Electrochemical studies on the corrosion resistance of mild steel in 1 M HCl solution before and after emulsion coating

N. Anitha,[1] A. Krishnaveni,[2] V. Prathipa,[3] S.S. Priya,[1] A.L. Jewelcy,[1] T.A. Arputha Anucia,[1] S.Parimala,[1] V.I. Jasmine,[1] V. Yuvarani,[1] M.V. Nivetha[1] and S. Rajendran[1,4]*

[1]PG Department of Chemistry, Corrosion Research Centre, St. Antony's College of Arts and Sciences for Women, Dindigul, 624005, India
[2]PG Department of Chemistry, Yadava College, Thiruppalai, Madurai, 625007, India
[3]Department of Chemistry, PSNA College of Engineering and Technology (Autonomous), Dindigul (Affiliated to Anna University), Chennai, India
[4]Adjunct Professor, Centre for Nanoscience and Technology, Pondicherry University, Puducherry, 605014, India
**E-mail: susairajendran@gmail.com*

Abstract

The corrosion resistance of mild steel immersed in 1 M HCl before and after coating of Durable exterior emulsion coating (Emulsion coating) has been evaluated by electrochemical studies such as polarization study and AC impedance spectroscopy. When a protective film (emulsion coating) is formed on metal surface, corrosion resistance of the metal increases and hence LPR value increases and corrosion current decreases. Similarly, when a protective film is formed on the metal surface, corrosion resistance increases, R_t values, impedance values and phase angle increase whereas C_{dl} values decrease. The study reveals that, after emulsion coating the corrosion resistance of mild steel in 1 M HCl increases because, the LPR value increases and corrosion current decreases as revealed by polarization study. It is also inferred from AC impedance spectra that when mild steel coated with emulsion coating is immersed in 1 M HCl the corrosion resistance of mild steel is increased. This is due to the fact that the emulsion coating on the mild steel is stable in the presence of 1 M HCl. The corrosion inhibition efficiency calculated from the charge transfer resistance values is found to be 99.99%. After emulsion coating corrosion resistance of mild steel increases, R_t values, impedance values and phase angle increase whereas C_{dl} values decrease. Electrochemical studies lead to the conclusion the mild steel tank used in pickling industry to store concentrated hydrochloric acid may be given a coat of emulsion coating to improve the life time of the mild steel tank in the pickling industry.

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Introduction

Paint is any pigmented liquid, liquefiable, or solid mastic composition that, after application to a substrate in a thin layer, converts to a solid film. It is most commonly used to protect, color, or provide texture. It has been used in the corrosion inhibition study also [1–10].

