CORROSION INHIBITION OF STAINLESS AND MILD STEEL BY IMIDAZOLIUM-BASED COMPOUNDS IN ACIDS

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Abstract

Inhibition of stainless and mild steel corrosion in 1 M HCl solution by 1-octyl-3-methylimidazolium bromide and 1-dodecyl-3-methylimidazolium bromide was investigated using electrochemical and weight loss methods. The qualitative surface analysis was carried out. The studied compounds showed appreciable inhibition efficiencies. Polarization measurements proved that they are mixed-type inhibitors with predominantly anodic action. The inhibition efficiency for mild steel is higher comparing with AISI 304 stainless steel. The Gibbs energy of adsorption was calculated by means of the Langmuir isotherm.

Keywords: Imidazolium-based compounds; corrosion inhibition; polarization curve; electrochemical impedance spectroscopy; stainless steel

1. INTRODUCTION

Corrosion prevention has received considerable attention in the past years due to the increased use of metals in all fields of science and technology. The utilization of organic inhibitors is a foremost corrosion prevention technique. Many of these agents are heterocyclic compounds containing polar groups such as -OH, OCH_3, -Cl, $-NO_2$, -CN, -C=N-, CH_3-, and $-NH_2$ can serve as adsorption centres using the lone pair of π electrons [1]. The adsorbed inhibitor molecules shield the metal surface from direct attack by corrosive ions. There are two main modes of adsorption - physisorption and chemisorption. Inhibition efficiency has often been assumed to depend on the strength of adsorption. Most studies also describe the inhibitive effectiveness on the basis of adsorption models that fit the experimental surface coverage [2], [3]. The more negative the Gibbs energy absorption derived from thermodynamics of the adsorption process, the higher the inhibition potential. The adsorption tendency depends on a number of molecular properties, including steric factors, electron density at donor atoms, planarity, aromacity, and π-orbital characters of the active/adsorption sites. The interaction between the inhibitor and metal surface can be estimated by means of several models. Quantum chemical calculations try to find the optimized structure of the inhibitors via the energy of the highest occupied and lowest unoccupied molecular orbitals. The charge distribution indicates the preferred sites for nucleophilic and electrophilic attack [4], [5] .Cluster model is focused on the geometry optimization [6]. The estimation of the inhibition efficiency can be also carried out via the presence of various functional groups [7]. An inhibitor molecule with large molecular area usually provides wider protective coverage for the metallic substrate compared to similar molecule with smaller molecular size. Excessively large size of a molecule can also be its weakness because of difficulty in fitting into a partially occupied site on metallic substrate due to steric hinderance between the incoming and already adsorbed molecules. The imidazolium based compounds constitute the most commonly used family of corrosion inhibitors in industrial applications. They are reported to show corrosion resistance on aluminium [8], copper [9], and mild steel [10], [11], [12], [13], [14]. Based on the good results with alkylimidazolium bromides in an acidic medium [15], this study is focused on the investigation of the inhibition efficiency of the 1-octyl-3-methylimidazolium bromide and the 1-dodecyl-3-methylimidazolium bromide for the stainless and mild steel in hydrochloric acid solution.

2. EXPERIMENTAL

2.1. Materials

AISI 304 stainless steel wire having composition (wt. %) of 0.05 C, 18 Cr, 8.4 Ni, 1.2 Mn, 0.8 Si, 0.03 S, 0.045 P, 0.7 Mo and balance Fe and a mild steel wire containing (wt. %) 0.1 C, 1.5 Mn, 0.9 Si, 0.03 S, 0.04 P and balance Fe were used for electrochemical studies. The specimens were abraded using various grades of emery papers, washed with distilled water, degreased in acetone and air-dried. The solutions were prepared by dilution of inhibitors in hydrochloric acid of 1000 mol m^{-3} concentration. Imidazolium-based compounds were prepared in the microwave reactor using alkylbromide and 1-butyl-3-methylimidazolium-bis(trifluoromethylsulphonyl)imide. 1-octyl-3-methylimidazolium bromide (C8) can be classified as an ionic liquid. 1-dodecyl-3-methylimidazolium bromide (C12) has similar properties but it is solid at 20°C.

