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Effect of Organic Solvent on Corrosion Inhibition of Mild Steel in CO_2 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 imidazolinium, 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 H_3PO_4 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 CO_2 or H_2S. 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 CO_2 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 N_2 or CO_2 for at least 2 hours prior to each experiment. During the experiment, the headspace of the glass cell was continuously purged with N_2 or CO_2 to prevent O_2 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 $NaHCO_3$ 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.
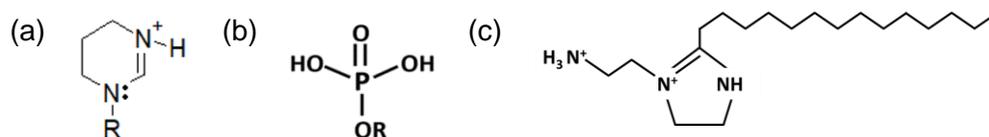

Figure 1: Chemical structure of inhibitor model compounds: (a) tetradecyl-tetrahydropyrimidinium (THP-C14), (b) tetradecyl phosphate ester (PE-C14), and (c) tetradecyl imidazolinium (IMID-C14). -R represents -$C_{14}H_{29}$.

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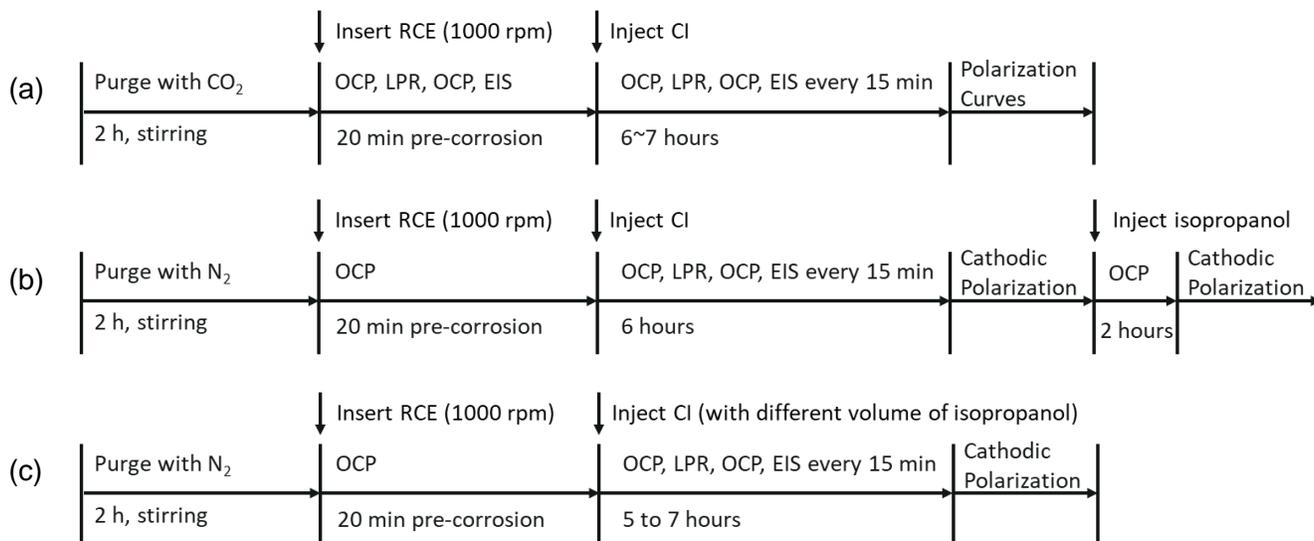
Figure 2: Experimental procedures. (a) General inhibition experiment in CO₂ environment. (b) Inhibition experiment to evaluate the effect of the injection of isopropanol at the end of experiment when corrosion rate stabilized in N₂ environment. (c) Inhibition experiment to evaluate effect of different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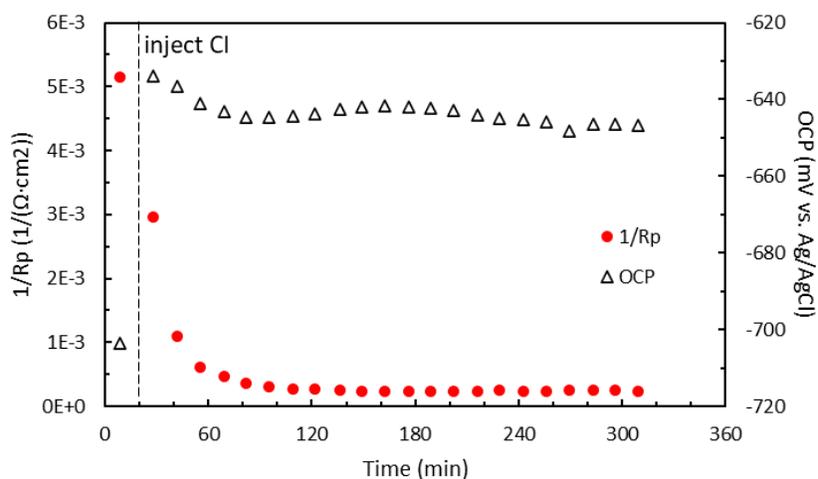

