Studies on New Ampholytic Cellulose Derivative as Clay-Hydration Inhibitor in Oil Field Drilling Fluid

XIANGCHUN YIN, LIMING ZHANG, ZHUOMEI LI

Institute of Polymer Science, Zhongshan University, Guangzhou 510275, People's Republic of China

ABSTRACT: A new ampholytic cellulose derivative (CAD) was prepared by grafting acrylamide and dimethyldiallylammonium chloride on carboxymethyl cellulose (CMC). The performance of CAD applied as a clay-hydration inhibitor in oil field drilling fluid was examined; the results showed that CAD had a hydration inhibitive property with better mud-making performance for low-solid mud. The mechanisms of the CAD inhibition of clay hydration were studied. The inhibiting-hydration performance of CAD was found to depend not only on cation, anion content, and molecular weight, but also on the cation–anion association in CAD chains. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 921–926, 1998

Key words: ampholytic cellulose derivative; hydration inhibitor; inhibitive property

INTRODUCTION

During oil well drilling, polymer-hydration inhibitors are usually used to protect the stability of the bore hole wall and prevent the drilling chips from dispersing.[1] At present, cationic polyelectrolytes remain dominant as hydration inhibitors. However, more and more complicate drilling strata have been met with the enlargement of drilling ranges, and many difficulties have emerged because of the weak mud-making ability of cationic polyelectrolytes. How to devise hydration inhibitors having inhibitive performance with good mud-making properties is very important. The ampholytic polyelectrolytes induce people's interest because of their good performance as hydration inhibitors in the drilling fluid.[2–4]

Carboxymethyl cellulose (CMC) is an additive widely used in drilling fluid to enhance the mud-making property of drilling mud.[5,6] Its hydratable —OH and —COO⁻ groups can stabilize the dispersion of clay particles in water favorable for mud making. But, on other hand, the inhibiting clay-hydration (or clay-swelling) property of CMC is poor, because CMC cannot be strongly adsorbed on the clay surface to form a film effective enough to protect the clay particles from hydration. It is thus expected that an ampholytic CMC derivative with cationic and anionic groups along the polymer chain may have good mud-making and clay-hydration inhibition. In this work we tried to prepare a new ampholytic cellulose derivative (CAD) by grafting acrylamide (Am) and dimethyldiallylammonium chloride (DMDAAC) on CMC and studied the relation between the clay-hydration inhibitive property of CAD and its structure. The reports about the grafting CAD have not been found in the literature.

EXPERIMENTAL

Materials

CMC was a commercial product obtained from Guangzhou Hong-Guang Chemical Factory; its

degree of substitution (DS) was 0.77, which was determined by conductometric titration.[7] The Am (Guangzhou Agent Factory) was used without further purification. DMDAAC (Guangzhou Nan-Zhong Plastic Factory) was a 60% aqueous solution. The clay (Shangdong An-Qiu Expansive Clay Factory) was Ca-montmorillonite.

Preparation of CAD

The graft copolymer CAD was prepared by grafting Am and DMDAAC on CMC initiated by $KMnO_4$. CMC and $KMnO_4$ were first mixed in water at room temperature for 20 min, then monomers (Am + DMDAAC) were added together with 0.1 mol L^{-1} H_2SO_4 to adjust the pH of the solution to 1–2. The graft polymerization was run at 50°C for 6 h under N_2. Seven CADs with various compositions were obtained by controlling the dosages of raw materials. The reaction product was precipitated in an excess of isopropanol, the precipitate was again slurred in acetone, and finally the precipitate was dried in a vacuum at 40°C to constant weight.

FTIR Spectra

CAD samples for FTIR analysis were purified by repeated extraction with mixed solvent (acetic acid : glycol = 60 : 40) in a Soxhlet extractor. FTIR spectra were obtained using a Nicolet model 205 spectrophotometer.

Anion and Cation Content Measurements

The anion content of the CAD was calculated according to the following equation based on the hypothesis that the DS of CMC remained unchanged during the reaction:

$$\text{anion content (mol g}^{-1}) = \frac{W_{CMC}}{M_c} \times DS/W_T$$

where W_{CMC} was the dosage of CMC, M_c was the molecular weight of the glucopyranose unit, and W_T was the weight of the reaction product.

