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EIS investigation of ammonium chloride corrosion on carbon steel under stirring condition

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ABSTRACT

Ammonium chloride (NH₄Cl) corrosion has plagued the oil refineries. In the present work, the effect of NH₄Cl on the corrosion behavior of carbon steel, under stirring condition, is investigated by potentiodynamic polarization, electrochemical impedance spectroscopy and other complementary techniques. It is found that the corrosion rate increases with the increase in the concentration of NH₄Cl. The polarization measurement implies that the carbon steel is vulnerable to uniform corrosion. The impedance analysis performed at various overpotentials (+0.05 V, +0.15 V and +0.25 V w.r.t OCP) shows multiple time constants, corresponding to capacitance and inductance. The total impedance decreases with the increase in overpotential, suggesting that no strong passivation layer is formed on the surface of carbon steel. In addition, reaction mechanism analysis (RMA) is employed to investigate the mechanistic reaction pathway. From RMA, a multi-step reaction mechanism with three intermediate adsorbed species is propounded to elucidate the patterns observed in impedance measurements. The kinetic parameters and the surface coverage by the adsorbed species are also obtained from RMA. The surface morphology of carbon steel are also reported using field emission scanning electron microscope.

Keywords: Carbon steel, Ammonium chloride, Electrochemical impedance spectroscopy, Reaction mechanism analysis

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1. INTRODUCTION

Corrosion of carbon steel associated with acidic constituents, salts deposits, sulfur compounds, amines, cyanides, carbon dioxide gas is a widely known problem in oil and gas industries. So, it is very important to study the corrosive behavior of these constituent species in order to find out as to which species might be responsible for greater degree of corrosion. Moreover, the evaluation of metallic materials construction in oil refineries as well as in other industrial environments is a very significant issue, particularly in pipelines and distillation plants, as this phenomenon is responsible for economic and human losses.

In oil refining industries, corrosion failures by means of ammonium chloride (NH₄Cl) salt deposits or aqueous solutions of NH₄Cl has increased considerably since many years. The NH₄Cl deposit leads to severe corrosion damages, resulting in discharge of flammable gases and oils, causing fires and explosions ^[1, 2]. In processes/streams where nitrogen and chlorides or ammonia and hydrochloric acid are present, the formation of NH₄Cl is feasible. The corrosiveness of streams containing NH₄Cl depends on several factors such as NH₄Cl concentration, temperature, hydrodynamic conditions, etc. NH₄Cl corrosion is generally observed in reactor effluent, pressure separator, and fractionator or stripper streams in hydro-processing units, hydro-processing reactor effluent air cooler (REAC) systems, crude unit overhead streams, fluid catalytic cracking unit overhead streams and other heat transfer equipments ^[1-5].

Corrosion of different alloys was probed in NH₄Cl solution, and it was found that both the corrosion nature (uniform or pitting corrosion) as well as the corrosion rate depends strongly on the composition of alloy [4]. Toba et al. [3] investigated the corrosion behavior of carbon steel under the effect of relative humidity and NH₄Cl concentration through weight loss measurement and water absorption experiments. The NH₄Cl corrosion of carbon steel was also characterized via polarization measurements under the influence of temperature and concentration and the results implies that both the parameters had a significant impact on the rate of corrosion ^[4]. The corrosion products examined via spectroscopic studies and thermo-gravimetric analysis (TGA) showed that it is a mixture, consisting of oxides and oxy-hydroxides ^[6, 7]

Carbon steel corrosion is extensively studied in chloride media viz. NaCl and HCl. The most commonly recognized mechanism is proposed by Li et al. ^[8] which is given below.

 $Fe(s) + 2Cl^{-}(aq) \longrightarrow FeCl_{2}(s) + 2e^{-}$

 $FeCl_2(s) \longrightarrow FeCl_2(interface) \longrightarrow FeCl_2(aq)$

 $\operatorname{FeCl}_2(s) + \operatorname{Cl}^{-}(aq) \xrightarrow{} \operatorname{FeCl}_3(s) + e^{-}$

 $FeCl_3(s) \longrightarrow FeCl_3(interface) \longrightarrow FeCl_3(aq)$

However, in the literature, only few works were found with respect to corrosion of carbon steel in NH_4CI solution. In particular, the reaction mechanism of carbon steel dissolution in NH_4CI solution under stirring condition is not reported yet to the best of author's knowledge. Thus, in the present work, propounding a kinetic model to elucidate the corrosion behavior of carbon steel in NH_4CI solution is of much interest.

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(1)

Electrochemical impedance spectroscopy (EIS) is one of the most powerful electrochemical technique to investigate the mechanistic reaction pathway ^[9]. The reaction mechanism of metal dissolution in various media is investigated successfully through EIS measurements at various overpotentials [10, 11, 12]. Therefore, in the present work, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were employed along with field emission scanning electron microscopy (FESEM) measurements and weight loss measurements to probe the corrosion behaviour of carbon steel in NH₄CI at room temperature.