Figure 3: Polarization resistance and open circuit potential evolution of C1018 inhibited with 10 ppm IMID-C14 above surface saturation concentration in 50 g/L NaCl electrolyte saturated with CO₂ at 25 °C.

RESULTS AND DISCUSSION

Three model inhibitor compounds, THP-C14, PE-C14, and IMID-C14, were tested above the surface saturation concentration, and their inhibition efficiencies were all above 95%.[7] The polarization curves collected after these inhibition experiments are shown in Figure 4. The anodic polarization curves were similar, but the cathodic polarization curves displayed some differences. The shape of the cathodic polarization curve of PE-C14 inhibited C1018 only had one Tafel slope, while the other two cathodic polarization curves of THP-C14 and IMID-C14 inhibited C1018 showed a very peculiar behavior: there seemed to be two Tafel slopes in the charge transfer parts of the cathodic curves. However, the same behavior could also be explained by the presence of two limiting currents, one around 0.1 A/m^2, and the other one around 2 A/m^2, and it is difficult at this stage to determine which mechanism is prevalent. This phenomenon was repeatable with IMID-C14 and THP-C14 of higher concentrations where the charge transfer dominates the cathodic reaction while PE-C14 had constantly one Tafel slope. Therefore, this phenomenon was further investigated in two ways. First, the cause of the limiting current or the Tafel slope change around 0.1 A/m^2 was unclear, while the limiting current around 2 A/m^2 was clearly the limiting current due to the hydrogen evolution reaction. Second, the double wave phenomenon was not universal and was observed with two out of three model inhibitor compounds. This paper focuses on what causes the double wave in the cathodic polarization curves.
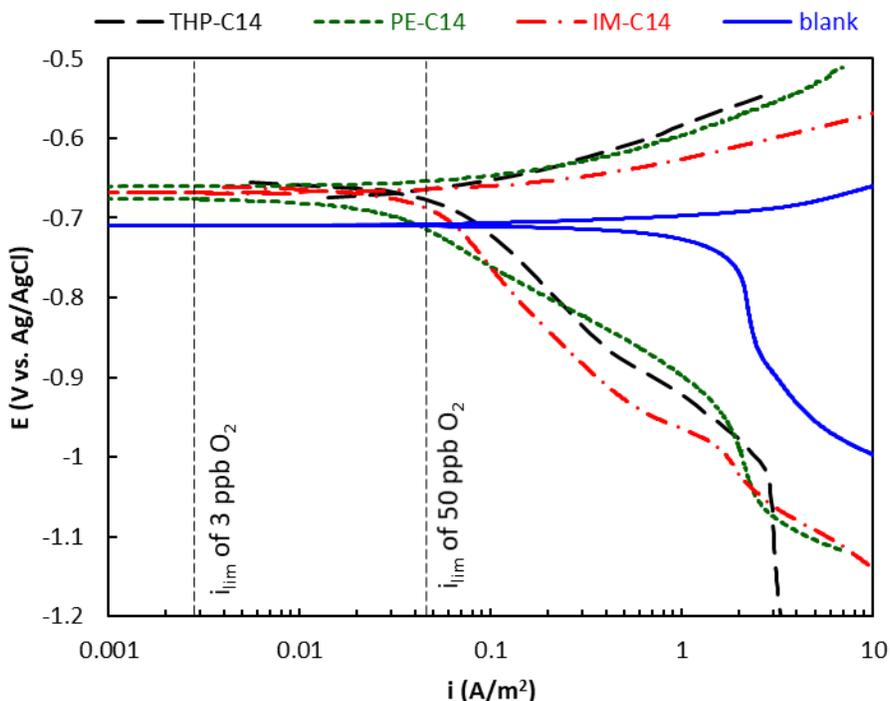

Figure 4: Polarization curves of uninhibited C1018 (blank with no inhibitor), and C1018 inhibited by THP-C14 (8 mg solid dissolved in 3 mL isopropanol), PE-C14 (100 mg solid dissolved in 3 mL isopropanol), and IMID-C14 (20 mg solid dissolved in 3 mL isopropanol) in 2 L 50 g/L electrolyte saturated with CO_2 at 25 °C. Vertical lines are the limiting current of oxygen reduction reaction.

