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Suspension of surface-modified nano-SiO_2 in partially hydrolyzed aqueous solution of polyacrylamide for enhanced oil recovery

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ABSTRACT

In high-temperature and high-salinity oil reservoirs, the poor thermal stability and salinity tolerance of partially hydrolyzed polyacrylamides (HPAM) solution hinder its efficiency in enhanced oil recovery (EOR). Therefore, a series of dispersible nano-SiO_2 (denoted as DNS) separately surface-modified by silane coupling agents hexamethyldisilazane (denoted as HMDS) and hexadecyltrimethoxysilane (denoted as HDTS) are prepared by in-situ surface-modification technique. The two types of surface-modified hydrophobic nano-SiO_2, i.e., DNS-HM (modified by HMDS) and DNS-HD (modified by HDTS), are separately added into HPAM solution to obtain the HPAM-based suspensions used for EOR. The effects of DNS-HM and DNS-HD on the thermal stability, apparent viscosity, and flooding performance of HPAM are investigated. The results indicate that the HPAM/DNS-HM8 and HPAM/DNS-HD16 (see Table 1) suspensions exhibit better apparent viscosity, storage stability and thermal stability than the HPAM/DNS-0 suspensions. Moreover, HPAM/DNS-HM8 suspension show better flooding performance and has a higher oil recovery factor (about 10.54%) than other HPAM-based suspensions.

1. Introduction

Enhanced oil recovery (EOR) is a technique to increase oil recovery by improving microscopic and macroscopic sweep efficiency [1]. As an important method to EOR, polymer flooding is applied to many oil fields [2,3]. Besides, as the most widely used polyacrylamide in polymer flooding, partially hydrolyzed polyacrylamides (HPAM) is drawing more and more attention [4,5]. However, with new oilfield exploitation and more and more reservoirs, featuring high-temperature environment and hard brines characteristics, are found around the world. Issues of HPAM, such as poor salt tolerance and weak thermal stability, have become increasingly prominent [6,7]. These disadvantages of HPAM solution limit its applications in the hostile environment oil reservoirs.

Numerous efforts have been made to improve the thermal stability and salinity tolerance of HPAM [8], and it has been primarily found that the suspensions of inorganic nanoparticles with polymer contributes to improving the thermal stability and salinity tolerance of HPAM as a medium of polymer flooding [9–12]. Particularly, due to the interaction between polymer and nano-SiO_2, HPAM/nano-SiO_2 suspensions exhibits better viscosity-temperature characteristics than HPAM solution under high-temperature and high-salinity conditions [13–15]. D. Zhu et al. studied the effect of unmodified silica nanoparticles on the rheological of hydrophobically associating polyacrylamides (HAPAM), it was found that the apparent viscosity and elastic modulus of HAPAM solution increased with addition of silica nanoparticles [9]. A Maghzi et al. explored the impact of silica nanoparticles on the performance of polymer solution in presence of salts, the results showed that silica nanosuspension in polyacrylamide have helped increase the viscosity of polyacrylamide and its viscosity increase with the concentration of silica nanoparticles [16]. A. Rezaei et al. used surface modified clay nanoparticles to improve rheological behavior of HPAM solution, the experimental result indicates that adding optimum concentration of surface modified clay nanoparticles improves rheological behavior and stability of polymer solution [17]. C.P. Whitby et al. reported similar action of nano-SiO_2 in increasing the structure stability and viscosity of polyacrylic acid suspensions and polyethylene suspensions [18]. The reason lies in that nano-SiO_2 is able to prevent polyacrylamide from degradation in brine, thereby resulting in increased oil recovery during flooding at a high concentration of nano-silica. Maurya et al. and Zhang et al. also independently claimed that nano-silica can not only increase the injected fluid viscosity but also lead to better salt tolerance for polymer solution, thereby showing potential for EOR [8,19]. However, nano-silica often exhibits poor compatibility with polymers, which does not favor its application in polymer-based flooding medium. On the other hand, as the increasingly rigorous situation of many new-found oil fields exploiting environment, there is no doubt that further research and development of HPAM with improved thermal stability and salinity

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tolerance is imminent.

There are some papers reported the application of hydrophobic nanoparticles of SiO_2 in EOR. Q. Di et al's experimental showed that the hydrophobic nanoparticles of SiO_2 could be adsorbed tightly on the surface of the porous wall to form a strong hydrophobic layer, which contributed to increase the water-phase effective permeabilities [20]. M.A. Ahmadi et al. studied the ability of hydrophobic nanoparticles of SiO_2 in EOR process though carbonate rock samples. Their observations indicated hydrophobic nanosilica can lower interfacial tension between oil and water and then reduce the mobility ratio between oil and nanofluid [21]. However, as far as we know, nano-SiO_2 surface modified by hydrophilic groups suspensions in HPAM solution, which is few reports in previous papers. Due to the formation of hydrogen bonds between the amide groups of HPAM and the hydroxyl groups of modified nano-SiO_2, the hydrophobic groups can be randomly distributed along the silica nanoparticles in polymer solution [10,22]. Because of the modified nano-SiO_2 suspensions in aqueous solution, hydrophobic groups tend to aggregate and form a micro-region by hydrophobic association action. Due to the hydrogen bonds, associating interactions and Van der Waals between silica nanoparticles and HPAM, a steadier three-dimensional association network structure is easily constructed in aqueous solution. Based on that analysis, it is concluded that nano-SiO_2 surface-modified by hydrophobic groups would act as physical cross-linkers between polymer molecules. These small amount of hydrophobic groups which on the surface of nano-SiO_2 will play an important role in improving thermal stability and salt tolerance of HPAM, so there is a wide application prospect in oil exploration.

