

Effect of Organic Solvent on Corrosion Inhibition of Mild Steel in CO₂ Environment

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ABSTRACT

Injection of inhibitors is an economic and efficient way to combat corrosion of tubular steels utilized in the production and transmission of oil and gas. Given variability in the physicochemical environments encountered in the field, small scale laboratory testing is necessary to determine the effectiveness of inhibitors in specific corrosive environments. To achieve ppm concentrations of an inhibitor in a small-scale lab setup, the inhibitor often needs to be pre-diluted before addition to the test electrolyte, which has the potential to introduce experimental errors. One factor that affects the repeatability of corrosion inhibition testing is the volume of solvent used to dilute or dissolve the small amount of inhibitor prior to addition to the test environment. In this study electrochemical measurements, including linear polarization and potentiodynamic polarization, were utilized to evaluate the effect of different volumes (0.1 mL to 3 mL) of isopropanol used as a solvent for imidazolium, pyrimidinium, and phosphate ester inhibitor model compounds in 2 L of a brine; a commercial corrosion inhibitor was also studied for comparison purposes. The cathodic charge transfer rate was affected more when a relatively large amount of isopropanol was used to dilute the inhibitor. However, in a well-inhibited system initially without

isopropanol, the cathodic charge transfer remained unaffected by the addition of isopropanol at the conclusion of the experiments. This suggests that the usage of organic solvents for dilution of inhibitors for small volume corrosion tests should be carefully reviewed before testing.

Key words: Corrosion inhibition, solvent effects, isopropanol, inhibitor model compounds

INTRODUCTION

Corrosion inhibitors is commonly used to combat internal corrosion of mild steel pipelines in oil and gas production and transmission systems. Since the corrosive environment and flow conditions could vary in different fields, small scale laboratory testing is essential to determine the effectiveness of inhibitors in specific corrosive environments. To ensure the accuracy of inhibitor dosage in a small-scale lab setup, the inhibitor often needs to be pre-diluted before addition to the test electrolyte. This pre-dilution has the potential to lead to experimental errors. However, little information can be found about pre-dilution steps, and their influence on inhibition phenomena, in the open literature.

Heitz categorized organic solvents as nonpolar aprotic, dipolar aprotic, and protic solvents.¹ Alcohols are protic solvents containing –OH groups, and they are very weak acids. Consequently, metallic corrosion can be hypothesized to occur in such organic solvents. Most studies about metallic corrosion involving organic solvents have been done with high concentrations of solvent, where water is treated as an impurity and the acidity of water phase is usually high, involving concentrated acids.^{2–5}

Khamis and Hosny studied the effect of various solvents up to 6 vol.% on the corrosion inhibition of mild steel in an aerated H₃PO₄ solution[6]. They found the dissolution of iron was greatly affected by the addition of organic solvents. In addition, the protection efficiency, treating organic solvents as inhibitors, was influenced by the protic and stereochemistry characteristics of the organic solvents. The overall protectiveness was rated as: butanol > butane 1,4-diol > isopropanol > butane 1,3-diol > propylene glycol.

Unfortunately, the above studies were conducted in highly acidic environments relative to those associated with aqueous CO₂ or H₂S. Some inhibitor studies in the oil and gas industry do not use such aggressive environments. In laboratory testing, alcohols are typically used to dilute inhibitors in small scale experiments. Recent experimental results have shown that one factor that affects the repeatability of corrosion inhibition testing is the volume of organic solvent used to dilute the liquid inhibitor or dissolve the solid inhibitor (lab-synthesized generic compound) prior to the addition into the test environment. Therefore, it is of interest to investigate the effect of such organic solvents on corrosion inhibition of mild steel.

A previous study pointed out the peculiar behavior of one inhibitor, tetradecyltetrahydropyrimidinium (THP-C14), which showed an unexpected double wave in the cathodic polarization curve, suggesting a change in the charge transfer kinetics or the occurrence of an additional cathodic reaction. The work was performed on carbon steel in a CO₂ saturated environment at 25°C, and isopropanol was used to solubilize the inhibitor.⁷ This was not the focus of that study but was a noteworthy observation. However, if the different shape of cathodic polarization curves is due to a different corrosion or inhibition mechanism, this phenomenon is certainly worth studying.

