



## Decrease in viscosity of partially hydrolyzed polyacrylamide solution caused by the interaction between sulfide ion and amide group

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### ARTICLE INFO

#### Keywords:

Amide group  
Interaction  
Mechanism  
Polyacrylamide  
Sulfide ion

### ABSTRACT

Viscosity of polymer solution is one of the key factors which, in some case, notably influence its application effect. However, it has been found that the viscosity drops significantly with sulfide ion. To better understand this phenomenon, the rheological behavior, dynamic light scattering (DLS), and <sup>1</sup>H NMR analysis were conducted. The results show that sulfide ion significantly reduced the viscosity of HPAM solution and this reduction was further enhanced under low pH and high O<sub>2</sub> content and, more specifically, could not be recovered by dialysis. The polymeric network structure of HPAM formed in water was apparently destroyed and the hydrodynamic radius was reduced by sulfide ion. Furthermore, <sup>1</sup>H NMR spectra indicated that the chemical environment of some protons in the methyne group connected to amide group in HPAM was modified by sulfide ion. The interaction between sulfide ion and the amide groups in side chain intra-/inter-molecule of HPAM reduces the hydrodynamic radius and destroys the three dimensional network structure and consequently decreases the viscosity of HPAM solution. These results are helpful for investigating the mechanisms of HPAM-sulfide interaction and optimizing the usage of HPAM for enhanced oil recovery in oil reservoirs with sulfide ions produced by sulfate reducing bacteria.

### 1. Introduction

Partially hydrolyzed polyacrylamide (HPAM) is a linear polymer with high molecular weight and plays an important role in enhanced oil recovery (EOR) by increasing the viscosity of flooding fluid (Wang et al., 2003, 2009a, 2009b). Usually, the viscosity of HPAM solution is determined by its chemical structure, molecular weight, degree of hydrolysis, concentration and further influenced by many factors including shearing force (Jung et al., 2013), temperature (Kamal et al., 2015; Rashidi et al., 2011), salinity (Sukpisan et al., 1998), etc. Recently, sulfide ion was found to be a factor affecting the viscosity of polymer solution in application (He et al., 2015; Yuan, 2013).

In oil reservoirs subjected to HPAM flooding and pipelines for transportation of HPAM solution, sulfide ion is usually presented as the metabolic product of in situ sulfate reducing microorganisms (Guan et al., 2013; Li et al., 2015). Oil field souring is the undesirable production of hydrogen sulfide (H<sub>2</sub>S) in oil reservoirs by sulfate-reducing bacteria (SRB) (Hubert et al., 2005). Taking into account of the amount of residue persulfate in HPAM products, which is used as trigger for

HPAM synthesis, HPAM flooding also introduces persulfate/sulfate into oil reservoirs and transportation lines, and thus stimulates metabolic activity of SRB to produce sulfide ions. Consequently, the produced sulfide ion influences the viscosity of HPAM solution and thus the flooding effect for oil recovery rate. Understanding the interaction between HPAM and sulfide ion is important not only in industrial processes such as EOR but also from the fundamental mechanisms of science. However, till now, study on this subject is still limited and its mechanism is not reported.

In this paper, the influence of sulfide ion on HPAM viscosity and the mechanism involved were studied by dynamic light scattering (DLS), <sup>1</sup>H NMR and etc. The results showed that the viscosity of HPAM solution decreased significantly with presence of sulfide ions through decreasing the hydrodynamic radius and destroying the network structure as a result of specific interaction between sulfide ion and the amide groups of HPAM side chain.

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<https://doi.org/10.1016/j.petrol.2018.07.017>

Received 23 October 2017; Received in revised form 4 April 2018; Accepted 5 July 2018

Available online 07 July 2018

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**Table 1**  
Composition of simulated formation water (mg/L).

Inorganic Salt	Brine-1	Brine-2
NaCl	1590	4899
KCl	0	1100
Na <sub>2</sub> CO <sub>3</sub>	380	590
NaHCO <sub>3</sub>	3170	5260
CaCl <sub>2</sub>	110	230
MgCl <sub>2</sub>	70	100
MgSO <sub>4</sub>	10	140
TDS	5330	12219

## 2. Materials and methods

### 2.1. HPAM and Brine

HPAM with different hydrolysis degree (60%, 20%, and 0% (NPAM)) and polyacrylic acid (PAA) used in this study were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) with an average molecular weight of 3000 kDa.

Two simulated formation water, namely Brine-1 and Brine-2, were prepared and their composition is shown in Table 1 below. All these solutions were filtered with polycarbonate membrane filters (0.45- $\mu$ m-pore-size, Millipore, Bedford, MA, USA) before usage.

### 2.2. HPAM solution preparation

The HPAM solution, was prepared by dissolving HPAM mentioned above in distilled water to a final concentration of 10000 mg/L. The HPAM solutions with different concentrations of sulfide ion (0, 2, 3, 5, 8, 10 mg/L) were prepared by adding an adequate volume of 500 mg/L sulfide ion (Na<sub>2</sub>S) solution into HPAM solutions, respectively, and mixed thoroughly to form the projected concentration of sulfide.

