Ionic Liquid-Modified Hydrophobic Layers for Enhanced Corrosion Inhibition

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Abstract

The aim of this study was to investigate the potential of the ionic liquid 1-methyl-3-n-octylimidazolium bis(trifluoromethanesulfonyl)imide (M3OITF), in combination with stearic acid (SA), to form self-assembled hydrophobic protective layers SAHL on AISI 316L stainless steel. The corrosion resistance of the resulting layers were evaluated in 1.0 M and 0.5 M HCl solutions using potentiodynamic polarisation measurements. Results show that immersing steel samples in ethanolic solutions of SA containing various concentrations of M3OITF leads to the formation of a hydrophobic layer that effectively suppresses anodic dissolution. Increasing the M3OITF concentration significantly decreased the anodic current density and enhanced inhibition efficiency. In 1.0 M HCl, inhibition efficiencies above 85% were achieved for all concentrations tested, while in 0.5 M HCl, efficiencies close to 99.9% were obtained. Contact angle measurements confirmed the hydrophobic nature of the modified surfaces, remaining above 105° even after five days of immersion in 0.5 M HCl. These findings demonstrate that M3OITF, when combined with stearic acid, can effectively form durable and highly efficient self-assembled anticorrosive coatings.

Keywords: *stainless-steel; HCl; ionic liquid; SAHL*

Introduction

The development of green chemistry and sustainable chemical engineering promotes the search for non-toxic substances and environmentally friendly technological solutions. In this context, ionic liquids (ILs) have emerged as a promising alternative to traditional, environmentally harmful organic corrosion inhibitors. ILs are salts composed of cations and anions with melting points below 100 °C. Their liquid state at room temperature results from weak electrostatic interactions between ions, caused by large, asymmetric ionic species that prevent the formation of an ordered crystalline structure. Due to these structural characteristics, ILs do not crystallise but remain liquid, enabling their efficient use as solvents or functional components in various applications, including corrosion inhibition. Ionic liquids possess several environmentally beneficial properties, such as non-toxicity, non-flammability, high stability across wide pH and temperature ranges, and very low vapour pressures, which significantly reduce evaporation into the environment and consequently limit air pollution by volatile compounds. Moreover, ILs serve as sustainable solvents for a wide variety of inorganic and organic compounds. They are anhydrous liquids with low oxygen content and a high concentration of ionic species. The cationic parts act as electron-accepting sites, while the electron-rich functional groups serve as adsorption centres during corrosion inhibition. The anion contributes to interfacial stabilisation throughout the adsorption process [1,2].

A key advantage of ionic liquids is their molecular tunability—they can be synthesised to possess specific, tailored properties. The appropriate selection of cations and anions allows adjustment of the structure and functionality of ILs according to the desired medium, material, or environmental requirements. In this way, their specificity, efficiency, and environmental compatibility can be optimised. Among the most efficient modern approaches for preparing such customised ionic liquids is microwave-assisted synthesis, which provides a rapid and energy-efficient process. Despite their

many advantages, the broader application of ILs is currently limited by their relatively high cost compared to conventional organic inhibitors [3,4].
The aim of this study was to investigate the use of the ionic liquid 1-Methyl-3-n-octylimidazolium bis(trifluoromethanesulfonyl)imide (M3OITF) in combination with stearic acid (SA) for the formation of self-assembled hydrophobic protective layer. The corrosive media used were 1.0 M HCl and 0.5 M HCl. The inhibition efficiency of the coatings was evaluated using the classical potentiodynamic method, while FTIR spectroscopy and scanning electron microscopy (SEM) were used to characterise the self-assembled layer.