The experimental environment was CO_2 saturated. A similar double wave shape had been reported before in certain CO_2 environments[9] and was attributed to a carbonic acid/bicarbonate buffering effect. In this scenario, the first limiting current was induced by H^+ reduction supplied by the H_2CO_3 dissociation reaction, and the second limiting current was induced by H^+ reduction supplied by the HCO_3^- dissociation reaction. However, this double wave only existed in the experiments with IMID-C14 and THP-C14, not

with PE-C14, where CO_2 saturation was consistent, and pH was the same as well. Therefore, this first hypothesis, stating that the H_2CO_3 buffering effect played a central role, could be eliminated.

Since the corrosion current densities of these inhibition experiments were low, the limiting current due to the oxygen reduction reaction might be observed if the oxygen content in the glass cell was high enough. Therefore, the second hypothesis was that the first limiting current was due to oxygen contamination. The glass cell was connected to an oxygen analyzer to monitor the oxygen content throughout the experiment. The oxygen concentration decreased to 1 to 5 ppb at the end of inhibition experiment. The highest oxygen concentration measured during the entire experiment was around 50 ppb when the working electrode was inserted into the glass cell, but the concentration quickly dropped below 10 ppb after the glass cell was sealed again. The injection step could introduce a measurement spike of roughly 30 ppb O_2 in the aqueous phase; however, the O_2 concentration decreased to the same level as before injection if the CO_2 or N_2 gas cap was maintained. The limiting current of the oxygen reduction reaction (ORR) was calculated using the Eisenberg equation.[10-12] The O_2 reduction limiting current was determined to be around 3×10^{-3} A/m^2 assuming 3 ppb oxygen, which was significantly smaller than 0.1 A/m^2. Therefore, the double wave was deemed not related to oxygen contamination in the system. However, if the experimental setup has more than 50 ppb oxygen present in aqueous phase, the impact of ORR will become significant around open circuit potential.

The third possibility was that the presence of isopropanol affected the limiting current or Tafel slope for certain pronated inhibitors, for example imidazolinium and pyrimidinium. However, dissolving solid inhibitor model compounds in water without organic solvent was challenging, and the phenomenon was only seen with certain model inhibitor compounds. A commercial corrosion inhibitor (CCI), rich in imidazolines as an active ingredient, was used to elucidate this aspect – this CCI was already soluble in water and contained only a small amount of organic solvent. It was proposed to inject the CCI, as is, or using 3 mL of isopropanol and to compare the results.

Figure 5 and Figure 6 present the electrochemical results of the two inhibition experiments with CCI in CO_2 environment. All experimental conditions of these two experiments, including the electrolytes and CCI concentrations, were the same, except that CCI was diluted with 3 mL isopropanol in one experiment, and in the other experiment CCI was injected without any dilution. The polarization resistance (R_p) and open circuit potential (OCP) for the experiment with CCI diluted with isopropanol changed more swiftly during the first hour after CCI injection than the one without dilution. However, the stabilized Rp values were similar for both experiments, while the OCP had a deviation of 40 mV. The OCP difference indicated a possible change in anodic and/or cathodic behavior.
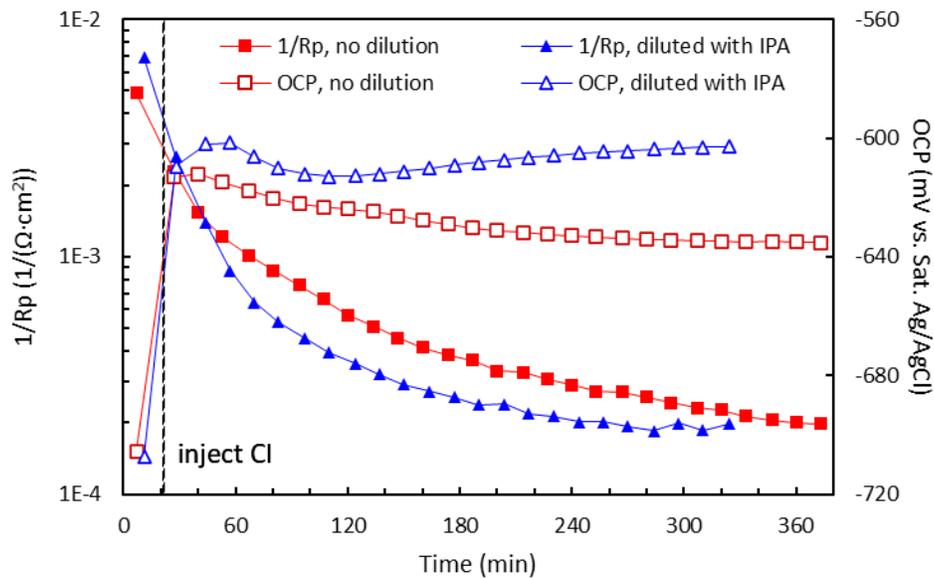
Figure 5: Polarization resistance and open circuit potential evolution of C1018 inhibited with 30 ppm CCI in 50 g/L NaCl electrolyte saturated with CO_2 at 30°C. IPA is short for isopropanol.

