

Inhibition of Water-Soluble Cationic Cellulosic Polymers to Clay Hydration

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ABSTRACT: The inhibition of water-soluble cationic graft terpolymers of hydroxyethylcellulose with the vinyl monomers dimethyldiallylammonium chloride and acrylamide to the hydration of water-sensitive clay in oilfields was investigated by clay hydration-swelling tests, XRD analyses, zeta-potential measurements, and SEM observation. It has been shown that grafting enhances the hydration-inhibition effectiveness and the performances of these cationic cellulosic polymers are strongly dependent on their cationicity, relative molecular weight, and solution concentration. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3088–3093, 1999

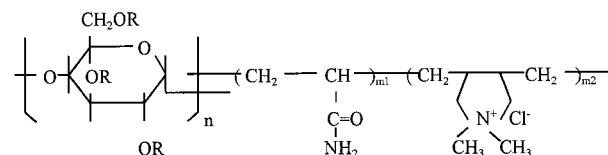
Key words: cationic cellulosic polymers; clay-hydration inhibition; environmental acceptability; water-based drilling fluids

INTRODUCTION

Over the last few years, positively charged synthetic polymers such as quaternary polyamine and cationic polyacrylamide, used for stabilizing water-sensitive shale formations containing large amounts of hydratable clay minerals, has received much attention in oilfields.^{1–6} Compared with conventional anionic polymers such as partially hydrolyzed polyacrylamide and polyanionic cellulose or nonionic polymers, these cationic polymers can provide more effective shale stabilization by attaching more strongly to the negatively charged clay surfaces to suppress effectively the hydration of swelling clays.^{3,6} More recently, however, growing concerns over their environmental impact have led to looking for the

modified natural polymers with cationic ions, which may guarantee biodegradability.^{7–11}

Water-soluble hydroxyethylcellulose (HEC) is used extensively as a drilling fluid additive with good environmental acceptability. Although it may be regarded as a shale-stabilizing polymer, its inhibition to the hydration of water-sensitive clay minerals is limited.^{12,13} In the present work, the modification of HEC was carried out by preparing water-soluble cationic graft terpolymers (HGAD) of HEC with the vinyl monomers acrylamide (AM) and dimethyldiallylammonium chloride (DMDAAC):



(R = -H or -(CH₂CH₂O)_xH, x ≥ 1)

It will be shown that grafting enhances the hydration-inhibition effectiveness, and that the

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performances of these cationic cellulosic polymers are strongly dependent on their cationicity τ (weight percentage of DMDAAC units), relative molecular weight (intrinsic viscosity $[\eta]$), and solution concentration.

EXPERIMENTAL

Materials

HEC is a commercial product obtained from Harbin Chemical Factory, with an average degree of substitution of 0.91 and a molar substitution of 1.65. The vinyl monomers DMDAAC and AM were generously supplied by Guangzhou Fine Chemical Industry Company. Potassium permanganate and sulphuric acid were of laboratory grade. Clay, containing 96 wt % calcium montmorillonite (a main water-sensitive clay mineral in shales), was generously provided by China National Oil & Gas Exploration & Development Corporation.

Preparation of Cationic Cellulosic Polymers

HGAD samples were synthesized in aqueous medium using a potassium permanganate/sulphuric acid redox system as the initiator. In a typical grafting experiment, an exact amount of dry HEC was first dissolved in a specific concentration of KMnO_4 solution using a four-necked flask, followed by adding the determined quantities of H_2SO_4 and the monomers in this order. Then, the flask content was stirred in a thermostatic water bath at 60°C for 4 h. Nitrogen gas was purged into the reaction mixture to avoid the presence of oxygen. After the polymerization, the graft sample was separated and extracted with mixed solvent (acetic acid : glycol = 60 : 40), and then dried at 35°C under vacuum to a constant weight. Four HGAD samples with various structural parameters, shown in Table I, were obtained by controlling the dosages of raw materials.

Clay Hydration-Swelling Tests

A WZ-2-type swellmeter, purchased from Nanjing Soil Instrument Factory, was adopted to measure the linear expansion of the clay pellet after the clay pellet had been in contact with deionized water or the sample solution. First, the clay pellet was prepared by compressing 40 g of clay, already dried at 120°C for 6 h, into a piece under 5 MPa pressure for 5 min, and was fixed in the swellme-

Table I Cationic Cellulosic Polymers with Various Structural Parameters

Sample No.	Cationicity ^a τ (%)	Intrinsic Viscosity ^b $[\eta]$ (dL/g)
HGAD-1	9.8	1.972
HGAD-2	14.2	1.949
HGAD-3	10.3	2.863
HGAD-4	15.1	3.026

^a τ was calculated from chloride analyses.

