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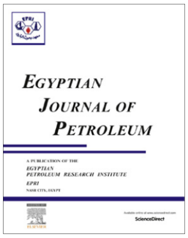

FULL LENGTH ARTICLE

Novel naphthenate surfactants based on petroleum acids and nitrogenous bases as corrosion inhibitors for C1018-type mild steel in CO_2-saturated brine

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Abstract The efficiency of two natural naphthenate surfactants (Naphthenic-dimethylamine and Naphthenic-diethylamine complexes), as corrosion inhibitors for mild steel in CO_2-saturated 1% NaCl solution, has been determined by linear polarization resistance corrosion rate and potentiodynamic polarization measurements. These compounds inhibit corrosion even at very low concentrations (25 ppm), and Naphthenic-diethylamine complex is the best inhibitor giving maximum inhibition efficiency (99.76) at 100 ppm. Polarization curves indicate that, the two investigated compounds are mixed inhibitors, affecting both cathodic and anodic corrosion currents. Adsorption of naphthenate surfactants on the mild steel surface is in good agreement with the Langmuir adsorption isotherm model, and the calculated Gibbs free energy values confirm the chemical nature of the adsorption. Energy dispersive X-ray fluorescence microscopy (EDRF) and scanning electron microscope (SEM) observations confirmed the existence of such an adsorbed film on the mild steel surface.

1. Introduction

Carbon dioxide (CO_2) corrosion of carbon steel pipelines and equipment in the oil and gas industry has been given much attention in recent years because of an increased tendency to inject CO_2 into oil wells to reduce the viscosity of oil and increase its production [1,2]. An important fact is that when CO_2 dissolves in water, carbonic acid (H_2CO_3) is produced with the characteristic that is more aggressive than hydrochloric acid at the same pH [3]. Despite the fact that carbon steel has low resistance to CO_2 environments, it is widely used in the petroleum industry mainly due to economical reasons [2]. What makes feasible the use of carbon steels is the natural precipitation of protective iron carbonate ($FeCO_3$) [4,5]. In order to reduce the corrosion of mild steel an alternative is to use inhibitor. The corrosion control by inhibitors is one of the most common, effective and economic methods to protect metals [6,7]. Corrosion inhibition of carbon steel is a result of a barrier film forming between the carbon steel and the environment.

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Surfactants are molecules composed of a polar hydrophilic group, the ‘head’, attached to a non polar hydrophobic group, the ‘tail’. In general, in aqueous solution the inhibitory action of surfactant molecules may also be due to physical (electrostatic) adsorption or chemisorption onto the metallic surface, depending on the charge of the solid surface and the free energy change of transferring a hydrocarbon chain from water to the solid surface. The adsorption of the surfactants markedly changes the corrosion resisting property of a metal, and for this reason, studies on the relation between adsorption and corrosion inhibition are of considerable importance [8–11]. The adsorption behavior of surfactants at the solid-solution interface is described by many authors [12,13]. The ability of a surfactant molecule to adsorb is generally related to its ability to aggregate to form micelles. Surfactants have been used for the corrosion inhibition of carbon steel in CO_2 environments [14–17].

The present study aimed to investigate the efficiency of some surfactants as corrosion inhibitors for mild steel in CO_2-saturated 1% NaCl solution. An attempt was also made to clarify the effects of concentration of the studied surfactants on the inhibition efficiency. The measurements of corrosion rate and percentage inhibition efficiency of different natural naphthenates surfactants toward corrosion of mild steel by linear polarization resistance corrosion rate and electrochemical polarization technique were performed in CO_2-saturated solution in the absence and presence of the investigated surfactants in the concentration range (25–100 ppm). Energy dispersive X-ray fluorescence (EDRF) was performed to verify the presence of the inhibitor on the carbon steel surface.

2. Experimental work

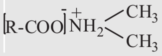
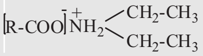
2.1. Chemical composition of mild steel alloy

The rotating disk working electrodes for tests were made of mild steel grade C1018 and have an area of 4.55 cm^2 with a chemical composition (wt%) C 0.18%, Si 0.17%, Mn 0.70%, P 0.011%, S 0.03%, Ni 0.0%, Cr 0.01% and Fe balance.

2.2. Synthesis of surfactant inhibitors

The surfactants used as inhibitors were synthesized in our laboratory based on petroleum acids and nitrogenous bases. The new series of the naphthenates surfactants were synthesized from naphthenic acids isolated from light oil fractions (Tb = 180–350 °C) [18]. Naphthenic acids were taken at molar ratio 1:1 with dimethylamine and diethylamine. The components of reactions were mixed well for a period of 30 min at 25 °C. Two complex surfactants were synthesized in high purity by the compositions as shown in Table 1. The chemical structure of the synthesized surfactants was characterized by using FT-IR, Spectrum BX spectrometer using KBr disks.

Table 1 List of the synthesized complex surfactants includes, code number, name and structure.

Code number of the inhibitor	Name and abbreviation	Structure
I	Naphthenic-dimethylamine complex (NDMC)	
II	Naphthenic-diethylamine complex (NDEC)	

2.3. Preparation of solutions

The aggressive solutions were made of AR grade 1% NaCl solutions saturated with carbon dioxide gas in 1% NaCl solution which was prepared by dissolving of analytical grade NaCl in distilled water. The concentration range of the prepared surfactants was from 25 to 100 ppm used for corrosion measurements. All inhibitors solutions were prepared using distilled water.

2.4. Corrosion measurements

The measurements were performed on the rotating cylinder electrode ($A = 4.55\ cm^2$). This electrode was used for one time. The reference electrode was Ag/AgCl electrode to which all potentials are referred.

Before beginning the experiment, the prepared 1% NaCl solution was stirred by a magnetic stirrer for 30 min in 1000 ml cell. Then this cell was thermostated at 50 °C for 1 h under a pressure of 0.9 bars. The solution was saturated with carbon dioxide. To remove any surface contamination and air formed oxide, the working electrode was kept at −1500 mV (Ag/AgCl) for 5 min in the tested solution, disconnected shaken free of adsorbed hydrogen bubbles and then cathodic and anodic polarization was recorded. ACM Gill AC instrument connected with a personal computer was used for the measurements.

The corrosion resistance of the investigated mild steel in 1% NaCl saturated with CO_2 was examined using two different techniques:

2.4.1. Potentiodynamic measurements

The potentiodynamic polarization curves were performed in a potential range ± 100 mV with respect to corrosion potential (E_{corr}) at temperature (50 °C). Three electrodes consisting of a reference electrode (Ag/AgCl), a working electrode (Mild steel) and a counter electrode (Pt electrode) at scan rate of 1 mV/s were used.

2.4.2. Linear polarization resistance corrosion rate

The linear polarization resistance (LPR) corrosion rate bubble-test method involves evaluating the corrosion of steel in simulated brine saturated with CO_2 at a temperature equivalent to that in the field. The LPR method is ideal for plant monitoring offering an almost instantaneous indication of corrosion rate, allowing for quick evaluation of remedial action and minimizing unscheduled downtime. The potential of the working electrode was varied by a CoreRunning programme (Version 5.1.3.) through an ACM instrument Gill AC. The CoreRunning programme converts a corrosion current in mA/cm^2 to a corrosion rate in mm/year. A cylindrical carbon steel rod of the composition 080A15 GRADE STEEL was used as a working electrode. Gill AC technology allows to