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New water-soluble ampholytic polysaccharides for oilfield drilling treatment: a preliminary study

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Abstract

New water-soluble ampholytic polysaccharides with carboxybetaine groups, which were prepared by grafting the zwitterionic monomer 2-(2-methacryloethyldimethylammonio)ethanoate onto hydroxyethyl cellulose, have been tested for their properties as a multifunctional drilling-mud additive regarding clay hydration inhibition and mud rheological control. For the ampholytic polysaccharides investigated, an increase in carboxybetaine groups results in an enhanced inhibitive ability and the pH of the medium has an effect on the inhibition. A strong viscosifying efficiency for low-solid muds, especially for saline mud, has been observed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ampholytic polysaccharide; Water-soluble copolymer; Carboxybetaine; Clay hydration; Mud rheology; Oilfield drilling

1. Introduction

Water-based drilling fluids with inhibitive property for oilfield applications require effective water-soluble polymers to suppress the hydration of clay or shale and to control the rheological property of muds (Yan & Huang, 1992; Zhang, 1997a,b). Both naturally occurring and synthetic polymers have been widely used. Among them, chemically modified polysaccharides are probably one of the most extensively studied due to their low cost, lack of toxicity and biodegradability.

According to the nature of their hydrophilic moieties polysaccharide materials can be distinguished as anionic polysaccharides, such as carboxymethyl cellulose (Akaranta & Osuji, 1997; Hughes & Jones, 1990; Palumbo, Giacca, Ferrari & Pirovano, 1989), polyanionic cellulose (Huang, Ma & Li, 1990; Palumbo et al., 1989), carboxymethyl starch (Sun, Deng, Li & Huo, 1992; Wu & Zhang, 1993; Yao & Ye, 1987) and xanthan gum (Thac, Ha & Chinh, 1996); nonionic polysaccharides such as hydroxyethyl cellulose or starch (Mou, Yang & Wang, 1991; Xu, 1995; Zhang, 1996); as well as cationic polysaccharides such as quaternary ammonium starch ethers (Zhang, 1997a,b), cationized hydroxyethyl cellulose (Zhang, 1998), cationic starch graft copolymers (Gao & Guo, 1995) and cationic cellulosic polymers (Zhang & Li, 1995). Conventional anionic and nonionic polysaccharides are usually characterized by good viscosity-increasing property and good compatibility with common drilling-fluid additives. But, they generally show weaker inhibitive ability. Recently developed cationic polysaccharides provide more effective inhibition by attaching to the negatively charged clay surfaces more strongly than anionic or nonionic polysaccharides. However, formulating practical drilling fluids using cationic polysaccharides is often difficult because they tend to react with bentonite, anionic polymers and weighting agents, resulting in severe flocculation and precipitation.

To overcome these problems and combine ionic and nonionic polysaccharide behavior advantageously, we explore preliminarily the possibility of a new family of water-soluble ampholytic grafted polysaccharides from hydroxyethyl cellulose (HEC) and the carboxybetaine-type zwitterionic monomer, 2-(2-methacryloethyldimethylammonio)ethanoate (MAEDAE), as the drilling-mud additive with improved properties.

2. Experimental

2.1. Materials

The raw material HEC was purchased from Hoechst Co.,

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Table 1
Preparation of three samples used in this study (the reactions were carried out in nitrogen atmosphere; 100 mL of distilled water was used as the solvent)

Sample	Concentration in reaction mixture (mol/L)			HEC (g/dL)	Reaction temperature (°C)	Reaction time (h)	Grafting parameters[a]		$[\eta]$[b] (dL g^{-1})
	($\times 10^{-2}$)	CAN ($\times 10^{-3}$)	EDTA ($\times 10^{-3}$)				%*G*	%*C*	
NWSAP-I	1.20	2.50	5.00	2.0	60	6	30.0	20.3	2.76
NWSAP-II	1.20	1.25	5.00	2.0	35	6	67.8	45.2	3.78
NWSAP-III	1.20	5.00	5.00	2.0	35	6	102.9	68.7	4.90

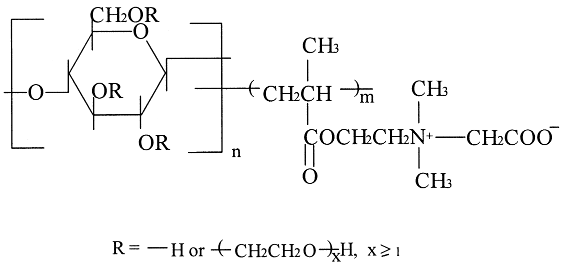
[a] The grafting parameters were determined as follows: %*G* (grafting percentage) = $(W_G - W_H) \times 100/W_H$; %*C* (monomer grafting conversion) = $(W_G - W_H) \times 100/W_M$. W_H, W_G and W_M are the weights of HEC, pure graft copolymer and monomer DMAEMA, respectively.

