

Preparation and Anti-Clay-Swelling Ability of New Water-Soluble Cellulose Derivatives Containing Quaternary Ammonium Groups

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ABSTRACT: New water-soluble cellulose derivatives containing quaternary ammonium groups were prepared by the heterogeneous reactions of hydroxyethyl cellulose with a quaternary chlorohydrin and characterized by reaction parameters and infrared analyses. The dependence of the heterogeneous reaction on the different affecting factors was studied. The cellulose derivatives obtained were investigated for their property as the water-soluble polymer for inhibiting the swelling of water-sensitive clay in oilfields. Based on the kinetic curves for clay hydration swelling, a mathematical model that relates linear clay expansion as a function of hydration rate and hydration equilibrium constant was developed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1416–1422, 2001

Key words: cellulose derivatives; cationic polymers; water-soluble; quaternary ammonium groups; clay-hydration inhibitor; oilfields

INTRODUCTION

The use of water-soluble polymers to suppress the hydration of clay minerals in shale is the most significant development in the oilfield drilling technology. It is known that positively charged polymers, especially the cationic polymers containing quaternary ammonium groups, can provide more effective clay-hydration inhibition than conventional anionic polymers or nonionic polymers.^{1–9} This fact arises primarily from their affinity for negatively charged clay surfaces. At present, numerous cationic synthetic polymers have been studied and used for this purpose. For example, Welch and Lee⁷ used a high-molecular-weight cationic polyacrylamide and a low-molecular-weight quaternary polyamine to control the

dispersion and swelling of gumbo shale from offshore Louisiana in North Sea; Beihoffer et al.⁸ developed an inhibitive cationic drilling fluid for slim-hole coring applications based on a combination of a synthetic polymer with quaternary ammonium groups and KCl and found that the fluid is highly inhibitive when compared to close offset well drilling with conventional water-based drilling fluids; Bailey et al.⁹ studied the effect of clay/polymer interaction on shale stabilization during drilling and confirmed that a cationic polyacrylamide containing 2% [(methacrylamido)propyl]trimethyl ammonium chloride groups limits clay-hydration swelling more effectively than a partially hydrolyzed polyacrylamide with a degree of hydrolysis of 27%, which is typical of the inhibitive polymers used in current drilling fluids, and a near neutral polyacrylamide (<3% acrylate groups). However, to date, very few studies have been conducted on modified naturally occurring polymers with cationic character and good environmental acceptability.

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Recently, we^{10,11} prepared some new cationic water-soluble cellulosic polymers by grafting a cationic monomer or a cationic monomer coupled with a neutral monomer onto nonionic hydroxyethyl cellulose (HEC), a common clay-stabilizing polymer for oilfield treatments¹² and investigated their properties as clay-hydration inhibitors. The experimental results^{10,11} showed that the grafting enhances the hydration-inhibition effectiveness. As another possible approach of preparing such materials, the present work deals with the introduction of quaternary ammonium groups onto HEC by the heterogeneous reaction of HEC with a quaternary chlorohydrin in alkaline medium and its ability to suppress clay hydration-swelling.

EXPERIMENTAL

Materials

Water-soluble hydroxyethyl cellulose (HEC) was used as the starting material. It was a commercial product obtained from Harerbin Chemical Factory (Heilongjiang, China), with an average molar substitution (*MS*) of 1.80 and the viscosity-averaged molecular weight of 3.52×10^5 (H₂O, 25°C). The quaternary chlorohydrin, 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHPTAC) was used as the cationizing agent and prepared according to Langher et al.¹³ The clay, containing 96 wt % calcium montmorillonite (a main water-sensitive clay mineral in shale), was kindly provided by National Oil and Gas Exploration and Development Corp. (Guangzhou, China). Sodium hydroxide and isopropanol were of laboratory grade.