2.2. Electrochemical measurements

All electrochemical measurements were carried out on Voltalab VM 40, Radiometer Analytical (France). A three-electrode electrochemical system was used with the steel wire as working electrode (0.4 cm^2), platinum wire as counter electrode and Ag / AgCl in 3 M KCl as reference electrode. All experiments were performed under atmospheric condition without stirring at 20 °C. Prior to the electrochemical measurements, a stabilization period of 45 min was allowed, which was proved to be sufficient to attain a quasi-equilibrium state for the open circuit potential (OCP) measurement. The potentiodynamic polarization curves were recorded in the potential range from −140 below to +140 mV above OCP at a scan rate of 1 $mV \cdot s^{-1}$ in the positive direction. The EIS measurements were carried out in a frequency range from 100 kHz to 100 mHz with an amplitude of 10 mV peak to-peak, using the AC signal at the OCP.

2.3. Weight loss measurements

Gravimetric measurements were performed with the samples prepared in the same way as the working electrode. The wires weighing about 0.2 g were immersed into the 1000 mol m^{-3} HCl solution (20 ml) with or without the inhibitor for seven days and the weight loss was determined. The inhibition efficiency for the weight loss measurements was calculated from the equation (1), where WL^0 is the weight loss in 1000 mol m^{-3} HCl solution and WL^i is the weight loss in the presence of the inhibitor.

$$IE_{WL} = \frac{WL^0 - WL^i}{WL^0} x100 \qquad (1)$$

2.4. Surface analysis

The surface analysis was carried out using a scanning electron microscope QUANTA 450 FEG EDX, equipped with the EDX analyzer. The snaps were acquired in the secondary electrons mode.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization curves and electrochemical impedance spectroscopy

The electrochemical parameters as corrosion potential E_{cor} (mV), corrosion current density i_{cor} (mA / cm^2), cathodic and anodic Tafel slopes β_c (mV) and β_a (mV) and polarization resistance R_p ($\Omega \bullet cm^2$) were calculated via the analysis tool incorporated in VM 40 software. The inhibition efficiency IE_i (%) was calculated from the following equation, where i^0 and i^i is the corrosion current density without and with the inhibitor:

$$IE_i = \frac{i^0 - i^i}{i^0} x100 \qquad (2)$$

Figures 1 and **2** present the polarization curves of mild and stainless steel in 1000 mol m^{-3} HCl (1 M HCl in the Figures) solution containing 1-dodecyl-3-methylimidazolium bromide. It can be seen that the corrosion potential is shifted slightly to the positive direction depending on the inhibitor concentration. The results for 1-octyl-3-methylimidazolium bromide were similar. Because the difference is less than 85 mV, both compounds can be classified as mixed type inhibitors with a predominant anodic action [12]. These results suggest that they can retard both the oxidation of the oxide-free iron and the discharge of the hydrogen ions to produce hydrogen gas on the metal surface. Both anodic and cathodic current densities are always lower in the presence of ILs. While anodic current densities decrease with increasing inhibitor concentration, especially for AISI 304, cathodic current densities exhibit the opposite trend. The inhibition efficiency increases with the inhibitor concentration and it is higher for mild steel than for AISI 304 stainless steel (**Figure 3**). There are not significant differences between C8 and C12. These experiments suggest that additional elongation of the alkyl chain is counter-productive because of difficulty in fitting into a partially occupied site on metallic substrate due to steric hinderance between the incoming and already adsorbed molecules.

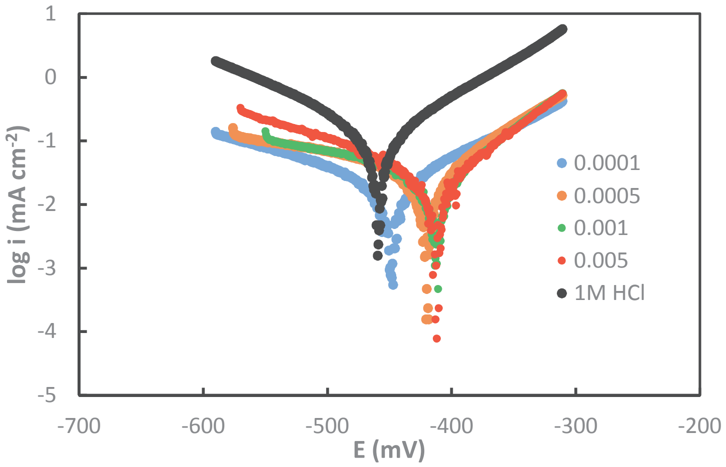

Figure 1 Potentiodynamic polarization curves of corrosion inhibition of mild steel in 1 M HCl in the absence and presence of 1-dodecyl-3-methylimidazolium bromide

