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Adsorption and inhibition effect of Ascorbyl palmitate on corrosion of carbon steel in ethanol blended gasoline containing water as a contaminant

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ABSTRACT

The adsorption and inhibition effect of Ascorbyl palmitate (AP) on carbon steel in ethanol blended gasoline containing water as a contaminant (GE10 + 1%water) was studied by weight loss and electrochemical impedance spectroscopic (EIS) techniques. The results showed that the addition of ethanol and water to gasoline increase the corrosion rate of carbon steel. AP inhibits the corrosion of carbon steel in (GE10 + 1% water) solution to a remarkable extent. The adsorption of AP on the carbon steel surface was found to obey the Langmuir adsorption isotherm model. The values of activation energy (E_a) and various thermodynamic parameters were calculated and discussed.

1. Introduction

The use of ethanol as transportation fuel is rapidly increasing because they can be obtained from different and widespread resources and because of the potential abatement of environmental pollution [1,2].

The main way that ethanol can be used as a transportation fuel is a blend of 10% ethanol with 90% unleaded gasoline called GE10 Unleaded. When mixed with unleaded gasoline, ethanol increases octane levels, decreases exhaust emissions, and extends the supply of gasoline [3].

Carbon steel pipelines are normally used for transporting and distributing traditional petroleum products [4]. One major concern in using carbon steel pipelines to transport fuel-grade ethanol or blended fuel is the corrosion of carbon steel pipelines in these environments [5,6].

Corrosion behavior of metals in blended fuel is different from those in aqueous media since they are highly dependent upon some physicochemical features such as dielectric constants, surface tension, conductivity of the corrosive media, and the solubility of the corrosion reactants and the corrosion products. In addition, water concentration and diffusion rates are also other factors that contribute to the corrosion process [7,8].

The corrosiveness of the ethanol blends fuel depends on the hydroscopic property of ethanol, meaning it absorbs water. In addition, water is expected to be present as a contaminant in small amounts in commercial fuels such as gasoline and this lead to the increase in the susceptibility of materials to localized corrosion [9].

One of the most important methods in corrosion protection of metals in fuel media is to use inhibitor [10]. The corrosion inhibitor should be included at a treat rate sufficient to provide corrosion protection comparable to that of other available motor fuels while protecting the transportation distribution system from corrosion concerns. The use of organic substances to inhibit corrosion of metals in fuel environments is well established [11–13]. The corrosion inhibition efficiency of organic substances is related to their adsorption properties. Generally, organic inhibitors act on the corrosion process by adsorption on the metal surface, forming a protective film and blocking the active sites [14]. Unfortunately most of the organic inhibitors are toxic in nature. The research in the field of eco-friendly corrosion inhibitors has been addressed toward the goal of using cheap, effective molecules at low or zero environment impact.

Ascorbyl palmitate could be deemed as good potential inhibitor owing to containing electronegative O-heteroatom, carbonyl group, heterocyclic ring and alkyl chain group. In addition, it is non-toxic and biodegradable [15]; this makes the investigation of its inhibiting properties significant in the context of the current priority to produce inhibitors with low environment impact. Nevertheless, data regarding the use of Ascorbyl palmitate as potent inhibitor for carbon steel corrosion appears to be very poor.

The aim of this study is to investigate the effect of addition ethanol and water on the corrosion behavior of carbon steel in gasoline. In addition, the adsorption of Ascorbyl palmitate on the carbon steel surface in ethanol blended gasoline containing water

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as a contaminant (GE10 + 1% water) and its corrosion inhibition properties has been investigated. These investigations have been evaluated by weight loss and electrochemical impedance spectroscopic EIS methods.

2. Experimental methods

2.1. Materials and chemicals

The corrosion tests were performed on carbon steel specimens with a composition (in wt.%) C 0.19, Si 0.35, P 0.018, Cr 0.04, Mo 0.03, Ni 0.017, Cu 0.02, Al 0.06, and Fe (balance). The carbon steel specimens with dimensions 2.2 cm × 2.0 cm × 0.03 cm were used for weight loss measurements. For electrochemical measurements, carbon steel specimens of 5.5 cm long stem with exposed surface area of 0.458 cm^2 (rest being coated with commercially available lacquer) were used.

The surface of working electrode was mechanically abraded using 600, 800, 1000 and 1200 grades of emery papers, prior to use. The disc was cleaned by washing with double distilled water and finally degreased with acetone and dried at room temperature. For each test, a freshly abraded electrode was used.

The corrosion media used this study were commercial unleaded gasoline (conductivity 25×10^{-12} S/m), ethanol (Anhydrous ethanol with a purity of 99.9%) blended gasoline GE10 (10 vol.% ethanol/90 vol.% gasoline; conductivity 255×10^{-8} S/m) and ethanol blended gasoline containing water as a contaminant (GE10 + 1 vol.% water; conductivity 678×10^{-7} S/m). The conductivity of the corrosion media was determined at 298 K using a Conductivity Meter LF 538 WTW".