The cation content was found from the following two equations based on the elemental analysis and the results of monomer conversion:

$$N\% = (14W_{Am}/71 + 14W_{DMDAAC}/162.5)/W_T \quad (1)$$

$$W_{Am} + W_{DMDAAC} + W_{CMC} = W_T \quad (2)$$

where N% was the nitrogen content in the CAD determined by elemental analysis (Perkin Co., model 240C); 71 and 162.5 were the molecular weights of Am and DMDAAC, respectively; W_{Am} was the conversion weight of Am; and W_{DMDAAC} was the conversion weight of DMDAAC in the reaction. Thus, W_{DMDAAC} could be obtained by solving eqs. (1) and (2) and

$$\text{cation content (mol g}^{-1}) = \frac{W_{DMDAAC}}{162.5}/W_T$$

CAD Inhibiting Clay-Swelling Studies

Forty grams of clay, which had already been dried at 120°C for 7 h, was pressed into a piece under 5-MPa pressure for 5 min and then fixed in a WZ-2 swelling apparatus (Nanjing Soil Apparatus Factory). The height readings were recorded before and after 100 mL of water or polymer aqueous solution was added. The swelling efficiency, V_f (%), was calculated by the following equation:

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

where H_0 was the height of the dry sample and ΔH_t was the increase of height due to clay swelling.

The morphologies of the clay and CAD/clay complex were observed by SEM (Hitachi model S-520), and the adsorption of CAD on clay was studied by wide angle X-ray diffraction (Rigaku model D/max-IIIA).

Mud-Making Studies

The low-solid mud was made up by stirring the clay mixture (clay : Na_2CO_3 : H_2O = 30 : 3 : 1000) at high speed for 20 min, then aging for 24 h at room temperature. Then 300 g of low-solid mud was mixed with the required quantity of polymer by stirring it at high speed for 10 min; the rheological behavior of the mixture was measured immediately with the rheometer (Qingdao Photometer Factory model ZNN-3). The parameters used to characterize the mud-making properties were apparent viscosity (η_a), plastic viscosity (η_P), and yield point (τ_0), which was obtained by the following equations:

$$\eta_a(\text{mPa s}) = \phi_{600}/2$$
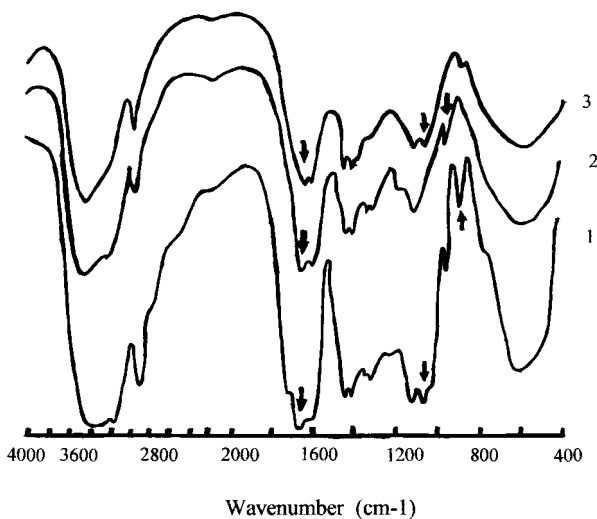
$$\eta_P(\text{mPa s}) = \phi_{600} - \phi_{300}$$

Figure 1 IR spectra: (1) CAD, (2) A-D, and (3) CAm.

$$\tau_0(\mathrm{Pa}) = 0.511(\phi_{300} - \eta_P)$$

where ϕ_{600} was the rheometer reading at the stirring speed of 600 rpm and ϕ_{300} was at 300 rpm.

RESULTS AND DISCUSSION

Identification of CAD

Figure 1 shows the IR spectra for CAD, Am-DMDAAC copolymer (A-D), and CMC-g-PAm (CAm). In contrast to the CAm spectrum, an obvious peak appears at circa 950 cm^{-1} in the CAD and A-D spectra due to $\gamma_{\mathrm{CH_2}}$ of —N$^+$—CH$_2$—, indicating the presence of DMDAAC units in the CAD chains. Both CAD and CAm spectra have peaks at circa 1060 cm^{-1} that is characteristic of the absorption of cyclic ether —C—O—C— in the glu-

copyranose units. In addition, all three spectra have peaks at circa 1680 cm^{-1} due to >C=O in the amide groups. These IR results imply that CAD contains CMC, Am, and DMDAAC units.