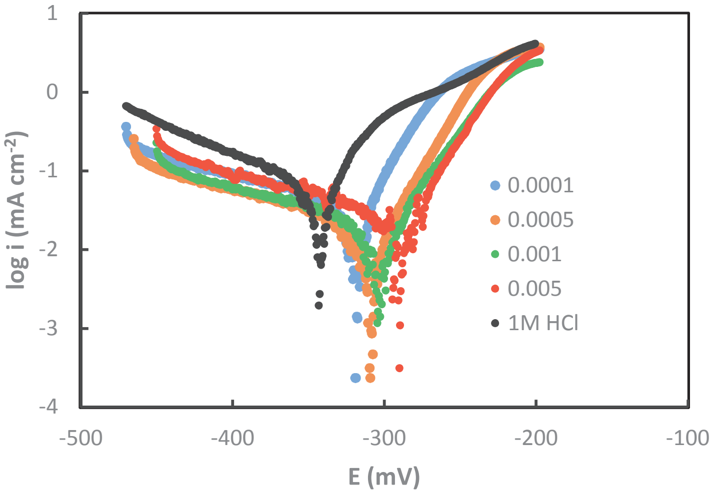

Figure 2 Potentiodynamic polarization curves of corrosion inhibition of AISI 304 stainless steel in 1000 mol m^{-3} HCl in the absence and presence of 1-dodecyl-3-methylimidazolium bromide

The Bode plots obtained from the EIS measurements in the absence and presence of 5 mol m^{-3} C12 are presented in **Figure 4**. The impedance spectrum of mild steel in the presence of C12 exhibits two time constants and a new phase angle shift and suggests the protective film formation. The impedance of the mild steel in the presence of the inhibitor in the low frequency region is higher than that of the AISI 304 stainless steel.

3.2. Surface analysis, weight loss measurements and adsorption isotherms

Figure 5 shows the surface of AISI 304 stainless steel after 7 days immersion in 1000 mol m^{-3} HCl solution and in 1 mol m^{-3} 1-dodecyl-3-methylimidazolium bromide solution. The surface in the presence of the inhibitor is less damaged than in 1000 mol m^{-3} HCl solution. The inhibition efficiencies calculated from the weight loss measurements for mild steel were slightly higher than those obtained from polarization curves (79 - 98%), while those for AISI 304 stainless steel were lower (30 - 60%). The inhibition efficiency can change with time and this problem is the subject of the present investigation.

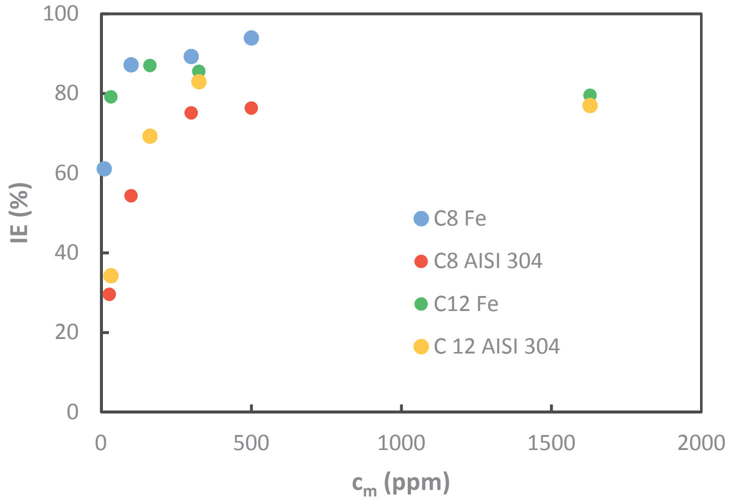

Figure 3 Inhibition efficiencies obtained from polarization curves for mild steel and AISI 304 stainless steels using 1-octyl-3-methylimidazolium bromide and 1-dodecyl-3-methylimidazolium bromide

