

Influence of Zinc Sulphate on the Corrosion Resistance of L80 Alloy Immersed in Sea Water in the Absence and Presence of Sodium Potassium Tartrate and Trisodium Citrate

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Abstract

In cooling water systems, seawater can be used. L 80 can be used as a pipeline for carrying sea water. However, this alloy will undergo corrosion. Corrosion can be prevented by the addition of inhibitors such as sodium potassium tartrate (SPT), trisodium citrate (TSC) and zinc sulphate. Corrosion resistance of L 80 alloy in sea water, in the absence and presence of the above inhibitors, has been evaluated by polarization study and AC impedance spectra. It was observed that SPT and TSC show better inhibition efficiency in the presence of Zn²⁺. Further, it was found that the SPT-Zn system is better than the TSC-Zn system.

Keywords: corrosion inhibition, seawater, sodium potassium tartrate, trisodium citrate, polarization study, AC impedance spectra, L80 alloy.

Introduction

Seawater makes up the oceans and seas, covering more than 70 percent of Earth surface. Seawater is a complex mixture of 96.5 percent of water, 2.5 percent of salts, and smaller amounts of other substances, including dissolved inorganic and organic materials, particulates and a few atmospheric gases [1]. Almost anything can be found in seawater. This includes dissolved materials from Earth crust, as well as materials released from organisms. The most important components of seawater that influence life forms are salinity, temperature, dissolved gases (mostly oxygen and carbon dioxide) and nutrients [2].

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Seawater can be used in cooling water systems, especially in ships and in marine environments. In these systems, L 80 alloy can be used to carry out seawater. Hence, knowledge of corrosion resistance of L80 alloy in seawater, in the presence of inhibitors, will be useful. Corrosion resistance of aluminium and its alloys [3, 4], zinc and its alloys [5, 6], copper and its alloys [7, 8], mild steel [9, 10], stainless steel [11, 12], nickel and its alloys [13, 14] in seawater has been evaluated. Corrosion inhibitors such as inorganic compounds [15, 16] and natural products [17, 18] have been used to prevent the corrosion of metals and alloys. In the present study, corrosion resistance of L 80 alloy in seawater, in the presence of sodium potassium tartrate (SPT) and trisodium citrate (TSC), has been evaluated by electrochemical studies, such as polarization study and AC impedance spectra. Influence of Zn^{2+} on the corrosion resistance of the above systems has also been evaluated.

Experimental

Electrochemical studies

In the present work, corrosion resistance of L 80 alloy immersed in various test solutions was measured by Polarization study and AC impedance spectra.

Polarization study

In the present study, polarization studies were carried out in a CHI Electrochemical work station/ analyzer, 660A model. It was provided with an automatic IR compensation facility. A three electrode cell assembly was used, as shown in Fig. 1.

The working electrode was L 80 alloy. SCE was the reference electrode. Platinum was the counter electrode. A time interval of 5 to 10 min was given for the system to attain a steady state open circuit potential. The working electrode and the platinum electrode were immersed in sea water, in the absence and presence of the inhibitor. Saturated calomel electrode was connected with the test solution through a salt bridge. From the polarization study, corrosion parameters, such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = b_a and cathodic = b_c and LPR (linear polarization resistance) values, were considered. The scan rate (V/S) was 0.01. Hold time at (E_{fcs}) was zero and quiet time (s) was two.

AC impedance spectra

In the present investigation, the same instrument and set-up used for the polarization study was used to record AC impedance spectra. A time interval of 5 to 10 min was given for the system to attain a steady state open circuit potential. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. AC impedance spectra were recorded with initial $E(v) = 0$, high frequency (Hz = 1×10^5), low frequency (Hz = 1), amplitude (V) = 0.005 and quiet time (s) = 2. From Nyquist plot, the values of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) were calculated.

$$R_t = (R_s + R_t) - R_s \quad (1)$$

where R_s = solution resistance.

C_{dl} values were calculated using the relationship:

$$C_{dl} = \frac{1}{2 \times 3.14 \times R_t \times f_{max}} \quad (2)$$

where f_{max} = frequency at maximum imaginary impedance.

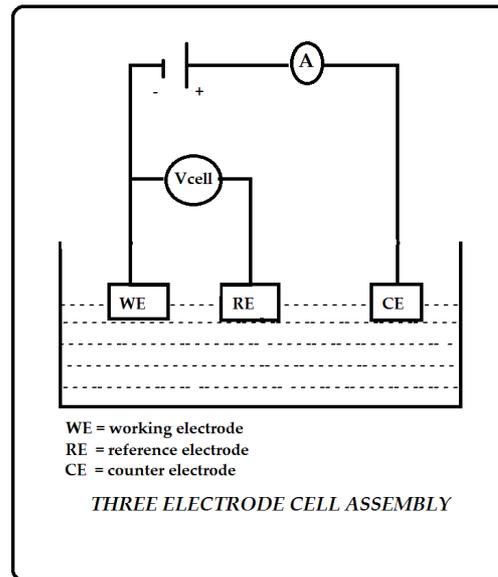


Figure 1. Three electrode cell assembly.

