such a way that the overall oil recovery was greatly improved. This attractive EOR technique was later referred to as polymer flooding. Extensive and comprehensive investigation into the mechanisms of polymer flooding has been conducted since it was proposed [10,11]. Firstly, the water soluble polymer was found to be capable of enhancing the viscosity of the displacing phase, thus the mobility ratio of the displacing phase to the displaced phase was noticeably reduced. Ideally, the mobility ratio would reach a value close to unity [12]. Furthermore, polymers would be allocated in the vertical layers by the crossflow between different layers if the polymer was injected into a heterogeneous formation. As a consequence, a greater volume of the target reservoir was swept by the polymer solution, leading to the improvement of both vertical and areal sweep efficiencies. In addition to modifying the mobility ratio, the polymer altered the formation permeability, which subsequently decreased the effective permeability of the injected brine. Most recently, it has been discovered that the polymer viscoelastic behaviour also contributed to the enhancement of oil recovery [13,14]. Due to the existence of the polymer viscoelasticity, a normal stress appeared at the interface of the polymer solution and oil, which enabled the polymer to pull the oil droplets or films out of the dead-end in the reservoir [15,16]. All of the mechanisms stated above contributed to the incremental oil production, although some might contribute more than the others do.

To date, hydrolysed polyacrylamide (HPAM) is still the most commonly utilized polymer in the petroleum industry due to its outstanding performance and relatively low cost [17–19]. However, both lab-scale investigations and field tests revealed the ultimate oil recovery of HPAM polymer floods barely reach 50%, suggesting a large portion of OOIP remains in the pay zone even after a significant volume of HPAM had been injected [20,21]. The poor recovery factor of polymer (HPAM) flooding arises from several factors: (1) HPAM is extremely sensitive to the brine salinity and its capability of thickening the displacing phase decreased at high salinity especially with the presence of Ca^{2+} and Mg^{2+} [22]; (2) elevated reservoir temperature is detrimental to the thermal stability of HPAM, leading to the breakdown of the molecular chain as well as the decrease in the thickening ability

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[23]; (3) the mechanical breakdown of the molecular chain by the shearing stress occurs during the HPAM injection [24]; (4) most of all, although HPAM remarkably improves the sweep volume of the displacing phase, it has little positive impact on the displacement efficiency. Due to all the drawbacks listed above, the residual oil saturation is still unsatisfactory even if a large quantity of HPAM solution is employed in the target formation.

This research proposes a new polymer that is not only able to thicken the formation brine in harsh reservoir conditions but is also able to emulsify the crude oil, in such a way that the accumulative oil recovery of polymer floods using this polymer is expected to be far greater than that of conventional polymer such as HPAM. This polymer, named AVS, is synthesized from acrylamide (AM), 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and one self-made monomer YS through free radical polymerization. The first part of this work evaluates the static characteristics of the AVS solution such as the thickening capability and emulsification in harsh conditions, and compares the outcomes with the commonly used HPAM. The second part investigates the displacement performance of AVS in porous media through performing core flooding experiments. Through systematic assessment, it is believed this proposed new polymer could be a promising alternative to the widely used HPAM in polymer flooding.

Experimental

Materials

An HPAM sample with a number average molecular weight of 2.5×10^7 and a hydrolysis degree of 21% was obtained from Beijing Hengju Chemical Company. AM, AMPS, potassium persulfate ($K_2S_2O_8$), ammonium hydroxide ($NH_3 \cdot H_2O$, 25 wt.%), sodium formate (HCOONa), sodium carbonate (Na_2CO_3), urea ($CO(NH_2)_2$), sodium chloride (NaCl), calcium chloride ($CaCl_2$) and distilled water were provided by Beijing Chemical Reagent Company. All the commercially available products were analytical pure (AR) and they were used as supplied without further purification. YS was a self-made hydrophobic monomer and its molecular structure was illustrated in Fig. 1. The crude oil was sourced from an eastern oil field in China and its specifications were listed in Table 1.