The grafting of DMDAAC to CMC in CAD can be further proved by the following experiments: when NaB(C$_6$H$_5$)$_4$ is mixed with the CAD solution, flocculates appear immediately due to the reaction of NaB(C$_6$H$_5$)$_4$ with the quaternary ammonium groups in the CAD[8]; some CAD aqueous solutions appear milky as a result of the association between cationic quaternary ammonium groups and anionic carboxymethyl groups that decrease the solubility of CAD in water, and the milky solution rapidly becomes transparent by adding NaCl to it. This is obviously due to the reduction of the cation–anion association in CAD molecules because cation and anion charges along the CAD chains can be shielded by the added salt ions.[9]

Solubility Property of CAD

Most CAD products are water soluble, and even in some milky CAD solutions no obvious precipitate appears (see Table I). It is very probable that the aqueous dispersion property of CAD derives from its characteristic molecular structure. Because Am is more reactive than DMDAAC and the dosage ratio of Am to DMDAAC in the reaction is 7 : 1, Am should first graft directly to CMC, and Am units become the main components in the grafting chain. Then the cationic quaternary ammonium groups and anionic carboxymethyl groups are separated by long (Am)$_n$ chains. The CAD molecular structure is shown simply by the following structure:

Table I Effects of CAD Structures on Inhibitive Properties

Sample	Anion Content (mol g^{-1})	Cation Content (mol g^{-1})	$[\eta]$ (dL g^{-1})	Solubility	V_f (%)
Water	—	—	—	—	70.00
CAD-1	5.82×10^{-4}	4.96×10^{-4}	1.94	Transparent	58.20
CAD-2	4.43×10^{-4}	9.37×10^{-4}	1.94	Transparent	52.20
CAD-3	4.90×10^{-4}	1.13×10^{-3}	1.94	Transparent	51.70
CAD-4	4.90×10^{-4}	1.02×10^{-3}	2.25	Milky	57.20
CAD-5	4.45×10^{-4}	8.25×10^{-4}	1.82	Transparent	58.70
CAD-6	8.09×10^{-4}	9.36×10^{-4}	1.51	Transparent	60.10
CAD-7	1.03×10^{-3}	1.65×10^{-3}	2.02	Milky	56.70

CAD concentration, 0.2%; pH 8.00; retention time, 12 h.
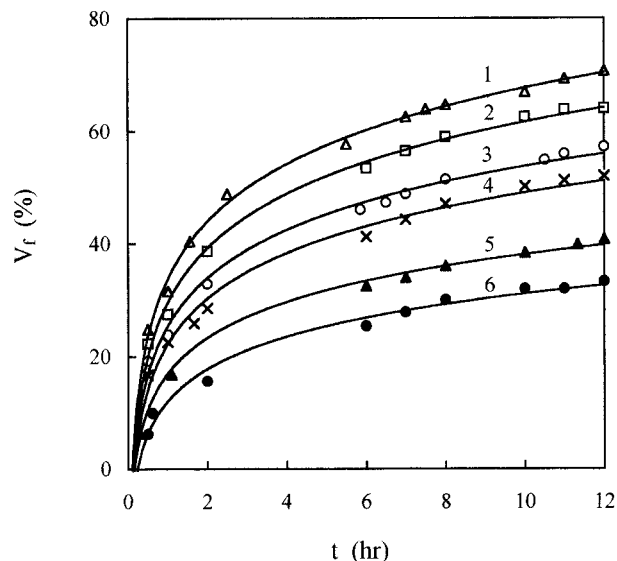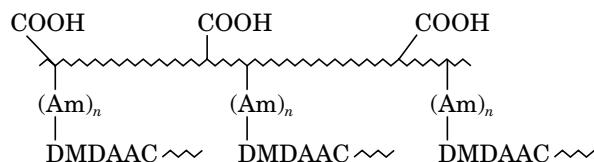
Figure 2 V_f for clay in water and different polymer solutions, pH 8.00: (1) H_2O, (2) 0.2% CAm, (3) 0.2% A-D, (4) 0.2% CAD-3, (5) 0.2% FA-367, and (6) 1.0% CAD-3.

There is be a thick hydration layer around the $(Am)_n$ due to its strong hydration ability, and it confines the intramolecular and intermolecular associations between the cationic and anionic groups to a limited extent. Then the hydration of free cationic and anionic groups, in addition to that of $(Am)_n$, results in the good solubility of CAD in water.

