

# Synthesis of fluorescent-tagged scale inhibitor and evaluation of its calcium carbonate precipitation performance



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## HIGHLIGHTS

- Preparation of water soluble copolymer scale inhibitor
- Characterizations of FT-IR and <sup>1</sup>H NMR methods
- The inhibition efficiency to calcium carbonate scale
- Could be used in the system of the high hardness water and accurate to determine concentration
- Scale inhibition mechanism

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## ABSTRACT

A novel fluorescent-tagged scale inhibitor, maleic anhydride–oxalic acid–allylpolyethoxy carboxylate–8-hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt (pyranine) (MA–APEM–APTA) was synthesized by maleic anhydride (MA), oxalic acid–allylpolyethoxy carboxylate (APEM) and 8-hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt (APTA). Structures of APTA, APEM, and MA–APEM–APTA were carried out by FT-IR and <sup>1</sup>H NMR. The observation shows that the dosage of MA–APEM–APTA plays an important role on CaCO<sub>3</sub> inhibition. It can be concluded that the order of preventing the precipitation from flask tests was MA–APEM > MA–APEM–APTA > T-225 > PESA > PAA ≈ HPMA. Relationship between MA–APEM–APTA's fluorescent intensity and its dosage was studied. Correlation coefficient R<sup>2</sup> of MA–APEM–APTA's is 0.9973. The effect on formation of CaCO<sub>3</sub> was investigated with combination of scanning electronic microscopy (SEM), transmission electron microscope (TEM), X-ray powder diffraction (XRD) and FT-IR analysis. MA–APEM–APTA can be used to accurately measure copolymer consumption on line besides providing excellent CaCO<sub>3</sub>.

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## 1. Introduction

In recent years, a common problem in circulating cooling water system is scale deposition. The commonly occurring scales are calcium carbonate, calcium sulfate, magnesium hydroxide, barium sulfate, calcium phosphate, calcium oxalate, etc., among which calcium carbonate is considered the most frequent. Scale can consist of one or more mineral combination [1–3]. When scale problems occur on the surface of the facilities, it could cause a total or partial obstruction of pipes and decrease the heat transfer, and even make the boiler burst [4–7]. The most common and effective method of scale controlling is the use of chemical additives as scale inhibitors that retard or prevent scale formation even in very small concentrations [8,9]. There are many classes of chemicals

used as scale inhibitors to prevent scale formation. These are water-soluble molecules or polymers with several functional groups, the most common groups being phosphonate, carboxylate and sulfonate.

Although the phosphonate and sulfonate containing scale inhibitor are highly efficient as a scale inhibitor, their use is being restricted due to environmental legislation, which restricts their application in cooling water system. In addition, phosphonates, when reverted to orthophosphates, are potential nutrients for algae [10]. As a result, the current trend for inhibitors' use is towards more environmental-friendly “green” chemicals that are undoubtedly the trend of development [11,12]. Recently, Kessler reported a novel nonphosphorus scale inhibitor. It is acrylic acid (AA)–ammonium allylpolyethoxy sulfate (APES) copolymer [13–15]. However, it is quite difficult to test for AA–APES by the traditional way because there is no phosphate active component in it. Improper feed rate of treating agent leads to serious problems. Another defect of AA–APES is that it still contains nitrogen nutrition.

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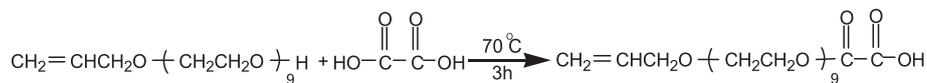


Fig. 1. Preparation of APEM.

For the concentration determination several analytical methods such as turbidimetric, potentiometric, fluorescent tracer and spectrometric methods are available [16]. Fluorescence methods provide direct measurement and control of a wide array of treatment actives [17–19]. Presently, there are two methods to prepare fluorescent polymers. One is the copolymerization of a monomer containing a fluorescent chromophore and other monomers, the other is chemical modification of polymers by fluorescent groups [20,21]. There exist some reports about the fluorescent scale inhibitor, generally focusing on polyacrylate and poly(maleic acid) [22,23]. Moriarty performed 8-allyloxy-1,3,6-pyrene trisulfonic acid trisodium salt (APTA) fluorescent monomers. Hydrophilic of APTA is strong because of sulfoacid hydrophilic groups [24].

In our previous work, no phosphate and nitrogen free scale inhibitor (APECn, APELn, APEG-PG-COOH) for cooling water systems were prepared from allyloxy polyethoxy ether, NaOH, and chloroacetic acid, glycidol or succinic anhydride (SA) and allylpolyethoxy carboxylate, a double-hydrophilic block copolymer, has a high molecular weight and the (-COOH) anionic active groups are at lateral and exposed [25–28]. However, the preparation process still has two defects: (a) chloroacetic acid is toxic, and harmful to human body and environment and (b) glycidol and succinic anhydride (SA) are very expensive, and difficult to turn into a large-scale business. Thus, new types of double-hydrophilic block copolymer need to be developed.