Cataphoretic deposition of an epoxy coating with the incorporation of Ti_3C_2Tx@Mg-Al layered double hydroxide for long-term active corrosion protection effect has been investigated by Li *et al.* [1]. The authors haveprovided a new way of using Ti_3C_2Tx MXene in the cathodic electrophoretic paint to prepare active anti-corrosive coating. Fourier transform infrared spectroscopy, X-ray diffraction, transmission electron microscope, scanning electron microscope, X-ray photoelectron spectroscopy, zeta (ζ) potentials test and UV-Vis spectroscopic analysis have been employed in this study [1]. Mamat *et al.* have investigated the "Anticorrosion performance of self-healing polymeric coating on low carbon steel substrates in 3.5 wt.% NaCl medium" [2]. The study revealed that the self-healing coating has sufficient corrosion resistance when compared to the coating without microcapsules [2]. Emad *et al.* have manipulated transport paths of inhibitor pigments in organic coating by addition of other pigments [3]. It was found that addition of soluble/sparingly soluble pigments into the organic coating results in increased leaching rate. This was attributed to the formation of clusters comprised of both the main inhibitor pigment and the additional pigment. The network of cavities and voids formed upon dissolution and removal of the soluble pigment introduces transport paths in the organic coating, and consequently, facilitated the leaching of the main inhibitor pigment [3]. Krishnan has explored the anti-corrosive activity of TP (*Thespesia populnea*)–TiO_2 composite coating for mild steel in aggressive environments. The proposed composite coating is unquestionably promising for industrial application and is also recommended by green protocols [4]. Griffiths *et al.* have investigated the contribution of Zn^{2+} and phosphate anions to the inhibition of organic coating cathodic disbondment on galvanized steel by zinc phosphate pigment. The most powerful inhibitory effect is obtained using in-coating Zn^{2+}, while ZnPhos pigments inhibit cathodic disbondment rather weakly and as such the principal function of phosphate is to control Zn^{2+} solubility [5]. Novel layered double hydroxides (LDHs) based coatings developed in-situ on aluminum alloys have been recognized by Fedel *et al.* to provide the substrate with improved corrosion protection. LDH layers have gained prominent attention due to their barrier properties and ions exchange capability, together with compositional flexibility and low environmental impact. The filiform inhibition was found to be qualitatively proportional to the pitting potential measured over the LDHs conversion layers [6]. Kavipriya *et al.* have studied the influence of a paint coating on the corrosion of hull plates made of mild steel in natural seawater. It is observed that after paint coating, the corrosion resistance of mild steel hull plates increases. Polarization study reveals that after paint coating, the linear polarization resistance increases and corrosion current decreases. AC impedance spectra reveal that in the presence of paint coating charge transfer resistance value increases, impedance value increases, phase angle increases and double layer capacitance value decreases. The corrosion resistance of mild steel (used to make hull plates in ship technology) in seawater before paint coating (Nippon paint, weather bond advance) and after paint coating has been measured by electrochemical studies such as Polarization study and AC impedance spectroscopy [7]. The current demand of the automotive industry for durable high-performance paints with self-healing ability and environmental compatibility has prompted Trentin *et al*. the research for the next-generation coatings. To achieve extended durability, the progress of smart coatings has been pursued, aiming to provide active protection after a corrosive or mechanical failure. Many approaches are used for developing smart/self-healing coatings, such as the addition of micro/nanocapsules containing organic or inorganic healing agents, vascular or shape memory polymers, polymers with reversible covalent bonds, and self-healing agents based on organic and inorganic compounds. The latter strategy, in particular, presents a brilliant cost-benefit and low complexity, making this approach very gifted for applications in the automotive industry [8]. Dorothy *et al*. proposed that the robots made of materials such as mild steel may also undergo corrosion when they come in contact with sea water, while in search. If a paint coating is given, it will control the corrosion of these proposed materials. Therefore this work is undertaken. Mild steel is coated with Asian guard red paint. Corrosion resistance of mild steel in 3.5% sodium chloride solution is calculated before coating and after coating by electrochemical studies such as polarization study and AC impedance spectroscopy. The corrosion inhibition efficiency obtainable by red paint to mild steel in 3.5% sodium chloride is 99.98% [9]. Zhang and Zhu have made a study on the synthesis of PANI/CNT (polyaniline/cabon nanotube) nanocomposite and its anticorrosion mechanism in waterborne coatings. The nanofibrous PANI/CNT nanocomposite benefits to form a conductive network in the organic coating, which determines the cathodic inhibition and the anodic passivation protection of PANI/CNT metal anticorrosion mechanism. This research provides a new idea for the preparation of environmentally friendly active anticorrosive materials [10].

The present work is undertaken to investigate the corrosion resistance of mild steel immersed in 1 M HCl before and after Emulsion coating. The corrosion resistance has been evaluated by electrochemical studies such as polarization study and AC impedance spectroscopy.

The findings will find applications in the pickling industry. Pickling is a metal surface treatment used to remove impurities, such as stains, inorganic contaminants, and rust or scale from ferrous metals, copper, precious metals and aluminum alloys. A solution called pickle liquor, which usually contains acid, is used to remove the surface impurities. It is commonly used to descale or clean steel in various steelmaking processes.