Performances of CAD Inhibiting Clay Swelling

Figure 2 shows the clay-swelling efficiency (V_f) in water and in aqueous solutions containing different polymers: CAm, A-D, and CAD-3. The structural parameters of CAD-3 are listed in Table I. CAm, A-D, and CAD-3 are the products synthesized at the same conditions. Their V_f values for 12 h are 63.5, 56.4, and 51.7%, respectively (curves 2–4 in Fig. 2), which are all less than V_f in water (70%) and show their inhibiting clay-swelling ability. Of these three polymers, the inhibiting ability order is CAD-3 (with cationic and anionic groups) > A-D (with cationic groups) > CAm (with anionic groups), indicating that the syner-

gistic effect of cationic and anionic groups exists in the inhibiting performances. CAD-3 is adsorbed on the clay through the interaction of its cationic groups and the negative charges on the clay surface, forming protective films around the clay particles. In the meanwhile, the anionic groups in CAD-3 are hydrated to form hydrated layers around the clay particles, which also prevents the free water from penetrating into the clay. CAD-3 has a more effective inhibiting clay-swelling function than A-D and CAm. FA-367, which is prepared by vinyl monomer copolymerization, is a commercial ampholytic hydration inhibitor applied successfully in drilling fluid. Its V_f at 0.2% for 12 h is 40% (curve 5 in Fig. 2), which is better than CAD-3 at 0.2% but worse than CAD-3 at 1% (curve 6 in Fig. 2). Because FA-367 was much more expensive than CAD-3, it is expected that CAD-3 would become a favorable new clay-hydration inhibitor in oil field drilling.

Mechanism of CAD Inhibiting Clay Swelling

The mechanism by which CAD inhibits clay swelling was studied in three respects: the effect of CAD structures on inhibitive clay swelling, SEM observation, and wide angle X-ray diffraction investigation. The results are now presented.

Effect of CAD Structure

The structural parameters and V_f for different CADs are listed in Table I. The V_f decreases with increasing cation content for CAD-1, CAD-2, and CAD-3. It is thus obvious that the high cation content does favor the inhibitive property. This may be attributed to two causes: the cation can neutralize the negative charges on the clay surface, resulting in lowering hydration of clay; and the cation can reinforce the adsorption of polymer and form a film around the clay, resulting in hindering water from diffusing into the clay.

The [η]s for CAD-5 and CAD-6 are lower than other CADs, corresponding to their higher hydration values of V_f. And CAD-5, with an [η] higher than CAD-6, has a V_f lower than CAD-6. All these facts reveal that the molecular weight of the polymer inhibitor also plays an important role in improving the inhibitive performances.

The [η]s for CAD-4 and CAD-7 are higher than CAD-3, but their inhibitive performances are inferior to CAD-3; CAD-3 has a lower V_f. This is caused by the presence of the cation–anion association in the milky solutions of CAD-4 and
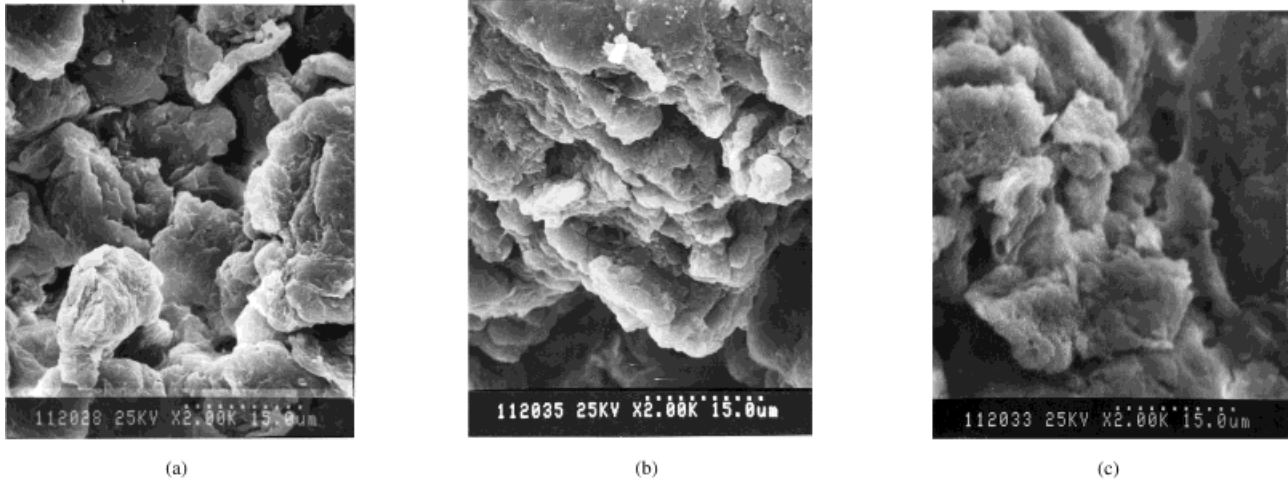
Figure 3 SEM photographs for clay treated by different solutions for 12 h: (a) water, (b) 0.2% CAD-3 aqueous solution, and (c) 1.0% CAD aqueous solution.

