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Enhanced corrosion inhibition effect of polypropylene glycol in the presence of iodide ions at mild steel/sulphuric acid interface

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ABSTRACT

The corrosion inhibition effect of polypropylene glycol (PPG) without and with addition of iodide ions at mild steel/0.5 M H_2SO_4 solution interface was investigated using chemical, electrochemical, and surface analysis methods at different temperatures. Results obtained showed that PPG inhibited the corrosion of mild steel in the acid environment. Addition of iodide ions to PPG is found to synergistically enhance the corrosion inhibitive ability of PPG with efficiency in the vicinity of 98.4%. Temperature–inhibition efficiency relationship suggest physisorption of PPG onto mild steel surface and chemisorption when PPG was combined with iodide ions. Potentiodynamic polarization results showed that PPG behaved as mixed type inhibitor but under anodic control when combined with iodide ions. The adsorption of PPG and PPG–iodide ions mixtures onto the metal surface followed Temkin adsorption isotherm model.

Introduction

The use of corrosion inhibitors in minimizing the loss of metals in areas deploy in service, due to corrosion has proven to be more practicable and cost effective than other methods [1]. Unfortunately, most substances which have been found to possess good inhibitory ability have come under severe criticism either for environmental issues or for exorbitant prices which undermined the primary aim of metal corrosion prevention which is economic maximization and environmental sustainability. For instance, chromium compounds were widely used as efficient metal corrosion inhibitors in aqueous systems [2–4] but have been found to possess high toxicity and have been band for industrial usage [5]. Lanthanide salts which were thought to be perfect replacement for chromium compounds [6,7] have already been found to exhibit toxicity that is comparable with sodium chloride [8]. In the category of organic inhibitors, the tedious synthetic procedures and high cost of synthesis reagents have been identified as major setback on the use of this class of inhibitors [9]. Also, polymers which many researchers [10–14] have advocated as possible replacement for organic metal corrosion inhibitors due to their low prices and environmental friendliness in addition to multiple adsorption centers appear to only moderately inhibit metal corrosion.

One of the steps taken by corrosion scientists to address the aforementioned challenges in recent times has been finding substances that can exert synergistic effect when combined with inhibitor such that the quantity of an expensive inhibitor could be reduced or the efficiency of a moderately performed inhibitor enhanced. Both cations and anions have been found to exert synergistic influence with organic species. Jeyaprabha et al. [15] reported that addition of 1×10^{-3} M ceric ions to 10 and 50 ppm of polyaniline increased the inhibition efficiencies from 53 and 71% to 88 and 90% respectively for iron in 0.5 M H_2SO_4 solution. The synergistic inhibition effect of rare earth cerium (iv) ions and anonic surfactant of sodium oleate on the corrosion of cold rolled steel in sulphuric acid solutions has been documented [16]. It was found that incorporation of cerium (iv) ions to sodium oleate significantly improved the inhibition effectiveness of the surfactant. Manimaran et al. [17] noted that formulation consisting of 250 ppm polyacrylamide and 50 ppm zinc (ii) ions could afford 98% protection to carbon steel deployed in service in water. In the category of anions, halide ions are the most investigated for possible synergistic influence with organic species. Several reports have shown that halide ions could remarkably improve the inhibitive performance of organic compound [18–21]. This has been attributed to the ability of halide ions to chemisorb on metal surface. The chemisorptions, according to Umoren and Solomon [9] diminished the repulsive influence of the metal ions exerted on the organic inhibitor molecules which by virtue of presence of some functional groups which are susceptible to protonation exist as cation species but created excess electron cloud on the metal

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surface. The electron cloud on the metal surface then induced the attraction of the cation species (the so-called coulombic attraction) on the metal surface which leads to the metal surface being covered and protected from aggressive agents present in the corrosive environment. However, the strength of the bond formed between halide ions and organic species is influenced by the electro-negativity and ionic radii hence the predisposition trend is $I^- > Br^- > Cl^-$. Most researchers have resorted to testing the synergistic influence of iodide ions with organic species in preference to the other halides. Fouda et al. [22] studied the synergistic influence caused by iodide ions on the inhibition of corrosion of C-steel in 1 M H_2SO_4 in the presence of some aliphatic amines using weight loss, potentiodynamic polarization, linear polarization, and a.c. impedance techniques. It was found that the corrosion performance of the aliphatic amines was remarkably enhanced by iodide ions. Also, Larabi et al. [23] noted that addition of 0.10% KI–5 mg/L poly (4-vinylpyridine) could upgrade the inhibition efficiency from 81.40% to 92.10%. Comprehensive information on the effect of addition of halide ions on the inhibition efficiency of different organic species including polymers can be found in our recent review paper [24].