Experimental

Composition of mild steel

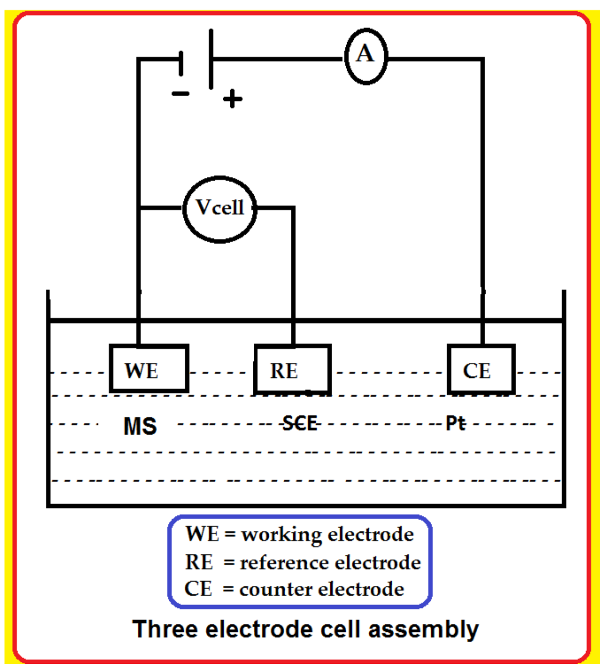
Mild steel with composition (wt.%) : C – 0.101%, Si – 0.055%, Mn – 1.629%, P –0.0087%, S – 0.0028, Fe – 97.74 and the rest being metals such as Cr, Ni, Cu *etc*., was used in the present study.

Duralife Asian paints

Exterior emulsions are water-based paints that offers protection for exterior masonry surfaces from the elements like sunlight, rainfall and algae/fungal attack (Duralife Asian paints) [11, 12]. This emulsion was used to coat on the mild steel surface. The effectiveness of this coating in 1 M HCl medium was measured by polarization study and AC impedance spectroscopy.

Potentiodynamic polarization study

In the present study, polarization studies were carried out in a CHI Electrochemical work station/analyzer, model 660 A. It was provided with automatic *iR* compensation facility. A three electrode cell assembly was used (Scheme 1).



Scheme 1. Three electrode cell assembly.

The working electrode was mild steel/coated mild steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode.

From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic = b_a and cathodic = b_c) and linear polarization resistance (LPR) were calculated. The experiment was carried out at room temperature. The details of the experimental set up are: the hold time (Start potential duration) at each frequency (s) = 0. Scan rate (V/s) = 0.01. Quiet time (Quiescent time before potential scan) (s) = 2.

AC impedance spectroscopy

The instrument used for polarization study was used to record AC impedance spectroscopy also. The cell setup was also the same. The real part (Z′) and imaginary part (–Z″) of the cell impedance were measured in Ohms at various frequencies. The details of the experimental conditions are as follows: initial E (V) = 0; high frequency (Hz) = $1\cdot10^5$; low frequency (Hz) = 10; amplitude (V) = 0.005; quiet time (s) = 2. Values of the charge transfer resistance (R_t), impedance value, phase angle and the double layer capacitance (C_{dl}) were calculated. C_{dl} was calculated using the formula: $C_{dl} = 1/2\pi R_1 f_{max}$, where f_{max} is the maximum frequency.

Results and Discussion

Analysis of polarization study

Corrosion resistance of mild steel immersed in 1 M HCl, before and after Durable exterior emulsion coating (Emulsion coating) has been evaluated by polarization study and AC impedance spectroscopy [13–35].

Analysis of results of polarization study

The polarization curves of mild steel immersed in 1 M HCl before and after Durable exterior emulsion coating (Emulsion coating) are shown in Figures 1 to 3.

The corrosion parameters, namely, corrosion potential (E_{corr}), Tafel slopes (b_c = cathodic; b_a = anodic), linear polarization resistance (LPR) and corrosion current density (i_{corr}) are given in Table 1.

According to the principles of polarization study, "When a protective film (emulsion coating) is formed on metal surface, corrosion resistance of the metal increases and hence LPR value increases and corrosion current decreases" (Scheme 1, Figures 1 to 3).

It is observed from Table 1 and Figures 1 to 3 that after emulsion coating, the corrosion resistance of mild steel in 1 M HCl increases because the LPR value increases and corrosion current decreases. Corrosion inhibition efficiency of 99.81% (calculated from LPR values) is offered by the emulsion coating. Inhibition efficiency was calculated using the relation $IE = \left[(R_1 - R_2)/R_1\right]\cdot 100\%$, where R_1 = LPR value in the presence of the coating and R_2 = LPR value in the absence of the coating.

