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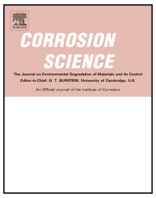

Insights into corrosion inhibition behavior of multi-active compounds for X65 pipeline steel in acidic oilfield formation water

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ABSTRACT

Inhibition behavior of new designed inhibitors for X65 steel in CO_2 saturated oilfield formation water containing acetic acid has been investigated by electrochemical measurements, surface characterization, scanning vibrating electrode technique, rotating electrochemical quartz crystal microbalance, and X-ray photoelectron spectroscopy. It is found the inhibition efficiency can exceed 95% for each inhibitor at a concentration of 3×10^{-4} mol/L. The inhibitor film exhibits a compact and uniform structure, which is more effective for the corroded rather than freshly prepared steel surface due to the facilitation of chemisorption. The active centers of inhibitor adsorption mainly focus on N, S atoms, and conjugation system.

1. Introduction

Carbon steel is high strength and high cost-effective therefore the most applicable pipeline material in petroleum industry [1]. However, carbon dioxide (CO_2), which is a naturally occurring or intentionally injecting constituent in oil and gas production, is very corrosive to carbon steel tubular, especially in some produced brines containing aggressive ions (Cl^-, SO_4^{2-}) [2,3]. It has been reported that CO_2 induced corrosion in aqueous solutions to carbon steel could cause more significant damage than hydrochloric acid at a given pH [4,5]. Moreover, the exacerbation of corrosion on carbon steel pipeline is directly related to the content of organic acids, which is commonly presented in produced brines of oilfield system [6,7]. In particular, acetic acid is the most abundant one that contributes 50–90% of organic acids [8]. It was found in the group's previous work that both cathodic and anodic corrosion reaction increase remarkably with addition of 5×10^{-4} mol/L acetic acid in oilfield formation water [9,10]. These problems have become a great concern in terms of economic losses, potential environmental impacts, and safety, due to the implementation of water-flooding systems for enhanced oil recovery.

The use of organic compounds as corrosion inhibitors, which usually contain polar functional groups such as nitrogen, sulfur and oxygen heteroatoms, remains the most economical practice for protection of carbon steel pipelines exposed to oilfield brines [11–13]. These corrosion inhibitors are believed to form self-assembled films that protect the steel surface against corrosion [14]. Typically, the amides and imidazoline derivatives are most frequently used in commercial inhibitor formulations for oil and gas industry because of their good adsorption and chemical film-formation characteristics [15–17]. However, it is found that single inhibitors are usually unable to retard the localized corrosion of steel effectively [18–20]. The synergistic inhibition agents such as thiourea and Gemini surfactant are generally used to promote the binding of inhibitor molecules to the steel surface, although some of them are inadequate to be both eco-friendly and high-efficient [21,22]. The development of new compounds with multiple active sites that can inhibit localized corrosion, and are environmental-friendly, has been a hot issue of inhibitor research. The combination of various functional groups, which have desirable adsorption ability on steel surface, to form a new multi-active compound could combine the inhibitive property of each component. The obtained inhibitors often provide superior inhibition to that found with the individual groups at the same concentration [23].

In this work, two types of newly synthesized compounds are introduced as promising corrosion inhibitors for pipeline steel, which consist of amino, imino, triazole, thiol, and olefin. Each func-

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Table 1
Chemical composition of the simulated oilfield formation water.

Salts	NaCl	$CaCl_2$	$MgCl_2$	KCl	$NaHCO_3$	$MgSO_4$
Concentration (mol/L)	1.55	0.156	0.056	0.03	0.006	0.003

tional group has been reported to be efficient corrosion inhibition center for carbon steel in acid or brine solutions [24–29]. Here, we designed the compounds by integrating these functional groups into a single molecule, which are expected to be highly potent inhibitors for CO_2 corrosion in acidic oilfield formation water system. Moreover, they have many additional advantages such as low cost, non-toxic, and easy production. A systematic investigation has been carried out in order to evaluate the inhibition performance and clarify how the inhibitor works, including electrochemical analysis and surface characterizations. To the best of our knowledge there has not been any research focused on the inhibition behavior in acidic oilfield brines related to the multi-activation of inhibitor molecule.

2. Experimental

2.1. Materials and sample preparation

The flowchart of synthesized process and the molecular structures of two inhibitors, namely CITT and CATA respectively, are demonstrated in Fig. 1. The inhibitors were characterized by ^1H NMR, IR and MS to confirm the proposed molecular structures.

Test solution was prepared to simulate formation water in oil and gas production, with the chemical composition shown in Table 1. The concentration of acetic acid added in test solution is 3×10^{-3} mol/L [30]. All solutions were made from analytical grade reagents and deionized water. The concentration of inhibitors employed is ranged from 2.7×10^{-5} to 7.7×10^{-4} mol/L. Prior to measurements, the test solution was deoxygenated by purging CO_2 (99.95%) for 4 h and maintained throughout the test to minimize possibility of air ingress. The pH value of solution without inhibitors is 3.53, which remains at 3.57 with slight changes in the measured range of inhibitor concentration. All measurements were performed at 60 °C which mimics actual conditions for oil and gas transportation in most case of oilfield [22].