^b $[\eta]$ was measured with an Ubbelohde viscometer at 25 ± 0.2°C (in 0.1M aqueous Na_2SO_4).

ter chamber, which confined it between screens and confined the swelling of the clay pellet to the vertical direction. Then deionized water or the sample solution was filled in the chamber when the test began. Thus, the swelling of the clay resulting from its hydration caused the sensor to rise, and the linear expansion of the clay pellet was recorded for the duration of the test.

XRD Analyses

The first-order basal spacing of wet clay ($d(001)_w$) was measured after the clay had been contacted deionized water or various sample fluids for 6 h at room temperature. The first-order basal spacing of dried clay ($d(001)_d$) was also measured after the wet clay had dried for 12 h at 120°C. The hydration level of the clay treated by deionized water or the sample solution was investigated by comparing the variation (Δd) between $d(001)_w$ and $d(001)_d$. A Rigaku D/max-1200 diffractometer equipped with a curved crystal AMR monochromator (copper Ka radiation) was used in all X-ray diffraction work.

Zeta-Potential Measurements

The zeta-potentials of the clay suspension before and after the addition of HEC or HGAD-4 were measured using a Model 501 Lazer Zee Meter™ made in Pen Kem, Inc. The clay suspension was prepared by mixing 1 g of the clay in 1000 cm³ of deionized water and shaken vigorously to obtain a uniformed suspension. To determine the effect of HEC or HGAD-4 concentration on the zeta-potential of clay suspension, the predetermined amount of HEC or HGAD-4 solution was added and stirred for 5 min.

SEM Observation

The grain structures and morphologies in the clay slurry untreated and treated by the HGAD-4