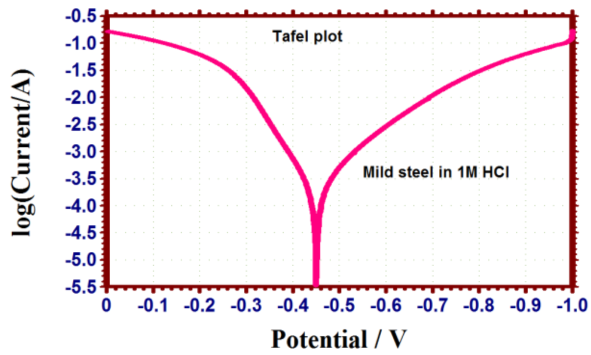


Figure 1. Polarization curve of mild steel in 1 M HCl.

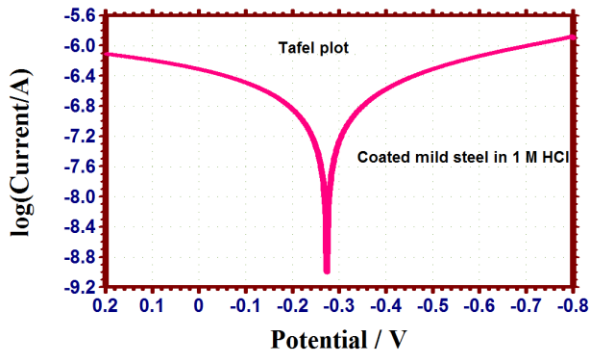
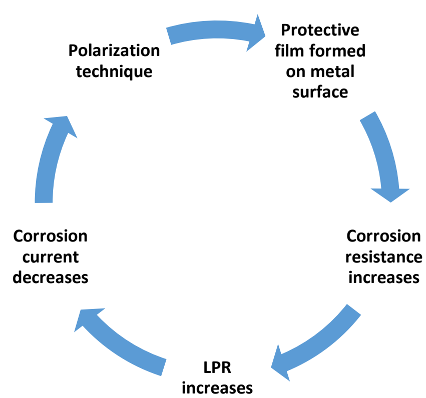


Figure 2. Polarization curve of coated mild steel in 1 M HCl.



Scheme 2. Correlation among corrosion parameters of polarization study.

Table 1. Corrosion parameters of mild steel immersed in 1 M HCl before and after emulsion coating, obtained from polarization study.

System	E_{corr} mV *vs* SCE	b_c mV/decade	b_a mV/decade	LPR Ohm·cm^2	i_{corr} A/cm^2
Mild steel in 1 M HCl	–450	129	74	98	$2.089 \cdot 10^{-4}$
Coated mild steel in 1 M HCl	–274	197	210	51099	$8.812 \cdot 10^{-8}$

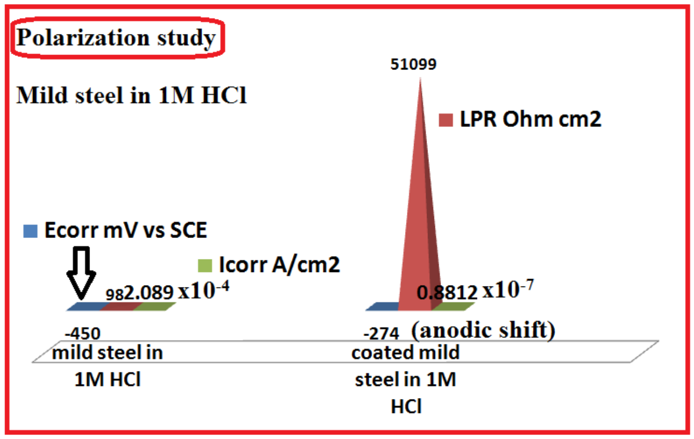


Figure 3. Comparison of corrosion parameters of polarization study.

Implication

In pickling industry, the mild steel vessel containing HCl may be coated with Emulsion coating. This will increase the life time of the mild steel vessel.

Analysis of results of AC impedance spectroscopy

The AC impedance spectra of mild steel immersed in 1 M HCl in the absence and presence of emulsion coating are shown in Figures 4–9. The Nyquist plots are shown in Figures 4 and 6. The Bode plots are shown in Figures 5 and 7. The interactive 3D plots are shown in Figures 8 and 9. The equivalent circuit diagram is shown in Figure 10. AC impedance corrosion parameters are compared in Figure 11.

The corrosion parameters such as charge transfer resistance (R_t) impedance value, phase angle values and double layer capacitance (C_{dl}) values are given in Table 2.