2. EXPERIMENTAL PROCEDURE

2.1 MATERIALS

Carbon steel [C (0.22-0.26) %; Si (0.11-0.14) %; Mn (1.03-1.06) %; P (0.04 % maximum); S (0.03 % maximum); Cr (0.03 % maximum); and rest Fe] was used for all the experiments in this present work. The electrolytes were prepared utilizing chemicals of analytical reagent grade (Ammonium Chloride - NH_4Cl : Himedia) and distilled water. All the experiments were conducted at natural pH of the solutions and under stirring conditions (300 rpm). The solution pH observed were 4.69 and 4.22, respectively for 10 and 20 wt. % NH_4Cl solutions.

2.2 ELECTROCHEMICAL MEASUREMENTS

Electrochemical measurements were carried out using a standard three electrode system and a potentiostat [Metrohm Autolab, PGSTAT 204] at (25.5 ± 1) °C. The working electrode was made of carbon steel with cross section dia. 9 mm. It was enclosed within a Teflon tube, allowing only the cross-sectionional area to interact with the electrolytic solution. Ag/AgCl (3 M KCl) was employed as the reference electrode, and a Pt wire was employed as the counter electrode. The corrosion cell was placed inside a Faraday cage in order to avoid the external noises from the surroundings, during all the experiments. Before each experiment, the working electrode was polished successively with 180, 320 and 600 and 1000 grades of emery paper, followed by 1.0 μ m and 0.3 μ m abrasive alumina powder. The electrode was then rinsed with distilled water, and ultrasonicated to remove any adhered particles. The electrode was finally rinsed and dried using tissue paper. The polarization and impedance measurements were performed once the open circuit potential (OCP) reached a stable value.

For investigating the dissolution behavior of carbon steel in pure NH₄Cl system, the potentiodynamic polarization measurements were performed by sweeping the potential from -250 mV to +500 mV (w.r.t. OCP), at a scan rate of 1 mV s⁻¹. The impedance measurements were performed by applying an amplitude of 10 mV (rms) for various overpotential (+ 0.05 V, + 0.15 V and + 0.25 V w.r.t. OCP). The frequency range considered was from 100 kHz to 1 mHz, with 6 frequencies per decade. All the experiments were performed atleast thrice and only the repeatable results are presented in this work. The measurements were conducted using naturally aerated electrolyte solutions.

2.3 FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM) MEASUREMENTS

In order to characterize the corrosion type, the images of surface morphology of carbon steel were taken using field emission scanning electron microscope [Zeiss, Sigma]. The carbon steel was dipped in nitric acid, polished with sand paper followed by abrasive powder, washed with water and air dried. Then the sample was immersed in the solution of interest. After 12 hours, the sample was taken out, washed with water, air dried and then images were taken.

3. RESULTS

3.1 POTENTIODYNAMIC POLARIZATION MEASUREMENTS

The polarization measurements were performed once the open circuit potential (OCP) reached a stable value within 300 s. Figure 1 illustrates the potentiodynamic polarization behavior of carbon steel in 10 wt. % and 20 wt. % NH₄Cl solutions under stirring condition. The curves shows that the corrosion potential (E_{corr}) shifts slightly towards positive potential on increase of concentration of NH₄Cl. However, both the cathodic and anodic current density increases with increase in the NH₄Cl concentration as the curve shifts towards right. This implies that with increase in the concentration of NH₄Cl, the corrosion rate increases. Another observation in the curve is that the increase in current density is almost linear with increase in potential, though a kink is observed in the anodic region over a few millivolt. This envisages that no passivation takes place on the carbon steel surface. Thus, it could be expected that the layer forming on the surface may be thin and non-protective in nature, thereby increasing the susceptibility of the carbon steel to undergo uniform corrosion.



Figure 1: Potentiodynamic polarization curve of carbon steel corrosion in NH₄Cl solution obtained at 300 rpm; Scan rate = 1mV s⁻¹

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3.2 FESEM measurements

The surface morphology of carbon steel after immersion in 10 and 20 wt. % NH_4CI concentrations are shown in Figure 2 (a-b). The result shows that the corrosion is more of uniform type in both the concentrations. This is in corroboration with the inference made from polarization measurements that uniform corrosion prevails over the carbon steel surface on reaction with NH_4CI species.



Figure 2: FESEM images of carbon steel, immersed in (a) 10 wt. % and (b) 20 wt. % NH₄Cl solutions for a period of 12 hours

