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SHORT COMMUNICATION

L.-M. Zhang

Inhibitive properties of amphoteric, water-soluble cellulosic polymers on bentonite swelling

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L.-M. Zhang
Institute of Polymer Science
Zhongshan University
Guangzhou 510275
China

Abstract Amphoteric, water-soluble cellulose derivatives were prepared by the quaternization of anionic carboxymethylcellulose (CMC) with 3-chloro-2-hydroxypropyltrimethylammonium chloride. These polymers suppress the swelling of bentonite more effectively than CMC and their inhibitive effect depends on the degree of quaternization, the molecular conformation and the type of counterions.

Key words Amphoteric cellulose derivative – Carboxymethylcellulose – Hydration suppressant – Drilling fluids

Introduction

The hydration of the clay minerals of shales is a major problem during drilling oil and gas wells in oilfields. On contact with water, the clay minerals can swell and eventually disperse into the fluid [1, 2]. This behavior often reduces the mechanical properties of the shale [3–5]. To prevent degradation of the wellbore wall and to minimize disintegration and dispersion of drilled cuttings during their removal from the borehole, drilling through reactive shale formations requires the use of an inhibitive drilling fluid [6].

Water-soluble polymers play an important role in the formulation of inhibitive drilling fluids [7–21]. Their inhibition mechanism to clay mineral swelling is commonly attributed to protective adsorption layers on the clay mineral particles [7–10]. Conventional anionic polymers such as partially hydrolyzed polyacrylamide, polyanionic cellulose, sodium carboxymethylcellulose (CMC) and recently developed cationic synthetic polymers such as quarternary polyamine and cationic polyacrylamide have been used for this purpose. However, shale inhibition with anionic polymers is limited because of the strong repulsion between the negatively charged clay mineral surfaces and anionic polymers. The cationic polymers usually show high toxicity to aquatic organisms and are incompatible with common drilling fluid additives such as anionic polymers and barite [16, 17].

Recently, a new class of water-soluble polymers, modified CMC with amphoteric character has been synthesized in our laboratory [22]. The polymer may overcome the limitations inherent in the above-mentioned additives and may be used as a new hydration suppressant in drilling fluids. The present paper describes its inhibition behavior on bentonite swelling.

Experimental

Materials

Modified amphoteric cellulose derivatives were prepared by the quaternazation of commercial CMC with 3-chloro-2-hydroxypropyl-trimethylammonium chloride in isopropanol water [22]. Samples of different degrees of substitution of quaternary (DSQ) ammonium groups per glucopyranose unit and counterions (K^+ or Na^+) were used (Table 1).

The bentonite was provided by China National Oil & Gas Exploration & Development Corporation. The cation exchange capacity was 82.3 mEq/100 g and the zeta potential was −42.5 mV at pH = 6.5.

Table 1 Original carboxymethylcellulose (*CMC*) and modified cellulosic polymers used in this study

Samples	CMC[a]	A[b]	B[c]	C[c]	D[d]
DSQ	0	0.22	0.16	0.21	0.38
Counterions	Na^+	Na^+	K^+	K^+	K^+

[a] The degree of substitution of carboxymethyl groups is 0.66 and the average molecular weight is 1.86×10^5 (0.1 M NaCl, 25 °C) [22]. Prior to modification, CMC was purified by sedimentation in 3 M HCl
[b] Prepared using NaOH as the alkalizing agent
[c] Prepared using KOH as the alkalizing agent
[d] Prepared by second quaternization of sample C (using KOH as the alkalizing agent)

Swelling tests

Bentonite (40 g), dried at 120 °C for 6 h, was pressed to a cake (5 MPa pressure for 5 min) and fixed in a WZ-2-type swellmeter (Nanjing Soil Apparatus Factory, China). The thickness changes of the bentonite were recorded in contact with 100 ml pure water or aqueous solution of the cellulose derivative for different time periods. The swelling efficiency, V_f (%), was calculated from

$$V_f = \Delta H_t / H_0 \times 100\ (\%)\ ,$$

where H_0 was the thickness of the dry bentonite cake and ΔH_t was the increase in thickness at time t due to swelling.

Viscometric measurements

Viscometric measurements were carried out with an Ubbelohde viscometer at 30 ± 0.05 °C. The modified cellulose samples were dissolved in 0.5 M NaCl aqueous solutions. The viscosity data were calculated according to the Mark–Huggins equation:

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C\ ,$$

where η_{sp} is the specific viscosity, C is the concentration of polymer, $[\eta]$ is the intrinsic viscosity, and k' is the Huggins constant. η_{sp}/C is plotted versus C, and $[\eta]$ and k' are determined from the intercept and slope of the straight line, respectively.

Results and discussion

The swelling of bentonite in 1.0% CMC aqueous solution or in 1.0% solutions of modified cellulose is less than in deionized water (Fig. 1). This result shows that the original CMC and the modified cellulosic polymers can inhibit clay swelling, in particular after quaternization. Samples B and C have the same counterions, but sample B with DSQ = 0.16 (curve e in Fig. 1) is less effective than sample C with DSQ = 0.21 (curve f in Fig. 1), indicating that an increase in DSQ increases the inhibition effect. From the adsorption point of view, the strong repulsion between the negatively charged clay mineral surfaces and anionic CMC makes it unlike that most of the CMC will be adsorbed. Thus, anionic CMC can only attach at the positive edge charges. In contrast with CMC, modified CMC with both anionic and cationic groups can adsorb on negatively charged clay mineral surfaces as well as at the positively charged edges. This is an advantage for forming a protective coating which suppresses swelling of the bentonite (Fig. 1).