The objective of this study is to evaluate the effect of organic solvent on corrosion inhibitor laboratory testing with electrochemical assessments, including linear polarization resistance and polarization sweeps. The focus of this study is not on the general inhibition test results, *i.e.*, efficiencies of certain inhibitors, but on the possible effect of organic solvent on the inhibited corrosion mechanism.

EXPERIMENTAL PROCEDURE

Carbon steel 1018 (UNS G10180⁽¹⁾) was manufactured to a cylindrical specimen (rotating cylinder electrode, RCE, 1.4 cm in height and 1.2 cm in outer diameter) for this study. The surface was finished with #600 grit silicon carbide abrasive paper in an isopropanol flow. The specimen was cleaned in isopropanol in the ultrasonic bath and dried in air prior to each experiment.

A 2 L glass cell with an electrode rotator was used in the study. The electrolyte for the experiment was a 50 g/L NaCl aqueous solution, deoxygenated with N₂ or CO₂ for at least 2 hours prior to each experiment. During the experiment, the headspace of the glass cell was continuously purged with N₂ or CO₂ to prevent O₂ ingress. A pH probe was inserted in the glass cell to monitor any pH changes. The electrolyte pH was adjusted to 4.5 ± 0.1 with deoxygenated NaHCO₃ or HCl solutions, as necessary, throughout experiments. The experimental temperature was 30°C.

Three corrosion inhibitor model compounds, tetradecyl imidazolinium (IMID-C14), tetradecyltetrahydropyrimidinium (THP-C14), tetradecyl phosphate ester type (PE-C14), and one commercial corrosion inhibitor (CCI) were used in this study. The model compounds were synthesized and characterized in-house, as reported elsewhere.^{7,8} The chemical structure of each model compound is shown in Figure 1. Pyrimidinium and imidazolinium type inhibitor are cationic in the aqueous environment. The solid inhibitor model compounds were dissolved or diluted in 3 mL deoxygenated isopropanol before injection for each experiment. The inhibitor concentrations used in this study were all above their surface saturation concentrations. The CCI were in liquid phase and soluble in water with imidazolines and quaternary ammonium salt as the active ingredients, and 2-butoxyethanol and ethylene glycol as solvent.

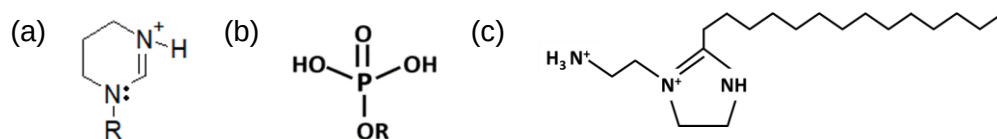


Figure 1: Chemical structure of inhibitor model compounds: (a) tetradecyltetrahydropyrimidinium (THP-C14), (b) tetradecyl phosphate ester (PE-C14), and (c) tetradecyl imidazolinium (IMID-C14). -R represents -C₁₄H₂₉.

A three-electrode electrochemical setup was used in this study. A Pt-coated mesh was used as counter electrode, a KCl saturated Ag/AgCl reference electrode was connected to the glass cell *via* a salt bridge and a Luggin capillary. The C1018 RCE was used as the working electrode. The electrochemical measurements were conducted using a potentiostat.

⁽¹⁾ 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.

