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Synergistic corrosion inhibition effect of quinoline quaternary ammonium salt and Gemini surfactant in H_2S and CO_2 saturated brine solution

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ABSTRACT

Corrosion inhibition of a quinolinium quaternary ammonium salt and a Gemini surfactant, 1,3-bis(dodecyldimethylammonium chloride)-2-propanol, for mild steel in H_2S and CO_2 saturated brine solution was investigated by using polarization test, EIS and XPS. The synergistic effect is found between these two compounds when the Gemini concentration is less than 50 mg L^{-1} in the solution containing 100 mg L^{-1} quinolinium quaternary ammonium salt, and it disappears when the Gemini concentration is larger than 50 mg L^{-1}. The synergistic mechanism is explained by competitive adsorption of these two compounds on steel surface.

1. Introduction

Typically, H_2S and CO_2 are intensively corrosive to carbon steel, and concentrations of these corrosive gases were increased in newly-discovered oil and gas fields. Their corrosivity to gathering and transportation facilities has already caused a huge economic loss in oil and gas industry [1].

In order to decrease the corrosion of H_2S and CO_2 to pipeline and other facilities, inhibitors are used as an economical and effective method. Many organic compounds with oxygen, nitrogen, sulfur heteroatoms and aromatic rings, through which these organic molecules can be adsorbed on the metal surface, are considered to be effective corrosion inhibitors [2–6]. Their inhibition efficiency can be influenced by varieties of factors, such as metallic sort [7–10], temperature of the system [11,12], testing media [13–16] and the structure of inhibitor molecule [17].

Synergistic inhibition effect, which is an improved performance of a mixture of inhibitors compared with the individual inhibitor, has been a focus of corrosion inhibition for decades. Most of the previous research has been focused on the synergism in inorganic acid solution (HCl, H_2SO_4, H_3PO_4, etc.) [18–22] and in CO_2-saturated brine solution [23,24]. However, the synergism in the solution containing H_2S and CO_2 has rarely been reported.

Since quinoline derivatives have outstanding inhibitive property in HCl and 3.5% NaCl solution [25–28] and Gemini surfactants are effective inhibitors in HCl, CO_2-containing, and H_2S and CO_2 coexistent solution [29–33], this research was designed to investigate the synergistic effect between quinoline quaternary ammonium salt (1-benzyl-quinolinium chloride, QB for short) and Gemini surfactant (1,3-bis(dodecyldimethylammonium chloride)-2-propanol, 12-3OH-12 for short) in a H_2S and CO_2 saturated brine solution via electrochemical measurements. X-ray photoelectron spectroscopy analysis (XPS) was also used to determine the adsorption behavior of inhibitors on steel surface. Their synergism was also explained with a proposed mechanism.

2. Experimental

2.1. Material preparation

Test specimens used in this work were cut from a L360 steel pipe with the following composition (wt.%): C 0.20, Si 0.45, Mn 1.60, S 0.01, P 0.02, V 0.10, Nb 0.05, Ti 0.04 and Fe balance. Specimens were machined into 10 mm × 10 mm × 3 mm sheets, embedded into epoxy resin with an exposed area of 0.5 cm^2, abraded with silicon carbide abrasive paper up to 800 grit, rinsed with distilled water and degreased with acetone, then air-dried.

The solution with 2.15 g L^{-1} of NaCl, 0.25 g L^{-1} of KCl, 11.63 g L^{-1} of $CaCl_2$, 5.32 g L^{-1} of $MgCl_2{\cdot}6H_2O$, 0.1 g L^{-1} of Na_2SO_4

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and 0.41 g L^{-1} $NaHCO_3$ was prepared to simulate the formation water of one oil field in China. Analytical grade chemicals and distilled water were used in solution preparation.

The structures of QB and 12-3OH-12 were shown in Fig. 1. QB was synthesized with quinoline and benzyl chloride. The chemical reaction was depicted in Fig. 2. Benzyl chloride was analytical pure. Quinoline and 12-3OH-12 were industrial products.

2.2. Electrochemical experiments

A three-electrode glass cell setup with the counter electrode made of platinum and a saturated calomel electrode as reference electrode was used during the electrochemical experiments. The glass cell was filled with the test solution, de-aerated with nitrogen for 1 h and then a mixture of H_2S (40 mL min^{-1}) and CO_2 (20 mL min^{-1}) was bubbled through the solution for 1 h. All components were assembled and sealed up with silicone sealant before the aeration process.

