ALKYLIMIDAZOLIUM BROMIDES AS CORROSION INHIBITORS FOR MILD STEEL IN ACIDIC MEDIUM

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Abstract

Inhibition of mild steel corrosion in 1 M HCl solution by alkylimidazolium bromides was investigated using electrochemical and weight loss methods. The studied ionic liquids showed appreciable inhibition efficiencies. Polarization measurements proved that the studied ILs are mixed-type inhibitors with predominantly anodic inhibition. The inhibition efficiency increased with the ionic liquid concentration and with the length of the alkyl chain. The values obtained from the polarization curves and Nyquist plots are in good agreement. The highest inhibition efficiency reached for the 1-octyl-3-methylimidazolium bromide was 93%. The Gibbs energy of adsorption was calculated by means of the Flory-Huggins isotherm and El Awady Thermodynamic-kinetic model.

Keywords: Alkylimidazolium bromides, corrosion inhibition, polarization curve, electrochemical impedance spectroscopy, hydrochloric acid

1. INTRODUCTION

The use of corrosion inhibitors is one of the most practical and economical methods of protecting metals. Ionic liquids are among the compounds that have been gaining increasing popularity in corrosion inhibition studied in the recent time. They often have a low vapour pressure and good thermal stability, so some of them belong among the environmentally friendly substances; nevertheless their toxicity must be verified yet. The action of an inhibitor is assumed to be due to its adsorption at the metal/solution interface via electrostatic attraction between the charged metal and charged inhibitor molecules, dipole-type interaction between unshared electron pairs in the inhibitor with the metal, Π-interaction with the metal or via combination of all of the above [1]. If the absorption process involves charge sharing or charge transfer from the inhibitor molecule to the surface, a coordinate-type bond is formed and the process is termed chemisorption. The main factors affecting the inhibition efficiency are the presence of the active centres with the high electron density (particularly heteroatoms such as O, N, S), and the length of the alkyl chain [2, 3,]. Despite the large amount of ILs known, the imidazolium based compounds constitute the most commonly used family of ILs in industrial applications. They are reported to show corrosion resistance on aluminium [4], copper [5], and mild steel [6 - 11]. The inhibition efficiency of various ILs based on methylimidazolium was higher than 92 % at 500 ppm. 1-ethyl-3-methylimidazolium ethylsulphate proved to be a very good inhibitor for mild steel in 1 M HCl. The aim of this study was to determine the inhibition efficiency of 1-alkyl-3-methylimidazolium bromides for mild steel in 1 M HCl solution at 20 °C, ΔG^0_{ads} and the mechanism of the adsorption reaction via the electrochemical and weight loss measurement.

2. EXPERIMENTAL

2.1. Materials

Mild steel wire having composition (wt. %) of 0.1 C, 1.5 Mn, 0.9 Si, 0.03 S, 0.04 P and balance Fe was 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 ILs in hydrochloric acid of 1 M concentration. Ionic liquids were prepared in the microwave reactor using alkylbromide and 1-butyl-3-methylimidazolium-bis(trifluoromethylsulphonyl)imide.

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 mild 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 −130 below to +130 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 0.22 g were immersed into the 1M HCl solution (25 ml) with or without the inhibitor for seven days. After the experiment, the oxide layer was removed and the weight loss was determined.

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 and β_a and polarization resistance R_p (Ω cm^2) were calculated via the analysis tool incorporated in VM 40 software. The corrosion rate was expressed as the penetration depth h (mm / year) from the equation (1), where ρ is density (g / cm^3), z number of exchanged electrons and M molar weight (g / mol) of iron:

$$h = 3.27 \cdot i_{cor} \cdot \frac{M}{z\rho} \tag{1}$$

The inhibition efficiency (%) was calculated from the following equation, where h^0 and h^i is the penetration depth without and with the inhibitor:

$$IE_h = \frac{h^0 - h^i}{h^0} x100 \tag{2}$$

It can be seen in the **Figure 1** that the corrosion potential is shifted slightly to the positive direction comparing with HCl solution. The results for C4 and C8 were similar. Because the difference is less than 85 mV, 1-alkyl-3-methylimidazolium bromides can be classified as mixed type inhibitors with a predominant anodic action [8]. 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. Tafel slopes do not change monotonously with the inhibitor concentration (**Table 1**); hence the inhibitive effect can involve some changes in the mechanism of the corrosion reaction. A hydrogen generation was observed at 10 ppm C4 and C6. This fact could make the electrochemical measurement less authentic. The inhibition efficiencies calculated from the penetration depth can be seen in **Figure 2**. They increase with the increasing inhibitor concentration and with the length of the alkyl chain. The 1-octyl-3-methylimidazolium bromide exhibits a very good inhibition activity at 500 ppm - about 94% both for the polarization measurement and for the weight loss measurement.