2.2. Conventional electrochemical measurements

The electrochemical experiments were conducted with Solartron 1280C system. A three-electrode cell was used, with a platinum plate as counter electrode, a saturated calomel electrode (SCE) as reference electrode and carbon steel as working electrode. The working electrodes were made from a sheet of API X65 steel, with a chemical composition (wt%): C 0.04, Si 0.2, Mn 1.5, P 0.011, S 0.003, Mo 0.02 and Fe balance. The test specimens were cut into a cylinder and embedded into epoxy resin with an exposed surface area of about 1 cm^2, which were ground up to 1000 grit silicon carbide paper, rinsed with deionized water and degreased in acetone. For each test, the electrode was immersed into the solution after adding the inhibitor, if there is no special instruction.

Prior to electrochemical tests, the open circuit potential of the steel electrode was monitored as a function of time for at least 1 h to ensure that a steady state condition was attained. EIS was measured at a sinusoidal excitation potential of 10 mV in the frequency ranging from 20 kHz to 10 mHz while the steel was kept at the corrosion potential. The inhibition efficiency obtained from EIS measurement was calculated as

$$\eta_{eR}\% = \frac{R_{ct} - R^{o}_{ct}}{R_{ct}} \times 100 \qquad (1)$$

where R_{ct} and $R^0{}_{ct}$ represent the resistance of charge transfer in the presence and absence of the inhibitor, respectively. Potentiodynamic polarization curves were then measured at a potential sweep rate of 1 mV/s. The obtained inhibition efficiency was calculated as

$$\eta_{ei}\% = \frac{i^{o}{}_{corr} - i_{corr}}{i^{o}{}_{corr}} \times 100 \qquad (2)$$

where i_{corr} and $i^0{}_{corr}$ are the corrosion current density of steel with and without inhibitors in the solution, respectively.

2.3. Weight loss measurement

X65 steel specimens in triplicate were immersed in the acidic oilfield formation water with different concentration of two inhibitors (2.7×10^{-5} to 7.7×10^{-4} mol/L) for 20 days. After that, the specimens were removed from the solution, rinsed in 0.1 mol/L HCl, water and acetone, finally dried and weighted. Weight loss experiments are used to calculate the mean corrosion rate (W, μg m^{-2} h^{-1}) and inhibition efficiency obtained are evaluated by:

$$\eta_{ew}\% = \frac{W^{o} - W}{W^{o}} \times 100 \qquad (3)$$

where W^0 and W are the corrosion rate of copper in the solution without and with the inhibitor, respectively.

2.4. SVET measurement

SVET was measured by a PAR Model 370 Scanning Electrochemical Workstation, where a Pt/Ir (80%/20%) probing electrode with a 10 μm micro-tip vibrated above the X65 steel electrode surface. The probe was located 100 μm above the steel sample mounted horizontally facing upwards and vibrated in the perpendicular direction to the sample surface with the amplitude (d) of 30 μm and the frequency of 300 Hz. A video camera connected to an optical microscope was used to control the distance during operation. The potential of the microprobe was directly proportional to its position in the vibrating plane. The potential difference (E), when the microprobe was located at vibrating peak and valley, was measured by an electrometer incorporated in M370. To obtain the current, a calculation was needed from the measured potential value and the solution conductivity (k). The solution resistance (R) between the vibrating peak and valley can be determined by $R = d/k$. The current is then obtained by $I = E/R$.

2.5. REQCM measurement

This study was based on methods and patents reported by Kern et al. [31,32]. The mechanical parts of experimental devices were provided by Lanxess Energizing Chemistry in Germany and CH Electrochemical Instruments in China. A Zahner potentiostat (IM6 Germany) was used, and a platinum wire served as the counter electrode with a SCE as the reference. Preparation of rotating EQCM electrodes were described elsewhere in detail [32,33]. The 10 MHz AT cut quartz crystals with a sensitivity factor of 0.217 Hz cm^2 ng^{-1} were contained in exchangeable holders mounted on a rotating shaft [33,34]. About 1 μm thick Fe electrode was prepared by an electrodeposition process on a 190 nm thick sputter deposited Au film with an adhesion layer of 30 nm Cr at a current density of 20 mA/cm^2 in pH 3.5, 350 g/dm^3 ferrous ammonium sulfate solution [35,36]. The studied inhibitors were injected into the testing solutions to reach a final concentration of 3×10^{-4} mol/L.

The frequency change Δf is given with respect to the absolute resonant frequency of the quartz crystal and contains two contributions [37]:

$$\Delta f = \Delta f_{m,ads} + \Delta f_{\eta} \qquad (4)$$

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