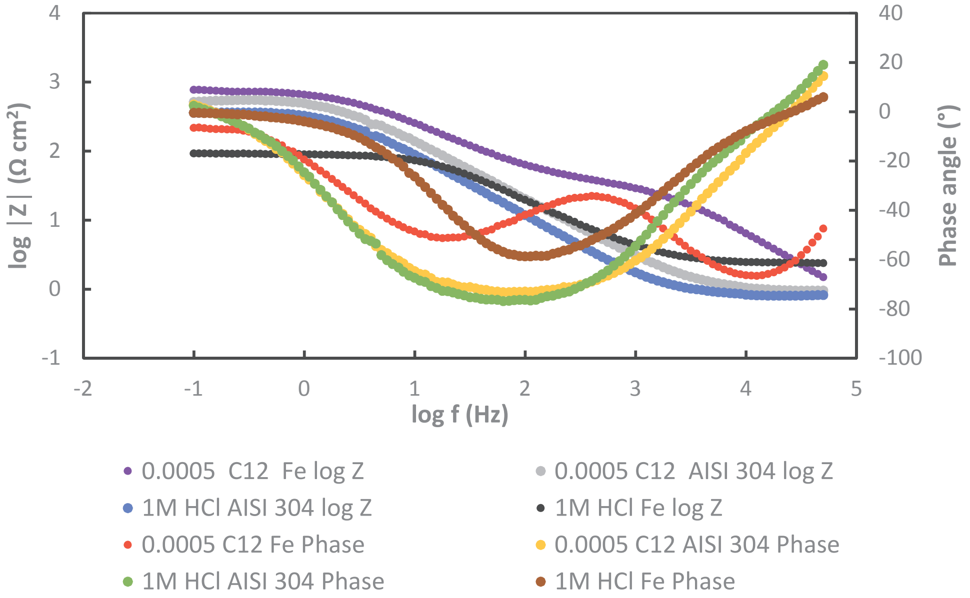

Figure 4 Bode plots of corrosion inhibition of mild and stainless steel in 1000 mol m^{-3} HCl in the presence and absence of 1-dodecyl-3-methylimidazolium bromide

The action of an inhibitor in aggressive acid media is assumed to be due to its adsorption at the metal/solution interface. Gibbs energy of adsorption represents the strength of adsorption or desorption between adsorbate and adsorbent. It has been reported [12] that the values of ΔG_{ads}^0 around -20 kJ / mol and lower indicate electrostatic interaction between charged metal surface and charged organic molecules in the bulk (physisorption process), while those around -40 kJ / mol or higher involve charge sharing or charge transfer (chemisorption process). The values of surface coverage, Θ (IE / 100) for the different concentration of 1-alkyl-3-methylimidazolium bromides proved to fit Langmuir adsorption isotherm (3). *C* is he molar concentration of the inhibitor and *K* is the equilibrium constant of the adsorption reaction (**Figure 6**). Linear dependences were obtained both for electrochemical and for weight loss measurements. The absolute values of Gibbs energies range from 30 to 40 kJ / mol. The interaction between the inhibitor and metal surface probably involves both physisorption and chemisorption.