### 2.3. Evaluation of sulfide on viscosity of HPAM at different time

The HPAM solution with different sulfide ion concentrations were incubated hermetically at 25 °C and the viscosity was detected respectively at different incubation time from 0 to 72 h.

### 2.4. Evaluation of sulfide on viscosity of HPAM under different temperature

HPAM solution prepared with brines and different sulfide ion concentrations were kept at 25 °C and 65 °C for 72 h, respectively, and their viscosity were determined.

### 2.5. Evaluation of sulfide ion on viscosity of HPAM

To evaluate the influence of sulfide ion on viscosity of HPAM solution, a four-step experiment was conducted. First, the HPAM solution with different sulfide ion concentrations were incubated at room temperature for 72 h and the viscosity of the solution systems was then determined. Secondly, these HPAM solution were dialyzed and the viscosities of these dialysates were determined. Thirdly, these dialysates, after viscosity measurement, were supplemented, respectively, with sulfide ion to achieve the same concentrations as they were before dialysis followed by another incubation at room temperature for 72 h and subsequent viscosity measurement. Finally, these HPAM solutions were subjected to dialysis and afterward viscosity determination again. The dialysis was conducted using dialysis bag with molecular weight cut-off of 3000 Da for 48 h with the interval of 8 h for replacement of deionized water. Viscosity was monitored by a rotary rheometer (Brookfield DV-III, USA) with a SC4-18 rotor at the testing temperature.

To evaluate the influence of pH and oxygen on viscosity of the HPAM solution in the presence of sulfide ions, the pH of polymer

solution was adjusted to pH 6, 7, 8 and 10 with 1.0 mM NaOH or 1.0 mM HCl solution, respectively. To prepare the nearly oxygen-free (oxygen lean) solution, the HPAM solution in bottle was continuously purged with high purity nitrogen gas for 30 min and then these bottles were sealed and incubated at testing temperature before its viscosity was determined.

To specifically determine the effect of sulfide ion on viscosity of HPAM, viscosity of two kinds of HPAM solution was analyzed, one solution was added with sulfide ion only and the other with simultaneously sulfide ion and certain amount of H<sub>2</sub>O<sub>2</sub> for stoichiometrical oxidation of sulfide ion added. Every solution was mixed thoroughly and incubated at room temperature for 72 h before its viscosity was determined. In addition, after 48 h incubation, the HPAM solution containing only sulfide ion was further mixed with added H<sub>2</sub>O<sub>2</sub> and kept for another 48 h followed by viscosity determination.

To specify the interaction site of HPAM molecule with sulfide ion, solutions were made either with HPAM of different hydrolysis degree (60%, 20%, and 0% (NPAM)) or with polyacrylic acid (PAA). These solutions were first dialyzed for 48 h. Then, different amounts of sulfide ions were added to each solution before its viscosity was determined.

### 2.6. Rheological measurements

Rheological measurements of HPAM solution amended with different concentration of S<sup>2-</sup> were performed on a rheometer (HAAKE MARS 3, ThermoFisher) with shear rates screening from 0.1 to 1000 s<sup>-1</sup> at 25 °C. Rheological data were obtained at 0.5 min intervals and ten readings were taken within an order of magnitude in shear rate.

### 2.7. Quantification of sulfide ions

The concentration of sulfide ion was determined by methylene blue method. First, 5.0 mL samples and 35 mL distilled water were put together into 50 mL colorimetric tube. Secondly, 5.0 mL N,N-dimethyl-p-phenylenediamine (2 g/L) were introduced into the tube and mixed thoroughly. Thirdly, 1.0 mL ammonium ferric sulfate solution (100 g/L) was added into the colorimetric tube, immediately closed, shaken well and stand for 10 min. Fourthly, deionized water was added to make the volume and thoroughly mixed. Finally, the absorbance was measured on a spectrophotometer (UNICO, 2000; USA) at 665 nm.

### 2.8. Hydrodynamic radius measurement

HPAM solution at concentration of 100 mg/L with different pH were used for hydrodynamic radius measurement by DLS instrument (Malvern Zetasizer Nano ZS90, Worcestershire, United Kingdom) with an He-Ne laser source ( $\lambda = 633$  nm) at 25 °C (controlled within 0.01 °C) and angular 173°. Every sample was analyzed in triplicate.

### 2.9. Microscopy and <sup>1</sup>H NMR analysis

The HPAM solution samples with 0 mg/L and 5 mg/L sulfide ions were dried at -60 °C in vacuum drying chamber, respectively. The obtained solid samples were analyzed with Environmental Scanning Electron Microscopy (FEI-Q45) working at accelerating voltage of 75 kv and pressures of 60–70 Pa. The surface micro-structure of HPAM samples were observed with a magnification of 3000 times.

The <sup>1</sup>H NMR spectra were obtained by AVANCE III 400 NMR (Bruker, Switzerland). Five mL of HPAM solution samples treated with 0 mg/L and 5 mg/L sulfide ions were dried at -60 °C in vacuum drying chamber and then the dried samples were dissolved in D<sub>2</sub>O (99.9%, Aldrich) in 5 mm NMR tubes at room temperature and analyzed, respectively.

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