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Hydrogen generation during the corrosion of carbon steel in crotonic acid and using some organic surfactants to control hydrogen evolution

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ABSTRACT

The purpose of this paper is to describe and evaluate the corrosion of carbon steel in crotonic acid for hydrogen production and using polysorbate 20 (NS), dioctyl sodium sulfosuccinate (AS) and benzalkonium chloride (CS) to control hydrogen evolution. Measurements were conducted in tested solutions using hydrogen evolution and electrochemical impedance spectroscopy (EIS) measurements and complemented by scan electron microscope (SEM) and energy dispersive X-ray (EDX) investigations. It is shown that the hydrogen generation rate obtained during the corrosion of carbon steel in crotonic acid increased with increase in acid concentration, temperature and immersion time. The addition of organic surfactants inhibits the hydrogen generation rate. The inhibition occurs through adsorption of organic surfactants on the metal surface. Adsorption processes followed the Langmuir isotherm. The order of effectiveness of the surfactants was AS > NS > CS. The values of activation energy (E_a) and heat of adsorption (Q_{ads}) were calculated and discussed.

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1. Introduction

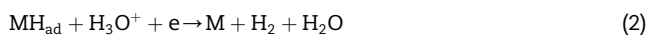
The concept of producing hydrogen by the reaction of certain metals with acids has intrigued researchers for many years [1–7]. The acidic conditions will result in corrosion of the carbon steel. Hydrogen evolution may also accompany the corrosion of carbon steel in an acidic solution. Many literatures revealed that the maximum ratio of moles of hydrogen evolved to moles of iron corroded is 1:1 [8,9]. This ratio would be observed in a de-aerated environment. If oxygen or other oxidizing species are present, the ratio could be much less than 1:1. Although the ratio of hydrogen evolution to iron corroded will not exceed 1:1, the total amount of hydrogen evolved can be influenced by such things as a decrease in the exposed surface area, suppression of hydrogen generation by corrosion inhibitor, the presence of corrosion products on steel surface, etc.

The following mechanisms can be proposed for hydrogen evolution reaction (HER) on electrodes in acidic media [10]:

1. A primary discharge step (Volmer reaction)



2. An electrochemical-desorption step (Heyrowsky reaction)



3. A recombination step (Tafel reaction)



In spite of three states for the formulation of the mechanism [11], no one of the three reactions formulated occurs as a

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single step but combines with another; i.e. Volmer reaction (slow) with the following Heyrowsky (faster) or Tafel (faster) reaction must be. If Volmer reaction is fast, Tafel and/or Heyrowsky reaction must be slow.

Reviews of the literature on the corrosion behavior of metals electrode in acidic media showed that the most of the work has been done in mineral acids [12–14]. Only very little work is available on the influence of crotonic acid on the corrosion behavior of metals [15].

Crotonic acid, or trans-2-butenic acid, is a short-chain unsaturated carboxylic acid, described by the formula $\text{CH}_3\text{CH}=\text{CHCO}_2\text{H}$. This acid is very important and having many industrial uses such as the preparation of a variety of industrial resins, pharmaceuticals, fungicides, surface coatings and rubber softener [16]. Crotonic acid is a medium-strong acid that reacts with bases and strong oxidants, and attacks many metals [16].

Inhibitors are used to prevent metal dissolution as well as acid consumption [17–19]. Most well known acid inhibitors are organic surfactants [20,21]. The organic surfactant inhibitor has many advantages such as high inhibition efficiency, low cost, low toxicity and easy production [22]. Surfactants exert their inhibition action by adsorption on the metal surface such that the polar or ionic group (hydrophilic part) attaches to the metal surface while its tail (hydrophobic part) extends to the solution.

The aim of this study is to investigate the hydrogen generation during the corrosion of carbon steel in crotonic acid solution and using some organic surfactants to control hydrogen evolution. The investigation was performed using hydrogen evolution and electrochemical impedance spectroscopy (EIS) measurements. Some SEM/EDX examinations of the electrode surface were also performed.

2. Experimental

Tests were performed on a carbon steel of the following composition (wt %): 0.06 C; 0.06 Si; 0.7 Mn; 0.005 P; 0.001 S; 0.012 Ni; 0.015 Cr; 0.004 Mo; 0.002 V; 0.02 Cu and Fe balance. The carbon steel specimens with surface area 4 cm^2 were used for hydrogen evolution measurements. For EIS 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.

Prior to each experiment, the working electrodes were abraded with successive grades of emery papers down to 1200 grit up to a mirror finish and then degreased with acetone and washed with running doubly distilled water.

The gasometric assembly is essentially an apparatus that measures the volume of hydrogen evolved from a corrosion reaction system. It consists of essentially a two necked round-bottom flask, a separating funnel and a graduated burette (filled with paraffin oil) fitted with taps [23]. In hydrogen evolution measurement, 100 ml of crotonic acid solution was introduced into the two-necked flask and carbon steel coupon was carefully dropped into the test solution and the reaction flask was quickly closed to avoid any escape of hydrogen gas. The volume of hydrogen gas evolved from the corrosion reaction was monitored by the depression (in cm^3) in the

paraffin oil level in the graduated burette at fixed time intervals.

The electrochemical impedance spectroscopy (EIS) measurements studies were carried out using a three-electrode cell assembly with platinum counter electrode and saturated calomel electrode (SCE) as reference electrode. Impedance spectra were measured on potentiostatic type (Potentiostat-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. The real part (Z_r) and the imaginary part (Z_i) were measured at various frequencies in the range of 30 KHz to 1.0 Hz with a voltage amplitude of 10 mV peak-to-peak.

The surface morphology of the carbon steel specimen immersed in 1.0 M crotonic acid solution in the presence and absence of organic surfactants were compared by recording the SEM images of the samples using JEOL-JEM 1200 EX II electron microscope.

Energy dispersive X-ray spectroscopy (EDS) investigations were carried out in order to identify the elemental composition of the species formed on the metal surface after its immersion in 1.0 M crotonic acid solution in the presence and absence of inhibitor. EDX examinations were carried out using a Traktor TN-2000 energy dispersive spectrometer.

The different concentration of crotonic acid solutions were prepared from of AR grade of crotonic acid (Merck).

The organic surfactants used in this study were poly-sorbate 20 (NS), dioctyl sodium sulfosuccinate (AS) and benzalkonium chloride (CS) as nonionic, anionic and cationic surfactants respectively. Scheme 1 shows the molecular structure of the organic surfactants.

The study was conducted at 303 and 333 K maintained using a thermostated water bath.

Each experiment was repeated three times to ensure reproducibility and the average values are reported.

3. Results and discussion

3.1. Effect of crotonic acid

For the corrosion of carbon steel in crotonic acid solution the anodic (metal dissolution) and cathodic (hydrogen evolution) half reactions are:



Hydrogen evolution reaction involves the following two step pathways proceeding alone or in parallel [24]:

- 1 Volmer-Tafel pathway: electro-adsorption followed by chemical combination.
- 2 Volmer-Heyrowsky pathway: electro-adsorption followed by electro-combination.

These steps are followed by transport of dissolved H_2 molecules away from the electrode via diffusion or gas

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