The polarization curves in Figure 6 also show some differences. The anodic kinetics on the specimen inhibited with isopropanol diluted CCI was retarded compared to the anodic kinetics on the specimen inhibited with CCI without dilution. On the contrary, the cathodic kinetics on the specimen inhibited with isopropanol diluted CCI was accelerated compared with the one without any dilution. These two changes led to the stabilized OCP deviation, yet similar stabilized R_p were observed in Figure 5. In addition, there was only one limiting current observed with the cathodic curve under no dilution condition, but there seemed to be an additional limiting current or a changed Tafel slope around 10^{-5} A/cm² on the cathodic polarization curve with isopropanol dilution.
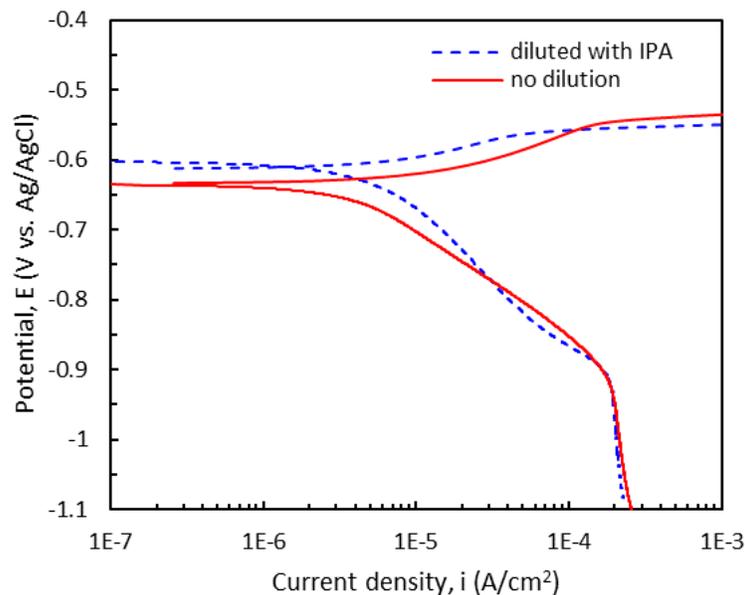

Figure 6: Potentiodynamic sweeps of C1018 inhibited with 30 ppm CCI in 50 g/L NaCl electrolyte saturated with CO_2 at 30 °C, collected after the inhibition test shown in Figure 5. IPA is short for isopropanol.

