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Effects of substitution degree and molecular weight of carboxymethyl starch on its scale inhibition☆

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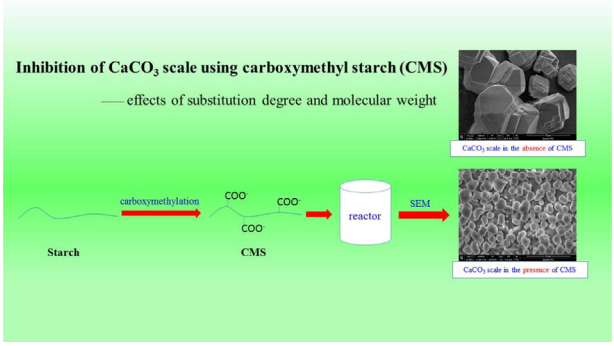
HIGHLIGHTS

- Carboxymethyl starch (CMS) as "Green" antiscalant was prepared simply.
- The effects of the structural factors of CMS on scale inhibition were evaluated.
- CMS with higher substitution degree owns higher scale-inhibition efficiency.
- Decrease of the molecular weight would evidently reduce the required CMS dose.
- CMS can disturb $CaCO_3$ crystal growth via chelating and complexing effects.

GRAPHICAL ABSTRACT



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ABSTRACT

"Green" antiscalants are gaining increased interest because of their environment-friendliness. In this work, various samples of carboxymethyl starch (CMS), with different substitution degrees of carboxymethyl groups and molecular weight were designed and prepared. The structures of these CMS samples were characterized by Fourier transform infrared spectroscopy, ^{1}H nuclear magnetic resonance, and viscosity. CMS was used as a green antiscalant for the inhibition of the growth and formation of calcium carbonate ($CaCO_3$) scale, as evaluated by a static test in laboratory scale. Apart from the environmental parameters, effects of structural factors of CMS, including the substitution degree of carboxymethyl groups and molecular weight, on its scale-inhibition performance were extensively studied. Results showed that increased substitution degree of carboxymethyl groups and decreased molecular weight of CMS samples favored the distortion of $CaCO_3$ crystal growth through chelating effects and improved the scale-inhibition efficiency. The morphology and crystal form of $CaCO_3$ scale were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively, to further investigate the scale-inhibition mechanisms of CMS.

1. Introduction

Scale deposition that mainly includes insoluble salts of calcium and magnesium, such as $CaCO_3$, $Ca_3(PO_4)_2$, $CaSO_4$, $MgCO_3$ and $Mg(OH)_2$, occurs frequently in circulating cooling water system, resulting in the reduction of heat transfer efficiency and the aggravation of corrosion of the operation equipment. Moreover, the scale in drinking water can

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do harm to human health, causing gastrointestinal diseases [1–2]. An effective approach for controlling scale formation is to add some antiscalants [3–6]. On the basis of widely accepted scale-inhibition mechanisms, which are the effects of chelation, dispersion, crystal distortion, and threshold, respectively [7,8], many inorganic phosphates and organic phosphorus compounds have been employed as efficient antiscalants for years. However, those phosphorus-containing materials can be harmful to the environment, especially eutrophication in water [9]. In addition, polyphosphate antiscalants are usually unstable and easily suffer hydrolysis, causing the phenomenon of calcium phosphate deposition [2]. Thus, the development of non-phosphorus antiscalants is of great significance in scientific research and practical applications. Many studies have been done on scale inhibition using synthetic polymers without phosphorus, such as poly(ethylene glycol), poly(acrylic acid), poly(citric acid) and poly(maleic acid), as antiscalants [10–13]. However, these polymeric antiscalants are usually non-biodegradable. Moreover, many of reported polymeric antiscalants are ter- or even tetra- copolymers, which are complicated and costly for obtaining higher scale-inhibition efficiency [9,14–16].

"Green" antiscalants, such as polyaspartic acid, polyalkylepoxysuccinic acid, and polyepoxysuccinic acid, have been receiving increasing attention owing to their non-phosphorus, low toxic, and biodegradable features [17–21]. These "green" antiscalants usually include abundant hydroxyl and carboxyl groups, which play critical roles in scale control because of their excellent chelation, dispersion, and crystal distortion effects. Furthermore, polysaccharides, a type of very important natural polymers, such as starch, cellulose, chitosan, pectin etc., possess many advantages, i.e. not only the various active groups they contain, including hydroxyl and carboxyl groups, but also their some distinct characteristics, such as environment-friendliness, widespread availability, biodegradability, and low cost. Also, due to containing abundant oxygen-containing groups, these polysaccharides can be chemically modified and introduced with various functional groups onto their backbones easily, using graft, etherification, esterification, oxidation etc., to further improve their application performance [22,23]. Some of works related to polysaccharides and their derivatives that act as antiscalants have been reported [5,16,20,24–26].