Experimental

The conventional three-electrode configuration was used for the potentiodynamic studies. All potentials were measured against the saturated calomel electrode (SCE), and the counter electrode was platinum. Measurements were conducted within a potential range of ±300 mV relative to the open circuit potential (OCP), with a scan rate of 1 mV s^{-1}. Polarisation plots were obtained 60 minutes after the working electrode was immersed in the solution, allowing the stationary potential to stabilise. All experiments were performed at 25 °C ± 1 °C. Potentiodynamic curve measurements were taken after 1 hour of immersion and after 1, 2, 3, 4, and 5 days of testing. The measurements were performed using a Gamry 600™ potentiostat/galvanostat controlled by electrochemical software. Data were collected and analysed using CorrView and CorrWare software developed by Scribner Associates, Inc. The samples intended for the formation of self-assembled coatings were immersed in an ethanolic solution of 0.05 M SA containing varying amounts of the ionic liquid M3OITF: (0.05 M SA + 1.0% M3OITF), (0.05 M SA + 2.0% M3OITF), and (0.05 M SA + 5.0% M3OITF). The specimens designated for electrochemical measurements in 1.0 M HCl were kept in these solutions for 24 hours. The same procedure was applied to another set of samples subsequently exposed to a 0.5 M HCl solution, which were also immersed for 24 hours in freshly prepared solutions. After immersion, the steel samples were carefully removed from the solutions using tweezers and dried with compressed air, resulting in a functionalised self-assembled surface layer.

Results and discussions

Electrochemical results

Figures 1a-c show the current–potential curves of AISI 316L steel in 1.0 M HCl, modified with a self-assembled coating prepared by immersing the metallic samples in an ethanolic solution of 0.05 M stearic acid (SA) with the addition of x wt% of the ionic liquid M3OITF. Measurements were performed after different immersion times (1 h, 2 days, 3 days, 4 days, and 5 days). All polarisation curves display a distinct anodic peak, indicating the material's susceptibility and the presence of anodic dissolution in the corrosive medium. After surface functionalisation with the self-assembled coating, the area under the anodic peak decreased significantly, suggesting improved corrosion resistance and reduced anodic activity. The formation of a hydrophobic layer by immersion in the ethanolic SA solution containing M3OITF effectively reduced surface hydrophilicity and enhanced the protective performance of the coating. Increasing the M3OITF concentration further decreased the anodic current, confirming higher inhibition efficiency of the coating at greater mass fractions of the ionic liquid. The inhibition efficiency was calculated according to Equation 1, based on integration of the area under the anodic peak of each polarisation curve, by comparing the untreated sample with those protected by the self-assembled coating. The integration limits were defined within the potential range between the open-circuit potential (OCP) and –0.1 V vs SCE.