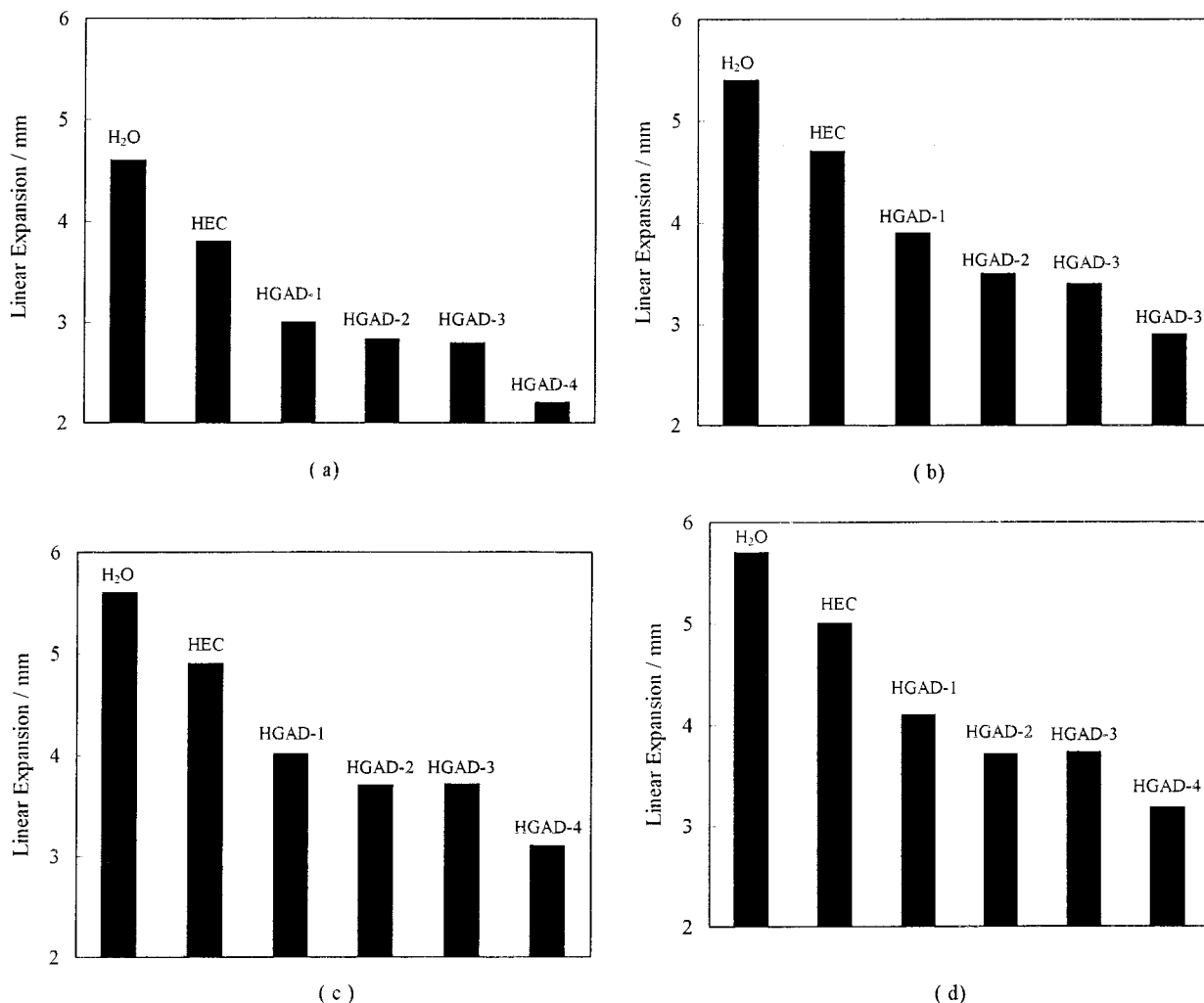


Figure 1 The linear expansion of the clay after it has contacted deionized water and sample aqueous solutions for different time: (a) for 2 h, (b) for 4 h, (c) for 6 h, (d) for 8 h. Polymer concentration: 1.0 wt %.

sample were examined by an Hitachi S-430 apparatus at an accelerating potential of 10 kV. The SEM photos had been reproduced at a magnification of 3000.

RESULTS

The linear expansion (Le) of clay after it has contacted deionized water and 1.0 wt % aqueous solutions of ungrafted HEC and HGAD for 2, 4, 6, and 8 h is given in Figure 1(a) to (d), respectively. It can be seen that the Le of the clay in the HEC solution or the solutions of HGAD with different structural parameters at each investigated time is smaller than the Le of the clay in deionized

water at a corresponding time, showing that HEC and HGAD have the inhibition activity to clay hydration. In comparison with the Le of the clay in the HEC solution, the Le of the clay in the HGAD solutions is lower, indicating that grafting can enhance the hydration-inhibition effectiveness. Among the HGAD samples evaluated, HGAD-4, with a higher τ and $[\eta]$, are the most effective. For HGAD-1 and HGAD-2 with equivalent $[\eta]$, HGAD-2 with $\tau = 14.2\%$ is more effective than HGAD-1 with $\tau = 10.8\%$, which suggests that the increase in τ can result in the enhancement of inhibition ability. For HGAD-3 with a lower τ but higher $[\eta]$ than HGAD-2 (Table I), its inhibition property is equivalent to HGAD-2, which indicates the contribution of the increase in

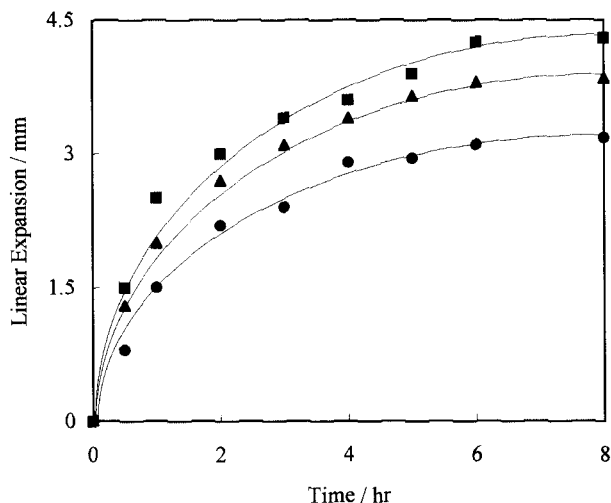


Figure 2 The effect of HGAD-4 concentration on the linear expansion of the treated clay: (■) 0.2%, (▲) 0.5%, (●) 1.0%.

$[\eta]$ to clay-hydration inhibition. In addition, the results in Figure 2 shows that the solution concentration of HGAD-4 influences its inhibition effect, and that HGAD-4 can provide better inhibibility when its concentration increases.

