Synthesis, characterization and emulsification properties of an amphiphilic copolymer for enhanced oil recovery

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Abstract. The present work was aimed at developing a copolymer oil-displacing agent for enhanced oil recovery (EOR). A novel amphiphilic polymer, AAO, was synthesized by radical copolymerization of acrylamide(AM), 2-acrylamido-2-methyl propane sulfonic acid (AMPS), and an amphiphilic monomer (OPMA), using 2,2'-Azobis (2-methylpropionamide) dihydrochloride (AIBA) as initiator. The structure of the sample was characterized by Fourier transform infrared spectrometer (FTIR). The surface/interface tension of AAO aqueous solutions was measured with surface/interface tensiometer. The viscometer was used to measure the apparent viscosity. The emulsifying capacity was researched by drainage rate, microscopy and particle size analyser. The results show that AAO has strong emulsification ability, good surface/interface activity, and thickening property. The emulsion consisting of AAO aqueous solution and cyclohexane was much more stable than that of HPAM (partially hydrolyzed polyacrylamide) which was widely used in EOR.

1. Introduction

Currently, with the increasing of the energy demand, the development of oil and gas resources has widely attracted the global attention. In order to meet growing energy demand, various enhanced oil recovery (EOR) have been developed over the past few decades. Chemical EOR is an interesting topic, as it helpful for exploiting heavy, unconventional and residual oils [1-3].

Among the chemical EOR methods, polymer flooding with high viscosity is widely used because it can improve the mobility ratio by enlarging the swept volume. The interfacial activity and ability of polymer to emulsify crude oil are also important for EOR. The surfactant-polymer (SP) or alkaline-surfactant-polymer (ASP) flooding systems were developed by adding surfactants. [4,5] These mixtures may have some disadvantages, such as the interaction between surfactant and polymer which may leading incompatibility, the loss of surfactant through adsorption on the rocks and the chromatographic separations of various components in porous medium. [6-8] Therefore, it is valuable to develop an amphiphilic polymer (also can be called polymeric surfactant) with both thickening property and interfacial activity.

In this work, an amphiphilic copolymer was synthesized trying to overcome the drawbacks of SP and ASP flooding mixtures. The amphiphilic polymer was composed of acrylamide(AM), 2-acrylamido-2-methyl propane sulfonic acid(AMPS) and an self-made monomer (OPMA). AM is a commonly used viscosity increasing monomer. OPMA was designed to provide polymer excellent interfacial activity.
which was prepared using MA to react with OP-10. AMPS is used to enhance temperature resistance and salt tolerant properties of copolymer by its high steric hindrance. Based on the relationship between the molecule structure and performance, the polymer AAO has abilities of thickening and emulsifying. The polymer can overcome the chromatographic separation effect and has great application potential in chemical EOR.

2. Experimental

2.1. Materials
Ethanol (AR), acrylamide (AM, AR), and 2,2'-Azobis(2-methylpropionamide) dihydrochloride (AIBA) were purchased from Sinopharm Chemical Reagent Co., Ltd. 2-acrylamido-2-methyl propane sulfonic acid (AMPS) was purchased from Aladdin Industrial Corporation, China. Maleic anhydride (MA), OP-10, p-Toluenesulfonic acid were obtained from Tianjin Guangfu Fine Chemical Research Institute, China.

2.2. Preparation of OPMA
32.3 g of dehydrated OP-10, 5.1 g of MA and 0.0051 g of p-toluene sulfonic acid were added to the three flasks of 50 mL. Then the mixture solution was heated at 90°C for 5 h under the stirring. The product was discharged to room temperature and was preserved in low temperature.

2.3. Preparation of AAO
AAO was prepared by micellar radical copolymerization in aqueous medium as previously reported[9]. The deionized aqueous solution of acrylamide was placed in a flask followed by magnetic stirring, and then monomers AMPS and OPMA were added to the reactant mixture at room temperature. After degassing with nitrogen for 30 min, initiator AIBA (0.3 wt% with respect to the total number of mass of the monomers) was introduced to the reactant solution. The copolymerization reaction was carried out for 10 hours. Then the synthesized samples were precipitated with ethanol for three times, and dried in vacuum drying oven at 50°C.

2.4. Emulsion Preparation
The emulsifying property of the polymeric surfactant in cyclohexane and water phase was studied. The surfactants were initially dispersed in the water phase, then the solution was homogenized with cyclohexane for 2 minutes at 8000 rpm using the high speed disperser of XHF-D. The volume ratio of cyclohexane to water is 1:1.

2.5. Characterization of AAO
A FTS-3000 (America) Fourier transform infrared spectrophotometer (FTIR) was used to obtain the infrared spectra of AAO (in the range of 4000 to 500 cm⁻¹). The molar mass and the intrinsic viscosity of the copolymer were measured with Ubbelohde viscometer in NaCl solution (1.0 mol/L) at room temperature. Particle size distribution of the emulsion was obtained by the Mastersizer 2000 (Malvern Instrument). Emulsion droplet images were observed by an optical microscope with a digital camera (OMEC Instruments Co., Ltd.). Apparent viscosity was measured with digital viscometer (DV-79+Pro, Ni Run Co., Ltd.). The surface/interface tensiometer (BZY-2, VITRON Co., Ltd.) was used to measure surface tension. Interface tension was measured with rotating drop meter interface tensiometer (TX500C, POWEREACH Co., Ltd.).
3. Results and discussion

3.1. FTIR analysis

FTIR spectrum of AAO terpolymer particles was shown in Fig. 1. Transmittance bands at 2924 cm\(^{-1}\) corresponded to C-H stretching, and a strong band at 3433 cm\(^{-1}\) represented N-H in AM. 1670 cm\(^{-1}\) represented stretching vibration of C=O in AM. Transmittance bands at 1451 cm\(^{-1}\) were associated with the C-N stretching of AM and AMPS. 1043 cm\(^{-1}\) was the C-O stretching vibration of the ethylene oxide in OPMA. 1214 cm\(^{-1}\) was the rocking vibration of the carbon-hydrogen bond in the nonyl of the OPMA. These showed that the AM, AMPS and OPMA were synthesized successfully.