The molecular structure is known to account for the final application performance of materials [27–30]. On the basis of structural features and final application performance of materials, the relationship between structure and activity can be properly built. Accordingly, a proper material can be selected or designed by precise structural control to achieve the optimal application performance. As for polymeric antiscalants, their structural factors, such as the various types of functional groups and their substitution degrees, as well as the molecular weight, are important for their scale-inhibition properties [18,21,27–29,31]. However, until now, little work concerning the aforementioned strategy has been reported on scale inhibition, especially for polysaccharide-based antiscalants.

Starch is a kind of popular and high-performance polysaccharides, which was recognized as a potential green antiscalant [32]. After suitable modification, the scale-inhibition performance of starch-based materials could be evidently improved. Among them, carboxymethyl starch (CMS) is one of simplest starch derivatives, which contains abundant hydroxyl and carboxyl groups on the chain backbone. Thus CMS may own good scale-inhibition performance and have significant application potentials as a commercial scale inhibitor. However, little work concerning CMS used as a scale inhibitor has been reported and studied systematically until now. In this current work, a series of CMS samples with different substitution degrees of carboxymethyl groups and molecular weight was obtained. These well-prepared starch-based samples were then characterized by Fourier transform infrared spectroscopy (FTIR), ^{1}H nuclear magnetic resonance (^{1}H NMR), and viscosity. The scale-inhibition performance of CMS was evaluated by a static test against calcium carbonate ($CaCO_3$) in the synthetic water sample. The effects of structural factors of CMS on scale control efficiency were studied in detail, in addition to external parameters. To further investigate the scale-inhibition mechanism of CMS, scanning electron microscope (SEM) and X-ray diffraction (XRD) were respectively used to characterize the $CaCO_3$ crystal morphology and structure. Accordingly, the structure–activity relationship of CMS was well established and effectively exploited.

2. Experimental section

2.1. Reagents and instruments

Starch, of which weight–average molecular weight is around 1.5×10^5 g/mol, was obtained from Jinhui Corn Development Co. Ltd., Binzhou. Monochloroacetic acid (Lushuo Economic Trade Co., Ltd., Zibo), calcium chloride (Xilong Chemical Reagent Co., Ltd., Shantou), sodium bicarbonate (Lingfeng Chemical Reagent Co., Ltd., Shanghai), and sodium borate (Lingfeng Chemical Reagent Co., Ltd., Shanghai) were used without further treatment. All other chemicals that were reagent grade and directly used as received were from Chemical Reagent Co. Ltd., Nanjing.

Instruments used in this research mainly included a Bruker model IFS 66/S FTIR, a Bruker AVANCE model DRX-500 NMR spectrometer, a FEI Quanta 250 FEG SEM, and a Shimadzu model XRD-6000 X-ray diffractometer. The detected wavelength range in FTIR measurement is from 600 cm^{-1} to 4000 cm^{-1}. D_2O is the solvent in ^{1}H NMR measurement at 500 MHz. SEM was carried out under a 5-kV acceleration voltage. XRD was operated at a voltage of 40 kV and a current of 30 mA, using Cu Kα radiation ($\lambda = 0.15418$ nm).

2.2. Preparation of CMS

CMS was synthesized based on the following method. Firstly, 8.0 g of starch and 4.0 g of NaOH were added into a 100 mL of 95% ethanol solution, then they were incubated under mechanical stirring for 1.0 h in a water bath at 50 °C to make the starch swelled and alkalized. A certain amount of monochloroacetic acid was dropwise added into the reaction phase. After a 4-h reaction at 50 °C, the mixture was adjusted to neutral pH with hydrochloric acid aqueous solution, and then deposited in 95% ethanol. The obtained product was purified by filtration and rinse to remove extra salt and unwanted byproducts, then vacuum-dried in an oven at 60 °C for 48 h. Finally, the target product, CMS, was successfully synthesized and stored at room temperature [33]. By adjusting the molar feeding ratio of monochloroacetic acid to starch according to Table 1, six CMS samples with different substitution degrees of carboxymethyl groups were obtained, which were named accordingly as CMS(1) to CMS(6).

2.3. Ultrasonic degradation of CMS samples

Ultrasonic irradiation treatment of CMS(3) and CMS(5) was conducted using a JY 99-IID ultrasonic reactor (200 W, Ningbo Xinzhi Biotechnology Co., Ltd.) to obtain two series of CMS samples with the

Table 1
Summary of the preparation conditions, structural parameters, and the scale-inhibition efficiency of various CMS samples with different substitution degrees of carboxymethyl groups.

Samples	Molar feeding ratio of choroacetic acid to starch	Substitution degree of carboxymethyl groups	[η] (L/g)	Scale-inhibition efficiency[a] (%)
CMS(1)	0.1:1	0.10	0.0277	13.03
CMS(2)	0.2:1	0.20	0.1046	17.39
CMS(3)	0.5:1	0.48	0.1446	35.71
CMS(4)	0.9:1	0.63	0.2679	44.05
CMS(5)	1:1	0.74	0.3812	72.81
CMS(6)	2:1	0.95	0.4655	89.80

[a] Scale-inhibition efficiency of various CMS samples at dose of 60 mg/L.