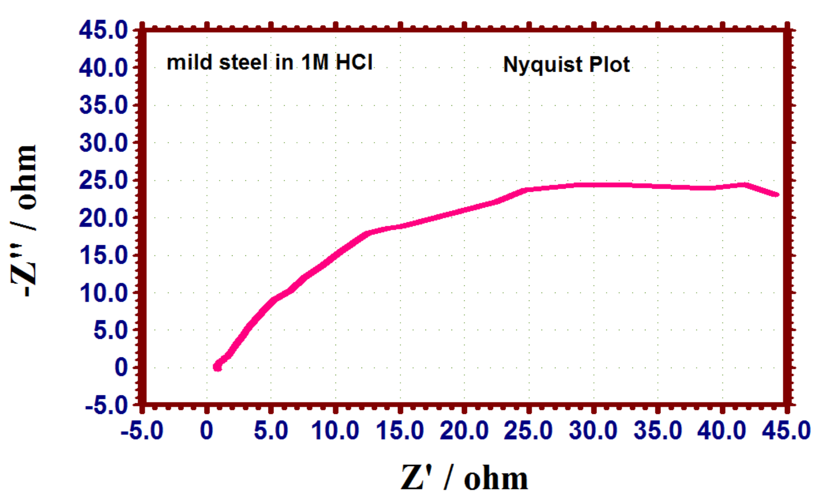


Figure 4. Nyquist plot of mild steel immersed in 1 M HCl.

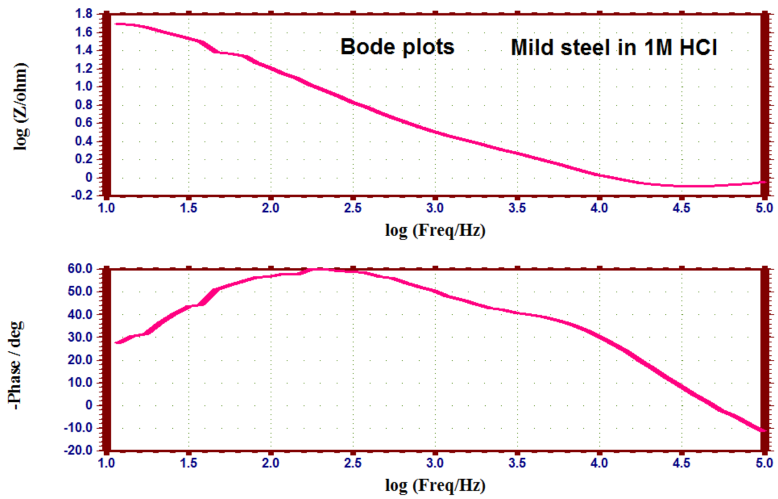


Figure 5. Bode plots of mild steel immersed in 1 M HCl.

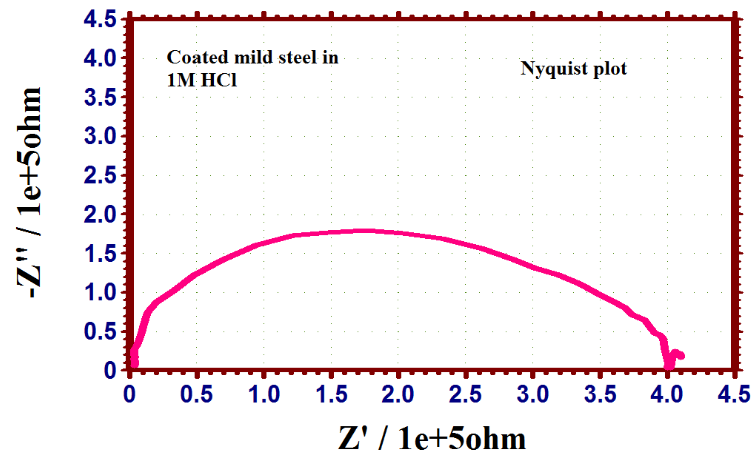


Figure 6. Nyquist plot of coated mild steel immersed in 1M HCl.