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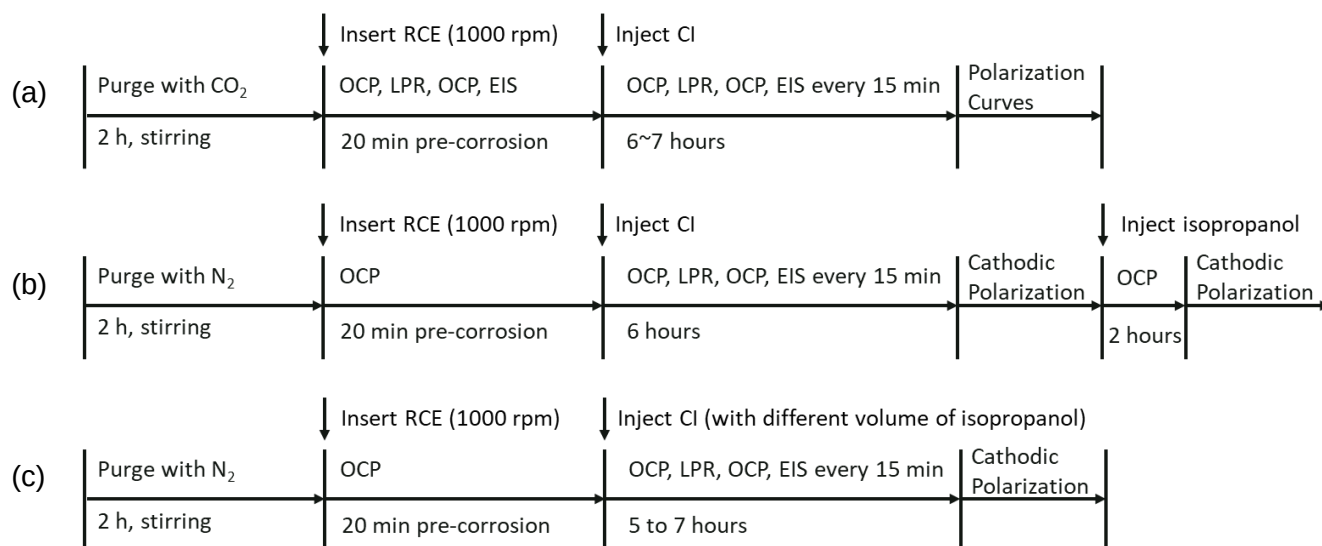


Figure 2: Experimental procedures. (a) General inhibition experiment in CO₂ environment. (b) Inhibition experiment to evaluate the effect of the injection of isopropanol at the end of experiment when corrosion rate stabilized in N₂ environment. (c) Inhibition experiment to evaluate effect of different volumes of isopropanol in N₂ environment.

Figure 2 summarizes the three experimental procedures. In general, after the insertion of the RCE specimen, the rotation speed was set at 1000 rpm. Initial measurements of open circuit potential (OCP) and linear polarization resistance (LPR) were collected using a potentiostat after the OCP stabilized. Then, the corrosion inhibitor was injected directly into the water phase after a 20-minute pre-corrosion period. Subsequently, the OCP and LPR were collected periodically for 5 to 7 hours until the LPR or R_p stabilized as exemplified in Figure 3. Since the inhibitor concentrations were all above their surface saturation concentrations and the stabilized corrosion rates were lower than 0.1 mm/year, the OCP and LPR evolution of each experiment are not presented in detail in this paper.⁷ Then, depending on the purpose of each experiment, the cathodic polarization curve or both cathodic and anodic polarizations were collected, always separately from OCP to cathodic or OCP to anodic potentials. Each experiment was repeated twice.

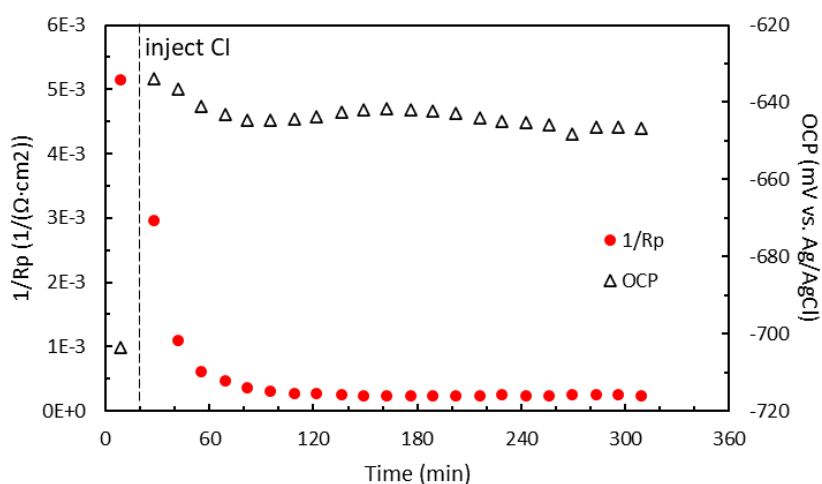


Figure 3: Polarization resistance and open circuit potential evolution of C1018 inhibited with 10 ppm IMID-C14 above surface saturation concentration in 50 g/L NaCl electrolyte saturated with CO₂ at 25 °C.