ECOTOXICITY AND CORROSION INHIBITION EFFECT OF QUINOLONIUM AND IMIDAZOLIUM SALTS

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https://doi.org/10.37904/metal.2020.3535

Abstract

The corrosion inhibition of steel in the hydrochloric acid solution by N-butylquinolinium bromide and 1-octyl-3-methylimidazolium chloride was investigated using electrochemical and weight loss methods. Both compounds under investigation act as mixed type inhibitors with predominantly anodic action. The Gibbs energy of adsorption was calculated by means of the Langmuir isotherm. The inhibition efficiency of 1-octyl-3-methylimidazolium chloride was higher. *Daphnia magna* was used as acute toxicity test organism. 1-octyl-3-methylimidazolium chloride was more toxic than N-butylquinolinium bromide. The LC_{50} value (48 hours) for 1-octyl-3-methylimidazolium chloride for acute test on *Daphnia magna* was 0.020 $mg \cdot l^{-1}$ and it was 1.271 $mg \cdot l^{-1}$ for N-butylquinolinium bromide. 1-octyl-3-methylimidazolium chloride can be classified as extremely toxic substance (LC_{50} is 0.01-0.1 $mg \cdot l^{-1}$) and N-butylquinolinium bromide can be classified as moderate toxic substance (LC_{50} is 1-10 $mg \cdot l^{-1}$).

Keywords: Daphnia magna; N-butylquinolinium bromide; 1-octyl-3-methylimidazolium chloride; corrosion inhibition; steel

1. INTRODUCTION

Iron and its alloys belong to the most used building materials due to high mechanical strength and low costs. However, these materials are highly reactive and undergo corrosive degradation during various industrial processes, such as acid cleaning, descaling or acid pickling. Imidazolium compounds are widely studied as corrosion inhibitors for mild steel and other materials. The inhibition efficiency depends on the strength of adsorption. The more negative the Gibbs energy adsorption derived from thermodynamics of the adsorption process, the higher the inhibition potential. The great advantage of ionic liquids (ILs) is the possibility to manage their characteristics through diverse combinations of cations and anions. They exhibit low melting points, negligible vapour pressures, low flammability, high thermal and chemical stability, high electrical conductivity, and high solvation ability for organic and inorganic compounds [1-3]. Some of them are called green solvents but their toxicity has not been sufficiently examined yet. The toxicity of alkylimidazolium ionic liquids usually increases with the increasing alkyl chain length which seems to be related to the high lipophilic character. The anion type also plays an important role but the toxicity impact depends on the tested organism. Acute test on *Daphnia magna* is usually performed according to ISO 6341 (2012), to determine the inhibition of the mobility of *Daphnia magna Straus* (acute toxicity test). This is a very sensitive test and is very suitable for these ionic liquids solutions [4-6]. The aim of this study was to compare acute toxicity of N-butylquinolinium bromide and 1-octyl-3-methylimidazolium chloride and to evaluate corrosion inhibition of steel in the hydrochloric acid solution by this ILs.

2. EXPERIMENTAL

2.1. Materials

The mild steel wire containing (wt. %) 0.1 C, 1.5 Mn, 0.9 Si, 0.03 S, 0.04 P and balance Fe was used for corrosion measurements. The steel 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. Ionic liquids were prepared by the microwave synthesis.

2.2. Ecotoxicity tests

Ecotoxicity tests on *Daphnia magna* was done according to ISO 6341 (2012). *Daphnia magna* organism is a suitable bio-indicator for ecological risk assessments for different or new chemicals and compounds (EC 2002). Ecotoxicological data were calculated as LC_{50} values (lethal concentration - mortality of 50% of individuals), with 95% confidence intervals calculated by non-linear regression.

2.3. 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 −150 below to +150 mV above OCP at a scan rate of 1 mV·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 5 mV peak to-peak, using the AC signal at the OCP.

2.4. 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 several 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.

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

3. RESULTS AND DISCUSSION

3.1. Ecotoxicological tests

The results for acute *Daphnia magna* test for tested ionic liquids solutions after 48 hours, LC_{50} (in mg·l^{-1}), with 95% confidence intervals can be seen in **Table 1**. The C4QUINBr ionic liquid was less toxic than C8MImCl. According to the study [7], ionic liquid C4QUINBr is moderately toxic and C8MImCl is extremely toxic. For C4QUINBr the LC_{50} value for *Daphnia magna* (48 hours) is 1.271 mg·l^{-1} and for C8MImCl the LC_{50} value is 0.020 mg·l^{-1}. The nonlinear curves of mortality depending on the molar concentration of ionic liquids solutions are represented in **Figures 1-2**.