The Nyquist plots obtained from the EIS measurements in the absence and presence of 100 ppm of 1-alkyl-3-methylimidazolium bromides are presented in **Figure 3**. The impedance spectra exhibit one semi-circular capacitive loop with one time constant. This indicates the corrosion is mainly controlled by a charge transfer process. The diameter of the capacitive loop increases with increasing inhibitor concentration and the length of the alkyl chain. This is an indication of the protective film formation. The charge transfer resistance R_{ct} (Ω cm^2), solution resistance R_s (Ω cm^2) and double-layer capacitance $\chi_{\delta\lambda}$ (μF cm^{-2}) were calculated via the analysis tool incorporated in the VM 40 software (**Table 1**). A common equivalent circuit with the solution resistance in series with the parallel combination of the charge transfer resistance and double layer capacitance was used. The inhibition efficiency was calculated from the ratio of the charge transfer resistances with and without the inhibitor. The measurement for 10 ppm of C4 and C6 was disturbed by the hydrogen generation and the corresponding values are rather unreliable. The inhibition efficiencies obtained from EIS are usually slightly lower than those from polarization curves.

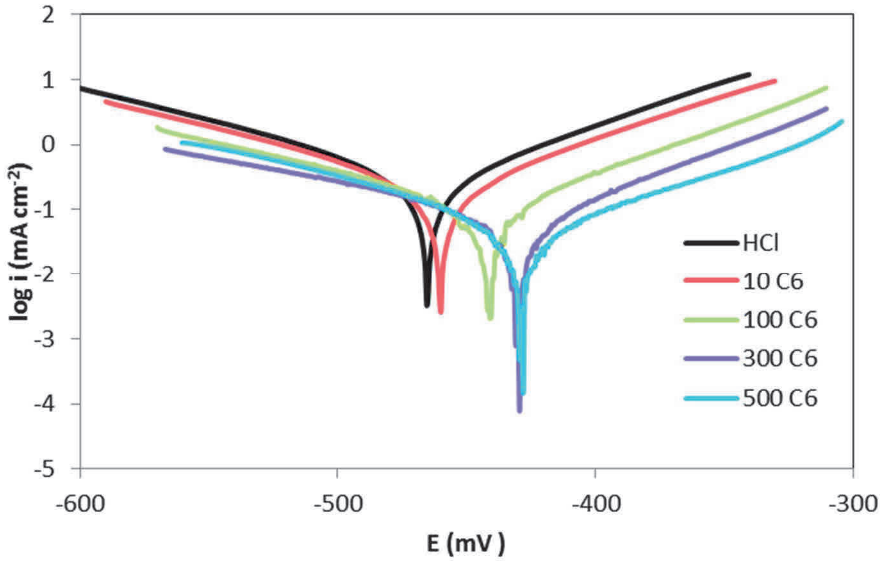

Figure 1 Potentiodynamic polarization curves of corrosion inhibition of mild steel in 1 M HCl in the absence and presence of 1-hexyl-3-methylimidazolium bromide

