



Utilization of sulfidated poly (acrylamide-vinyl acetate) as a new corrosion inhibitor for carbon steel in acidic media



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ABSTRACT

This paper study the utilization of sulfidated poly (acrylamide-vinyl acetate) (SG), which is previously prepared by the expose of poly (acrylamide-vinyl acetate) copolymer (AG) to H₂S gas (15 ppm), as a new corrosion inhibitor for carbon steel in acidic media. The corrosion inhibition efficiency of these inhibitors is detected in carbon steel surface in 1 M HCl solution by the weight loss and electrochemical techniques. Untreated and treated steel surfaces were examined by scanning electron microscopy (SEM). The obtained results show that the maximum inhibition efficiency (η_p) by SG inhibitor in 1 M HCl solution at 500 ppm and 303 K was 96.71%. Also, the potentiodynamic polarization curves indicated that the investigated inhibitors behave as a mixed type inhibitor. Adsorption of these inhibitors on the carbon steel surface was found to obey Langmuir's adsorption isotherm. Both of the computed quantum chemical properties viz., electron affinity (EA), highest occupied molecular orbital (E_{HOMO}), the lowest unoccupied molecular orbital (E_{LUMO}), energy gap $\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$, dipole moment (μ), $\log P$ and ΔN showed good correlation with experimental inhibition efficiency.

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Introduction

Hydrogen sulfide (H₂S) and other compounds containing sulfur can be found in natural gas and other industrially important hydrocarbon feedstock [1]. H₂S is considered as one of the most noxious industrial gases for the atmosphere [2,3]. Its removal from natural gas is particularly required for reasons of health (e.g., sore throats, breathing difficulties, respiratory infections), odor problems and safety; it also causes pipeline corrosion that limits plant lifetime [1] and might poison many industrial catalysts [4,5]. In the petroleum industrial facilities, the steel is widely used as a construction material. Due to the low installation costs, mild steel is especially preferred. However, the main problem with the use of mild steel is its low resistance to corrosion. Therefore, it must be protected against corrosion in especially aggressive media. The use of organic inhibitors is one of the most practical and effective methods for the protection of the mild steel [6]. The selection of appropriate molecules as an inhibitor depends absolutely on

structure and formulation. Generally, molecules containing nitrogen, sulfur, oxygen and aromatic rings are preferred. The efficiency of these molecules depends mainly on their abilities to adhere onto the metal surfaces [7–9]. The researches show that these molecules adsorb on the metal surface by displacing water molecules on the surface and forming a protective film [10,11]. The ability of organic inhibitors to protect carbon steel pipelines in acid media using polarization, open circuit potential, weight loss and surface tension measurements have been studied [12], as well as quantum chemical investigation [13]. In recent studies, the quantum calculation methods are used for detailed explanation of the inhibition efficiency mechanism. In this approach, the electronic properties relevant to the inhibiting action are calculated [14]. The goal of this work is to utilize a new corrosion inhibitor (as a byproduct), results from the expose of poly (acrylamide-vinyl acetate) to H₂S gas, emitted from the gas plant as a source of sulfur and to study the inhibition performance of their inhibitors poly(acrylamide-vinyl acetate) and sulfidated poly (acrylamide-vinyl acetate) on carbon steel in 1 M HCl solution using weight loss and electrochemical techniques. Also, the correlations between the inhibition efficiency of the prepared inhibitors for the corrosion of carbon steel in 1 M HCl and some quantum parameters have been discussed.

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Experimental

Materials

Two monomers namely; acrylamide (AM) and vinyl acetate (VA) obtained from Fluca (England) and Sigma-Aldrich (Germany), respectively were freshly distilled under reduced pressure and stored at -10°C . The initiator, azobisisobutyronitrile (AIBN) purchased from Sigma-Aldrich (Germany), has been recrystallized from methanol. The water used in all experiments was double distilled, deionized and filtered prior use. A natural feed gas of varying H_2S and CO_2 concentrations was obtained from natural gas field, Western desert, Egypt.

Copolymerization of acrylamide with vinyl acetate

Into 100 ml Pyrex glass reactor equipped with a condenser under nitrogen gas in water bath at 60°C and maintained constant within $\pm 0.1^{\circ}\text{C}$ of the desired temperature, a typical polymerization batch of (0.5) and (0.5) moles of acrylamide and vinyl acetate, respectively were dissolved in 200 ml acetone. 0.01% (weight ratio with respect to the monomers of 2,2'-Azobisisobutyronitrile (AIBN)) as initiator was added to the monomers solution at desirable temperature. The reaction mixture was purged with N_2 gas for about 5 min and then kept at 60°C . After 120 min, the polymerization was stopped by cooling and the copolymer was precipitated in acetone [15,16]. The product was purified by reprecipitation from acetone/ethanol mixture (60/80). Finally, the precipitated copolymer was dried in vacuum until a constant weight was obtained, with a molecular weight of 3.05×10^5 g/mol.

