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Inhibitory effect of xanthan gum and synergistic surfactant additives for mild steel corrosion in 1 M HCl

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ABSTRACT

Natural polymer xanthan gum (XG) was investigated as eco friendly corrosion inhibitor for mild steel in 1 M HCl at 30 °C, 40 °C, 50 °C and 60 °C, respectively. The inhibition studies were performed using gravimetric analysis, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), quantum chemical calculations, scanning electron microscopy (SEM), and UV–visible spectrophotometry. XG significantly reduces the corrosion rates of mild steel. The inhibition efficiency (IE) of the XG increased with increase in concentration, but decreased with temperature; the maximum IE of 74.24% was obtained at concentration of 1000 ppm at 30 °C. The inhibiting action of XG is synergistically enhanced on addition of very small amount of surfactants sodium dodecyl sulfate (SDS), cetyl pyridinium chloride (CPC) and Triton X-100 (TX). The effect of SDS is more pronounced than other surfactants. Potentiodynamic polarization studies confirm XG as a mixed type inhibitor. Results of weight loss measurements are in good agreement of the results of electrochemical measurements. The UV–visible spectroscopic results indicate the formation of complex between XG and Fe^{2+} ions during corrosion reaction. Mechanism of inhibition was also investigated by calculating the thermodynamic and activation parameters like ΔG^0, E_a, ΔH and ΔS. The adsorption of inhibitor on mild steel surface obeys Langmuir adsorption isotherm. SEM micrographs show a clearly different morphology in presence of XG and XG-surfactant additives and confirmed the existence of an adsorbed protective film on the mild steel surface.

1. Introduction

Mild steel is an important engineering material used in a variety of industries such as petroleum, automotive, and power and water generation. During its applications it may come in contact with aggressive acid solutions and corrode heavily. Hydrochloric and sulphuric acids are the two mineral acids which are generally used in the various industries to remove undesirable scales and rusts from steel and ferrous alloys surfaces at temperatures up to 60 °C. However, these acid solutions are quite corrosive and their corrosiveness needs to be controlled by adding appropriate corrosion inhibitors in small concentrations. The selection of a corrosion inhibitor is governed by its economic feasibility, efficiency and effects on the environment. The use of certain compounds like chromates as corrosion inhibitors is of great concern as the compounds are toxic and hazardous to human beings as well as the environment. They need to be replaced by non-toxic, environment friendly compounds (Abiola & James, 2010; de Souza & Spinelli, 2009; Singh & Quraishi, 2010). In recent times, polymers have been found to be attractive as corrosion inhibitors as they are cost effective. They are inherently stable and non-toxic and exhibit superior corrosion inhibition properties in contrast to simple organic molecules. The polymers provide two advantages: (i) a single polymeric chain displaces many water molecules from the metal surface thus making the process entropically favorable and (ii) the presence of multiple bonding sites makes the desorption of polymers a slower process. The application of water-soluble polymers having functional groups (–OH, –COOH, $–NH_2$, etc.) have been reported as corrosion inhibitors in different aggressive media (Ashassi-Sorkhabi & Ghalebsaz-Jeddi, 2005; Bello et al., 2010; Deng, Li, & Xie, 2014; El-Haddad, 2013, 2014; Guilminot, Delard, & Degrigny, 2002; Khairou & El-Sayed, 2003; Rajeswaria, Kesavan, Gopiraman, & Viswanathamurthia, 2013; Umoren, Ogbobe, Ebenso, & Okafor, 2007). The polymers through their functional groups form complexes with metal ions. On the metal surface these complexes occupy a large surface area, thereby, blanketing the surface and protecting the metal from corrosion.

The idea of synergistic corrosion inhibition studies for metals is of great importance as it leads to a decrease in the amount of inhibitor usage, diversifies the application of the inhibitor and

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improves the inhibitive force of the inhibitor. Earlier studies have shown that halide ions synergistically increase the IE of some polymers for mild steel corrosion in acidic media (Arukalam, 2014; Larabi, Harek, Traisnel, & Mansri, 2004; Rajeswaria, Kesavan, Gopiraman, & Viswanathamurthia, 2013; Umoren & Solomon, 2015; Umoren, Ogbobe, Igwe, & Ebenso, 2008). Surfactants, which have a remarkable ability of influencing the properties of surfaces and interfaces, have recently been shown to synergistically improve the inhibition effect of some natural and synthetic polymers (Mobin & Khan, 2011, 2013a, 2013b; Mobin, Khan, & Parveen, 2011). The natural polymer, XG is a microbial desiccation-resistant polysaccharide, prepared commercially on a large scale by aerobic submerged fermentation of corn, soy or other plant materials using *Xanthomonas campestris* as fermenting agent. It is composed of pentasaccharide repeat units, comprising glucose, mannose, and glucuronic acid in the molar ratio of 2.0:2.0:1.0 (Garcia-Ochoa, Santos, Casas, & Gomez, 2000). The polymer has chemical formula, $C_{35}H_{49}O_{29}$ (monomer). The backbone of the polymer is similar to that of cellulose. The side chains are β-D-mannose, 1,4 β-D-glucuronic acid and 1,2 α-D-mannose. The polymer is soluble in cold and hot water but needs intensive agitation upon introduction into the aqueous medium in order to avoid agglomeration. Under certain conditions the thermal stability of XG against hydrolysis is superior to many other water-soluble polysaccharides or polymers in general. It is stable over a broad range of pH values. As XG is a naturally occurring polymer it is fully biodegradable (Palaniraj & Jayaraman, 2011). The chemical structure of the polymer suggests that it can act as good corrosion inhibitor. In this paper we are reporting the use of XG as corrosion inhibitor for mild steel in 1 M HCl solution. The corrosion inhibition of XG has also been established in the presence of surfactants, specifically SDS, CPC and TX respectively (chemical structure of XG, SDS, CPC and TX are shown in Fig. S1 in supporting information). The techniques used to assess the performance of XG and XG-surfactants additions include: weight loss, potentiodynamic polarization, EIS, UV visible spectroscopy, SEM, quantum chemical analysis and thermodynamic and activation parameters.

