ORIGINAL ARTICLE

Polyvinyl alcohol–sulphanilic acid water soluble composite as corrosion inhibitor for mild steel in hydrochloric acid medium

M. Srimathi *, R. Rajalakshmi, S. Subhashini

Department of Chemistry, Avinashilingam University for Women, Coimbatore 641 043, India

Abstract   The inhibitive action of synthesised polyvinyl alcohol–sulphanilic acid (PVASA) composite on the corrosion of commercial mild steel in 1 M HCl medium has been investigated by weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopic (EIS) methods. Characterization of PVASA composite has been carried out using Fourier transform infrared spectroscopy (FTIR). Experimental results reveal that PVASA composite acts as an inhibitor in the acid environment. The inhibition efficiency increases with an increase in the concentration of the inhibitor. Maximum inhibition efficiency of PVASA composite was found to be 84% at 6000 ppm. Thermodynamic and kinetic parameters have been obtained from temperature studies. Electrochemical measurement reveals that PVASA composite acts as a mixed inhibitor and the adsorption follows Langmuir adsorption isotherm.

© 2010 Production and hosting by Elsevier B.V. on behalf of King Saud University.

1. Introduction

Corrosion is a serious environmental problem in the oil, fertilizer, metallurgical and other industries (Eddy and Mamza, 2009; Eddy, 2009, 2010; Aytac et al., 2005). Valuable metals, such as mild steel, aluminum, copper and zinc are prone to corrosion when they are exposed to aggressive media (such as, acids, bases and salts) (Ebenso et al., 2009; Odoemelam et al., 2009; Odiongenyi et al., 2009). Therefore, there is a need to protect these metals against corrosion. The use of inhibitors has been found to be one of the best options available for the protection of metals against corrosion (Eddy et al., 2009a). The most efficient corrosion inhibitors are organic compounds containing electronegative functional groups and π electrons in their triple or conjugated double bonds (Emregu et al., 2006). The initial mechanism in any corrosion inhibition process is the adsorption of the inhibitor on the metal surface (El Ashry et al., 2006; Eddy et al., 2009b; Khaled, 2008; Xia et al., 2008). The adsorption of the inhibitor on the metal surface can be facilitated by the presence of hetero atoms (such as N, O, P and S) as well as an aromatic ring. The inhibition of the corrosion of metals

* Corresponding author. Tel.: +91 9942460747.
E-mail addresses: srimathichem@gmail.com (M. Srimathi), raji_adu@yahoo.com (R. Rajalakshmi), subhashini_adu@yahoo.com (S. Subhashini).

can also be viewed as a process that involves the formation of a chelate on the metal surface, which involves the transfer of electrons from the organic compounds to the surface of the metal and the formation of a coordinate covalent bond. In this case, the metal acts as an electrophile while the nucleophilic centre is in the inhibitor.

Polymers find applications as effective corrosion inhibitors for steel (Olivares et al., 2006). The use of polymers as corrosion inhibitors have drawn considerable attention recently due to their inherent stability and cost effectiveness. Owing to the multiple adsorption sites, polymeric compounds adsorb more strongly on the metal surface compared with their monomer analogues (Ali and Saeed, 2001). Therefore, it is expected that the polymers will be better corrosion inhibitors.

The Literature reveals that a wide range of polymeric compounds have been successfully investigated as potential inhibitors for the corrosion of metals in aggressive media. Polymers such as polyethylenimine and polyvinylpyrrolidone, poly(o-phenylenediamine), polyanthranilic acid, polyacrylic acid, polyvinyl pyridine and polyvinylpyrrolidone, maleic anhydride and N-vinyl-2-pyrrolidone, polyamino-benzoquinone, polyvinyl alcohol, and polyethylene glycol have been reported (Schweinsberg et al., 1996; Abd El Rehim et al., 2010; Shukla et al., 2008; Amin et al., 2009; Mostafa Abo El-Khair, 1986; Achary et al., 2008; Muralidharan et al., 1995; Umoren et al., 2006a,b).

