

The Change of Corrosion Inhibition Behavior of Tetradecyl Phosphate Ester at Elevated Temperatures

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ABSTRACT

Having a better understanding of the effect of increased temperature on the performance of organic corrosion inhibitors (CIs) is beneficial for their usage in high temperature environments. The present work focuses on studying the effect of temperature on inhibition behaviours of an in-house synthesized CI model compound, tetradecyl phosphate ester (PE-C14), in a simulated refinery environment. Surface saturation concentrations at three temperatures (25°C, 55°C, and 80°C) are determined by exploiting corrosion rate evolution. At low temperature (25°C), a gelatinous film formed on the rotating cylinder electrode (RCE) surface that significantly affected the limiting current, although the PE-C14 layer was poorly adherent. At elevated temperatures (55°C and 80°C), a thick, adherent and readily detectable by EDS and Raman spectroscopy, PE-C14 layer formed on the RCE surface to achieve much lower corrosion rate (inhibition efficiency close to 100%) with relatable surface saturation concentrations.

Keywords: corrosion inhibition, phosphate ester, surface saturation concentration, temperature, inhibitor film

INTRODUCTION

Organic corrosion inhibitors (CIs) are widely employed in the oil and gas industry to protect carbon steel pipelines against internal corrosion. The high inhibition efficiency of organic CIs at extremely low concentration can be attributed to their amphiphilic molecular structures. This structure enables the formation of self-assembled films that act against corrosion *via* the adsorption of their hydrophilic head group on the steel substrate and the repellence of aqueous corrosive species by their hydrophobic tail. Consequently, any factors affecting the film formation of organic CIs could lead to changes in inhibition behaviors.

The use of organic CIs in high-temperature environments, *i.e.*, up to 80°C here, has particular challenges: not only uninhibited corrosion rates (CRs) are largely accelerated, but also inhibition performance could be affected dramatically. The high temperature could affect the organic CIs inhibition performance from different aspects, such as influencing the adsorption process,^{1–5} inducing chemical degradation,^{6, 7} enabling polymerization,^{8, 9} etc. Even through the performances of organic CIs at elevated temperatures have been extensively studied,^{1–9} the mechanisms behind these effects require further elucidation. Moreover, the effects of temperature on inhibition are often different from inhibitor to inhibitor. Consequently, more research work about the effect of high temperature on organic CIs will be beneficial for their optimal usage.

The research described herein focuses on studying the effect of temperature on inhibition behaviours of an in-house synthesized CI model compound, tetradecyl phosphate ester (PE-C14), in a simulated refinery environment. Surface saturation concentrations at three temperatures are identified in relation to corrosion rate over time measurements obtained by linear polarization resistance (LPR). Potentiodynamic sweeps were collected after the corrosion rate stabilized. Surface analysis techniques, including scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and Raman spectroscopy, were employed to characterize the specimen surfaces after their exposure to the experimental environment at the selected temperatures. This paper mainly focuses on describing experimental observations and raising relevant research questions, mechanistic interpretation is ongoing and will be the subject of a future publication.

EXPERIMENTAL SETUP AND METHODOLOGY

Materials and Chemicals

Steel specimens used for electrochemical measurements were machined from UNS G10180* carbon steel (C1018) with a ferritic-pearlitic microstructure. The in-house synthesized CI model compound, tetradecyl phosphate ester (PE-C14), was employed in this work. The composition of PE-C14 consists of 73.5% monoester and 26.5% diester. Their molecular structures are shown in Figure 1. Its synthesis, purification, and characterization are described elsewhere.¹⁰

* UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.



Figure 1: Molecular structures of in-house synthesized tetradecyl phosphate ester (PE-C14) (monoester and diester present as 3:1 mixture)

Apparatus and Electrochemical Techniques

The electrochemical measurements were carried out using a three-electrode glass cell (Figure 2) with a platinum grid as a counter electrode, saturated KCl Ag/AgCl reference electrode, and a C1018 rotating cylinder electrode (RCE) with an outer diameter of 12 mm and a height of 14 mm as a working electrode. All potentials reported in this paper are in reference to a saturated KCl Ag/AgCl electrode. The reference electrode was connected to the corrosion cell *via* a KCl salt bridge and a Luggin capillary.