3.2. Molar mass

By analyzing the line of the viscosity against concentration of AAO solution, the intrinsic viscosity was obtained. The viscosity-average molecular weight of AAO was calculated by the following Equation:

\[ [\eta] = 4.75 \times 10^{-5}M^{0.80} \]

As shown in Fig. 2, the viscosity average molecular weight and intrinsic viscosity of AAO were respective 6.14 \(\times\) 105 g/mol and 203 mL/g.
3.3. Apparent viscosity, surface/interface tension of AAO

The relationships between the polymer concentration and the surface/interface tension of AAO solution were demonstrated in Fig. 3 and Fig. 4. At room temperature, with the increasing of concentration, the surface tension of AAO solution first decreased obviously then increased slightly. After the concentration exceeded 1000mg/L, the surface tension was rising slightly which was likely to the increasing of the solution viscosity. Therefore, the critical micelle concentration was 1000mg/L, and the surface tension was 32.7mN/m. As was shown in Fig.4, the interfacial tension between the AAO solution and cyclohexane decreased with the increasing concentration, and changed slightly when concentration exceeded 6000mg/L. When the concentration was greater than 1000mg/l, the interfacial tension was lower than 101mN/m.

The correlations between the polymer concentration and the apparent viscosity of AAO solution were demonstrated in Fig.5. The apparent viscosity of AAO solution increased with the increasing concentration. The low surface/interfacial tension and the thickening property will play an important role in EOR.

3.4. Emulsifying properties of AAO

Emulsion was prepared by cyclohexane (simulated crude oil) and polymer solution. Fig.6 revealed that the emulsifying capacity of HPAM (2000mg/L) and AAO at different concentration (2000mg/L, 4000mg/L) were evaluated by recording the amount of water coming out of the emulsion over time. The stability of the mixture of HPAM and cyclohexane was low. Compared with HPAM, the emulsifying ability of the polymeric surfactant AAO was great stronger and increased significantly with the concentration going up.
3.5. *Particle size distribution of emulsion*

As was shown in Fig.7 and Fig.8, the AAO and cyclohexane formed an emulsion with a relatively uniform droplet size distribution and the mixtures was stable. The volume weighted mean diameter of the droplet in the AAO/ cyclohexane emulsion was $21.68\,\mu\text{m}$. The particle size distribution was match with the results showed in the image measured with microscope. The results indicated that AAO has the strong ability to emulsify oil.

![Figure 7. Microscope image: oil in water.](image1)

![Figure 8. Droplet size distribution of AAO emulsion.](image2)

4. **Conclusion**

The amphiphilic copolymer AAO was synthesized by copolymerization of AM, AMPS and OPMA. The synthesized polymer could reduce the surface/interface tension, increase the viscosity of the polymer solution, and have a strong emulsification ability. This research provided an effective candidate agent for enhanced oil recovery.

**Acknowledgments**

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51674270), National Major Project (Grant No. 2017ZX05009–003), Major project of the National Natural Science Foundation of China (No.51490650), and the Foundation for Innovative Research Groups of the National Natural Science Foundation of China (Grant: No. 51521063).

**References**

[1] S. Thomas, Enhanced Oil Recovery-An Overview, Oil Gas Sci. Technol. 2007, 63(1):9-19.
[2] L. Kapetas, S. Vincent Bonnieu, S. Danelis, et al. Effect of temperature on foam flow in porous media, J. Ind. Eng. Chem. 2016, 36(1):229-237.
[3] O. Karatum, S.A. Steiner, J.S. Griffin, et al. Flexible, Mechanically Durable Aerogel Composites for Oil Capture and Recovery, ACS Appl. Mater. Interfaces , 2015, 8(1):215.
[4] P. Raffa, A.A. Broekhuis, F. Picchioni, Polymeric Surfactants for Enhanced Oil Recovery: a Review, J. Petrol. Sci. Eng. 2016, 145:723-733.
[5] P.P. Liu, S. Zhang, N. Yang, C.M. Xiong, A novel surface active polymer oil displacement agent, Petrol. Explor. Dev. 2012, 39(5):619-623.
[6] X. Xu, O.Y. Jian, Y.Y. Wang, C. Wang, Experimental investigation using an acrylamide-based polymer with emulsifying capability for enhanced oil recovery: A preliminary study, J. Ind. Eng. Chem. 2017, 57.
[7] Y. Guo, W.D. Liu, L.H. Suni, et al. Chromatographic separation of components of ASP flooding system for conglomerate reservoir in Xinjiang Oil Fields, Oilfield Chemistry. 2008, 25(4): 362–365.
[8] J.J. Sheng. Modern Chemical Enhanced Oil Recovery. 2011:569–600.
[9] Z.L. Gui, Q.F. An, J.W. Qian, H.J. Zhu, Synthesis and characterization of polymer surfactant p(AM-co-OPMA), Acta Poly. Sin. 2008, 29(10):955-960.