Sea water

The composition of sea water used in this study is given in Table 1. Sea water was collected in the Bay of Bengal, located at Kanampadi, East Coast Road, Chennai, India.

L80 alloy

L80 alloy was manufactured according to 5CT API specification. This is a controlled yield strength material with a hardness testing requirement.

L80 is usually used in wells with sour (hydrogen sulfide) environments. Chemical composition of L80 alloy is given in Table 2.

The remaining Wt % was iron.

Used inhibitors

Pure samples of Sodium Potassium Tartrate (SPT), Tri Sodium Citrate (TSC) and Zinc Sulphate were used as corrosion inhibitors.

Table 1. Composition of sea water.

Physical examination	Acceptable limit	Permissible limit	Sample value
Colour			Colourless and clear
Odour	Unobjectionable		Unobjectionable
Turbidity NT units	1	5	0.2
Total dissolved solids mg/l	500	2000	29400
Electrical conductivity micro mho/cm			42000
Chemical examination			
pH	6.5 – 8.5	6.5 – 8.5	7.46
pH Alkalinity as CaCO ₃		0	0
Total Alkalinity as CaCO ₃	200	600	140
Total Hardness as CaCO ₃	200	600	4000
Calcium as ca	75	200	1200
Magnesium as Mg	30	100	240
Iron as Fe	0.1	1	0
Magnesium as Mg	0.1	0.3	NT
Free Ammonia as NH ₃	0.5	0.5	0.48
Nitrite as NO ₂	0.5	0.5	0.104
Nitrate as NO ₃	45	45	25
Chloride as Cl	250	1000	15000
Fluoride as F	1	1.5	1.8
Sulphate as SO ₄	200	400	1170
Phosphate as PO ₄	0.5	0.5	1.47
Tids Test 4hrs as O ₂			NT

Table 2. Chemical composition of L80 alloy.

	C	Mn	Mo	Cr	Ni	Cu	Ti	P		S	Si	V	Al
Min	-	-	-	-	-	-	-	-		-	-	-	-
Max	0.430	1.900	-	-	0.250	0.350	-	0.030		0.030	0.450	-	-

Results and discussion

Electrochemical studies

In the present work, corrosion resistance of L80 alloy immersed in various test solutions was measured by polarization study and AC impedance spectra.

L80 alloy –sodiumpotassium tartrate (SPT) system

Polarization study

It is seen from Table 3 that when SPT is added to sea water, the corrosion resistance of L80 alloy increases. This is revealed by the fact that when SPT is added to sea water, LPR values increases and I_{corr} value decreases, as shown in Figs. 2 to 5.

Table 3. Corrosion parameters of L80 alloy immersed in sea water, in the absence and presence of SPT and Zinc sulphate ($ZnSO_4 \cdot 7H_2O$), obtained by polarization study.

System	E_{corr} mV SCE	b_c mV/decade	b_a mV/decade	LPR Ohm cm^2	I_{corr} A/ cm^2
Sea water	-830	161	221	355	1.138×10^{-4}
Sea water + SPT (300 ppm)	-822	119	212	677	4.908×10^{-5}
Sea water + SPT (300 ppm) + $ZnSO_4$ (100 ppm)	-537	209	252	23882026	2.079×10^{-9}

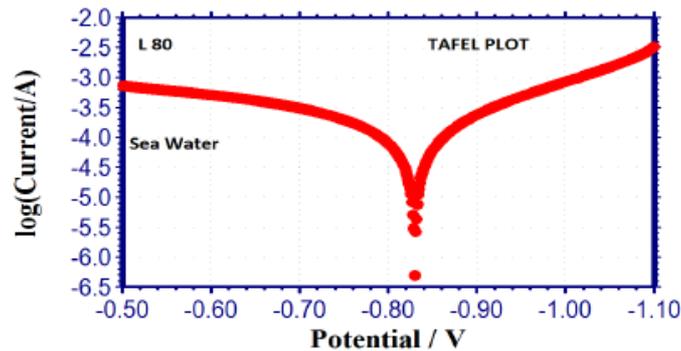


Figure 2. Polarization curve of L80 alloy immersed in sea water.