The $d(001)$ spacings of wet/dried clay, treated by deionized water and by 1.0 wt % aqueous solutions of ungrafted HEC and HGAD samples, are listed in Table II. In the case of deionized water, the variation (Δd) between $d(001)_w$ and $d(001)_d$ is the biggest, suggesting the highest hydration capacity. In contrast, the Δd in the case of the HEC solution or the HGAD solutions is relatively small, and is found to be in the following order: HEC (0.093 nm)

Table II First-Order Basal Spacings of the Clay Treated by Deionized Water or Various Sample Solutions

Sample Fluids	$d(001)_w$ (nm)	$d(001)_d$ (nm)	Δd (nm)
H ₂ O	1.943	1.547	0.396
1% HEC aqueous solution	1.633	1.540	0.093
1% HGAD-1 aqueous solution	1.586	1.533	0.053
1% HGAD-2 aqueous solution	1.571	1.528	0.043
1% HGAD-3 aqueous solution	1.574	1.530	0.044
1% HGAD-4 aqueous solution	1.553	1.521	0.032

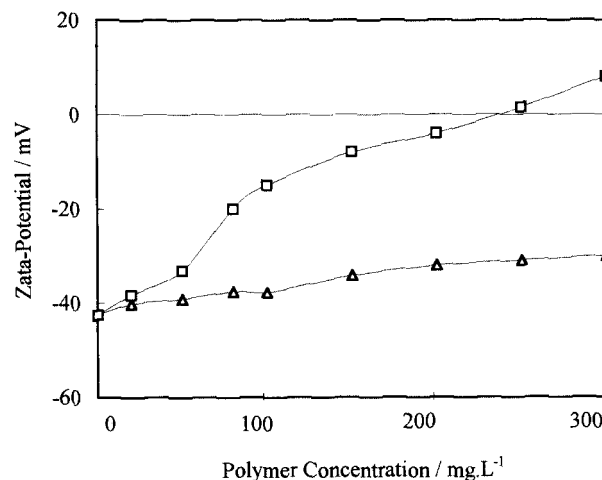


Figure 3 The effect of HEC or HGAD-4 concentration on the zeta-potential of the clay suspension: (Δ) HEC, (□) HGAD-4.

> HGCA-1 (0.053 nm) > HGAD-2 (0.0043), HGAD-3 (0.044 nm) > HGAD-4 (0.032 nm).

It is understood that the clay-hydration capacity is weaker when the Δd is smaller.¹⁴ Therefore, the X-ray diffraction analyses are very consistent with the clay hydration-swelling tests.

The zeta-potentials of the clay suspension before and after the addition of HEC or HGAD-4 are shown in Figure 3. In the untreated clay suspension, the zeta-potential is very negative (−42.5 mV), suggesting that the clay minerals have many negatively charged surfaces. In the clay suspension treated by HEC, the zeta-potential is relatively unaffected by the addition of HEC. In the clay suspension treated by HGAD-4, however, the zeta-potential increases from −38.3 to +8.0 mV as the concentration of HGAD-4 increases from 20 to 300 mg/L with a point-of-zero charge (PZC) at about the concentration value of 245 mg/L, which can be attributed to the neutralization of the cationic groups along the HGAD-4 chains to the negative charges on the clay surfaces.

The grain structures and morphologies in the clay slurry untreated and treated by HGAD-4 are observed with the help of scanning electron microscopy (see Fig. 4). In the untreated clay slurry, the clay grains are relatively fine and distribute uniformly, and the coagulation among the grains is rare. But in the treated clay slurry, the clay particles cluster together, forming a relatively compact texture.