[b] Viscosity measurements were carried out in distilled water at 30 ± 0.5°C using an Ubbelohde viscometer.

Germany. Its average molecular weight is 4.56×10^5 (H_2O, 25°C) as determined by the viscosity method (Sato & Nalepa, 1978). The carboxybetaine-type zwitterionic monomer MAEDAE was synthesized in our laboratory by the reaction of 2-(dimethylamino)ethyl methacrylate with sodium monochloroacetate. Ceric ammonium nitrate (CAN) and ethylenediamine tetraacetic acid (EDTA) were of analytical grade. Shale samples and Anqiu bentonite were obtained from Drilling Mud Company of Shengli Petroleum Administration, China. Commercial polymeric additive, carboxymethylcellulose (CMC) and FA367, were provided by the Southwest Petroleum Institute in China, and were used for a comparative study.

2.2. Graft copolymerization

The new water-soluble ampholytic polysaccharides (NWSAP) with carboxybetaine lateral groups were synthesized by grafting MAEDAE onto HEC using CAN/EDTA initiation system. The following procedure has been adopted in carrying out the reactions: in a 250-mL four-neck round-bottom flask equipped with a mechanical stirrer, 2.0 g HEC was dissolved in distilled water with stirring and warming, while the flask was purged with N_2. After 30 min, the required quantities of CAN and EDTA (Table 1) were added successively to the reaction system. After 10 min, a definite amount of MAEDAE (Table 1) was added. The flask content was kept in a thermostatic water bath at a certain temperature for 6 h. After completion of the reaction, the products were precipitated by the addition of acetone and separated by filtration. After complete removal of the homopolymer, the pure graft copolymers were dried at 40°C under vacuum to a constant weight. Their infrared spectra as well as that of the purified HEC (Fig. 1) were obtained using a Nicolet FT-20SX spectrophotometer (KBr pellet). These ampholytic polysaccharides are water-soluble and the schematic representation of their structure is shown as follows:



2.3. Clay swelling tests

Anqiu bentonite (40 g) dried at 120°C for 6 h was pressed into a cake (5 MPa pressure for 5 min.) and fixed in a WZ-2 type swelling apparatus (Nanjing Soil Apparatus Factory, China). The thickness changes of the betonite were recorded in contact with 100 mL pure water or polymer aqueous solution for 12 h. The swelling efficiency, %SE, was calculated as follows:

$$\%\mathrm{SE} = (\Delta H/H_0) \times 100 \tag{1}$$

where H_0 is the height of the dried betonite cake and ΔH is the increase in height at 12 h due to hydration swelling. The smaller the %SE is, the stronger the inhibiting-swelling ability of the polymeric additive.

2.4. Shale rolling tests

Weathered shale was ground and sieved to yield suitable mesh size granules for the rolling tests. A 5.0 g portion of this shale was added to the test fluid in a stainless steel aging jar and the system was rolled for 12 h at 120°C. After the rolling, the jar content was passed over an 80-mesh screen. The retained shale was then dried to constant weight at 100°C. The shale recovery (%SR) was calculated for each sieve on a dry mass basis as follows:

$$\%\mathrm{SR} = (W/W_0) \times 100 \tag{2}$$

where W, W_0 denote the weight after and before hot-rolling,

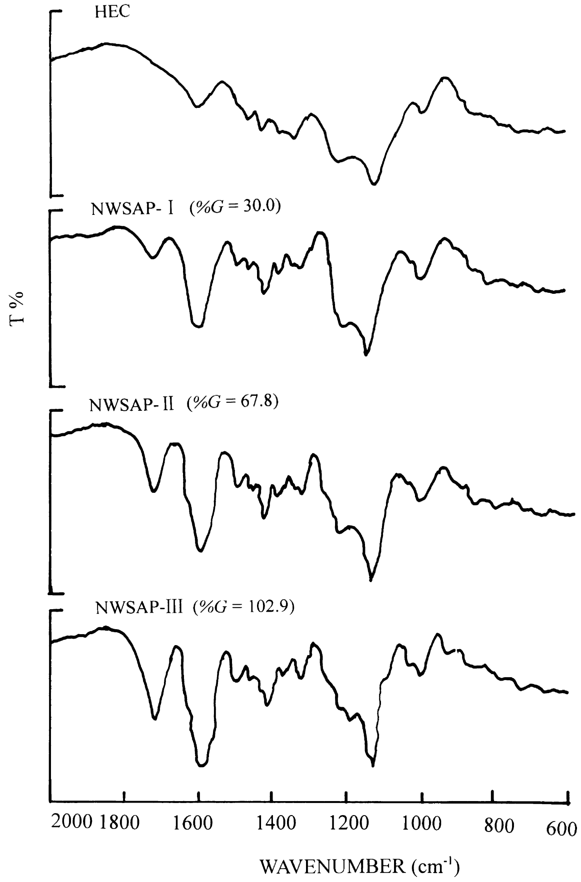


Fig. 1. Spectra of HEC and its graft copolymers.

respectively. The greater the %SR is, the stronger the inhibiting-dispersion ability of the polymeric additive.

2.5. Mud rheology tests

Two kinds of low-solid base muds, fresh-water-based mud (Anqiu bentonite:Na_2CO_3:$H_2O = 4:0.2:100$ by weight) and saline-based mud (4% prehydrated Anqiu bentonite +4% NaCl) were made. Prior to use, these base muds were aged for 24 h at room temperature to hydrate the bentonite. The required quantity of polymer was added to the base mud and stirred at high speed for 10 min. Then, the rheological property of the treated mud as well as that of the base mud were measured using a DNN-Z_6 type rotating viscometer. The rheological parameters such as apparent viscosity (η_a), plastic viscosity (η_b) and yield point (τ_0) can be determined as follows (Zhang & Chen, 1988):

$$\eta_a = \Phi_{600}/2 \text{ (mPa s)} \quad (3)$$

$$\eta_p = \Phi_{600} - \Phi_{300} \text{ (mPa s)} \quad (4)$$

$$\tau_0 = 0.511\,(\Phi_{300} - \eta_p) \text{ (Pa)} \quad (5)$$

where Φ_{600} is the viscosity at the rotating rate of 600 rpm and Φ_{300} is the viscosity at the rotating rate of 300 rpm.

3. Results and discussion

3.1. Preparation and characterization of NWSAP

Numerous methods have been reported in the literature for initiating graft copolymerization (Battaerd & Tregear, 1976). When polysaccharides such as xanthangum, guargum, starch and carboxymethylcellulose are the substrates, the ceric ion initiation method has been used extensively due to minimized homopolymer formation and higher grafting efficiency (Deshmukh & Singh, 1986, 1987; Deshmukh, Sudhakar & Singh, 1991). In the present investigation, three graft copolymers with various %*G* and intrinsic viscosity $[\eta]$ have been prepared (Table 1) in order to relate their structural parameters to their properties as the drilling-mud additive. CAN in combination with EDTA was used as the initiation system. The details of the graft copolymerization are given in Table 1. To obtain the pure graft copolymers, the resulting products were extracted with an appropriate solvent to remove the homopolymer produced. It was found that extracting with a mixture of methyl alcohol and water (9:1 by volume) for 48 h was quite enough to remove the poly (MAEDAE) (homopolymer).

The infrared spectra of the substrate HEC and three graft copolymers are presented in Fig. 1. After grafting, a new band appears at 1728 cm^{-1}, which is the characteristic of ester C=O from MAEDAE unit. Moreover, the intensity of the new band increases with the increase of the grafting percentage (%*G*). These testified to the existence of the grafting reaction.

3.2. Evaluation as drilling-mud additive

To explore the possibility of NWSAP as a drilling-mud additive, three graft copolymers, shown in Table 1, have been tested for their inhibitive and mud rheological properties. The inhibitive property was evaluated by means of commonly used clay-swelling tests and shale hot-rolling tests. The mud rheology tests were performed according to American Petroleum Institute (API) specifications. Meanwhile, two commercial polymeric additives, CMC and FA367, were used for a comparative study. It was reported that FA367, an acrylamide-based polyampholyte, has enhanced drilling-fluid properties and has been applied successfully in many drilling treatments (Niu, Zhang, Luo & Li, 1995; Yan, Jiang & Zong, 1995).