CAD-7, which results in the decrease of free anion and cation along the polymer chain that is very unfavorable for the adsorption of CAD on the clay surface and also unfavorable to forming protective films. It is obvious that the inhibiting clay-hydration performance of CAD depends not only on cation content, anion content, and molecular weight, but also on the distribution of cation and anion along the polymer that closely relates to the cation–anion association.

SEM Observation

The results of the SEM observation of the clays treated by different solutions for 12 h are presented in Figure 3. It can be seen that the clay is porous and distributes separately in water [Fig. 3(a)]. In the CAD solutions the clay particles cluster together and form a compact texture [Fig. 3(b,c)], especially in the 1% CAD solution; almost no obvious space can be found between the clay particles [Fig. 3(c)], indicating that CADs have bridged the clay particles to form a compact texture. Such a texture is very favorable to prevent free water from penetrating into the clay.[10]

Then, on the basis of the SEM observation and CAD structure studies, the mechanisms of the CAD inhibition of clay swelling can be considered as follows: the quaternary ammonium groups in CAD chains neutralize some negative charges on the clay surfaces, resulting in a decrease of the clay hydration; CAD is adsorbed firmly on the clay and forms protective films, which could be called the hydration inhibitive barrier, that can prevent water from penetrating into the clay; and CAD molecules bridge clay particles, forming a compact texture that can also impede the diffusion of water into the cluster of clay particles.

Wide Angle X-Ray Diffraction Investigation

The data of the d^{001} space of clay treated by different solutions for 12 h was measured by the wide angle X-ray diffraction method and are listed in Table II.

Table II d^{001} Space of Treated Clay

Sample	d^{001} (nm)
Clay treated by	
Fresh water	1.547
0.2% CAD-3 aqueous solution	1.530
1% CAD-3 aqueous solution	1.525

Table III Effects of CAD on Mud-Making Properties of Low-Solid Mud

Polymer Dosage	η_a (mPa s)	η_P (mPa s)	τ_0 (Pa)	pH
0	6.0	4.0	2.0	9.40
0.05% CAD-3	9.0	5.0	4.1	9.40
0.10% CAD-3	17.0	7.0	10.2	9.40
0.15% CAD-3	26.0	8.0	18.4	9.40
0.10% FA-367	11.0	7.0	4.1	9.40

Low-solid mud, 3% clay + water.

Table IV   Tolerance of Polymer Mud to NaCl

Polymer Dosage	NaCl Concn (%)	η_a (mPa s)	η_P (mPa s)	τ_0 (Pa)	pH
0	0	6.0	4.0	2.0	9.40
0.1% CAD-3	0	17.0	7.0	10.2	9.40
0.1% CAD-3	1.0	14.5	6.0	8.7	9.40
0.1% CAD-3	2.0	13.0	6.0	7.5	9.40
0.1% CAD-3	4.0	10.5	6.0	6.6	9.40
0.1% FA-367	4.0	8.0	5.0	3.1	9.40

Low-solid mud, 3% clay + water.

The d^{001} values of clay treated by water or CAD solutions are almost unchanged, revealing that CAD molecules do not enter the interlayer of the clay.[11,12] This result also relates to CAD structure. There are semirigid cellulose cycles with anionic groups and five-member quaternary ammonium cycles with two hydrophobic methyl groups in CAD chains. It is obvious that such a large molecular volume would impede the penetration of CAD into the interlayer of the clay.

Mud-Making Property of CAD Drilling Fluids

The mud-making property for a drilling mud is usually evaluated by the rheological parameters (η_a, η_P, τ_0) of mud containing a low clay content (low-solid mud). The high values of η_a, η_P, and τ_0 imply that a network structure may be present between the clay particles that makes the mud stable and viscous. The effect of CAD on the mud-making property of low-solid mud (3% clay + water) is listed in Table III. It can be seen that CAD-3 is very effective in improving the mud-making property (even better than FA-367), and its effect increases with increasing dosage. This result is consistent with the SEM photo shown in Figure 3(c). The clay particles bridged by the CAD molecules forms a compact texture that is very favorable for stabilizing the mud and raising the viscosity of the mud.

The effect of NaCl on the mud-making property of CAD-3 is shown in Table IV. The η_a, η_P, and τ_0 for CAD-3 mud decrease rather slowly when the concentration of NaCl increases from 0 to 4%, indicating that CAD-3 mud can tolerate NaCl quite well, even more so than FA-367 mud.

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