Table 1 Results for acute *Daphnia magna* test of ionic liquids solutions, 48 hours, LC_{50} ($mg \cdot l^{-1}$) and hazard ranking, 95% confidence intervals

Ionic liquids solutions	LC_{50} ($mg \cdot l^{-1}$)	Lower limit-upper limit ($mg \cdot l^{-1}$)	Hazard ranking+ (according to [7])
C8MImCl	0.020	0.011-0.029	extremely toxic
C4QUINBr	1.271	0.549-6.315	moderately toxic

+LC_{50} is 0.01-0.1 $mg \cdot l^{-1}$ – extremely toxic, 0.1-1 $mg \cdot l^{-1}$ - highly toxic, LC_{50} is 1-10 $mg \cdot l^{-1}$ - moderately toxic, LC_{50} is 10-100 $mg \cdot l^{-1}$ - slightly toxic and LC_{50} is 100-1000 $mg \cdot l^{-1}$ - harmless (non-toxic)

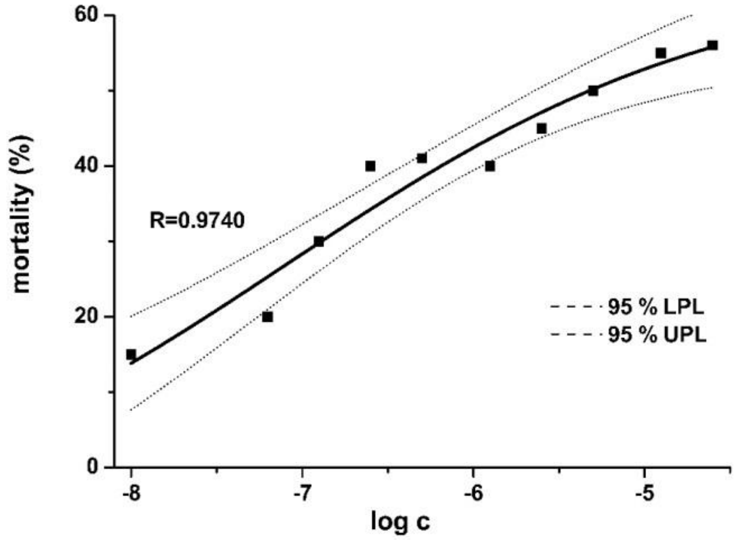

Figure 1 Nonlinear curves of mortality depending on concentration for C4QUINBr, acute *Daphnia magna* test, 48 h

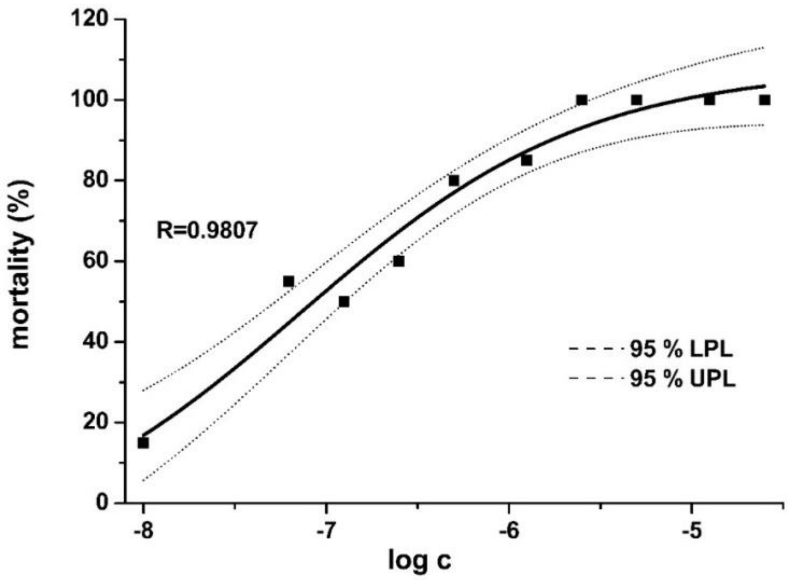

Figure 2 Nonlinear curves of mortality depending on concentration for C8MImCl, acute *Daphnia magna* test, 48 h

3.2. Potentiodynamic polarization curves and electrochemical impedance spectroscopy

Figure 3 presents potentiodynamic polarization curves of corrosion inhibition of mild steel in 1000 mol·m^{-3} HCl in the absence and presence of C4QUINBr. The corrosion potential is shifted slightly to the positive direction depending on the inhibitor concentration. Because of the difference is less than 85 mV, C4QUINBr can be classified as mixed type inhibitor with a predominant anodic action. The same trend can also be observed for C8MImCl. Inhibition efficiency (IE_i) is dependent on the inhibitor concentration, the values are reported in **Table 2**.