Fig. 2 shows the dependence of the %*G* of NWSAP on the %SE and %SR. An increase in the %*G* leads to a decrease in the %SE and an increase in the %SR. This implies that polymerizing the carboxybetaine monomer on HEC contributes to the inhibition of the clay swelling and shale dispersion resulting from hydration. It is known that polymeric hydration inhibitors appear to form a protective layer of hydrated polymer retarding clay or shale hydration by attaching or adsorbing onto exposed clay particles (Shen & Perricone, 1988). For the NWSAP sample containing

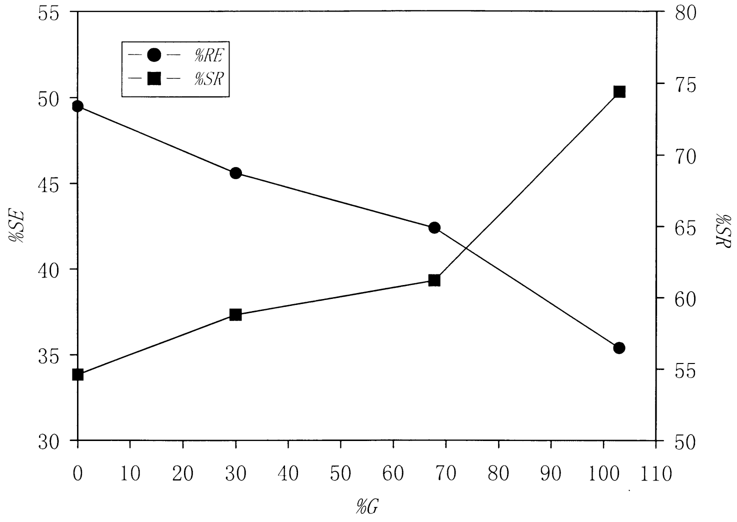


Fig. 2. Effect of the grafting percentage (%*G*) of ampholytic polysaccharides on the swelling efficiency (%SE) and the shale recovery (SR). Polymer concentration, 0.2 wt%; pH, 6.0.

both carboxybetaine groups and polar hydroxy groups, the positive charge is provided by a quaternary ammonium group and the negative charge is provided by a carboxylate group. Thus, it may be adsorbed effectively on the negatively as well as the positively charged clay edges via electrostatic attraction and hydrogen bonding. Obviously, this becomes an advantage when compared with nonionic HEC or anionic CMC because nonionic HEC can be adsorbed on the clay particles only via hydrogen bonding, while anionic CMC can attach only the clay edges via electrostatic attraction. The comparative study (Fig. 3) shows that NWSAP-III suppresses the hydration of clay and shale more effectively than CMC and has a matched inhibitive ability to FA367.

Fig. 4 gives the effect of the pH medium on the inhibition of NWSAP-II. With the increase of pH from 6.0 to 10.0, the %SE increases and the %SR decreases, corresponding to a decrease of the inhibitive ability of NWSAP-II. This phenomenon may result from two causes. Firstly, higher pH environment favors the hydration of clay or shale in itself (Chesser, 1986). Secondly, the pH increase results in the gradual conversion of carboxylate groups in the carboxybetaine monomer units from the associated state to the dissociated state. This strengthens the intramolecular ionic attraction of NWSAP-II but weakens the interaction of the NWSAP-II molecules with the clay or shale due to the corresponding decrease of the coulombic attraction between them.

Unlike the dispersed or high-solid mud formulated with bentonite, the rheological behavior of inhibitive polymer mud with low bentonite content is largely controlled by the viscosifying effect of the dissolved high molecular weigh polymer (Kadaster, Guild, Hanni & Schmidt,

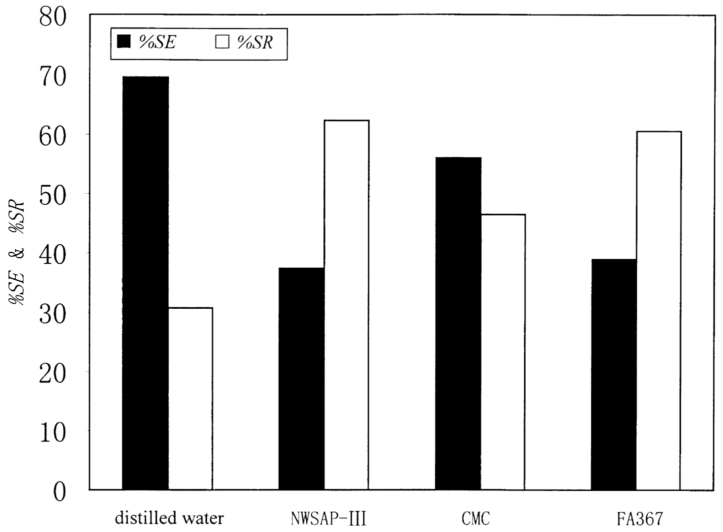


Fig. 3. Comparison of inhibitive properties among NWSAP-III, CMC and FA367. Polymer concentration, 0.2 wt%; pH, 8.0.