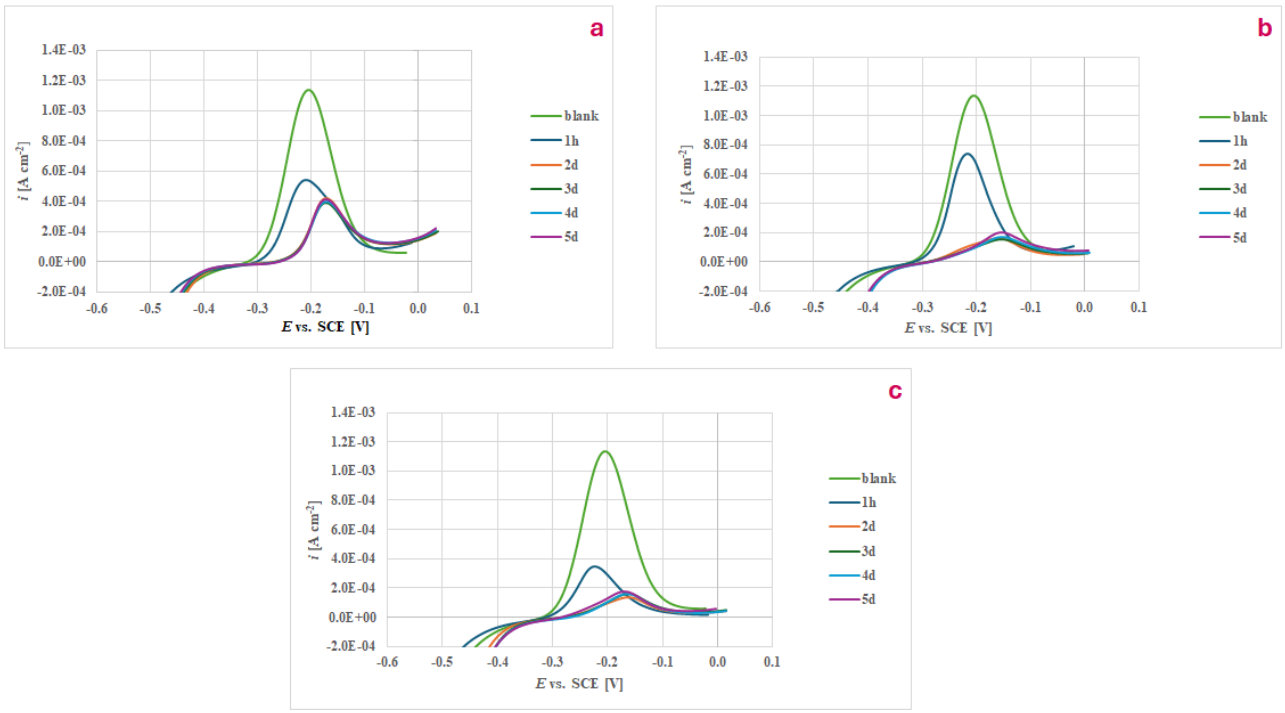

Figure 1. *Potentiodynamic polarisation curves (1 mVs^{-1}) of AISI 316L in 1.0 M HCl at 25°C, after 1h, after 2-, 3-, 4-, and 5-days duration test. a.) (0.05 M SA + 1.0% M3OITF), b.) (0.05 M SA + 2.0% M3OITF), c.) (0.05 M SA + 5.0% M3OITF).*

$$\eta_a = \frac{A - A'}{A} \cdot 100\% \qquad (1)$$

where:
η_a – inhibition efficiency of the anodic part
A – area under the curve of the unprotected sample surface
A' – area under the curve of the inhibited sample surface

Figure 2 shows that the self-assembled hydrophobic layers effectively inhibit the development and progression of anodic reactions after two days of immersion in the selected corrosive medium. The lowest addition of M3OITF forms a protective coating that inhibits dissolution of the steel sample by more than 70.0%. The two higher concentrations of ionic liquid achieve inhibition efficiencies above 85.0% in 1.0 M HCl. All three concentrations demonstrate the durability of the coatings even after five days, as there is no significant decrease in inhibition or increase in the area under the anodic peak. In addition, it can be concluded that a higher concentration does not result in a significant improvement in η.

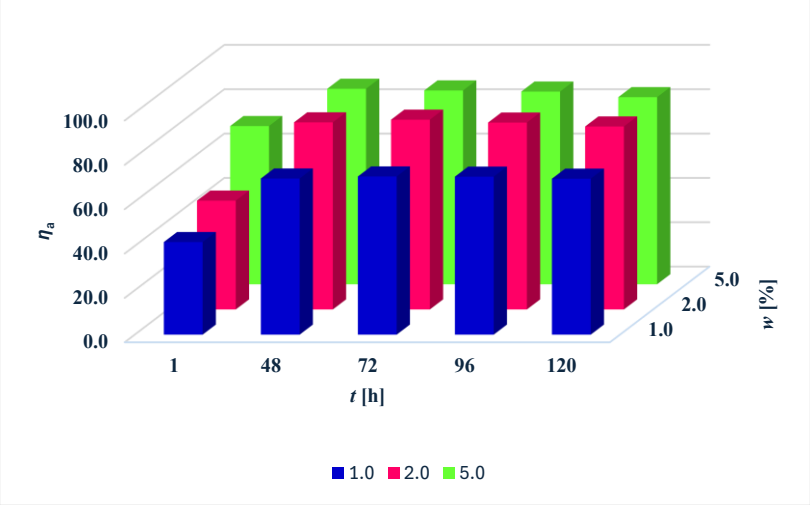

Figure 2. *Dependence of inhibitory effectiveness, determined from the charge involved in the surface anodic reaction, on time and concentration of M3OITF in 1.0 M HCl at 25°C, after 1h, after 2-, 3-, 4-, and 5-days duration test.*