The EIS measurements were evaluated by means of EIS analyser software. **Figure 4** presents Nyquist plots of corrosion inhibition of mild steel in 1000 mol·m^{-3} HCl in the absence and presence of C4QUINBr. The values of inhibition efficiency (IE_{EIS}) obtained from EIS measurements are presented in **Table 2**. The differences between the voltammetric and EIS measurements can be explained by the unequal time of measurement.

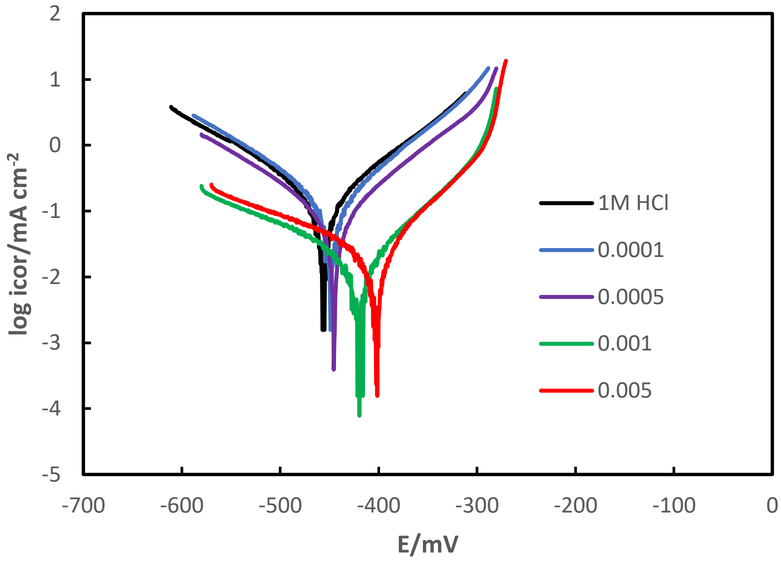

Figure 3 Potentiodynamic polarization curves of corrosion inhibition of mild steel in 1000 mol·m^{-3} HCl in the absence and presence of N-butylquinolinium bromide

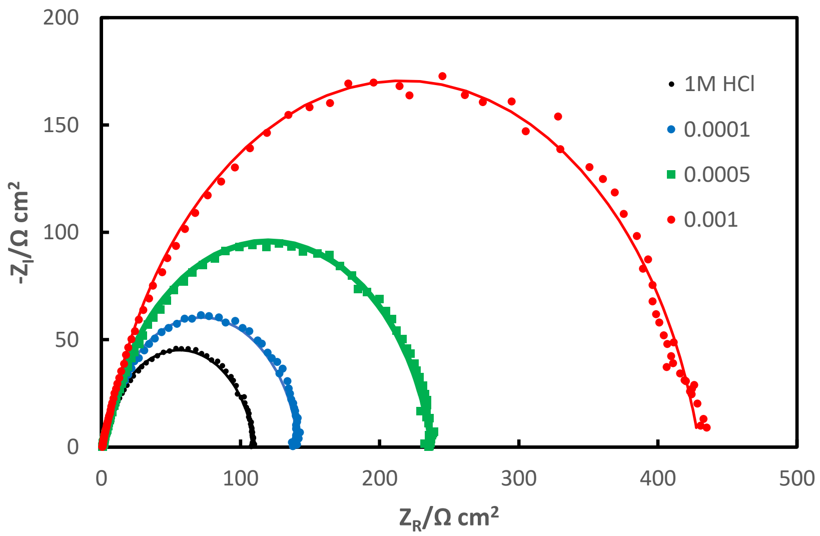

Figure 4 Nyquist plots of corrosion inhibition of mild steel in 1000 mol·m^{-3} HCl in the absence and presence of N-butylquinolinium bromide

Table 2 Inhibition efficiency for mild steel in 1000 mol·m^{-3} HCl solution in the absence and presence of N-butylquinolinium bromide and 1-octyl-3-methylimidazolium chloride at 20°C obtained from electrochemical measurements and weight loss measurements

	c (mol dm^{-3})	IE_i (%)	IE_{EIS} (%)	IE_{WL} (%)
C4QUINBr	0.0001	25	36	20
	0.001	89	79	66
	0.005	90	90	81
C8MImCl	0.0001	62	67	80
	0.001	86	92	96
	0.005	86	90	94

3.3. Weight loss measurements and adsorption isotherms

The results of the weight loss measurements (IE_{WL}) after seven days are shown in **Table 2**.