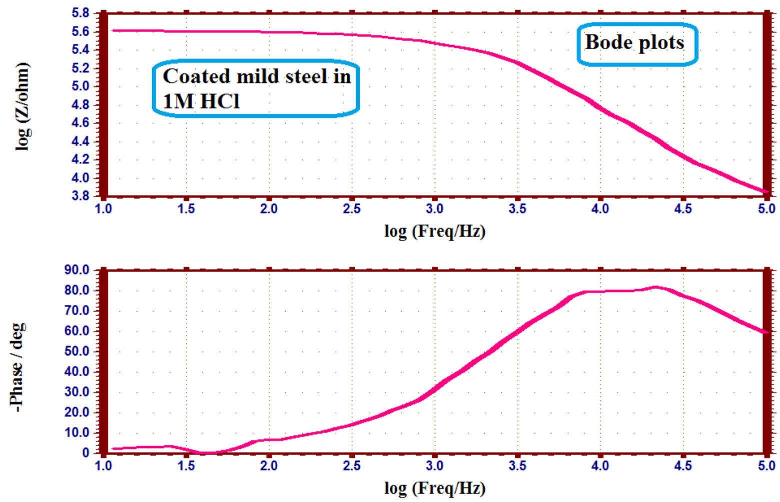


Figure 7. Bode plots of coated mild steel immersed in 1 M HCl.

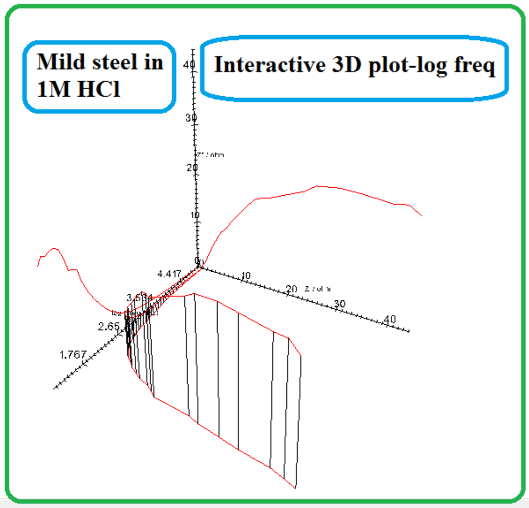


Figure 8. Interactive 3D plot-log freq of mild steel in 1 M HCl.

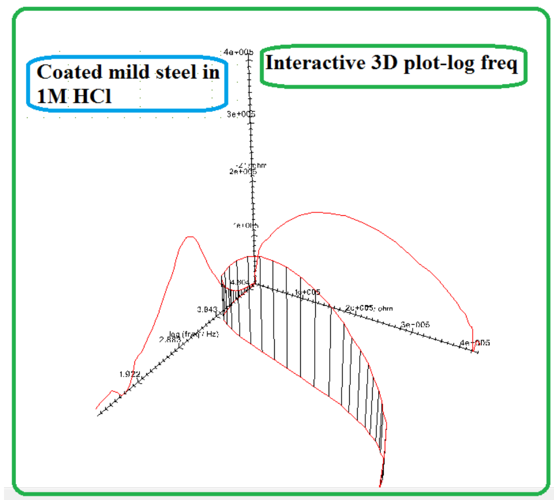


Figure 9. Interactive 3D plot-log freq of mild steel in 1 M HCl.

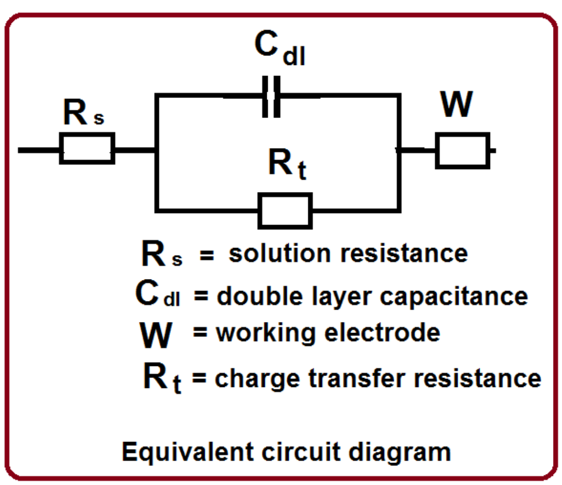


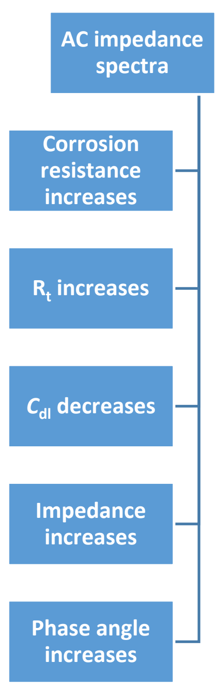
Figure 10. Equivalent circuit diagram for Nyquist plot.