Preparation of Cationic Cellulose Derivatives

In a 250-mL round-bottomed flask equipped with a stirrer, a condenser, a thermometer, and a dropping funnel, a predetermined weight of dry HEC was dispersed in aqueous isopropanol. The resulting slurry was stirred for 1 h and then a certain volume of sodium hydroxide solution of known concentration was added gradually with continuous stirring. After stirring for an additional 1 h, the required amount of CHPTAC was introduced. The reaction mixture was heated to 65°C and maintained at this temperature for 2 h while stirring consistently. At this end, acetic acid was added to neutralize the mixture. The reaction product was collected by filtration, washed sev-

eral times with alcohol : water mixture (80 : 20), purified with acetonitrile, and dried to constant weight in a 45°C vacuum oven to obtain the cationic cellulose derivative. It was found that the products have good water solubility.

Characterization by Reaction Parameters and IR analyses

The average molar substitution (*MSQ*) of quaternary ammonium groups of the products was determined on the basis of the analysis of nitrogen content (%N):

$$MSQ = \frac{(162 + MS \times 44)\%N}{100 \times 14 - 152.5 \times \%N} \quad (1)$$

where 162 is the average molecular weight (*MV*) of the cellulose anhydroglucose unit (*AGU*), 44 is the *MV* of hydroxyethyl substituent, 152.5 is the *MV* of quaternary ammonium substituent, 14 is the atomic mass of nitrogen, and %N was measured by Carlo Erda Elemental Analysis Model 1106.

The reaction efficiency (*RE*) was calculated as:

$$RE(\%) = \frac{\text{Amount of } \text{---CH}_2\text{CH(OH)CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^- \text{ bounded to HEC}}{\text{Amount of } \text{---CH}_2\text{CH(OH)CH}_2\text{N}^+(\text{CH}_3)_3\text{Cl}^- \text{ taken initially}} \times 100 \quad (2)$$

The IR spectra of the products and unmodified HEC were run on NICOLET FT-20SX spectrophotometer using KBr pellets in the range of 400 to 4000 cm⁻¹.

Clay Hydration-Swelling Tests

A WZ-2 type swellmeter, purchased from Nanjing Soil Instrument Factory, was used to measure the linear expansion of the clay pellet after the clay pellet had been in contact with freshwater water or the sample solution. First, the clay pellet was prepared by compressing 40 g clay, already dried at 120°C for 6 h, into pieces under 5 MPa pressure for 5 min, and was fixed in the swellmeter chamber, which confined it between screens and confined the swelling of the clay pellet to the vertical direction. Then, freshwater water or the sample solution filled the chamber when the test began. Thus the swelling of the clay resulting from its

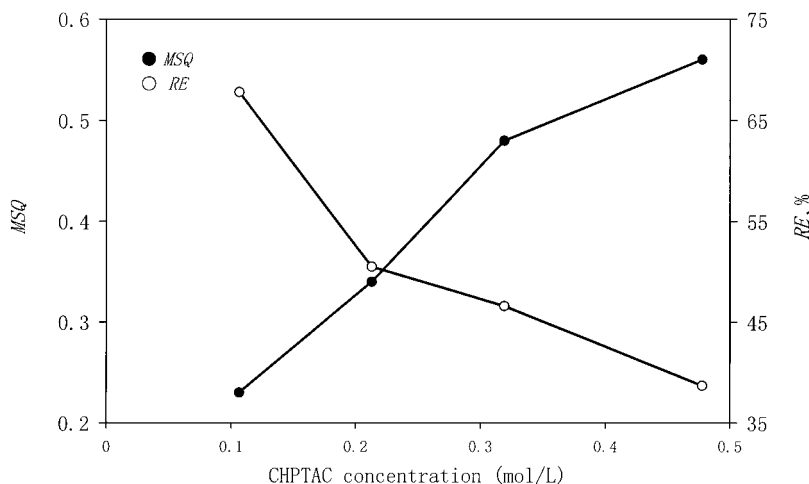


Figure 2 Effect of CHPTAC concentration on the *MSQ* and *RE*. Reaction condition: HEC, 6 g/dL; NaOH, 5.556×10^{-1} mol/L; isopropanol/water (molar ratio), 3 : 1; 65°C.

site holds true for the *RE*. The enhancement in the *MSQ* can be interpreted in terms of greater availability of CHPTAC molecules in the proximity of the HEC molecules. The decrease in the *RE* may be due to the increased chances of CHPTAC hydrolysis or not enough HEC reacted with CHPTAC.