In furtherance of our quest to explore the metal corrosion inhibition ability of polymers, and enhancement of their corrosion inhibition efficiency by combination of halide ions, the present work reports on the synergistic corrosion inhibition effect of polypropylene glycol in the presence of iodide ions for mild steel in acid environment. Gravimetric and electrochemical techniques of corrosion monitoring were employed. Surface morphological characterization of the mild steel specimens exposed to the acid corrodent without and with polypropylene glycol and polypropylene glycol–iodide ions combination were carried out using scanning electron microscopy and water contact angles surface analysis techniques.

Experimental

Materials and materials preparation

The percentage composition of the mild steel used in this study is as follow: C, 0.05; Mn, 0.6; P, 0.36; and Si, 0.03. The mild steel was mechanically press-cut into coupons of 3 × 3 cm (surface area = 9 cm^2) in dimension, for weight loss study and 1 × 1 cm for electrochemical measurements. These coupons were wet ground using different grades (#120–#800) of silicon carbide paper, decreased in absolute ethanol and air dried. The cleaned coupons were preserved in a dessicator prior to corrosion studies.

The mild steel coupons that were used for electrochemical measurements were embedded in two component epoxy resin and mounted in a PVC holder. A copper wire was used to solder to the rear side of the coupon as an electrical connection. The exposed surface of the coupons (of area 1 cm^2) was wet ground with silicon carbide abrasive paper up to 800 grits, rinsed with ethanol and air dried. This was used as the working electrode during the electrochemical test.

The corrodent was 0.5 M H_2SO_4 solution prepared from 98% analytical grade H_2SO_4 (Sigma–Aldrich) with double distilled water. Polypropylene glycol (average M_n = 2000) with the chemical structure of repeat unit shown in Fig. 1 was used as test corrosion inhibitor in the concentration range of 50–1000 ppm. Potassium iodide (KI) (Sigma–Aldrich) was used in the concentration range of 0.5–5 mM to evaluate the synergistic corrosion inhibition effect on addition to the test inhibitor.

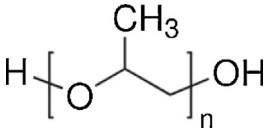

Fig. 1. Chemical structure of PPG repeat units.

Weight loss experiments

In the weight loss experiments, the pre-cleaned mild steel coupons were suspended freely in glass reaction vessels containing 200 mL of different test solutions at 303 K. The coupons were retrieved after 2 h progressively for 10 h. The influence of temperature on the corrosion inhibition effect of different test solutions was carried out at 303–333 K maintained using a thermostated bath. The coupons were however, retrieved after 2 h of immersion. In each case, the retrieved coupons were washed thoroughly in 20% NaOH solution containing 200 g/L zinc dust with bristle brush, rinsed severally in distilled water, dried with warm air and then re-weighed. The weight loss, in grammes, was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions.

The corrosion rate (CR) (mpy) in the absence and presence of inhibitor was calculated using Eq. (1):

$$CR(\text{mpy}) = \frac{3.45 \times 10^6 \times W}{\rho A T} \quad (1)$$

where CR is the corrosion rate, W is the average weight loss (g), ρ is the density of metal specimen (g cm^{-3}), A is the surface area of the specimen (cm^2) and T is the exposure time (h). The inhibition efficiency (η%) of PPG and PPG + KI respectively was evaluated from Eq. (2):

$$\eta(\%) = \left(1 - \frac{CR_1}{CR_0}\right) \times 100 \quad (2)$$

where CR_o and CR_1 are the weight losses of the coupons in the absence and presence of inhibitor, respectively, in the 0.5 M H_2SO_4 solutions at the same temperature.

Electrochemical measurements

The electrochemical impedance spectroscopy (EIS) experiments were performed using a VERSASTAT 400 complete dc voltammetry and corrosion system, with V3 Studio software. Potentiodynamic polarization (PDP) linear polarization resistance (LPR) experiments were carried out using Gamry potentiostat/galvanostat/ZRA (Reference 3000) embedded with Gamry framework system composed of ESA410 with DC105 software application and Echem Analyst 6.0 for data fittings. A conventional three-electrode Pyrex glass cell was used for the experiments. Test coupons with 1 and 0.7855 cm^2 exposed areas for EIS and polarizations measurements respectively were used as working electrode and a graphite rod as counter electrode. The reference electrode was a saturated calomel electrode (SCE), which was connected via a Luggin's capillary for EIS experiments. The test electrolyte was 0.5 M solution of H_2SO_4. All experiments were undertaken in stagnant aerated solutions at 303 K. The working electrode was immersed in a test solution for 1 h until a stable open circuit potential was attained. Potentiodynamic polarization studies were performed in the potential range ±250 mV versus open circuit potential (E_{corr}) at a scan rate of 0.5 mV/s. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (I_{corr}). Electrochemical impedance spectroscopy (EIS) measurements were made at corrosion potential E_{corr} over a frequency range of 100 kHz–100 mHz, with a signal amplitude perturbation of 10 mV. Spectra analyses were performed using

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