In this article, a series of hydrophobic nano-SiO_2 (DNS) surface modified by different hydrophobic groups and various modified amount were prepared. The effect of DNS-0 and modified nano-SiO_2 (DNS-HM, DNS-HD) on the HPAM viscosity behaviors in the high-temperature and high-salinity is investigated. Additionally, in order to examine the effect of nano-SiO_2 on the HPAM performance in EOR, a number of core flooding tests were carried out. Then, the efficacy of pure HPAM solution, HPAM/DNS-0, HPAM/DNS-HM and HPAM/DNS-HD suspensions to EOR are compared in harsh conditions. For simplicity, the above nano-SiO_2 modified by different modifier and various modified amount have been named as Table 1 shows.

2. Experimental

2.1. Materials

Dispersible nano-SiO_2 (DNS) was prepared with the method established at our laboratory [23]. Silane coupling agents HMDS and HDTS were purchased from Nanjing Pinning Coupling Agent Company (Nanjing, China). The two series of nano-SiO_2 (DNS-HM and DNS-HD) were prepared at our laboratory. HPAM with an average molecular weight of 2×10^7 g/mol was purchased from Henan Wujiangshui Materials Company (Gongyi, China). The quartz sand with a size of 200–300 mesh was purchased from Zhenxing Quartz Sand Factory (Luoyang, China). The crude oil was provided by Shengli oilfield in China, with a viscosity of 479.8 mPa s at 25 °C. The water used in this experiment was distilled followed by deionization.

Table 1
Abbreviations of HM-modified and HD-modified DNS samples.

Abbreviations	Modifying agent	Molar ratio of DNS-0 to modifying agent
DNS-0	–	–
DNS-HM32	HMDS	1/32
DNS-HM16	HMDS	1/16
DNS-HM8	HMDS	1/8
DNS-HM4	HMDS	1/4
DNS-HD32	HDTS	1/32
DNS-HD16	HDTS	1/16
DNS-HD8	HDTS	1/8

2.2. Preparation of surface-modified nano-SiO_2

DNS-0, DNS-HM and DNS-HD were prepared by in-situ surface modification method. Fig. 1 schematically shows the processes for fabricating DNS-0, DNS-HM and DNS-HD. Briefly, sodium metasilicate is hydrolyzed to generate $Si(OH)_4$ monomer. Resultant $Si(OH)_4$ monomer undergoes condensation polymerization to afford silica spheres containing active hydroxyl group on the surface, that is the DNS-0 (Fig. 1(a)). Then silane coupling agent HMDS or HDTS was added into the three-neck flask charged with resultant DNS-0 solution and using ammonia to adjust the pH value close to 9, the flask was then placed in water bath at 50 °C with a stirring rate of 400 ± 20 rpm for 1 h and then heating up to 80 °C for another 1 h. At the end of the surface-modification reaction, the product was washed with distilled water to obtain the target product DNS-HM and DNS-HD, as shown in Fig. 1(b) and (c).

2.3. Preparation of HPAM/DNS suspensions and simulated Shengli brine

HPAM/DNS suspensions were prepared in two steps: firstly, the filtered cake of DNS was fully dispersed in distilled water with the assistance of 30 min of ultrasonic vibration; secondly, the mother liquor of HPAM (5000 mg/L) was added into the aqueous dispersion of DNS and gently stirred for 48 h. The obtained HPAM/DNS suspensions should meet the requirements of no visible macroscopic phase separation after storage for 12 h at room temperature.

Simulated Shengli brine (total dissolved solids: 5727 mg/L; $[Ca^{2+} + Mg^{2+}]$: 108 mg/L) was composed of 0.1330 g of sodium sulfate, 4.6880 g of sodium chloride, 0.2220 g of anhydrous calcium chloride, 0.2370 g of magnesium chloride hexahydrate, 0.5510 g of sodium bicarbonate, and 994.17 g of deionized water. These solid chemicals were sequentially dissolved into the distilled water under mechanical stir to obtained stable and transparent solution.

2.4. Measurements

2.4.1. Contact angle measurement

The contact angle measurement was performed using a drop shape analyzer 25 (KRÜSS, Germany). The films were prepared by dipping the mud of modified nano-SiO_2 evenly on the surface of the slide, and then dried under suitable temperature. About 6 μL of distilled water was carefully dropped through the 0.5 mm outer diameter needle tip on the top surface of the modified nano-SiO_2, and the photographs of the contact angle was measured after 3 seconds. The two series of modified nano-SiO_2 DNS-HM, DNS-HD and unmodified nano-SiO_2 DNS-0 were measured at room temperature.

2.4.2. Structure characterization

The Fourier transform infrared spectra (FT-IR) of DNS-HM and DNS-HD were registered in solid sate using a KBr pellet method in the transmittance mode. A Nicolet FT-IR (AVATAR360, Nigaoli Instrument Company, USA) was used to record the spectra within the scanning range of 400–4000 cm^{-1}. Thermogravimetric analysis (TGA) of DNS-HM and DNS-HD in nitrogen atmosphere was conducted with an EXSTAR 6000 thermal analysis system (Seiko Instrument Inc, Japan) in the temperature range of 25–800 °C at a heating rate of 10 °C/min.

2.4.3. Evaluation of viscosity-temperature characteristics

The effects of DNS-0, DNS-HM, and DNS-HD on the viscosity of HPAM under high-temperature and high-salinity conditions were investigated with a NDJ-8S digital viscometer (Shanghai Ande Instrument Equipment Company; Shanghai, China). The viscosity of various HPAM/DNS suspensions in distilled water and simulated oilfield brine was measured in the temperature range of 30–80 °C. A