Electrochemical impedance spectroscopy (EIS) tests were conducted at the open circuit potential (OCP) with an ac amplitude of 10 mV in the frequency range from 64 kHz to 10 mHz. Before each test, the electrode was immersed in solution for 30 min to reach a stable state (the OCP fluctuation was less than ±5 mV) [24]. The Nyquist representations of the impedance data were analyzed with Z-View software. At the end of experiment, potentiodynamic polarization was conducted over a potential range from −0.2 to +0.2 V vs. open-circuit potential at a scan rate of 0.5 mV s^{-1}. Then corrosion current density and other electrochemical parameters were determined by fitting the curves in weak polarization zone using Gauss-Newton method [34,35]. All the tests were performed at 60 ± 1 °C which represented the actual conditions for oil and gas transportation in most of oil and gas fields.

The solution and working electrode were changed after each sweep. Three to four measurements were performed for each experimental condition to estimate the repeatability, with a relative standard deviation of less than 5%.

Given the potential hazards of working with H_2S, an experimental setup was designed as shown in Fig. 3.

2.3. X-ray photoelectron spectroscopy (XPS) analysis

The XPS spectra of all samples were obtained by using a PHI-5300ESCA spectrometer (Perkin–Elmer, USA) with Al Kα as excitation source. The survey scan was from 0 to 1350 eV binding energy with a step size of 1 eV. The high-resolution spectra of N 1s was acquired over 392.3–414.3 eV with a step size of 50 meV.

In the calibration, the binding energy of C 1s was set at 284.5 eV.

The XPS spectra were deconvolved with a nonlinear least squares curve-fitting program (XPSPEAK software, Version 4.1). With a Shirley type background baseline, an asymmetrical Lorentzian–Gaussian sum function fitting program was used to process the XPS data.

3. Results and discussion

3.1. Potentiodynamic polarization

Potentiodynamic polarization experiments were performed in order to investigate the synergistic effect between QB and 12-3OH-12 at 60 °C. The polarization curves of mild steel in H_2S and CO_2 saturated brine solution with different concentrations of inhibitors are shown in Fig. 4.

As shown in Fig. 4, both the anodic and cathodic reactions are inhibited, and the corrosion potential (E_{corr}) is shifted toward positive direction when either QB or 12-3OH-12 is added into the solution. Therefore, QB and 12-3OH-12 should belong to mixed-type inhibitors which preferentially restrained the anodic process of corrosion.

From the fitted corrosion current densities (i_{corr}), the inhibition efficiency (η_p) is defined as follows:

$$\eta_p = \left(1 - \frac{i_i}{i_u}\right) \times 100\%, \qquad (1)$$

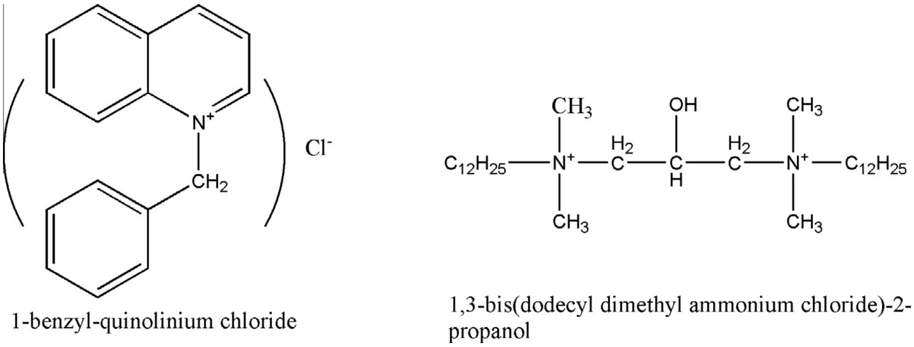

Fig. 1. Structures of QB and 12-3OH-12.

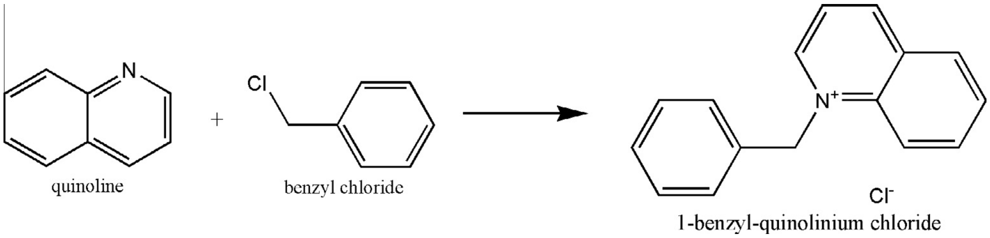

Fig. 2. Chemical reaction between quinoline and benzyl chloride.