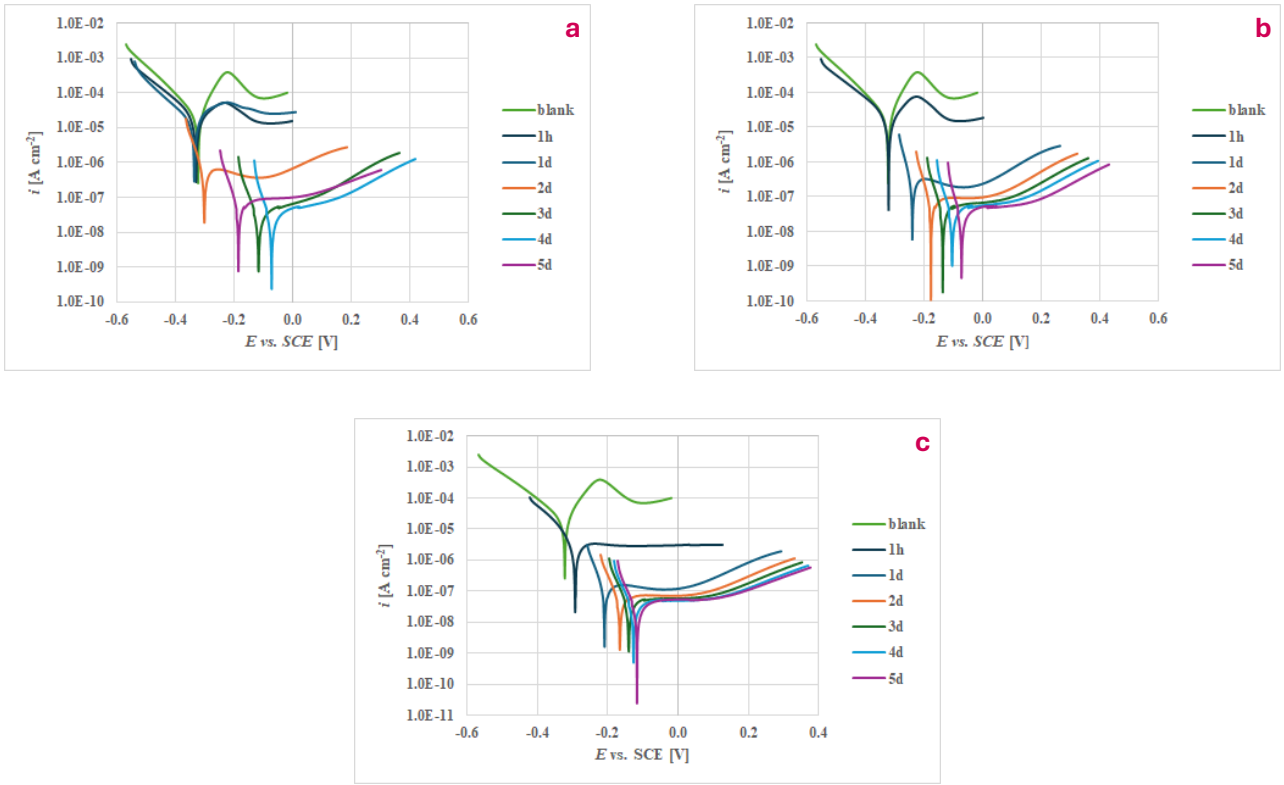

Figure 3. *Potentiodynamic polarisation curves (1 mVs^{-1}) of AISI 316L in 0.5 M HCl at 25°C, after 1h, after 1-, 2-, 3-, 4-, and 5-days duration test. a.) (0.05 M SA + 1.0% M3OITF), b.) (0.05 M SA + 2.0% M3OITF), c.) (0.05 M SA + 5.0% M3OITF).*