Formation of sulfidated poly (acrylamide-vinyl acetate)

Preparation and evaluation of poly (acrylamide-vinyl acetate), **AG**, as H_2S scavenger and sulfidated poly (acrylamide-vinyl acetate), **SG**, as bi-product compounds that used in this study have been described in detail in [16]. One gram of the prepared copolymer was loaded into the reactor (Fig. 1). The operating pressure was set using the pressurized nitrogen gas stream and adjusting the back pressure regulator. Once the pressure stabilizes the natural gas, which has a known concentration of H_2S gas (15 ppm), was fed into the reactor [16]. The structural formulae of (**AG**) and (**SG**) are shown in (Scheme 1).

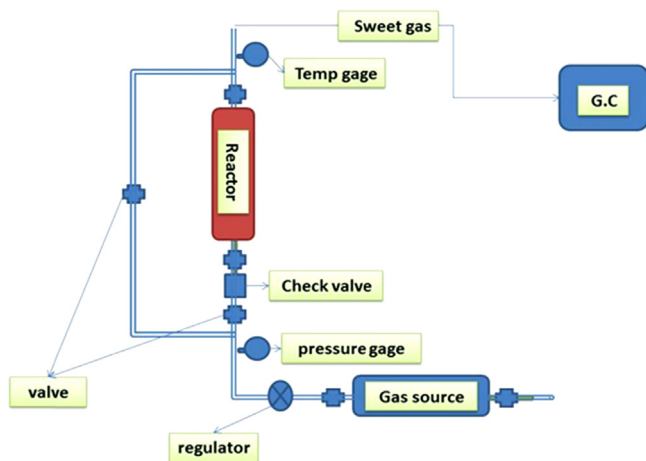


Fig. 1. Schematic diagram of experimental setup.

Solutions

The aggressive solution, 1 M HCl, was prepared by dilution of analytical grade, 37% HCl with distilled water. The concentration range of the prepared compound was from 100 to 500 ppm used for corrosion measurements. All solutions were prepared using distilled water.

Evaluation of weight loss

A fresh 1 M HCl solution was made of HCl (concentration of 37%). The concentrations of the inhibitors employed were varied from 100 to 500 ppm in 1 M HCl. The carbon steel sheets of ($7.0 \times 2.0 \times 0.3$ cm³) dimensions were immersed in a closed beaker in 1 M HCl with and without the addition of different concentrations of inhibitors for 4 h at 303 K. Experiments were carried out in triplicates. The average weight loss of the three parallel carbon steel sheets was calculated as follows [17]:

$$\Delta W = W_1 - W_2 \quad (1)$$

where, W_1 and W_2 are the average weight of specimens before and after exposure, respectively.

Electrochemical measurements

Carbon steel working electrode of the following chemical composition (wt%) was used in the experiments: 0.07% C, 0.24% Si, 1.35% Mn, 0.017% P, 0.005% S, 1006% Cr, 1008% Ni, 1002% Mo, 0.01% Cu and the remainder Fe. A pre-treatment was carried out prior to each experiment, in which specimen surface was mechanically ground with 400, 600, 800 and 1000 emery paper, washed with acetone and bidistilled water then dried and put into the cell [18]. The electrochemical measurements were carried out using Volta lab 40 (Tacussel-Radiometer PGZ301) potentiostat and controlled by Tacussel corrosion analysis software model (Volta-master 4) under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solutions for 30 min to establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp} , the electrochemical measurements were performed. The polarization curves were obtained in the potential range from -850 to -350 mV(SCE) with a 1 mV s^{-1} scan rate.

Surface morphology studies

The surface morphology of the steel specimens was examined after exposure to 1 M HCl in the absence and presence of a certain concentration of the selected inhibitor (SG). JEOL 5410 scanning electron microscope SEM (JEOL, Japan) was used for this investigation.

Quantum chemical study

All required molecular parameters were carried out based on MINDO3 semi-empirical method ever used for organic inhibitor's calculation [19] at an Unrestricted Hartree Fock (UHF) level which are implemented in Hyperchem 8.0. The molecule 2D sketch was obtained by ISIS Draw 2.1.4.

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