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Amphiphilic amido-amine as an effective corrosion inhibitor for mild steel exposed to CO_2 saturated solution: Polarization, EIS and PM-IRRAS studies

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ABSTRACT

The corrosion behavior of mild steel in CO_2-saturated 5% NaCl solution with N-[2-[(2-aminoethyl) amino] ethyl]-9-octadecenamide corrosion inhibitor at 25 °C has been studied by using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) measurements. Both potentiodynamic polarization and EIS measurements reveal that this amido-amine precursor inhibits the carbon steel corrosion and the inhibition efficiency increases with increasing the inhibitor concentration. The corrosion inhibitor exhibits high corrosion efficiencies as a mixed-type inhibitor, with a predominant influence on the anode process. The organic inhibitor acts blocking surface sites at low concentrations and by modifying the adsorption mechanism forming a protective barrier against corrosive ions at high concentrations. EIS results show that the mechanism of its corrosion inhibition at concentrations higher than 0.82×10^{-5} M is by forming a protective bilayer with small pore sizes that hinders the passage of the reactive species. PM-IRRAS measurements demonstrate that the inhibitor is chemisorbed to surface steel. Therefore, its spectrum reveals that the inhibitor monolayer has an amorphous structure.

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1. Introduction

Corrosion has a very important economic impact in the petroleum industry. Carbon dioxide (CO_2) is a naturally occurring constituent in oil and gas production and is found in amounts varying from trace levels to as much as 50%. Besides, CO_2 could be intentionally added as part of secondary enhanced oil recovery processes. Dissolved carbon dioxide in the produced brines is very corrosive to carbon and low alloy steel tubulars employed in the process equipment in this industry. CO_2 corrosion has become of great concern mainly to the increasing production of water due to the ageing of fields as well as the implementation of water-flooding systems for enhanced oil recovery. These problems have caused the consideration of many corrosion control methods and research in various oilfields around the world. The most popular control method is the use of organic inhibitors in combination with low alloy or C–Mn steels. It is generally accepted that organic molecules inhibit corrosion via adsorption at the metal–solution interface. The mode of adsorption is dependent on the following factors: structure of the molecule, solution chemistry, characteristics of the metal surface, and electrochemical potential at the interface. Four primary modes of adsorption are associated with organic compounds at surfaces: electrostatic adsorption, π-back bonding, chemisorption, and organometallic complex formation. In the study and prevention of corrosion, an understanding of the mechanism of both corrosion and corrosion inhibition is essential.

Organic nitrogen-based compounds such as imidazolines, amides, amido-amines and amines, and their salts have been used successfully as corrosion inhibitors in oilfield systems. Nowadays, there is not a conclusive answer about the stability (hydrolysis) of imidazolines and imidazoline formulated products and the activity of the hydrolyzed products. The hydrolysis of imidazoline-based corrosion inhibitors is considered negligible under most conditions, but the presence of significant amounts of water and high temperatures can hydrolyze them to form their amide precursor. There are controversial results in literature about the performance of imidazoline and amide based products. Martin et al. [1] studied several amides and imidazolines compounds, some of them prepared in the laboratory and others obtained from commercial sources. According to these authors, the studied imidazolines, whether alone or formulated into corrosion inhibitors, are spontaneously and fairly rapidly converted into their amide precursor. Therefore, the performance of inhibitors formulated with an imidazoline or its amide precursor would be similar. They suggest that these results can be used to reduce the cost of the imidazoline-based corrosion inhibitor

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by replacing the imidazoline with its cheaper amide precursor. Butler et al. [2] reported a high-rate conversion (up to 80%) from imidazoline to amide within a period of 2–9 days under atmospheric conditions because of the low stability of the imidazoline cycle. Jovancicevic et al. [3] studied the effect of hydrolysis of imidazoline on corrosion inhibition by using the Linear Polarization Resistance (LPR) method with the Rotating Cylinder Electrode (RCE) assembly in CO_2 containing brines. They found that the hydrolysis of saturated straight chain imidazolines plays an important role in their inhibition. Thus, under those test conditions, stearic imidazoline hydrolyzes fairly rapidly to a product equivalent in performance to stearic amide.

A detailed understanding of the mechanism of adsorption for corrosion inhibitors requires the characterization of corrosion inhibitor films by using surface analytical techniques. Electrochemical Impedance Spectroscopy (EIS) has proved to be a powerful technique to study corrosion processes and inhibitor performance in different environments [4–6]. For metal substrate supported organic thin films, one of the IR techniques most widely used is the Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) method [7]. The surface sensitivity of PM-IRRAS is very high, allowing characterizing of adsorbed molecules monolayers.

Taking into account that amido-amine compounds can be effective and economic corrosion inhibitors, a clear understanding of the mechanism of action of the corrosion inhibition process is still needed for reliable field applications [8]. At present, there is no general or specific explanation reported yet for the performance of the amide precursor N-[2-[(2-aminoethyl) amino] ethyl]-9-octadecenamide as corrosion inhibitor in mild steel in CO_2 saturated media at 25 °C. Because of that, it is of interest to carry out a systematic study. In the present work, PM-IRRAS, EIS technique and some electrochemical DC methods were employed in order to go forward to clarify how this inhibitor works.