Table 1 presents the electrochemical parameters and the calculated inhibition efficiencies for three concentrations of M3OITF, which, together with SA, formed an anticorrosive self-assembled coating. The inhibitor concentrations were 1.0%, 2.0%, and 5.0%. The corrosive medium was 0.5 M HCl.

Table 1. Kinetic parameters for corrosion of SS AISI 316L obtained from potentiodynamic polarisation curves for the bare and modified surfaces in the 0.5 M HCl 25°C at

selected concentrations of M3OITF ionic liquid, after 1h, and after 1-, 2-, 3-, 4-, and 5-days duration test

time	β_C [V/dekada]	β_A [V/dekada]	i_{kor} [µA cm^{-2}]	R_p [kΩ cm^2]	E_{kor} [mV]	η_{ikor} [%]	η_{Rp} [%]
brez prevleke							
blank	0.133	0.077	26.96	0.746	-321.1	-	-
1.0 % M3OITF							
1h	0.145	0.225	21.17	1.167	-328.4	21.48	36.10
1d	0.134	0.128	13.22	1.328	-336.4	50.96	43.85
2d	0.045	0.488	0.512	24.37	-301.0	98.10	96.94
3d	0.047	0.157	0.022	534.0	-114.9	99.92	99.86
4d	0.042	0.139	0.018	612.4	-70.43	99.93	99.88
5d	0.043	0.271	0.050	210.5	-184.3	99.81	99.65
2.0 % M3OITF							
1h	0.146	0.155	20.20	1.178	-320.9	25.06	36.70
1d	0.032	0.165	0.195	40.6	-242.5	99.28	98.16
2d	0.034	0.226	0.055	154.6	-178.5	99.80	99.52
3d	0.038	0.201	0.033	272.0	-135.1	99.88	99.73
4d	0.039	0.142	0.024	375.2	-103.6	99.91	99.80
5d	0.035	0.150	0.021	410.1	-72.08	99.92	99.82
5.0 % M3OITF							
1h	0.067	0.457	2.53	6.469	-292.6	90.62	88.47
1d	0.035	0.207	0.095	93.17	-207.7	99.65	99.20
2d	0.039	0.269	0.044	222.8	-164.7	99.84	99.67
3d	0.041	0.182	0.030	335.3	-141.0	99.89	99.78
4d	0.041	0.169	0.024	412.0	-125.4	99.91	99.82
5d	0.039	0.147	0.021	461.5	-117.0	99.92	99.84

With 1.0% and 2.0% M3OITF incorporated into the self-assembled hydrophobic layer with stearic acid, we observed that one hour after exposure to 0.5 M HCl, there was almost no effect. However, with 5.0% M3OITF, an inhibition efficiency greater than 90.0% was achieved within one hour. As the inhibitor concentration increased, the time required for the coating to effectively suppress corrosion processes decreased. All concentrations of M3OITF reached similar inhibition efficiency values, around 99.9% (Fig.4). This indicates that the anticorrosive coating almost completely prevents corrosion of the metal sample.