Table I lists the results concerning the heterogeneous quaternization of HEC with CHPTAC in isopropanol–water mixtures of various proportions as the reaction media. It is noticed that the *MSQ* and *RE* are both dependent on the medium composition. Among the reaction media investigated, the solvent system containing the molar ratio of isopropanol to water of 3 is the most convenient to obtain high *MSQ* and *RE*. It may be expected that the importance of the water–organic solvent mixtures results from the fact that many physicochemical properties can be changed by varying their composition, which has an important role in controlling the quaternization reaction.¹⁴

Table I Variation of *MSQ* and *RE* with Aqueous Isopropanol Composition

Isopropanol/Water (molar ratio)	%N	<i>MSQ</i>	<i>RE</i> (%)
3:1	2.13	0.48	46.6
2:1	1.70	0.36	34.5
1:1	1.03	0.21	21.2

Reaction conditions: HEC, 6 g/dL; CHPTAC, 3.191×10^{-1} mol/L; NaOH, 5.556×10^{-1} mol/L; 65°C.

Figure 3 represents the spectra of the product (*MSQ* = 0.30) and unmodified HEC. The characteristic adsorption bands of HEC are located at frequencies 3425 cm^{-1} (hydrogen bonded O—H stretching), 2879 cm^{-1} (C—H stretching in methylene groups), 1637 cm^{-1} (H_2O molecules in non-crystalline cellulose), and 1063 cm^{-1} (C—O stretching). In contrast, the IR spectrum of the product shows not only the characteristic adsorption bands of HEC but also the characteristic adsorption bands of quaternary ammonium C—N stretching at 960 and 910 cm^{-1} .¹⁵ Thus the chemical modification of HEC by quaternization reaction is confirmed by IR analyses.

Investigation for Anti-Clay-Swelling Ability

The hydration-swelling of clay minerals has always been a major concern when using water-based mud to drill oil and gas wells. It is known that water adsorption of clay minerals can result in many drilling problems such as disintegration of cutting, balling, high torque and drag, and stuck pipe.^{6,8} Therefore, the search for suitable chemicals or water-soluble polymers to retard the hydration of clay minerals is a continuous endeavor.

Figure 4 shows the kinetic curves for hydration-swelling of the clay in freshwater and various sample solutions. The hydration-swelling processes are characteristic of some initial rapid hydration of the clay followed by the uptake of additional water molecules at a lower rate. At each hydration time *t* investigated, the *Le* of the clay in 1.0% HEC aqueous solution or in 1.0%

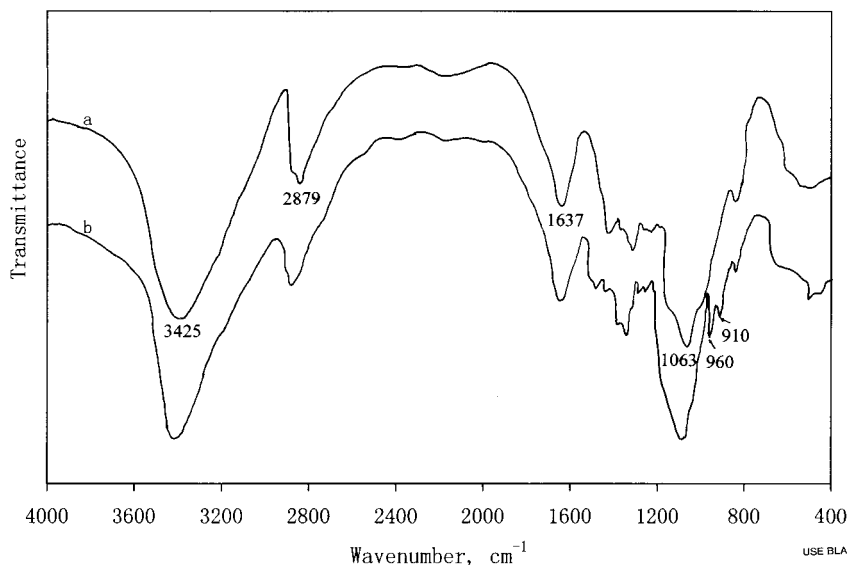


Figure 3 IR spectra of (a) HEC and (b) Product I ($MSQ = 0.30$).

aqueous solutions of the products is less than the Le of the clay in freshwater. This fact suggests that the original HEC and the products can suppress the clay swelling, in particular, after the quaternization modification. Compared with the swelling of the clay in 1.0% solution of Product I with the MSQ of 0.30, the Le of the clay in 1.0% solution of Product II with the MSQ of 0.48 is lower. This result indicates that an increase in the MSQ leads to the enhanced ability of inhibiting the clay swelling.