Table 2. Corrosion parameters of mild steel immersed in 1 M HCl before and after durable exterior emulsion coating (emulsion coating) obtained by AC impedance spectroscopy.

System	R_t Ohm·cm²	C_{dl} F/cm²	Impedance Log(Z/Ohm)	Phase angle°
Mild steel in 1 M HCl	43	$1.186 \cdot 10^{-7}$	1.697	39
Coated mild steel in 1 M HCl	412300	$0.1237 \cdot 10^{-10}$	5.617	83

According to the principles of AC impedance spectroscopy, "when a protective film is formed on the metal surface, corrosion resistance increases, R_t values, impedance values and phase angle increase whereas C_{dl} values decrease" (Scheme 3).

It is inferred from Figures 4–9 and Table 2 that, when mild steel coated with emulsion coating is immersed in 1 M HCl the corrosion resistance of mild steel is increased. This is due to the fact that the emulsion coating on the mild steel is stable in the presence of 1 M HCl. The corrosion inhibition efficiency calculated from the charge transfer resistance values is found to be 99.99%. Inhibition efficiency calculated from the formula, $IE = \left[(R_t 1 - R_t 2)\right] / R_t 1 \cdot 100\%$, where $R_t 1$ - charge transfer resistance value in the presence of coating and $R_t 2$ - charge transfer resistance value in the absence of coating.



Scheme 3. Correlation among corrosion parameters of AC impedance spectroscopy.

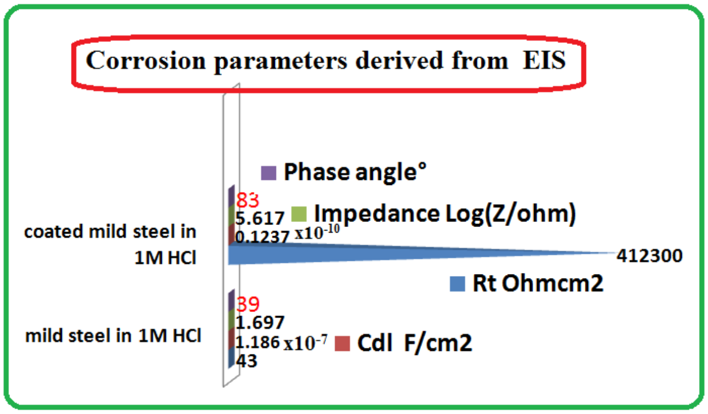


Figure 11. Comparison of corrosion parameters of AC impedance spectroscopy.

Implication

It is inferred from AC impedance spectral studies that the mild steel tank used in pickling industry to store concentrated hydrochloric acid may be given a coat of emulsion coating to improve the life time of the mild steel tank in the pickling industry.

Conclusions

- The corrosion resistance of mild steel immersed in 1 M HCl before and after Emulsion coating has been evaluated by electrochemical studies such as polarization study and AC impedance spectroscopy.
- When a protective film (emulsion coating) is formed on metal surface, corrosion resistance of the metal increases and hence LPR value increases and corrosion current decreases. Similarly, when a protective film is formed on the metal surface, corrosion resistance increases, R_t values, impedance values and phase angle increase whereas C_{dl} values decrease.
- The study reveals that, after emulsion coating the corrosion resistance of mild steel in 1 M HCl increases because, the LPR value increases and corrosion current decreases as revealed by polarization study.
- It is also inferred from AC impedance spectroscopy that when mild steel coated with emulsion is immersed in 1 M HCl the corrosion resistance of mild steel is increased. This is due to the fact that the emulsion coating on the mild steel is stable in the presence of 1 M HCl.
- The corrosion inhibition efficiency calculated from the charge transfer resistance values is found to be 99.99%. After emulsion coating corrosion resistance of mild steel increases, R_t values, impedance values and phase angle increase whereas C_{dl} values decrease.
- ***Electrochemical studies lead to the conclusion that the mild steel tank used in pickling industry to store concentrated hydrochloric acid may be given a coat of emulsion coating to improve the life time of the mild steel tank.***

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