In this contribution, a new calcium carbonate scaling inhibitor was studied. The purpose of the present study presents the results of no phosphate and nitrogen free chemicals study that was undertaken to investigate the ability of new inhibitors (Maleic anhydride-Oxalic acid-Allylpolyethoxy carboxylate (MA-APEM)) to inhibit the scale problems found in cooling water systems. MA-APEM-APTA compensates the weaknesses of AA-APES which contain nitrogen and cannot be monitored.

## 2. Experimental

### 2.1. Materials

8-hydroxy-1,3,6-pyrene trisulfonic acid trisodium salt (pyranine) was purchased from Xuhua Chemical (Shanghai, China). Allyloxy polyethoxy ether (APEG) was purchased from Zhongshan Chemical (Nanjing, Jiangsu, China). Other reagents such as maleic anhydride, oxalic acid, potassium peroxydisulfate, allyl chloride, and ammonium persulfate are of AR grade and were obtained from Zhongdong Chemical Reagent (Nanjing, Jiangsu, China). Poly(acrylic acid) (PAA, 1800 MW), hydrolyzed polymaleic acid (HPMA, 600 MW), polyepoxysuccinic acid (PESA, 1500 MW), and acrylic acid-hydroxypropylacrylate (AA-HPA or T-225, 2100 MW) were of technical grade and were supplied by Jiangsu Jianghai Chemical Co., Ltd. Distilled water was used for all the studies.



Fig. 2. Preparation of APTA.

### 2.2. Preparation of APEM, APTA and MA-APEM-APTA

The carboxylic acid functionalization of the surface hydroxyl groups was realized by reaction with oxalic acid (OA). The synthesis procedure of APEM is shown in Fig. 1. APTA was synthesized according to Moriarty [24]. Synthesis procedure of APTA from pyranine and allyl chloride is shown in Fig. 2. The synthesis procedure of MA-APEM-APTA from MA, APEM and APTA is shown in Fig. 3.

### 2.3. Measurements

The samples were analyzed using a FT-IR spectroscopy (VECTOR-22, Bruker Co., Germany) in the region of 4000–500  $\text{cm}^{-1}$ . Prior to the measurement, the samples were dried under vacuum until reaching to a constant weight. The dried samples were pressed into the powder, mixed with KBr powder, and then compressed to make a pellet for FT-IR characterization. Structures of APEG, APEM and MA-APEM-APTA were also explored by a Bruker NMR analyzer (AVANCE AV-500, Bruker, Switzerland) operating at 500 MHz.

Thermogravimetric analysis (TGA) was performed on samples at temperatures ranging from 25  $^\circ\text{C}$  to 750  $^\circ\text{C}$ . Such signals were obtained at a heating rate of 20  $^\circ\text{C}/\text{min}$  in air using a Perkin-Elmer Derivatograph instrument. X-ray diffraction (XRD) patterns of the  $\text{CaCO}_3$  crystals were recorded on a Rigaku D/max 2400 X-ray powder diffractometer with  $\text{Cu K}\alpha$  ( $\lambda = 1.5406$ ) radiation (40 kV, 120 mA).

Scanning electron microscopy (SEM) images were recorded using a field emission scanning electron microscope (S-3400 N HITECH SEM). Prior to imaging by SEM, the scale samples were sputtered with a thin layer of gold. The shape of  $\text{CaCO}_3$  scale was observed with a transmission electron microscope (TEM, JEM-2100SX, Japan). Fluorescence measurements were carried out on a luminescence spectrometry (LS-55, Perkin-Elmer, UK) with a xenon lamp as a light.

### 2.4. Precipitation of calcium carbonate experiments

All precipitation experiments were carried out in flask tests and all inhibitor dosages given below are on a dry-inhibitor basis. Tests of the inhibitors were carried out using supersaturated solutions of  $\text{CaCO}_3$  at 60  $^\circ\text{C}$ . The solutions were prepared by dissolving in distilled water reagent grade  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  (Zhongdong Chemical Reagent Co.) at equivalent concentrations of 24 milli-equivalent/L (cooling water code GB/T 16632–2008). The supersaturation level of the solutions corresponded to a Langelier Index of 2.1. Each inhibition test was carried out in a flask of 500 mL immersed in a temperature-controlled bath for 10 h. Precipitation of  $\text{CaCO}_3$  was monitored by analyzing aliquots of the filtered (0.22  $\mu\text{m}$ ) solution for  $\text{Ca}^{2+}$  ions using EDTA complexometry as specified in code GB/T

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