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Chemical Structure of Surfactant-Grafted Polyacrylamide Used in Oilfields

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Abstract

Surfactant-grafted Polyacrylamide (S-PAM) flooding is a new technique used in Daqiang Oil Field in China and also a novel way for improving the recovery efficiency of primary oil layer after polymer flooding. S-PAM flooding technology is perfected gradually with the proceeding of multiple polymer surfactant oil displacement tests. Test results showed that the S-PAM used in field was greatly different with conventional ones. Therefore, it is necessary to study the chemical structure of S-PAM. Aiming at making clear the chemical structure of S-PAM, this study characterized the two commonly used S-PAM in oil field through chemical analysis and Fourier infrared spectrometer detection and analyzed the main composition and chemical structure of the two S-PAM.

Keywords

Surfactant-Grafted Polyacrylamide, Chemical Structure, Oilfield

1. Introduction

Relevant data reveal that Surfactant-grafted Polyacrylamide (S-PAM) has a framework constituted by ordinary polyacrylamide hydrocarbon chains. By grafting and copolymerizing the functional monomers and functional group to the lateral groups of the molecular chains, the original polymer hydrocarbon chains can be converted into the hydrocarbon chains containing a large amount of surfactants. Therefore, the aqueous solution of S-PAM is provided with the physical and chemical properties of the polymer and surfactant, as well as the new properties which are absent in the two agents. Generally, surfactant reduces the interfacial tension between oil and water in oil-water two-phase system to improve oil displacement efficiency. The S-PAM disperses the nonpolar substances in non-water system (including crude oil, coal power, cement, pigment, and so on) into emulsion and

thus overcomes the application limitations of conventional surfactants in non-aqueous system [1] [2].

As for unhydrous oil, the S-PAM can unify the phase viscosity, phase activity, thickening (water) ability, and solubilizing (oil) ability and reduced the tension of oil-water interface significantly in the aqueous solution with low molecular weight and concentration. The chemical agent of single component formed by special molecular design is called as multivariate graft polymer surfactants. Since the molecules contains hydrophilic and lipo-philic groups (also known as hydrophobic group), such surfactants are known as parent molecule.

The molecular structures of polymer surfactants include random form, blocking form, and grafting form etc. This study investigated the Surfactant-grafted Polyacrylamide. Grafting surfactant is a kind of functional poly-mer compound with clear structure and also shows certain special effects in aspect of surface activity. According to the differences of the hydrophilic radicals in the molecules, the S-PAM can be generally classified into cati-onic surfactant, anionic surfactant, nonionic surfactant, and amphoteric surfactants. In broad sense, there are also surfactants composed of cationic and nonionic surfactants and those composed of anionic and nonionic surfac-tants.

The application performance of S-PAM greatly depends on the molecular structure and application condition. The molecular structure therein is the most fundamental factor and also the primary study aim for developing functional, efficient and new products. The molecular structure of S-PAM mainly includes the chemical compo-sition of chains, the sequence distribution of chain structure, and the iconicity, charge density, and geometric structure (linear, branched, and cross linked) of molecular chains etc. It is of great significance of determining and characterizing the chemical structure of S-PAM for grasping the relationship between the chemical structure and performance of S-PAM, selecting S-PAM, optimizing usage mode and usage condition, improving synthesis methods and polymerization condition, as well as developing new S-PAM [3]-[8].

This study analyzed the composition and structure of Lianhua S-PAM and Haibo S-PAM using chemical analysis method (chemical surfactant group identification method) and instrument analysis method (infrared spectroscopy) etc.

2. Experimental

2.1. Materials and Instruments

Two origins of S-PAM were used in this experiment: Daqing Refining & Chemical Company S-PAM (Lianhua type III), which is called Lianhua S-PAM ;Shanghai Haibo company S-PAM (Haibo type III), which is called Haibo S-PAM; polymer: polyacrylamide (the Fourth Oil Plant of Daqing Oilfield Company Limited, at molecu-lar weight of 35,000,000); surfactants: cetyl trimethyl ammonium bromide(CTAB) (cationic surfacant), petro-leum sulfonate surfactants (anionic surfactant, the Fourth Oil Production Plant); Main instrument: Btuker Ten-sor27 infrared spectroscopy.

2.2. Methods

The structure and composition of the S-PAM were firstly studied using chemical analysis method to analyze the surfactant types in the two S-PAM on whole and accurately determine the group type in the following infrared spectrum test.