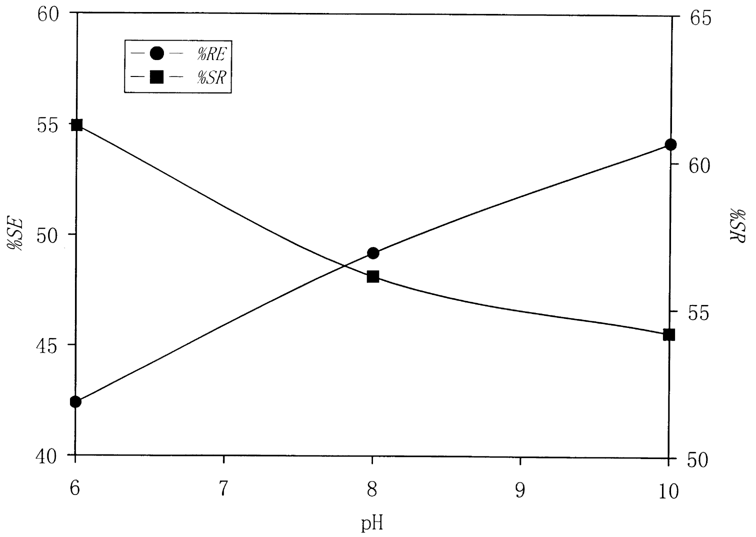


Fig. 4. Effect of pH of the NWSAP-II solution on the swelling efficiency of clay (%SE) and the shale recovery (%SR). Polymer concentration, 0.2 wt%.

1989). Table 2 gives the rheological properties of the fresh-water-based mud and the saline-based mud before and after treatment with different polymers (NWSAP-I, NWSAP-II, NWSAP-III, CMC, FA367), respectively. For the NWSAP samples investigated, the strong thickening efficiency characteristic of high values of η_a, η_b and η_0 for low-solid muds, especially for saline mud, has been observed. In contrast, CMC and FA367 demonstrate weaker viscosity-building ability in these muds, in particular FA367 in the saline mud. It seems that NWSAP with carboxybetaine groups has an obvious advantage in viscosifying the salt-containing drilling-fluids. The fact may be ascribed to NWSAP's "antipolyelectrolyte" behavior in an aqueous medium. Previous studies have revealed that the betaine-type ampholytic polymers can exhibit enhancement in viscosity and solubility in the presence of added electrolytes due to shielding of coulombic attractions (Kathmann, White & McCormick, 1997a,b). In addition, the $[\eta]$ of NWSAP seems to have an effect on the mud rheological property. As shown in Tables 1 and 2, the greater the $[\eta]$, the stronger the viscosification.

Table 2
Rheological property of the bentonite muds and the bentonite-polymer muds

Mud formulation	Rheological parameters			pH
	η_a (mPa s)	η_b (mPa s)	τ_0 (Pa s)	
Fresh-water-based mud (A)	6.0	4.0	2.0	8.5
(A) + 0.2 wt% NWSAP-I	29.5	4.0	25.5	8.5
(A) + 0.2 wt% NWSAP-II	35.0	9.0	26.0	8.5
(A) + 0.2 wt% NWSAP-III	33.0	10.0	23.0	8.5
(A) + 0.2 wt% CMC	9.3	7.0	2.3	8.5
(A) + 0.2 wt% FA367	16.3	13.0	3.3	8.5
Saline-based mud (B)	2.0	1.5	0.5	8.0
(B) + 1.0 wt% NWSAP-I	37.0	33.0	4.1	8.0
(B) + 1.0 wt% NWSAP-II	55.0	46.0	9.0	8.0
(B) + 1.0 wt% NWSAP-III	46.0	38.0	8.0	8.0
(B) + 1.0 wt% CMC	22.0	19.0	3.0	8.0
(B) + 1.0 wt% FA367	10.5	9.0	1.5	8.0

From the above mentioned results and discussion, it is expected that the NWSAP with suitable structural parameters may have a potential use as the drilling-fluid additive with both good inhibitive and mud properties. Further studies on the aqueous solution property, adsorption behavior on the clay minerals, and structure/property relationship of this ampholytic polysaccharide will be favorable to understand better its action mechanism and put its applications into effect.

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