As a further investigation, the data shown in Figure 4 were treated by the plots of the recip-

cal linear expansion versus the reciprocal hydration time (Fig. 5). It is found that $1/Le$ is a linear function of $1/t$ for each test system studied. Thus the clay hydration-swelling may be modeled by the following kinetic equation:

$$Le = \frac{kKt}{1 + kKt} \quad (8)$$

where k is a hydration rate constant and K is the hydration equilibrium constant. Based on the regression analysis, the k and K values along with

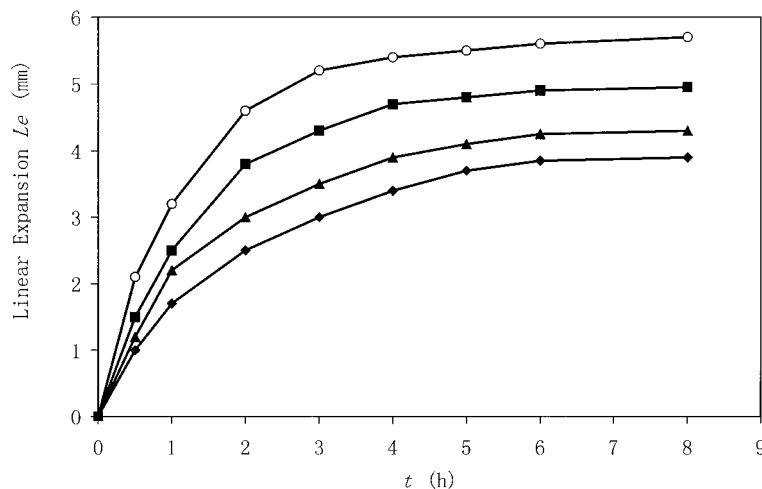


Figure 4 Kinetic curves for the hydration-swelling of the clay in water and various sample solutions at room temperature. (○) H_2O ; (■) 1.0% HEC; (▲) 1.0% Product I ($MSQ = 0.30$); (◆) 1.0% Product II ($MSQ = 0.48$).

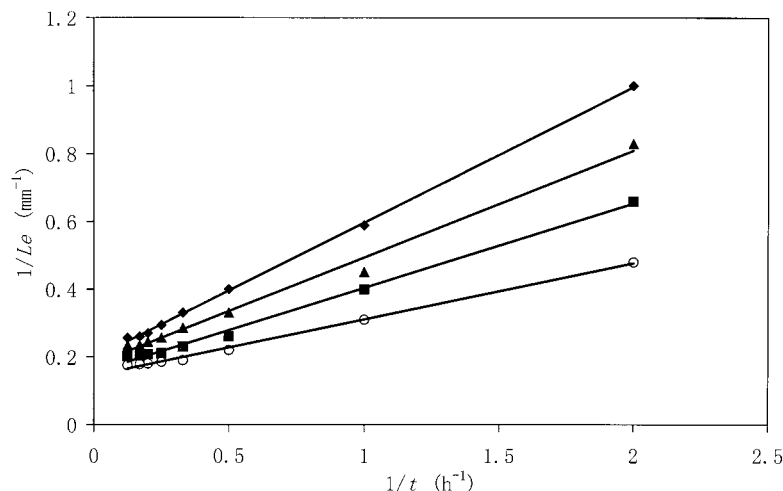


Figure 5 Plots of the reciprocal linear expansion ($1/Le$) versus the reciprocal hydration time ($1/t$). (○) H_2O ; (■) 1.0% HEC; (▲) 1.0% Product I ($MSQ = 0.30$); (◆) 1.0% Product II ($MSQ = 0.48$).