Ascorbyl palmitate (Fig. 1), which was obtained commercially from ScienceLab.com, Inc., was added to the corrosion medium (GE10 + 1 vol.% water) in concentrations ranging from 20 to 120 mg l^{-1} and the solution in the absence of Ascorbyl palmitate was taken as blank for comparison.

Experiments were carried out using calibrated thermostat at temperatures 298 and 323 K (±0.5 °C).

All chemicals were of analytical reagent grade and were used without further purification. The solutions were prepared using double distilled water and all experiments were carried out in unstirred solutions. All the test solutions were open to air.

2.2. Weight loss measurements

The weight loss was determined by weighing the cleaned carbon steel specimens before and after immersion in the tested medium for 1500 h using an analytical balance (GM1502- Sartorius). Weight loss measurements were conducted under total immersion using 250 ml capacity beakers containing 200 ml test solution. In order to get good reproducibility, experiments were carried out in triplicate. The corrosion rate (C_R) in mg cm^{-2} h^{-1} has been calculated using the following equation:

$$C_R = \frac{W}{St} \tag{1}$$

where W is the weight loss of the samples in mg, S is the total surface area of specimens in cm^2 and t is the immersion time in h.

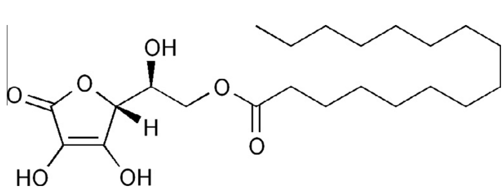

Fig. 1. Molecular structure of Ascorbyl palmitate.

Table 1
The corrosion rate of carbon steel after immersion in pure gasoline, ethanol blended gasoline GE10 (10% ethanol/90% gasoline) and ethanol blended gasoline containing water as a contaminant (GE10 + 1 vol.% water) at 298 K.

Solution	Corrosion rate (mg cm^{-2} h^{-1})
Gasoline	12.1×10^{-5}
GE10	17.8×10^{-5}
GE10 + 1 vol.% water	50.1×10^{-5}

2.3. EIS measurements

The electrochemical studies were carried out using a three-electrode glass cell assembly with platinum counter electrode and Ag/AgCl electrode (SSCE) in which the outer compartment is filled with 3.0 M LiCl in ethanol was used as the reference electrode. SSCE was used as a reference electrode in this study to avoid contact between ethanol blended gasoline and water from the reference electrode. The reference electrode (SSCE) separated from the test solution by Vycor junction (frit) that serves as a salt bridge. The liquid junction potential was not taken in account since that the experiments were performed comparatively in absence and in the presence of the corrosion inhibitor.

The glass cell contained 250 ml of the test solution (GE10 + 1 vol.% water). The supporting electrolyte was not used in this study to avoid any possible effect on the corrosion activity of carbon steel.

In order to achieve reliable electrochemical measurement in extremely low conductivity of ethanol blended solution and to minimize IR drop, the salt bridge frit and counter electrode were placed in close proximity to the test sample. The distances between counter, working electrodes and the salt bridge tip were kept constant for every test. The cell system was linked electrically to an impedance analyzer.

Impedance spectra were measured on potentioscan type (Potentio-Galvanostat EG&G model 273) connected with a personal computer and equipped with electrochemical impedance software (M 398) from EG&G Princeton Applied Research. All EIS measurements were performed at the open circuit potentials (OCP). The real part (Z_r) and the imaginary part (Z_i) were measured at various frequencies in the range of 100 kHz to 1.0 mHz with ac voltage amplitude of 10 mV peak-to-peak. The experimental impedance data obtained were represented using Nyquist plots.

3. Results and discussion

3.1. Weight loss measurements

3.1.1. Effect of ethanol and water on corrosion of carbon steel in gasoline

The effects of ethanol and water in gasoline solution on carbon steel corrosion were evaluated by weight loss measurements at 298 K after 1500 h immersion. The corrosion rates of carbon steel after immersion in pure gasoline, ethanol blended gasoline GE10 and ethanol blended gasoline containing water as a contaminant (GE10 + 1% water) are presented in Table 1. As seen from Table 1, it is apparent that the addition of ethanol and water to gasoline increase the corrosion rate of carbon steel. The corrosion rate of carbon steel increases in the sequence: GE10 + 1% water > GE10 > pure gasoline. This result suggests that the presence of ethanol and water as a contaminant in gasoline fuel plays a very significant role in the corrosion of the carbon steel. This is due to the tendency of ethanol to absorb water and dissociate slightly into anions and cations, contributing to the electrochemical process and increasing the corrosion rate [16]. In addition,