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The effect of ethylene oxide groups in alkyl ethoxy carboxylates on its scale inhibition performance

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HIGHLIGHTS

- We study the effects of EO number on the scale inhibition performance of AEC.
- The scale inhibition performance of AEC actually depends on EO number.
- The scale inhibition performance of AEC decreases with increasing EO number.
- The corrosion inhibition of AEC shows a critical threshold regarding concentration.
- The corrosion inhibition is actually determined by EO number of AEC.

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ABSTRACT

To study the effects of ethylene oxide (EO) number in alkyl ethoxy carboxylates (AEC) on scale inhibition, ten AEC compounds are prepared. The effect of EO number on the scale inhibition against $CaCO_3$, $CaSO_4$ and $Ca_3(PO_4)_2$ scales and effects of the operating conditions on scale inhibition against $CaCO_3$ are investigated by static test. The effect of EO number on the corrosion inhibition is measured by the weight loss of rotating hung steel slices. The influence of AEC on formation of $CaCO_3$, $CaSO_4$ and $Ca_3(PO_4)_2$ is investigated using scanning electronic microscopy (SEM). The results indicate that the scale inhibition of AEC depends actually on EO number, the scale inhibition against $CaCO_3$ and $Ca_3(PO_4)_2$ scales decreases with increasing EO number. The ability of the inhibitors to tolerate high alkalinity and high hardness reduces with increasing EO number. AEC-3, AEC-4 and AEC-5 have good performance with scale inhibition more than 80% at the pH, concentration of calcium carbonate and temperature ranges of 7.0–9.0, 250–750 mg/L and 50–80 °C, respectively. Morphologies of the scales are highly modified in the presence of AEC. The corrosion inhibition of AEC shows a significant critical threshold regarding the concentration of AEC, the corrosion inhibition increases with increasing EO number.

Contents

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1. Introduction

Scale is a common problem in water cooling system and in detergent industries, which diminishes the heat transfer and reduces the efficiency of surfactant. The commonly occurring scales are calcium carbonate, calcium sulfate, magnesium hydroxide, barium sulfate, calcium phosphate, calcium oxalate, etc., and these salts often deposit as the mixed fouling, which are combined with particulate and products of corrosion and biological accumulating [1]. Calcium carbonate is the predominant component of scales deposited from natural water, especially in cooling water systems and in detergent industries. 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 [2].

There are many classes of chemicals with water-soluble molecules or polymers with several functional groups (such as phosphonate, carboxylate, sulfonate and etc.) used as scale inhibitors to prevent scale formation [3,4]. Because of their strong scale inhibition performance and dispersing capability, phosphorus scale inhibitors [5], such as phosphonates and organic phosphorus containing copolymers [6,7], have been used satisfactorily in the circulating cooling water systems and in detergent industry. For example, Kjellin [6] has investigated a water soluble copolymer that consists of a poly (ethylene glycol) chain containing phosphate groups attached to a methyl terminated poly (propylene) glycol as scale inhibitor. This copolymer is found to adsorb strongly onto the metal surface and prevent crystallization by a surface competitive effect. However, phosphorus is eventually discharged with wastewater, resulting in environmental pollution and ecological imbalance in water. Therefore, high levels of phosphonates are becoming increasingly restricted.

Maleic acid, acrylic acid and acrylamide homopolymers and their copolymers are usually used as carbonate scale inhibitors [8–11]. The quality of these functional polymers is determined by the copolymer architecture, the product purity and a narrowing of the molecular weight band. For instance, Yousef et al. [12] have studied the effect of the low molecular weight maleic anhydride copolymers (YMR-polymers) on $CaSO_4$ scales in the artificial cooling water for steel (316 L) and copper (90/10, Cu–Ni alloy) pipes. The results show that the low molecular weight YMR-polymers are excellent calcium sulfate scale inhibitors in the copper and the steel pipe flow systems, and have inhibition up to 95% at 70 °C. These polymers can be safely used up to a temperature of 70 °C and up to a pH of 10.45 at a very low dosage level. Besides it also observed that the anti-scaling effect of the copolymers depends greatly on the molecular weight, and the optimum range of the molecular weight is 700–2000.