the corresponding determination coefficient R^2 were obtained (Table II). For the test systems investigated, the k and K values were both found to be in the following order: clay/1.0% Product II < clay/1.0% Product I < clay/1.0% HEC < clay/freshwater. Obviously, the clay hydration-swelling can be suppressed more effectively by the products, especially by the product with higher MSQ . It is known that 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.¹⁶ For the product containing both cationic quaternary ammonium groups and polar hydroxy groups in macromolecular chains, it can be adsorbed on the negatively charged clay surfaces via electrostatic attraction and hydrogen bonding. This becomes an advantage when compared with unmodified HEC because nonionic HEC can be adsorbed into the clay surfaces only via hydrogen bonding. Such an advantage will be reinforced with the increase of the MSQ . As a result, the

product would be easier to form a protective layer retarding the clay hydration than HEC, resulting in enhanced anticlay-swelling ability.

CONCLUSION

New water-soluble cellulose derivatives containing quaternary ammonium groups can be prepared by the quaternization reactions of HEC with the quaternary chlorohydrin, CHPTAC, in the presence of sodium hydroxide by using aqueous isopropanol as the reaction medium. Such factors as NaOH concentration, CHPTAC concentration, and the composition of the reaction medium were found to affect the quaternization extent and quaternization reaction efficiency. IR spectroscopy and elemental analysis were used to confirm the modification reaction of HEC. The products with two levels of substitution were studied for their effectiveness as the water-soluble polymer for inhibiting clay swelling. The quantitative data obtained with a model clay system were used to develop a mathematical model, which relates linear clay expansion as a function of hydration rate and hydration equilibrium constant.

Table II Regression Coefficients for the Kinetic Equation of Clay Hydration-Swelling

Test System	k	K	R^2
Clay/freshwater	6.91	0.87	0.997
Clay/1.0% HEC	6.50	0.62	0.995
Clay/1.0% Product I	5.65	0.56	0.991
Clay/1.0% Product II	5.11	0.49	0.999

REFERENCES

1. Pu, C. H. *Drill Fluid Complet Fluid* 1990, 7(1), 25.
2. Wen, L. W. *Drill Fluid Complet Fluid* 1991, 8(1), 41.

3. Liu, Y. Q. *Nat Gas Ind* 1992, 12, 46.
4. Du, D. L. *Drill Fluid Complet Fluid* 1993, 10(2), 14.
5. Gao, J. P.; Guo, D. R. *Drill Fluid Complet Fluid* 1995, 12(1), 22.
6. Retz, R. H.; Friedheim, J.; Lee, L. J.; Welch, O. Presented at the Offshore Europe Conference, Aberdeen, SD, 1991; SPE 23064.
7. Welch, O.; Lee, L. J. *Oil Gas J* 1992, July, 53.
8. Beihoffer, T. W.; Dorrrough, D. S.; Schmidt, D. D. Presented at the IADC/SPE Drilling Conference, Houston, TX, 1990; IADC/SPE 19953.
9. Bailey, L.; Keall, M.; Audibert, A.; Lecourtier, J. *Langmuir* 1994, 10, 1544.
10. Zhang, L. M.; Sun, B. W. *J Appl Polym Sci* 1999, 74, 3088.
11. Zhang, L. M.; Li, Z. M. Preprints of First East-Asian Polymer Conference; Shanghai, China, 1995; p 112.
12. Zhang, L. M. *J Cellulose Sci Technol* 1996, 3, 1.
13. Langher, R. R.; Jackson, L.; Walling, J. C.; McFadden, R. T. U.S. Pat. 3,532,751, 1970.
14. Mansour, O. Y.; Nagaty, A.; El-Zawawy, W. K. *J Appl Polym Sci* 1994, 54, 519.
15. Zhong, L.; Ding, Y. D. *Surfactants and Their Additives—Chemical Analysis*; Press of Zhejiang Science and Technology: Hangzhou, 1985; p 290.
16. Shen, J. J.; Perricone, A. C. Presented at the 63rd Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Houston, TX, 1988; SPE 18033.