The adsorption of inhibitors never reaches the real equilibrium but tends to approach an adsorption steady state. The values of surface coverage, Θ (IE/100) for the different concentration of C4QUINBr and C8MImCl proved to fit Langmuir adsorption isotherm (2). *C* is the molar concentration of the inhibitor and *K* is the equilibrium constant of the adsorption reaction. The absolute values of Gibbs energies can be seen in **Table 3**. The interaction between the inhibitor and metal surface probably involves both physisorption and chemisorption. Although Langmuir isotherm is usually used for chemisorption, in case of monolayer physisorption can be involved.

$$\frac{c}{\theta} = c + \frac{1}{K} \tag{2}$$

The results obtained from the voltammetric and weight loss measurements can be seen in **Figure 5**.

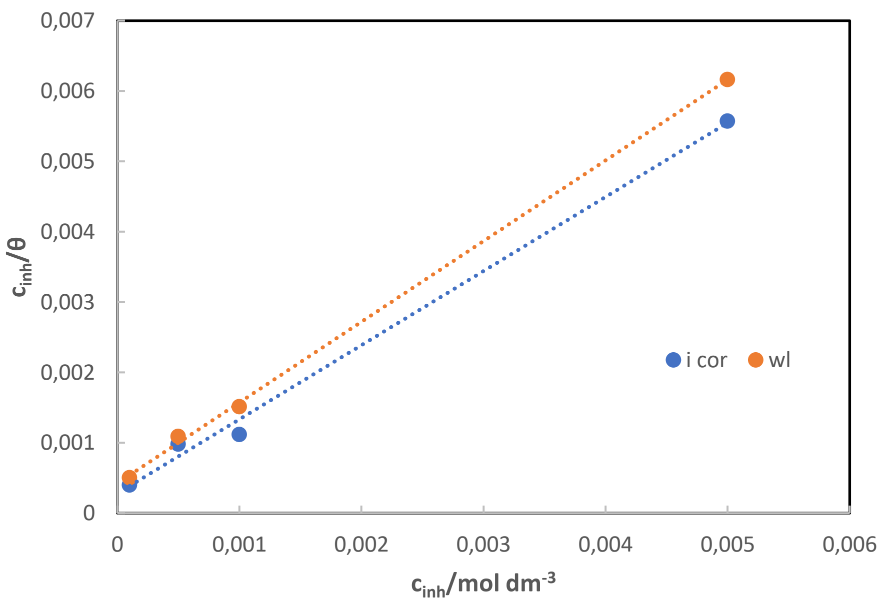

Figure 5 Curve fitting of the data obtained from polarization curves (i cor) and weight loss (wl) measurements to Langmuir isotherm for mild steel in 1000 mol·m^{-3} HCl and N-butylquinolinium bromide

Table 3 Gibbs energy of adsorption obtained from Langmuir isotherms (kJ·mol^{-1}).

	i_{cor}	wl
C4QUINBr	-29.5	-28.8
C8MImCl	-37.8	-35.1

4. CONCLUSION

The acute toxicity of N-butylquinolinium bromide and 1-octyl-3-methylimidazolium chloride was measured using *Daphnia magna Straus* test, 48 hours. It was found that C4QUINBr is moderately toxic and C8MImCl is extremely toxic. For C4QUINBr the LC_{50} value for *Daphnia magna* is 1.271 mg·l^{-1} and for C8MImCl the LC_{50} value is 0.020 mg·l^{-1}.

The corrosion inhibition efficiency of the C4QUINBr and C8MImCl was investigated by means of the potentiodynamic polarization curves, EIS and weight loss measurements. Both ionic liquids were proved to be mixed-type inhibitors with the predominant anodic inhibitive effect for the mild steel. The inhibition efficiency of both ionic liquids is about 90% for the highest concentration 5 mol·m^{-3}. The inhibition efficiency decreases with decreasing concentration of ionic liquid. A more significant decline can be seen for C4QUINBr. The absolute values of Gibbs energies of adsorption obtained from the Langmuir isotherms ranged from 28.8 to 29.5 kJ·mol^{-1} for C4QUINBr and from 35.1 to 37.8 kJ·mol^{-1} for C8MImCl. The interaction between the inhibitor and metal surface probably involves both physisorption and chemisorption.

ACKNOWLEDGEMENTS

This work was financially supported by the Ministry of Industry and Trade, project No. FV10089 Synthesis of ionic liquids in microwave reactor. Experimental results were accomplished by using Large Research Infrastructure ENREGAT supported by the Ministry of Education, Youth and Sports of the Czech Republic under project No. LM2018098. This work was also financed by the project of Specific research: SP 2018/79 and SP 2018/60.

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