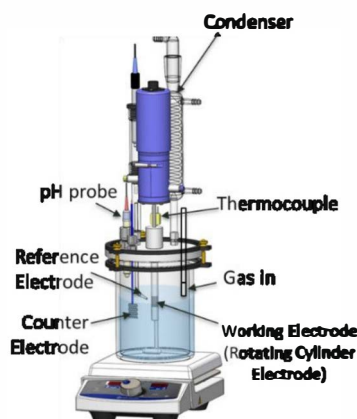


Figure 2: Schematic of the setup for electrochemical experiments[†]

Corrosion rate was assessed by linear polarization resistance (LPR) measurements, with a scan range from -5 mV to +5 mV vs. OCP, a scan rate of 0.125 mV/s and a B value of 26 mV. Cathodic potentiodynamic polarization sweeps were conducted at the end of each experiment when the corrosion rates were stable, by starting from the OCP down to -0.6 V vs. OCP at a scan rate of 0.125 mV/s. The anodic potentiodynamic sweeps were taken subsequently when the OCP returned to the original value before the cathodic sweep; they were taken from the OCP up to +0.2 V vs. OCP. The ohmic drop was compensated for in all the presented curves. All electrochemical measurements were carried out *via* a potentiostat (Gamry Interface 1010[‡]). The error bars shown on the curves throughout this paper indicate the minimum and maximum values from multiple measurements.

[†] Image courtesy of Cody Shafer, ICMT, Ohio University.

[‡] Trade name

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Test Matrix and Procedure

The corrosion experiments were performed in a simulated refinery environment containing low NaCl concentration (0.1 wt.%) with NH_4OH (ammonium hydroxide) and CH_3COOH (acetic acid) as other aqueous components. The full experimental matrix is shown in Table 1. A schematic of the experimental procedure is shown in Figure 3. Prior to each experiment, the RCE was sequentially polished with 180, 400 and 600 grit silicon carbide abrasive papers, cleaned with isopropanol in an ultrasonic bath after polishing, and air-dried before insertion into the cell. The solution was deoxygenated for 2 hours by sparging with N_2 prior to the introduction of the working electrode. Before the injection of PE-C14, there was 20 minutes of pre-corrosion, in which LPR, OCP and EIS measurements were taken to ensure that there was no contamination from previous experiments and the surface conditions of the steel specimens were consistent among all sets of tests. After the injection of CIs, LPR and EIS data were taken every 30 minutes until the corrosion rate became stable (± 0.01 mm/year). At the end of each test, potentiodynamic polarizations were conducted. The N_2 saturated solution was maintained at pH 3.8 by injecting NaOH and HCl solutions. Sparging with N_2 was maintained throughout the test to prevent air ingress and maintain the saturation of the test electrolyte with N_2 . The rotation speed of the working RCE was set at 1000 rpm before starting the electrochemical measurements. The PE-C14 inhibitor model compound was dissolved in isopropyl alcohol first and then this mixture was deoxygenated with N_2 and injected into solution directly using a long syringe needle.

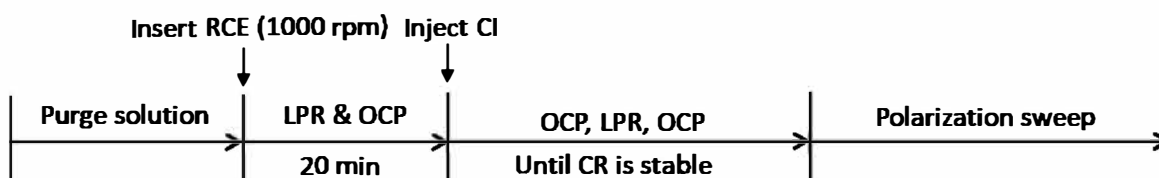


Figure 3: General experimental procedure for electrochemical experiments

Table 1. Experimental matrix for electrochemical experiments

Description	Parameters
Working solution	0.1 wt.% NaCl, 30 mg/L HCl 37%, 10 mg/L NH_4OH , 50 mg/L HAc
Material	UNS G10180
Spurge gas	N_2
Total pressure	1 bar
Temperature	25°C, 55°C and 80°C
pH	3.8 $\pm$ 0.1
CI model compound	PE-C14

Other analytical techniques were also used for post-exposure analysis. Raman spectroscopy was conducted to capture the Raman peaks of surface products using 532 nm laser with 2.5 mW and 3 s dwell time. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were also used to capture secondary electron images and elemental information. The secondary electron images were taken with an accelerating voltage of 15 kV, and spot size of 60.