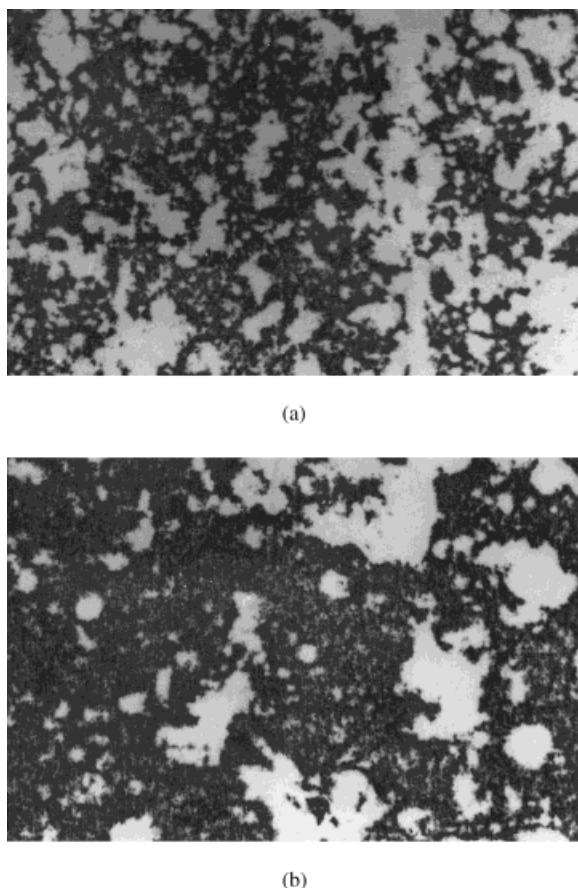


Figure 4 The grain structures and morphologies in the untreated and treated clay slurries: (a) untreated; (b) treated.

DISCUSSION

Water adsorption by clay minerals is considered a major cause of many shale problems. Among the common clay minerals, montmorillonite and its mixed-layer species are the most reactive and troublesome. It is well known that montmorillonite belongs to the 2 : 1 layer clay family. Each of its unit layers is composed of an Al—O—OH octahedral sheet sandwiched between two Si—O tetrahedral sheets. The surface of the layers has many negative charges because of the isomorphous substitution of some of the atoms in the crystal lattice, and the adjoining clay layers are held together more loosely by weak electrostatic forces.

When montmorillonite is exposed to water, the water can be drawn into the interlayer region by hydration of the exchange cations and the silicate surfaces causing its swelling. This behavior has

been described by some investigators.¹⁵ Most polymeric clay-hydration inhibitors appear to form a protective layer of hydrated polymer retarding clay swelling by attaching or adsorbing onto many exposed clay particles.^{3,6,13}

HGAD, containing both cationic quaternary ammonium groups, polar hydroxy, and amide groups in macromolecular chains, can be adsorbed on the negatively charged clay surfaces via electrostatic attraction and hydrogen bonding. This becomes an advantage when compared with unmodified HEC, as nonionic HEC can be adsorbed the clay surfaces only via hydrogen bonding. As a result, HGAD would be easier to form a protective layer retarding clay hydration, and easier to negate the reactive sites of a clay particle than HEC, resulting in better inhibibility, shown in Figure 1 and Table II. The data from zeta-potential measurements (see Fig. 3) provide indirect evidence for the interaction of clay with HGAD or HEC.

The attachment effectiveness of HGAD on the clay surfaces can be affected by their cationicity, molecular size, and solution concentration. It is conceivable that the attachment effectiveness of HGAD will be reinforced with the increase of τ , $[\eta]$, or solution concentration. This is because that the increase in τ , $[\eta]$, or solution concentration can result in stronger electrostatic attraction, more multisegment adsorption, and more accessibility of polymer chains, respectively.

Obviously, the attachment effectiveness plays a very important role in the inhibition of clay hydration. The experimental results, given in Figure 1 and Table II, has made this behavior clear.

The $d(001)$ spacings of the dried clay treated by HGAD solutions do not increase (see Table II), revealing that HGAD cannot penetrate the clay layers because of a large molecular size.^{16,17} For cationic HGAD with high molecular weights, the adsorption occurs primarily on the exterior surfaces of swelling clay. This is verified by SEM observation (see Fig. 4) that this attachment can link or “bridge” clay particles together, which is favorable to form a compact protective coating retarding clay hydration.

CONCLUSIONS

To improve its inhibition property to the hydration of water-sensitive clay minerals in oilfields, HEC was modified by grafting the vinyl monomers acrylamide (AM) and dimethyldiallylammo-

nium chloride (DMDAAC). It was found that grafting enhanced the hydration-inhibition effectiveness, and that the performances of prepared cationic cellulosic polymers were followed as a function of their cationicity, relative molecular weight, and solution concentration. Further experimental investigations about the adsorption of modified HEC onto clay surfaces, the solution properties of modified HEC, and the structure of clay/modified HEC complexes would be helpful to better understand their inhibition behavior and optimize their application as new clay-hydration suppressant.

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