Determination of cationic surfactants: we took a certain volume of S-PAM solution and adjust the pH value to 7. Then we added 10 ml bromophenol blue reagent into the solution. In case of cationic surfactant, the solution shows blue color.

Determination of anionic and nonionic surfactants: we took a certain volume of S-PAM solution and added 10 mL methylene blue solution and 5 mL chloroform into the solution. The solution obtained was violently oscil-lated for 2 - 3 s and then stayed for layering. The colors of the two layers were observed. In case of cationic sur-factant, the chloroform layer was blue. Then we added surfactant solution again and repeated the operations above. The chloroform layer then turned dark blue. In case of nonionic surfactants, the solution was milky solu-tion or the two layers present the same color.

To further determine the group types in the surfactants produced by Daqing and Shanghai, instruments were used for analysis. In S-PAM analysis field, infrared spectra were mainly used for quantitative analysis, espe-cially for the quantitative analysis of the functional groups of S-PAM. According to the characteristic absorption of compounds, it was aware of the functional groups in the compounds, which were conductive to determine and

verify the types of related compounds. This section used the infrared spectrum analysis method to analyze the compositions of the two surfactants.

3. Results and Discussion

3.1. The Compositions and Structure of S-PAM

3.1.1. Determination of Cationic Surfactant

The solutions in **Figure 1** are distilled water blank control, Lianhua S-PAM, Haibo S-PAM, polyacrylamide (used by the Fourth Oil Plant of Daqing Oilfield Company Limited, at molecular weight of 35,000,000), CTAB (cationic surfactant) in turn from left to right.

The experiments preliminarily showed that there was no cationic surfactant involved in above two S-PAM.

3.1.2. Determination of Anionic and Nonionic Surfactants

As shown in **Figure 2**, the solutions are distilled water blank control, Lianhua S-PAM, Haibo S-PAM, polyacrylamide (used by the Fourth Oil Plant of Daqing Oilfield Company Limited, at molecular weight of 35,000,000), CTAB (cationic surfactant) in turn from left to right.

As shown in this figure, Lianhua S-PAM contains nonionic surfactant and possibly contains cationic surfactant; Haibo S-PAM contains both nonionic surfactant and cationic surfactant.
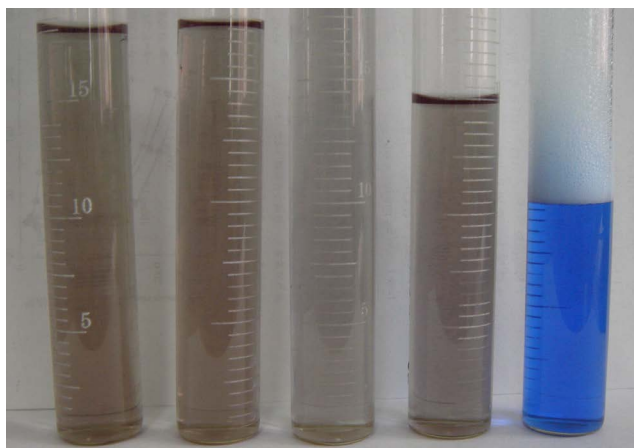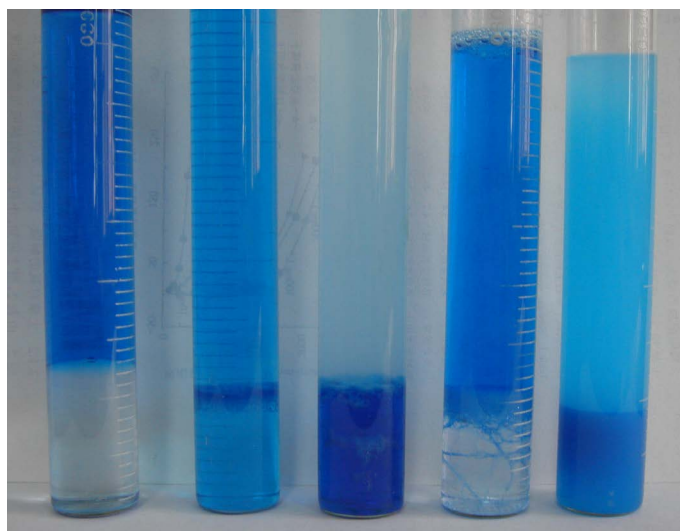

Figure 1. Determination of cationic surfactant.

Figure 2. Determination of anionic and nonionic surfactants.