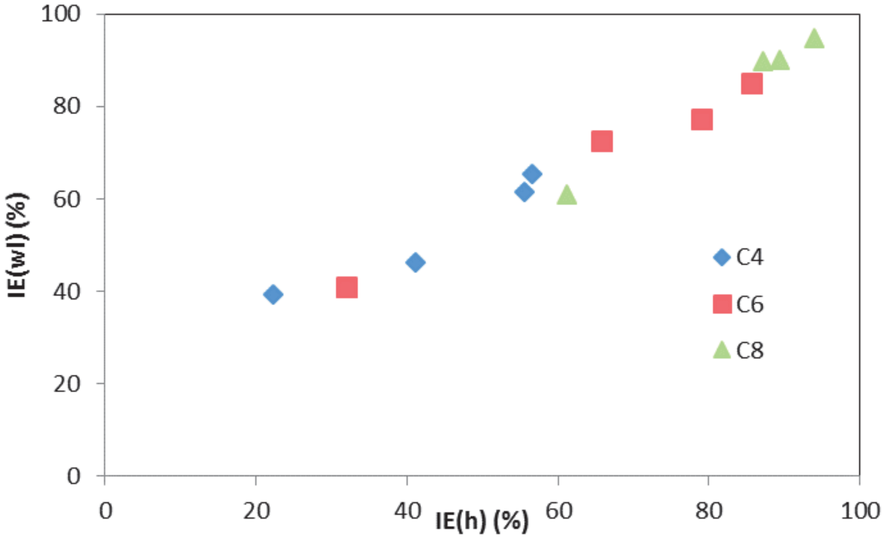

Figure 2 The inhibition efficiency from the weight loss measurements and penetration depth

Table 1 Electrochemical polarization and EIS parameters for mild steel in 1 M HCl solution in the absence and presence of 1-alkyl-3-methylimidazolium bromides at 20°C

	Concentration (ppm)	β_a (mV / dec)	$-\beta_c$ (mV / dec)	E_{cor} (mV)	c_{dl} (μF cm^{-2})	R_{ct} (Ω cm^2)	R_s (Ω cm^2)	IE_{EIS} (%)
	blank	77.5	103.4	-465	145	60.4	0.9	
C4	10	84.3	111	-455	182	54.2	0.9	-11.0
	100	92.3	101.8	-443	142	88.8	1.1	32.0
	500	73.5	108.9	-452	99	127.7	0.9	52.7
C6	10	74.8	92.2	-460	148	66.8	1.0	9.6
	100	71.5	103.7	-443	100	126.1	1.0	52.1
	500	80.4	83.9	-430	45	280.9	1.7	78.5
C8	10	79.9	124.2	-449	95	124.0	1.0	51.3
	100	121.2	212.8	-437	56	632.7	0.7	90.5
	500	89.4	174.8	-420	41	966.2	2.4	93.7

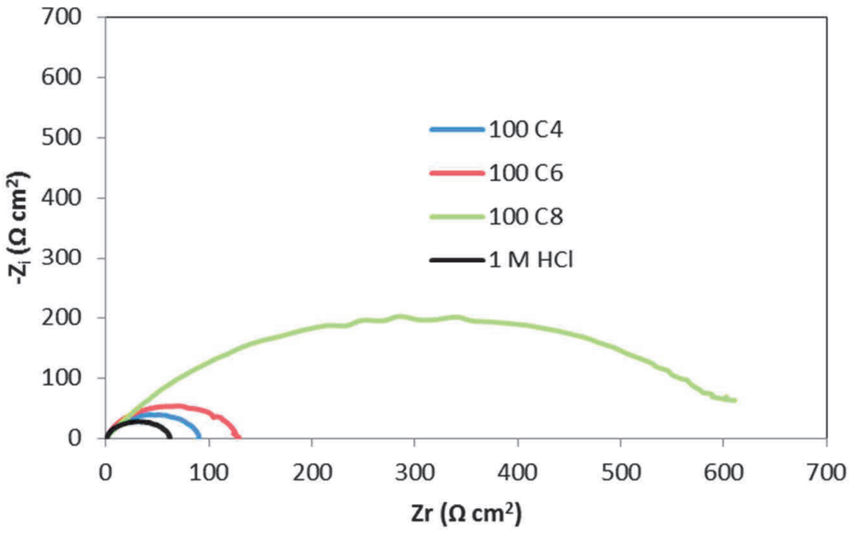

Figure 3 Nyquist plots of corrosion inhibition of mild steel in 1 M HCl in the absence and presence of 100 ppm of 1-alkyl-3-methylimidazolium bromides

3.2. Weight loss measurements

The inhibition efficiency for the weight loss measurements was calculated from the equation (3):

$$IE_{WL} = \frac{WL^0 - WL^i}{WL^0} x100 \qquad (3)$$

The relation between the efficiency obtained from the penetration depth and weight loss measurements can be seen in **Figure 2**. The solutions contained 10, 100, 300 and 500 ppm of 1-alkyl-3-methylimidazolium bromides and the inhibition efficiency increased with the increasing inhibitor concentration for every alkyl chain. The discrepancy between these two methods can be seen for 10 ppm of C4 and C6 because of the reasons mentioned above.