$$\frac{c}{\theta} = c + \frac{1}{K} \qquad (3)$$

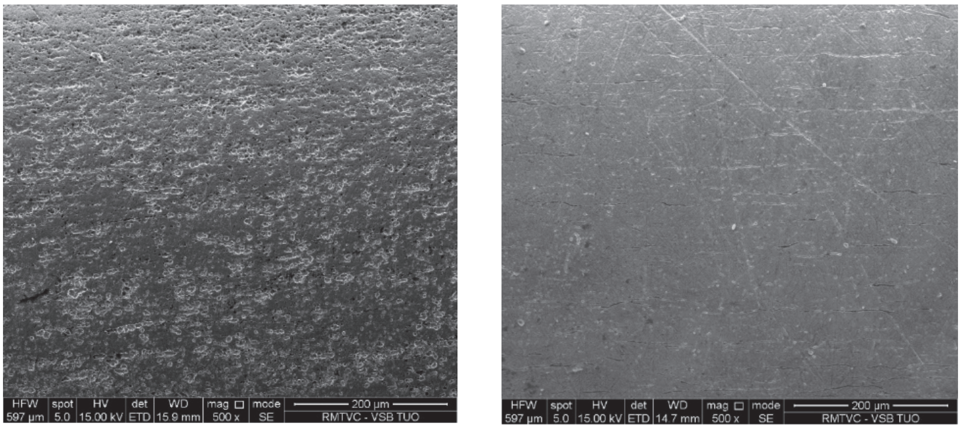

Figure 5 SEM analysis of AISI 304 stainless steel after 7 days immersion in 1000 mol m^{-3} HCl solution and in 1 mol m^{-3} 1-dodecyl-3-methylimidazolium bromide solution.

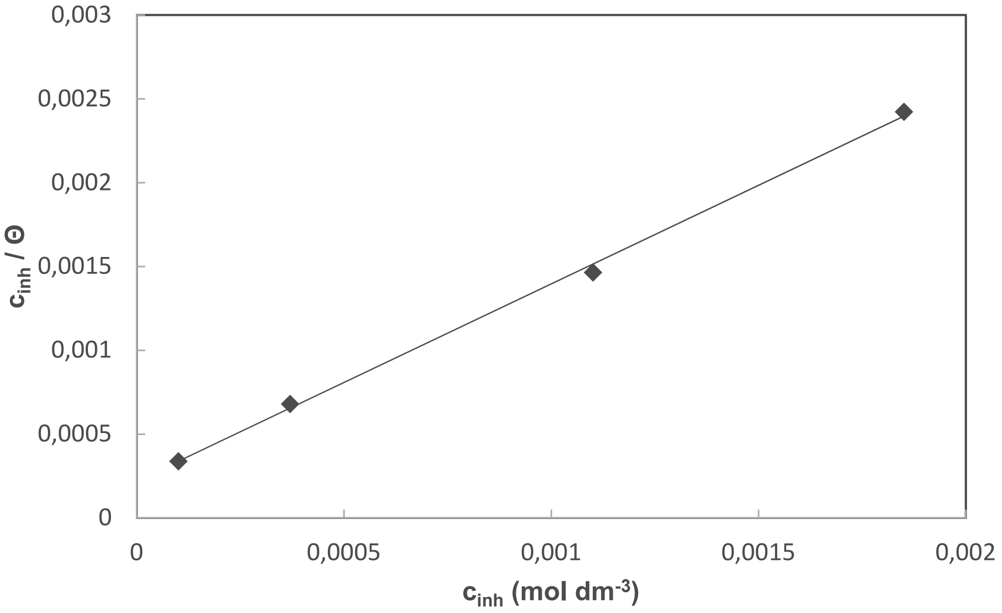

Figure 6 Curve fitting of the data obtained from polarization curves to Langmuir isotherm for AISI 304 in 1000 mol m^{-3} HCl and 1-octyl-3-methylimidazolium bromide

4. CONCLUSION

1-octyl-3-methylimidazolium bromide and 1-dodecyl-3-methylimidazolium bromide proved to be mixed-type inhibitors with predominant anodic inhibitive effect. The inhibition efficiency increases with the inhibitor concentration and it is higher for mild steel than for AISI 304 stainless steel. The values are higher than 80% for high inhibitor concentration for mild steel and 70-80% for AISI 304 stainless steel. There are not significant differences between C8 and C12. These experiments suggest that additional elongation of the alkyl chain is counter-productive because of difficulty in fitting into a partially occupied site on metallic substrate due to steric hinderance between the incoming and already adsorbed molecules. In the presence of low concentrations of 1-octyl-3-methylimidazolium bromide and 1-dodecyl-3-methylimidazolium bromide, mild steel has a higher polarization resistance and lower corrosion current density than AISI 304.The absolute values of Gibbs energies obtained from the Langmuir isotherm range from 30 to 40 kJ / mol. The interaction between the inhibitor and metal surface probably involves both physisorption and chemisorption.

ACKNOWLEDGEMENTS

This work was financially supported by the Ministry of Education, Youth and Sports of the Czech Republic in the "National Feasibility Program I", project LO1208 "TEWEP" and by Ministry of Industry and Trade, project TRIO FV10089, and by the project of Specific research : SP 2018/79.

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