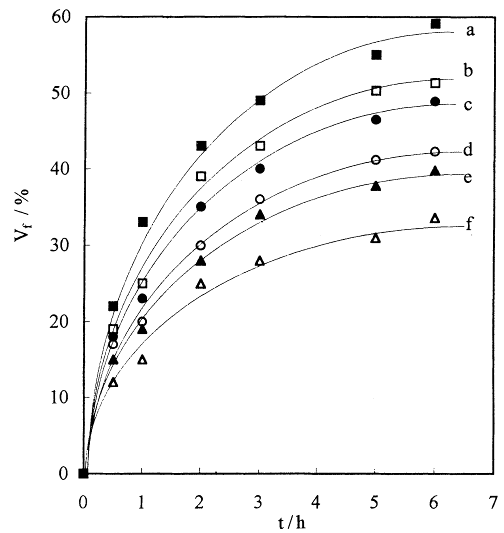

Fig. 1 The swelling curves of bentonite in deionized water and aqueous solutions of cellulose derivatives. (*a*) deionized water, (*b*) 1.0% CMC, (*c*) 1.0% modified cellulose, sample D, (*d*) 1.0% modified cellulose, sample A, (*e*) 1.0% modified cellulose, sample B, (*f*) 1.0% modified cellulose, sample C

Among the modified cellulosic polymers investigated, sample D has the highest DSQ but the worst antiswelling property (curve c in Fig. 1). Evidently, an intermediate value of DSQ is the optimum. According to Shen and Perricone [10], the extended conformation of shale stabilizing polymers in aqueous solution is favorable for forming an adsorbed protective layer on many exposed clay minerals or shale particles. For an amphoteric polymer, the solution property is closely related to its conformation [23]. When the net charge is large enough, a polymer chain behaves like a nonamphoteric polyelectrolyte, and due to the electrostatic repulsive forces the polymer chain takes an extended conformation in dilute solution. At low net electrical charge density, coulombic attraction between oppositely charged sites affords inter- and intramolecular interactions, which promote the association between the polymer chains, and the conformation of the polymer chains becomes more globular. In 0.5 M NaCl aqueous solution the intrinsic viscosity of the samples decreases (Fig. 2) and the Huggins constant (k') increases with increasing DSQ (Table 2). The result implies that sample D takes a fairly tight conformation compared with sample B or C.

Samples A and C have equivalent DSQ but different counterions. Sample C with K^+ as the counterion

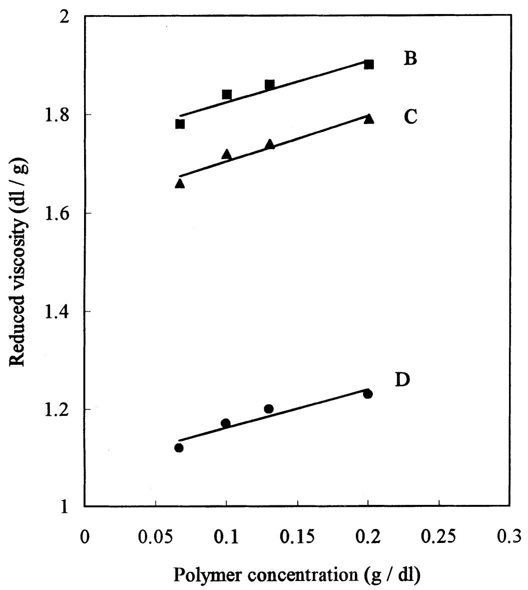

Fig. 2 Reduced viscosity of modified cellulosic polymers as a function of concentration in aqueous salt solution (0.5 M NaCl)

Table 2 Intrinsic viscosity and Huggis constant of modified cellulosic polymers in aqueous salt solution (0.5 M NaCl)

Samples	Slope	$[\eta]$ (dl g^{-1})	k'
B (DSQ = 0.16)	0.84	1.76	0.27
C (DSQ = 0.21)	0.92	1.61	0.35
D (DSQ = 0.38)	0.79	1.08	0.68

(curve f in Fig. 1) is more effective than sample A with Na^+ ions (curve d in Fig. 1). As a matter of fact, the oilfield industry shows a growing interest in the use of sodium-free, potassium-based chemicals, examples of which are potassium lignite, potassium asphalt sulphonates, potassium CMC, potassium hydrolyzed polyacrylamide and potassium compounds [11]. Therefore, the combined effects of K^+ and the cationic groups in the modified cellulosic polymer can markedly improve the inhibition of the swelling.

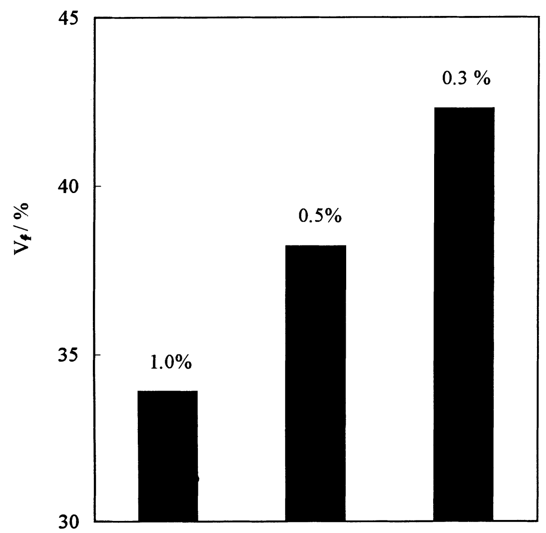

Fig. 3 Swelling efficiency V_f when the bentonite was contacted with aqueous solutions of modified cellulose, sample C, for 6 h

The values of V_f as a function of the concentration of sample C are shown in Fig. 2. An increase in the concentration increases the inhibitive effect.

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