Clearly, 3 mL isopropanol used to dilute CCI played a role in the anodic and cathodic kinetics of C1018 in the presence of CCI. In addition, this CCI could be used to evaluate the effect of organic solvent in this study, since the difference of CCI between in the presence or absence of isopropanol was obvious. Therefore, an experiment with CCI in a less corrosive N_2 environment, where the cathodic kinetics was simpler and would not be affected by the buffering effect of carbonic acid and bicarbonate ions, was carried out to see if isopropanol alone could cause the acceleration of cathodic kinetics.
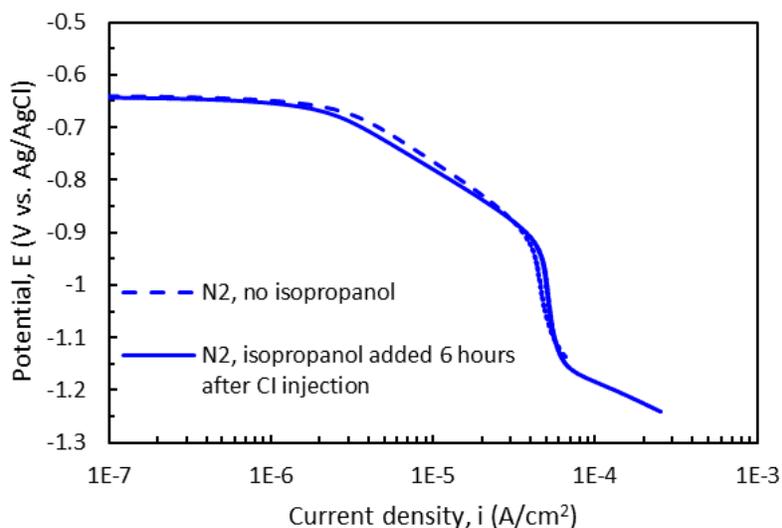

Figure 7: Cathodic polarization curves of C1018 inhibited by 30ppm CCI in 50 g/L NaCl electrolyte deoxygenated with N_2 at 30°C. The polarization curves were obtained sequentially in the same experiment as described in Figure 2b. Dashed line was collected first after addition of 30 ppm CCI, and solid line was collected after 3 mL uninhibited isopropanol was added.

Though the hypothesis of the buffering effect of H_2CO_3 and HCO_3^- has been eliminated, the cathodic polarizations of Figure 7 were collected in a N_2 environment, as described in Figure 2b. CCI without dilution was injected into the water phase directly after 20 minutes pre-corrosion. After 6 hours over which the corrosion rate had stabilized, a cathodic polarization curve was collected. Then, an additional 3 mL isopropanol without inhibitor was injected into the water phase. After the electrolyte was homogenized, another cathodic polarization curve was collected. The cathodic polarization sweep collected without isopropanol almost overlaps with the one collected after the addition of isopropanol. Therefore, isopropanol alone did not cause the double wave phenomenon, at least if the isopropanol is added after CI adsorption and desorption has reached equilibrium.

Since the injection of CCI diluted in 3 mL of isopropanol seemed to affect the cathodic sweep (as compared to without isopropanol), another series of experiments was conducted in the same conditions but with different volume of isopropanol. The expected result was that the observed deviation in the cathodic sweep behavior would be stronger as the amount of isopropanol used to dilute the same dosage of CCI would increase. The experimental procedure is described in Figure 2c. 0 to 3 mL isopropanol was used to dilute the CCI prior to the injection into glass cell. The results, shown in Figure 8, indicate that the cathodic kinetics was accelerated as more isopropanol was used to dilute the CCI. In addition, the cathodic reaction at OCP shifted from activation control to mixed or concentration control, which indicated possibly less inhibition of the cathodic reactions, with more isopropanol used. The tolerance for oxygen contamination is less in N_2 environment, but at least 20 ppb dissolved oxygen (limiting current of 2×10^{-6} A/cm^2 in Figure 8) is needed in the electrolyte to see the onset of ORR. After continuous purging with N_2 throughout the inhibition experiment, the oxygen concentration should be readily decreased to less than 5 ppb.
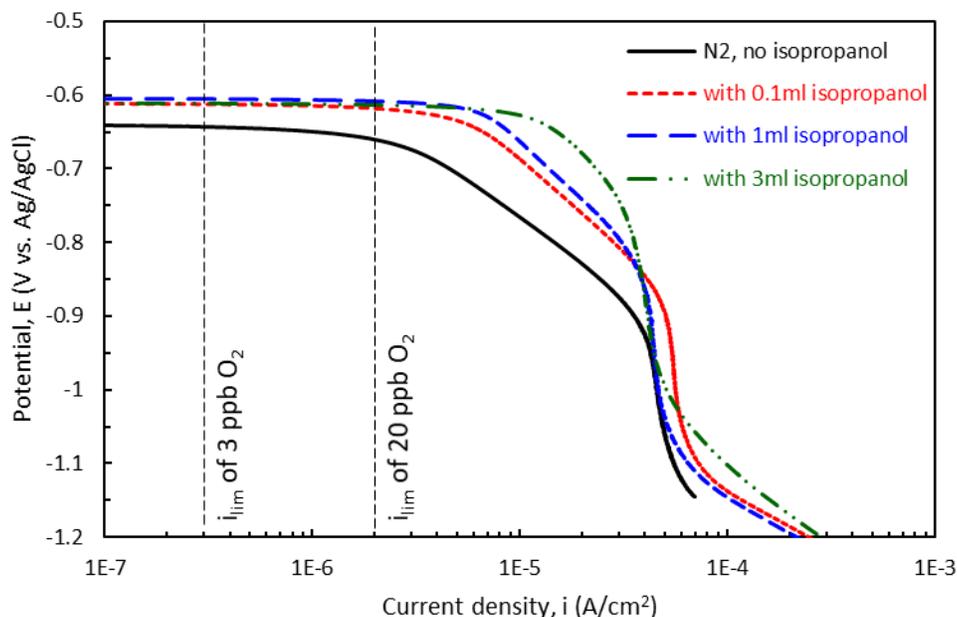
Figure 8: Cathodic polarization curves of C1018 inhibited with 30 ppm CCI in 50 g/L NaCl electrolyte deoxygenated with N_2 at 30 °C. The CCI were diluted with different volume of isopropanol as indicated in the graph.