3.1.3. Identification of the Anions in S-PAM Solution

The anions were primarily examined to obtain the grafting groups in S-PAM solution. The primary examination results showed that the anions included sulfate radical ions (SO_4^{2-}) and chloride ions Cl^-. The barium chloride and silver nitrate at certain concentrations were mixed with S-PAM solutions at certain concentration. The reaction phenomena were observed. In case of white precipitate and the precipitate that were insoluble after the hydrochloric acid and barium chloride were added in, it was proved that there were SO_4^{2-} and Cl^-. **Table 1** shows the test results:

3.1.4. Infrared Characterization

The compositions of the two S-PAM were analyzed using infrared spectrum in this section. **Figure 3** and **Figure 4** show the infrared spectra of the two S-PAM (**Table 2** and **Table 3**).
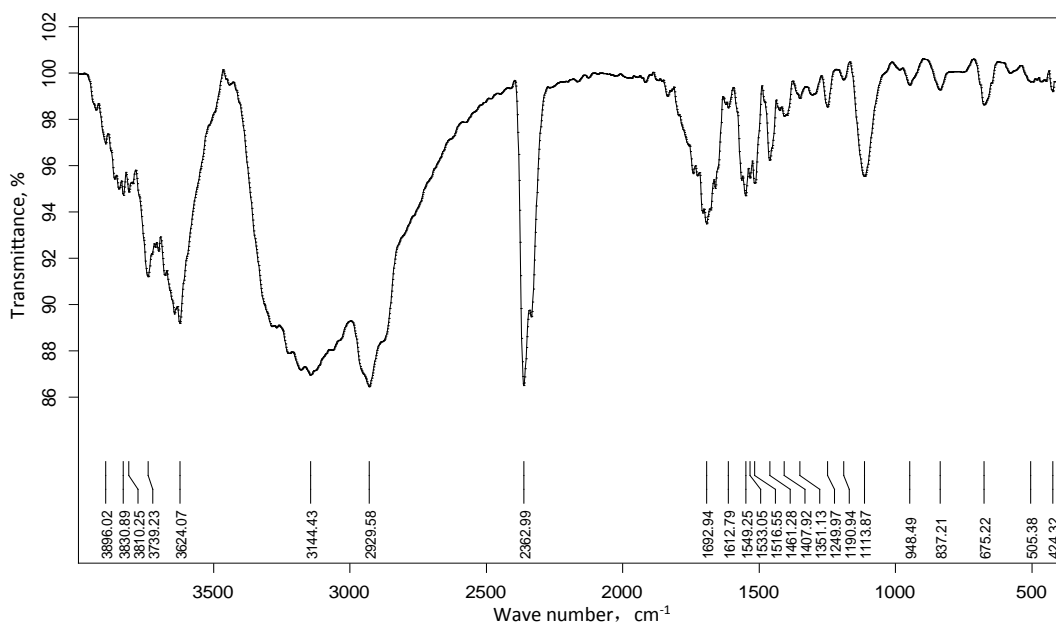

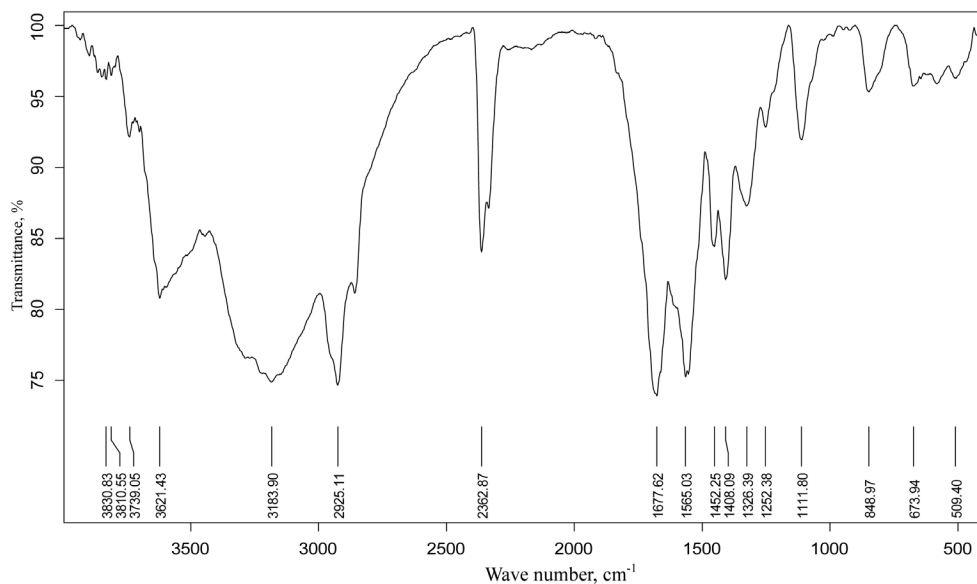**Figure 3.** The infrared spectra of Lianhua S-PAM.