In continuation of our quest for developing corrosion inhibitors with high effectiveness and efficiency, the present paper aims at the utilization of oxidatively polymerized PVASA composite as corrosion inhibitor by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. The effect of temperature on corrosion and inhibition processes are thoroughly assessed and discussed. Thermodynamic parameters governing the adsorption process were also calculated and discussed. FTIR spectroscopic technique was used to reveal the formation of PVASA composite.

2. Experimental method

2.1. Chemicals and reagents

Ammonium per sulphate (APS), p-sulphanilic acid (p-amino-benzene sulphonic acid), polyvinyl alcohol (Mw = 14,000) from Merck chemicals.

2.2. Polyvinyl alcohol–sulphanilic acid composite preparation (PVASA composite)

A standard procedure was adopted to prepare polyvinyl alcohol–sulphanilic acid polymer composite (Trivedi, 1997; Gangopadhyay et al., 2001; Mirmohseni and Wallace, 2003). 1% p-Sulphanilic acid was well mixed with 10% polyvinyl alcohol solution. The system was cooled at 0–5 °C followed by the addition of 20 ml of aqueous oxalic acid solution of ammonium persulphate. Sulphanilic acid to ammonium persulphate mole ratio was maintained 1:1. Polymerization was allowed to proceed for 3 h. The polymer composite was formed. This was treated with ammonium hydroxide for deprotonation. The pH of this solution was kept around 9.0 by adding drops of 1 M NH_4OH and kept for 5 h. It was iso-

lated from the medium by precipitation technique using a non-polar solvent and dried under vacuum.

2.3. Weight loss methods

Weight loss measurements were carried out using a Denvar balance. The mild steel samples were obtained from a locally available industrial Fe–C steel with very low concentration of carbon. A large sheet of cold rolled mild steel coupons with a chemical composition of carbon 0.106%, manganese 0.196%, silicon 0.006%, phosphorus 0.027%, sulphur 0.016%, chromium 0.022%, molybdenum 0.003%, nickel 0.012% and iron 99.612% were utilized for the present study. The mild steel samples, with an active surface of 1×5 cm^2 were mechanically abraded, degreased, washed in double distilled water and dried in warm air.

The experiments were performed in 1 M HCl solution without inhibitor and in the presence of PVASA composite at different concentrations: 600, 1200, 1800, 2400, 3000, 3600, 4200, 4800, 5400 and 6000 ppm at various immersion times: 0.5, 1, 3, 6, 12, 24 and 48 h and at various temperatures 303, 313, 323, 333 and 343 K.

2.4. Electrochemical measurements

2.4.1. Polarization and impedance studies

The experiments were performed in a classical three-electrode electrochemical cell. Mild steel specimen of 1 cm^2 area was used as the working electrode and platinum electrode as a counter electrode and saturated calomel electrode as a reference electrode. Prior to each experiment the working electrode surface was polished with emery paper. Solartron Electrochemical analyzer (model 1280B) interface with an IBM computer and corrware and z-plot corrosion software were used for data acquisition and analysis. For polarization and impedance studies the period of immersion was for 30 min. Polarization technique was carried out using corrware software from a cathodic potential of -0.1 V to an anodic potential of -1 V with respect to corrosion potential at a sweep rate 2 mV/s. AC signals of 10 mV amplitude and a frequency spectrum from 20 to 0.1 Hz were impressed and the Nyquist representation of the impedance data were analysed with Z view software.

2.5. FTIR spectra

To characterize the synthesized PVASA composite, the FTIR analysis of PVA, SA and PVASA were carried out (Fig. 1). The important peaks are assigned and discussed with references.

A broad and strong peak centred at 3291 cm^{-1} is due to the stretching vibrations of –OH group with strong hydrogen bonding of intra and inter types in PVA. This peak is found to be shifted to 3188 cm^{-1} in the PVASA composite (Chen, 2002). The adsorption peak at 2924 cm^{-1} assigned to –CH and –CH$_2$ asymmetric stretching vibrations in PVA has been shifted to 2972 and 2845 cm^{-1} in PVASA composite (Rajendran et al., 2004a). A peak at 1718 cm^{-1} associated with C=O stretching vibrations of PVA backbone is found to be shifted to a lower wave number in (1696 cm^{-1}) in the PVASA composite (Gandhi et al., 2011). The absorption peak due to –CH$_2$ bending observed in PVA at 1427 cm^{-1} is