Table 1
Property of the crude oil.

Test	Unit	Result
API gravity	°API	33.5
Density @ 15 °C	Kg/L	0.90
Viscosity @ 50 °C	cp	33.7
Sulphur content	%mass	0.89
Water content	%mass	0.09
Wax content	%mass	2.9
Asphatents content	%mass	0.9
Neutralization number	Mg KOH/g	1.12
Arsenic content	Mg/kg	2.3

Methods

Synthesis of the ter-polymer AVS

Given amount of AM, AMPS, YS (12.0 wt.%, 4.0 wt.% and 2.0 wt.%) and Na_2CO_3 (pH modifier, 1.0 wt.%) were well agitated in the distilled water. Next, $CO(NH_2)_2$ (500 mg/L) and HCOONa (60 mg/L) which were the solubility booster and chain transfer agent respectively, were added into the prepared solution. Nitrogen was then injected into the obtained solution for 30 min to remove the residual oxygen. At the end point of nitrogen injection, the $K_2S_2O_8/NH_3 \cdot H_2O$ initiator was applied with a mole ratio of 1/1 (0.5 wt.%/0.5 wt.%) which allowed the reaction to start at the ambient condition. A period of around 2 h was required to complete the polymerization. The chemical reaction formula was given in Fig. 1. The number average molecular weight and hydrolysis degree of AVS are identified to be 1.1×10^6 and 17% respectively.

Subsequently, IR spectra analysis was performed using a Fourier Transform Infrared (FTIR) Spectroscopy (FT/RI-660PLNS, JASCO) and the result was shown in Fig. 2. The absorption peak at 1620 cm^{-1} could be attributed to $\upsilon_{C=O}$ of the ester group. The two

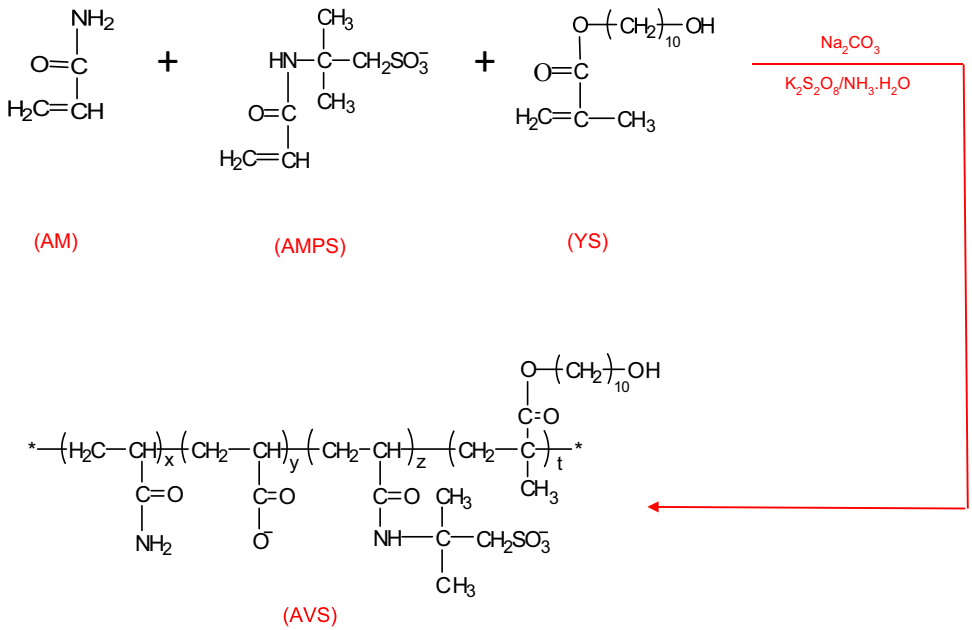

Fig. 1. Chemical formula of the polymerization process.
Note: the sodium acrylate in AVS comes from the hydrolysis effect due to the presence of Na_2CO_3.

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