Figure 4. The infrared spectrum of Haibo S-PAM.

Table 1. Primary determination results on anions.

	Lianhua S-PAM	Haibo S-PAM
SO_4^{2-}	Exclude	Include
Cl^-	Include	Include

Table 2. The analysis result on the infrared spectra of Lianhua S-PAM.

| No	Wave number range (cm^{-1})	Functional groups
1	Near 500 (intensive)	-C-I
2	Near 690	-CH=CH-(cis-)
3	890 - 820 (extremely weak)	Alkyl peroxide
4	970 - 960 (intensive)	-CH=CH-(trans-)
5	1150 - 1060 (extremely intensive)	Alkyl ethers
6	1220 - 1150	Alkane sulfonate
7	Near 1250 (intensive)	Cyclic ethers (epoxy compound)
8	1420 - 1330 (intensive) 1610 - 1550 (intensive)	-COO-
9	1660 - 1480 (variable)	Ring-like conjugated compound
10	1667 - 833	acylamino
11	1685 - 1665	-CH=CH-CO-
12	2640 - 1630	COOH oscillation in acylamino acid
13	2700 - 2560 (wide and low)	P-OH
14	3300 - 3030 (extremely intesive), 1430 - 1390 (intensive)	Ammonium salt

Table 3. The analysis results on the infrared spectra of Haibo S-PAM.

No	Wave number (cm^{-1})	Functional groups
1	Near 500 (intensive)	-C-I
2	Near 690	-CH=CH-(cis-)
3	890 - 820 (extremely weak)	Alkyl peroxide
4	1150 - 1060 (extremely weak)	Alkyl ethers
5	1250 ± 5 (intensive), near 1250 - 1200 (intensive)	$(CH_3)_3$-C-R
6	1340 - 1250 (intensive)	Secondary aromatic amines
7	1610 - 1550 (intensive) 1420 - 1300 (intensive)	-COO-
8	1465 - 1340	C-H alkanes with flexural vibration
9	1685 - 1665	-CH=CH-CO-
10	2440 - 2350 (medium)	P-H
11	3000 - 2850	CH alkanes with stretching vibration
12	3030 - 2500 a series of continuous bands (weak)	Amino acid hydrochloride

3.1.5. The Structure and Composition of S-PAM

By means of chemical analysis, IR spectra analysis, as well as related data concerning S-PAM synthesis, the chemical structures of two S-PAM are indicated as follows:

The structure and compositions of Lianhua S-PAM:
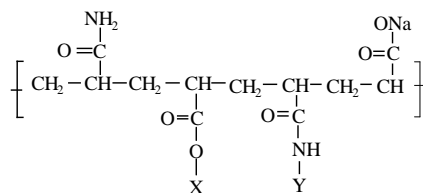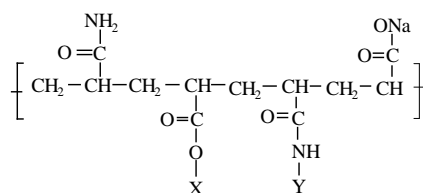

where X: Alkyl ethers—$(CH_2CH_2O)_m$—R, nononic

sulphosalts , anionic

Y: Ringlike conjugated compound , nonionic

Ployester , nonionic

Carboxylates , anionic

The structure and compositions of Haibo S-PAM:

where: X: Alkyl ethers —$(CH_2CH_2O)_m$—R, nononic

Trimethyl alkane , nonionic

Carboxylate , cationic

Y: Polyester , nonionic

Aromatic secondary amines, , nonionic

Amino acid hydrochloride , cationic

Analysis above showed that Lianhua S-PAM refining factory polymerized the nonionic and cationic surfactants, while that Haibo S-PAM polymerized the nonionic surfactants on the main chain of polyacrylamide. Moreover, the functional groups of the two S-PAM are different.

4. Conclusion

Analysis on the compositions of S-PAM implied that, Lianhua S-PAM polymerized the nonionic and cationic

surfactants, while Haibo S-PAM polymerized the nonionic surfactants on the main chain of polyacrylamide. Moreover, the functional groups of the two polymer surfactants were different.

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