This agrees with the accelerated cathodic kinetics around OCP observed with CCI inhibition experiments done in CO_2 environment (Figure 6). It can be speculated that the adsorption of inhibitors was affected by the isopropanol. Moreover, such change in kinetics was only observed with certain inhibitor compounds as exemplified in Figure 4. When inhibitor molecules are dissolved in isopropanol, they form hydrogen bonding with isopropanol. The affected compounds were all protonated, and it could be hypothesized that their bonding with isopropanol prior to exposure to water could be stronger than for unprotonated molecules. The nature of this stronger bond is not identified with certainty at this stage of the study. When they were exposed to water, at least some isopropanol molecules may still be attached to the inhibitor molecules and thus adsorb as-is on the specimen surface, resulting in a different cathodic behavior.

Nevertheless, the stabilized R_p measured in the inhibition experiment without isopropanol was one order of magnitude lower than what was measured with 3 mL isopropanol. According to cathodic polarizations in the N_2 environment shown in Figure 8, it can be suggested that the corrosion current density differed more in the N_2 environment than what was observed in the CO_2 environment (Figure 5 and Figure 6). The reasons governing such differences remain unclear and are the subject of ongoing investigation, separate anodic sweeps may be conducted to clarify the observed phenomena. It can be speculated that the surface pH of mild steel in CO_2 environment could be lower than it in N_2 environment, since the H^+ in CO_2 environment could also be supplied by bicarbonate ions and carbonic acid, which do not exist in N_2 environment. The potential higher surface pH in N_2 might lead to pronounced loss of inhibition by cationic inhibitor on mild steel surface.

On the other hand, in spite of the above findings about the role of organic solvent in the corrosion inhibition, the experiments in this study were conducted at room temperature, where isopropanol was present in liquid phase. If the inhibition experiment is conducted at high temperature above the boiling point of isopropanol (82.5 °C), isopropanol will likely evaporate and stay in vapor phase, and the impact of organic solvent may be minimized. Therefore, for lower temperature experiments, methanol might be a good alternative, since its boiling point is 64.7 °C.

Additionally, the influence of O_2 should not be neglected. The limiting current due to oxygen reduction reaction could influence the corrosion rate, if significant amount of oxygen, is present in the electrolyte. The aqueous oxygen concentration should be carefully monitored to address such impact.

CONCLUSIONS

The effect of organic solvent on corrosion inhibition was demonstrated in this paper, the following conclusions can be made:

- Diluting corrosion inhibitors with organic solvent could affect the cathodic and anodic kinetics of inhibition mechanisms, and thus could affect the overall inhibition efficiency, especially in N_2 environment. In CO_2 environment, further study is needed to evaluate the impact of organic solvent on stabilized corrosion rate. Therefore, laboratory testing should include an additional experiment with organic solvent to evaluate such an effect in case the inhibitor would be used with some amount of organic solvent.

- Organic solvent alone did not cause the change in cathodic kinetics. The change only occurs when a considerable amount of organic solvent was used to dilute the inhibitor.

- Not all inhibitors are affected. Some inhibitors, including phosphate ester, did not exhibit such behavior.

- Further studies are needed to clarify the reasons behind such phenomenon.

ACKNOWLEDGEMENTS

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