2. Experimental

2.1. Materials and medium

A mild steel SAE/AISI grade 1018 (Metal Samples) was used as working electrode. It was machined into 7 mm diameter bar, cut and mounted with epoxy resin in a disc electrode holder with an exposed area of $0.38\,cm^2$. Electrical contact between the sample and holder was obtained with silver loaded epoxy resin.

For the electrochemical tests, surfaces were polished with 600-grit SiC paper, washed with distilled water and rinsed with ethanol. Experiments were conducted at atmospheric pressure, 25 °C and under low speed magnetic stirring. Three-electrode jacketed test cells with a working volume of 0.5 l and a concentric Pt ring as counter electrode were employed. A saturated calomel electrode (SCE) was chosen as reference. Testing solution was deaerated by purging CO_2 (99.95%) for 2 h prior to the experiments. The oxygen concentration of the solution was measured with a Fibox 3-trace v6 (PreSens GmbH) instrument with an accuracy of 0.3 parts per billion (ppb), and it was kept below 40 ppb during the experiments. Test solution was 5 wt% NaCl (analytical-reagent grade) saturated with deoxygenated CO_2. A positive pressure of deoxygenated CO_2 was maintained throughout the experiments to avoid air ingress. All the electrochemical experiments were performed at atmospheric pressure. The pH was adjusted to 6 adding 10–15 ml of deoxygenated 1.0 M $NaHCO_3$.

The inhibitor used in this study was N-[2-[(2-aminoethyl) amino] ethyl]-9-octadecenamide (AAOA) whose molecular formula is shown in Fig. 1. AAOA was synthesized from oleic acid and diethylenetriamine according to Ref. [9]. The target compound was successfully synthesized as can be seen from the IR spectrum (showed as reference in Fig. 7). A stock solution was prepared by dissolving AAOA in isopropanol to 0.625 M. The inhibitor was used in a concentration range of 6.8×10^{-7} to 5.5×10^{-5} M.

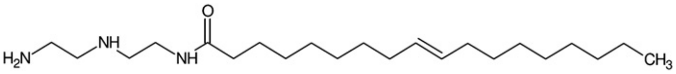

Fig. 1. N-[2-[(2-aminoethyl) amino] ethyl]-9-octadecenamide.

The inhibitor was added at the beginning of the experiments and the formation of the inhibitor film was evaluated after 2 h of immersion period. The samples were kept at open circuit potential (E_{corr}) during their exposure to the corrosive medium.

2.2. Electrochemical measurements

A Voltalab PGZ 402 unit was used for electrochemical measurements. The linear polarization method was used for the determination of the polarization resistance (Rp) by polarizing the working electrode ±0.010 V vs. E_{corr} with a sweep rate of $10^{-4}\,V\,s^{-1}$. The slope of the tangent at the origin provided the value of Rp. EIS was measured at the E_{corr} using an applied potential of ±0.01 V rms with a frequency range of 100,000–0.01 Hz. The corrosion potential was also monitored before and after DC and AC analyses.

Potentiodynamic polarization curves were drawn at the end of the experiments, with a sweep rate of $10^{-3}\,V\,s^{-1}$. The scanning range was from E_{corr} to −0.45 V (SCE) for cathodic curves and from E_{corr} to 0.45 V (SCE) for anodic ones. The electrochemical data were analyzed using the VoltaMaster 4 and Zview 2 software.

At least four replicas were tested for each experimental condition and the surface morphology of the mild steel samples after immersion in CO_2 saturated solution in the absence and presence of AAOA, was examined using an Olympus MG optical microscope.

2.3. Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS)

Chemical identification of the adsorbed AAOA layer was done *ex situ* employing PM-IRRAS. Measurements were performed using a step scan interferometer (Bruker Vertex 70) with a resolution of $4\,cm^{-1}$ and an angle of incidence of 80° relative to the substrate surface normal. For p-polarization of the IR light, an aluminum wire grid was used and modulated at 50 kHz with a ZnSe photoelastic modulator (PEM, Bruker PMA-50). Light reflected from the sample was focused with a ZnSe lens onto a cryogenic mercury cadmium telluride (MCT) detector. All presented spectra were averaged from 1024 scans. PM-IRRAS spectra were processed using the OPUS 6.5 software.

Before tests, samples were abraded using wet emery papers up to 2500 mesh. Then, they were polished with polycrystalline diamond suspension having a particle size of 1 μm. The surface was rinsed with distilled water and ethanol, and cleaned in ethyl alcohol for 10 min using an ultrasonic bath. After that, samples were immersed in the inhibited solution. Spectrum of each sample was obtained in three different conditions: (i) before immersion into the solution, (ii) dried with a stream of pure nitrogen after 2 h of inhibition, and (iii) washed with a small amount of ethanol and dried with pure nitrogen after recording the previous spectrum.

Surface analyses were undertaken immediately after the test was finished.

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