Some natural organic molecules can be used as scale inhibitors that are environmentally acceptable compared with conventional inhibitors [13–15]. For instance, Wada et al. [16] have studied the influence of five natural carboxylic acids, namely malonic acid, maleic acid, succinic acid, tartaric acid and citric acid, on $CaCO_3$ crystallization. The results show that citric acid is quite effective scaling at concentration 0.2 mg/L on a total calcium concentration of 800 mg/L. Calcium carbonate growth is inhibited by the adsorption of the carboxylic acids onto the $CaCO_3$ surface. The inhibition ability of the carboxylic acids largely depends on the number of carboxyl groups in the molecule.

PASP, CMI and PESA are three typical representatives of green inhibitor derived from petroleum [17–19]. Poly (aspartic acid) (PASP) and Poly (aspartic acid) (PESA) are developed in the early 1990s and have numerous applications, including scale and corrosion inhibition, water softening and green chemical for detergent formulations. They are representative of green scale inhibitors given their non-nitrogenous, non-phosphorus and biodegradable features. Carboxymethylinulin (CMI) is a good inhibitor of $CaCO_3$ precipitation by modifying the morphology of crystals and influencing the growth rate of calcium carbonate seed crystals.

Above-mentioned literatures addressed the scale inhibitors come from phosphorus, some natural organic acids, polymers with several functional groups and green inhibitors derived from petroleum. The degree of scale inhibition provided by a specific scale inhibitor depends on a large number of parameters: its chemical formulations, its concentration, its narrowing of the molecular weight band and chemical characteristics of scaling water [12].

Surfactants are one unique class of chemicals, with water-soluble molecules or polymers having several functional groups, are widely used in all walks of life. Household detergent industry is the largest user of the surfactant. Surfactant consumption of worldwide is about 12.5×10^6 t in 2005, wherein the household and personal care products are about 6.1×10^6 t, accounting for 48.8% [20]. In household detergents, the most commonly surfactants are non-ionic and anionic surfactants. According to different anionic groups, nonionic-anionic surfactants can be broadly divided into the following categories. (1) non-ionic phosphate type $RO(CH_2CH_2O)_nPO_4M_2$. (2) non-ionic sulfate type $RO(CH_2CH_2O)_nSO_4M$. (3) non-ionic carboxylates type $RO(CH_2CH_2O)_n CH_2COOM$. (4) non-ionic sulfonate type $RO(CH_2CH_2O)_nR'SO_3M$, wherein R is an alkyl or alkyl phenyl group, the total carbon number is 8 to l8, n is the degree of polymerization of ethylene oxide and the number is 1 to 20, M is a monovalent metal cation or an ammonium ion, R′ is generally a carbon number in the range of 1 to 6. These surfactants have excellent salt tolerance, and their salt tolerance can be enhanced with the increase of EO number [21]. For the past many years, more attentions are paid to improve their activity and enlarge their adaptability [22]. In the 1990s, one kinds of alkyl epoxy carboxylate (AEC) is developed by GE-Betz Company of U.S.A. AEC has proven to be an extremely effective scale inhibitor, especially in high pH, high alkalinity, and at high calcium levels and temperature conditions. Because of the proprietary and the patented nature of most of the chemicals, a systematic and scientific approach for their working behavior is lacking, there are a few reports that are focused on studying the effect of EO number on the scale inhibition performance of these surfactants.

Motivated by the facts mentioned above, ten alkyl ethoxy carboxylates (AEC) with different EO number are synthesized in the laboratory. The primary objective of this study is to determine the effect of EO number on the scale inhibition performance of AEC against $CaCO_3$, $CaSO_4$ and $Ca_3(PO_4)_2$ scales by conducting static test with artificial cooling water. The effect of EO number on the corrosion inhibition of AEC is also studied by the weight loss of rotating hung steel slices. The influence of AEC