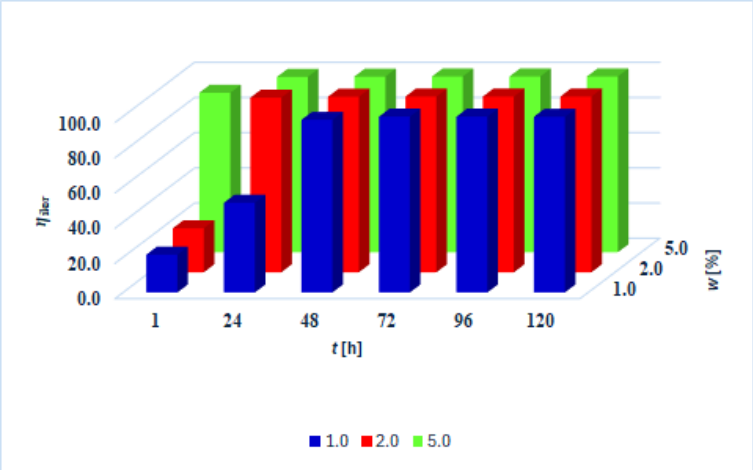

Figure 4. *Dependence of inhibitory effectiveness, on time and concentration of M3OITF in 1.0 M HCl at 25°C, after 1h, after 1-, 2-, 3-, 4-, and 5-days duration test.*

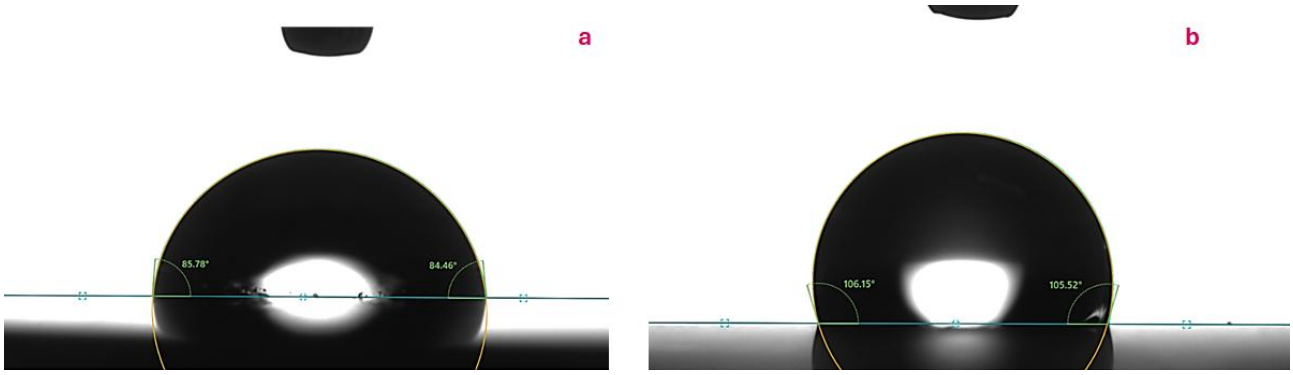

Figure 5. *a.) Contact angle of the polished sample surface of the AISI 316L, b.) Contact angle of the modified sample surface of the AISI 316L (0.05 M SA + 2.0% M3OITF).*

Figure 5a shows the measured contact angle of the polished surface of AISI 316L without a protective layer. As this angle is 85°, the sample surface exhibits hydrophilic properties. Figure 5b shows the measured contact angle of the SAHL coating containing 2.0% M3OITF after 5 days of immersion. After 5 days, the contact angle exceeds 105°, confirming that the surface of the modified sample retains its hydrophobic properties even after 5 days of immersion in 0.5 M HCl. This is also reflected in the high inhibition efficiency of over 99%.

Conclusions

- In 1.0 M HCl, the SAHL with M3OITF significantly reduced anodic dissolution, achieving inhibition efficiencies above 70% for 1.0% M3OITF and over 85% for 2.0% and 5.0% concentrations. The SAHL remained stable after five days of immersion.

In 0.5 M HCl, the SAHL showed superior performance. The 5.0% M3OITF layer achieved over 90% inhibition within one hour, while all concentrations reached efficiencies of around 99 % after five days, maintaining strong hydrophobicity (contact angle >105°).

- Overall, combining stearic acid with M3OITF enables the formation of durable, hydrophobic, and highly efficient anticorrosive self-assembled coatings for stainless steel in acidic environments.

Acknowledgements

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