3.3. Adsorption isotherms

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 [8] 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 have been used to find the best adsorption isotherm. The experimental data fit Flory-Huggins adsorption isotherm [12]:

$$\log\frac{\Theta}{c} = \log K + x\cdot\log(1-\Theta) \qquad (4)$$

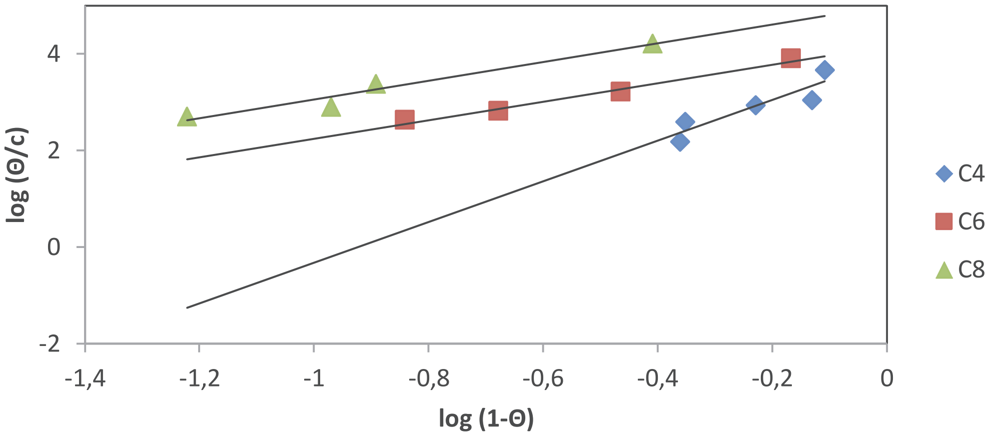

Figure 4 Curve fitting of the data obtained from polarization curves to Flory-Huggins isotherm at 20 °C

K is the equilibrium constant of the adsorption reaction, c is the inhibitor molar concentration and x is the size parameter (or a measure of adsorbed water molecules replaced by a given molecule of inhibitor. A linear dependence was found also for the thermodynamic-kinetic model [1], where 1/y =x and $K=K'^{(1/y)}$.

$$\log\frac{\Theta}{1-\Theta} = \log K' + y\cdot\log c \qquad (5)$$

Y is the number of inhibitor molecules occupying one active site. Curve fitting of data to Flory-Huggins isotherm are given in **Figure 4**. Gibbs energies and size parameters can be seen in **Table 2**.

Table 2 Gibbs energy of adsorption and inhibitor size parameters obtained from polarization curves

	Flory-Huggins isotherm		Kinetic-thermodynamic model	
	$-\Delta G_{ads}^0$(kJ / mol)	x	$-\Delta G_{ads}^0$ (kJ / mol)	y
C4	20.4	3.8	15.3	0.41
C6	22.4	1.9	20.7	0.64
C8	27.2	1.9	26.2	0.55

4. CONCLUSION

All the 1-alkyl-3-methylimidazolium bromides under investigation proved to be mixed-type inhibitors with predominant anodic inhibitive effect. The inhibition efficiency increases with the alkyl chain length and reaches

94% for 500 ppm of 1-octyl- 3-methylimidazolium bromide. A good data correlation was found as to the inhibition efficiency calculated from the penetration depth and weight loss except the low concentration of 1-butyl-3-methylimidazolium bromide, where the hydrogen evolution disturbing the electrochemical measurement was observed. Probably for the same reason, the inhibition efficiencies calculated from R_{CT} show even higher deviation from the weight loss and polarization experiments at the low inhibitor concentration because of the long EIS measurement duration. The data obtained for 1-hexyl-3-methylimidazolium bromide and 1-octyl- 3-methylimidazolium bromide fit well Flory-Huggins adsorption isotherm and El Awady thermodynamic-kinetic model, the data for 1-butyl 3-methylimidazolium bromide are closer to the Langmuir isotherm. The values of ΔG^0_{ads} for 1-butyl 3-methylimidazolium bromide ranging from -15- -20 kJ / mol indicate that the studied inhibitor molecules are mainly physisorbed onto the mild steel surface. The absolute values for 1-hexyl-3-methylimidazolium bromide and 1-octyl-3-methylimidazolium bromide are slightly higher than 20 kJ / mol. This fact probably means that the interaction between the inhibitor and metal surface involves both physisorption and chemisorption. The values calculated for 1-octyl- 3-methylimidazolium bromide are similar to the Gibbs energies obtained for mild steel in the sulphuric acid solution in [7].

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