3.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) MEASUREMENTS

Prior to EIS measurements, OCP was measured to allow the system to attain its stable OCP value. The impedance analysis was performed at various overpotentials (dc potential) viz. +0.05 V, +0.15 V and +0.25 V above OCP, to understand the dissolution behavior of carbon steel at the metalelectrolyte interface in 10 and 20 wt. % NH₄Cl solutions. The results obtained are shown in Figure 3 (a-f). The following observations were drawn from the impedance data: (a) three time constants are observed at lower dc potentials i.e., 0.05 V and 0.15 V w.r.t. OCP for both the concentrations; (b) at 0.25 V w.r.t. OCP, four time constants are observed in both the systems; (c) the total impedance for both the concentrations decreases with increase in overpotential, thereby implying increase in dissolution rate with overpotential; (d) at any overpotential, the total impedance decreases for 20 wt. % NH₄Cl as compared to 10 wt. % NH₄Cl, indicating higher dissolution rate in 20 wt. % NH₄Cl system, as observed in potentiodynamic polarization studies. In addition to this, it is to be noted that the EIS pattern changes with increase in overpotential from three to four loops. In both the systems, at 0.05 V and 0.15 V w.r.t OCP, two capacitance loops are observed in the high and mid frequency region, and 1 inductance loop in the low frequency region. However, at 0.25 V w.r.t. OCP, four loops viz. capacitance-inductance-capacitance-inductance are observed. The loops arising in the higher frequency region corresponds to electrical double layer (EDL) and faradic reactions at the metalelectrolyte interface. While the one's arising in the mid and low frequency region corresponds to various faradic and non-faradic reactions at the interface as well as in the bulk electrolyte.

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Before analyzing the EIS data by various modelling approaches, it should be validated by Kramers – Kronig Transformation (KKT) in order to ensure the causality, linearity and stability of the electrochemical system. All the data reported here are validated with the same. In the present work, the commonly employed modelling approach, electrical equivalent circuit (EEC) could not be adopted to fit the EIS data. It is difficult to capture all the experimental trends (number of time constant and patterns) using a single circuit. Therefore, in this study, a reaction mechanism analysis (RMA) approach is considered to elucidate the processes occurring at the carbon steel – solution interface for 10 and 20 wt. % NH₄CI system via. the impedance data attained.



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Figure 3: EIS measurement of carbon steel at various overpotentials in (a-c) 10 wt. % and (d-f) 20 wt. % NH₄CI solutions, obtained under stirring condition

3.4 Reaction mechanism analysis (RMA)

In this approach, the EIS data is simulated for the propounded mechanism and then compared with the experimental EIS data, in particular for the patterns observed [9, 13, 14]. Following presumptions were made in developing the impedance equations for the mechanism proposed.

1. The electrochemical system being studied is perturbed using sinusoidal voltage signal with small amplitude. This is to consider only linear terms in the equations.

2. The kinetic parameters vary exponentially with voltage and the forward reaction has a nonnegative component.

3. Langmuir adsorption isotherm is considered to model the adsorption of species on the surface i.e., surface coverage is restricted to unity.

In the present work, a maximum of four time constants are observed in both the systems. Thus, we have proposed a following six step reaction mechanism with three intermediate adsorbed species and Fe^{2+} as the dissolution species to capture all the aforementioned experimental trends.

$\operatorname{Fe}_{\overbrace{k_{-1}}}^{\underline{k_1}}\operatorname{Fe}_{ad}^+ \xrightarrow{\underline{k_2}} \operatorname{Fe}_{ad}^{2+} \xrightarrow{\underline{k_3}} \operatorname{Fe}_{sol}^{2+}$	
$Fe_{ad}^{+} \xrightarrow{k_{4}} Fe_{sol}^{2+}$	(2)
$Fe_{ad}^{+} \xleftarrow{k_{5}}{k_{.5}} Fe_{ad}^{2+*} \xrightarrow{k_{6}} Fe_{sol}^{2+}$	(-)
$\operatorname{Fe}_{\operatorname{ad}}^{2+*} + \operatorname{Fe} \xrightarrow{k_6} \operatorname{Fe}_{\operatorname{ad}}^{2+*} + \operatorname{Fe}_{\operatorname{sol}}^{2+} + 2e^{-}$	

Here, Fe_{ad}^{+} and Fe_{ad}^{2+} are the metal ions adsorbed on the surface, while Fe_{sol}^{2+} represents the metal ion dissolved in solution. Fe_{ad}^{2+*} corresponds to the intermediate adsorbed species, which also acts as a catalyst for the kinetic step k_6 .

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In the above mechanism, step k_3 is a chemical reaction, while the remaining steps are electrochemical reactions. For the proposed reaction mechanism, the overall impedance equation is derived. The best fit RMA parameters are obtained by employing an optimization technique, sequential quadratic programming (SQP).

4. CONCLUSIONS

Corrosion of carbon steel in 10 and 20 wt. % NH₄Cl solution under stirring condition is investigated. The corrosion rate increases with increase in the concentration of NH₄Cl. The polarization measurement and the FESEM images confirms that uniform corrosion occurs over the carbon steel surface. Impedance measurements performed at various dc potential shows that a minimum of three time constant appears at all the overpotentials, indicating that the dissolution rate increases both with increase in overpotential as well as concentration. Therefore, a six step reaction mechanism is utilized to understand the corrosion behavior of carbon steel in NH₄Cl solution stirring at 300 rpm. The mechanism analysis implies that the carbon steel undergoes dissolution by means of three steps including both chemical and electrochemical reaction paths. The dissolution species is Fe²⁺.

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