2. Experimental methods

2.1. Solutions and sample preparation

ASTM A1020 low carbon steel specimens of size 2.5 cm × 2.0 cm × 0.03 cm (weight % composition: 0.06841 C, 0.039397 Mn, 0.00080 S, 0.02197 P, 0.04561 Cr, 0.06743 Mo, 0.01539 Al, 0.03347 V and remainder Fe) were utilized in weight loss experiments. For electrochemical experiments the dimension of working electrode was 1 cm^2. The coupons were progressively polished on SiC papers of grades N°320, N°400, N°600 and N°1200, rinsed with double distilled water, de-greased with acetone and dried with warm air. Before conducting corrosion experiments, the specimens were prepared as above and used with no further storage. 1 M HCl solution prepared from 37% analytical grade reagent was used as the corrosive solution. Pure XG was obtained from Otto Chemicals. Stock solutions of 1000 ppm of XG was prepared in 1 M HCl and the desired concentrations (100, 200, 500, 800 and 1000 ppm) were obtained by appropriate dilution. Each set of XG solutions were also prepared by separately adding 5 ppm each of SDS, CPC and TX. All solutions were prepared using double distilled water.

2.2. Gravimetric measurements

After accurate weighing, the freshly prepared mild steel coupons were immersed in 100 ml each of test solution contained in a beaker maintained at 30, 40, 50 and 60 °C, respectively using a thermo-stated water bath. After 6 h of immersion, the coupons were retrieved, the corrosion products were removed from the surface mechanically using a nylon brush, dried and loss in weight was recorded. The weight loss taken was the difference between the weight at a given time and the original weight of the specimen. Runs were performed on triplicate samples and the average corrosion rate was calculated. The deviation for triplicate measurements was less than 5%. The corrosion rate was determined using the following equation:

$$\text{Corrosion rate (mpy)} = \frac{534W}{\rho At} \quad (1)$$

where W, is weight loss in mg, ρ, is the density of specimen in g/cm^3, A, is the area of specimen in sq. in and t, is exposure time in h. The % IE was calculated by using the following equation:

$$(\%\text{IE}) = \frac{CR_0 - CR_i}{CR_0} \times 100 \quad (2)$$

where CR_0 and CR_i are the corrosion rates of mild steel in the absence and presence of the inhibitor, respectively. Surface coverage (θ) was evaluated from weight loss measurements according to equation:

$$\theta = \frac{CR_0 - CR_i}{CR_0} \quad (3)$$

The synergism parameter S_1 was calculated using the following relationship (Arukalam, 2014; Umoren et al., 2008):

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \quad (4)$$

where, $I_{1+2} = (I_1 + I_2)$, I_1 is the IE of XG, I_2 is the IE of surfactant and I'_{1+2} is the measured IE for XG in combination with surfactant. S_1 approaches 1 when no interaction between inhibitor and the surfactant exists, while $S_1 > 1$ indicates a synergistic effect. In the case of $S_1 < 1$, antagonistic behavior prevails, which may be attributed to competitive adsorption.

2.3. Electrochemical measurements

The electrochemical measurements were performed using a conventional three electrode cell assembly, using an Autolab Potentiostat/Galvanostat Model 128N with inbuilt impedance analyzer FRA 2. The experiments were carried out using Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and mild steel specimens of exposed surface area 1 cm^2 as working electrode in an AUTOLAB 1 L corrosion cell. The polarization studies were carried out by sweeping the potential between −250 and 250 mV with respect to the steady-state potential at a scan rate of 0.001 V/s. The linear Tafel segments of the anodic and cathodic curves were extrapolated to obtain corrosion potential (E_{corr}) and corrosion current densities (I_{corr}). The %IE was calculated from the measured I_{corr} values using the relationship:

$$\%\text{IE} = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100 \quad (5)$$

where, I^0_{corr} is corrosion current density in the absence of inhibitor and I_{corr} is corrosion current density in the presence of inhibitor. Impedance measurements were implemented at open circuit potential within frequency range of 10^{-2}–10^4 Hz with 10 mV perturbation. All the experiments were performed at room temperature (30 °C ± 1 °C) under aerated, unstirred conditions.

2.4. SEM analysis

The surface morphology of mild steel specimens immersed in uninhibited and inhibited acid solution was evaluated using