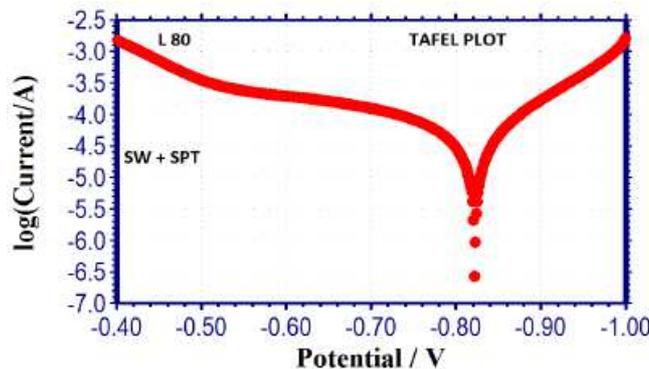


Figure 3. Polarization curve of L80 alloy immersed in sea water + SPT.

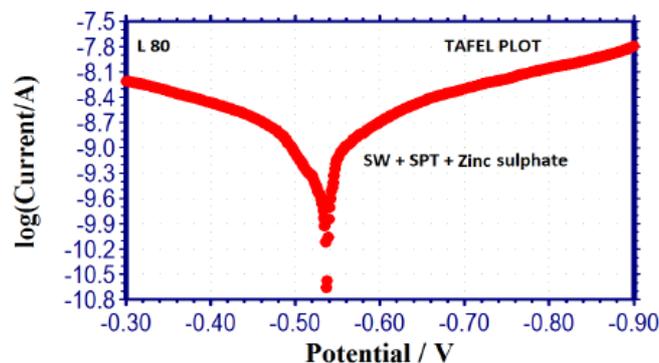


Figure 4. Polarization curve of L80 alloy immersed in sea water + SPT+ zinc sulphate.

Influence of Zinc sulphate ($ZnSO_4 \cdot 7H_2O$)

When $ZnSO_4 \cdot 7H_2O$ was added to the above system, LPR value increased to a great extent (Fig. 5) and I_{corr} decreased considerably. This indicates that, in the

presence of SPT - $ZnSO_4 \cdot 7H_2O$ system, the corrosion resistance of L80 alloy in sea water increases to a great extent. A protective film is formed on the metal surface. This prevents transfer of electrons from anodic site to cathodic site. Hence, LPR value increases, which results in a decrease in the corrosion current value.

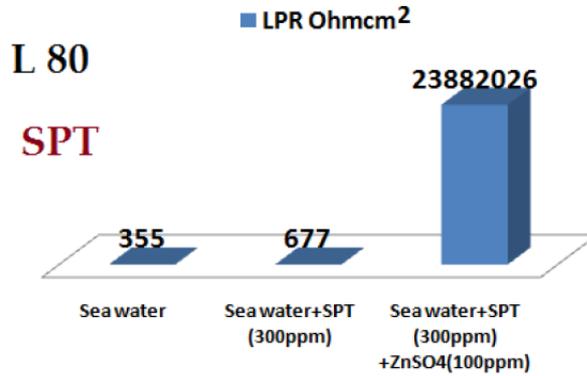


Figure 5. Comparison of LPR values.

AC impedance spectra

The AC impedance spectra (Nyquist plots, Bode plots) of L80 alloy immersed in various test solutions are shown in Figs. 6 to 11. The corrosion parameters are given in Table 4. It is observed from Table 4 that, when SPT is added to sea water, the corrosion resistance of L80 alloy increases. This is revealed by the fact that there is an increase in R_t value, impedance value and decrease in C_{dl} value.

Table 4. Corrosion parameters of L80 alloy immersed in sea water, in the absence and presence of SPT and Zinc sulphate ($ZnSO_4 \cdot 7H_2O$), obtained by AC impedance spectra.

System	R_t Ohm cm ²	C_{dl} F/cm ²	Impedance log (z/ohm)	Phase angle degree
Sea water	5.026	0.010×10^{-4}	0.9149	22.03
Sea water + SPT (300ppm)	5.653	9.021×10^{-7}	0.9604	24.01
Sea water + SPT (300ppm) + ZnSO ₄ (100ppm)	12808933	3.982×10^{-13}	7.123	96.33

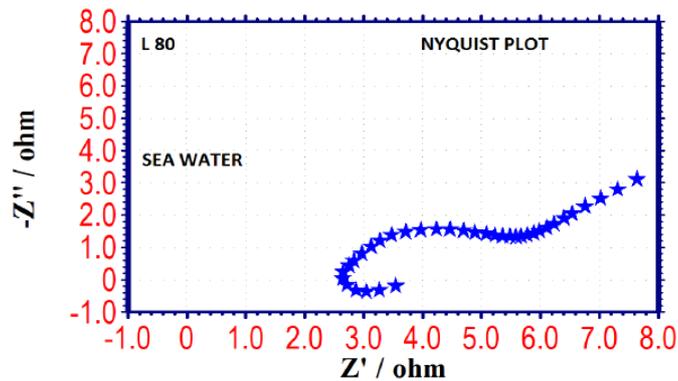


Figure 6. AC Impedance spectra (Nyquist plot) of L80 alloy immersed in sea water.

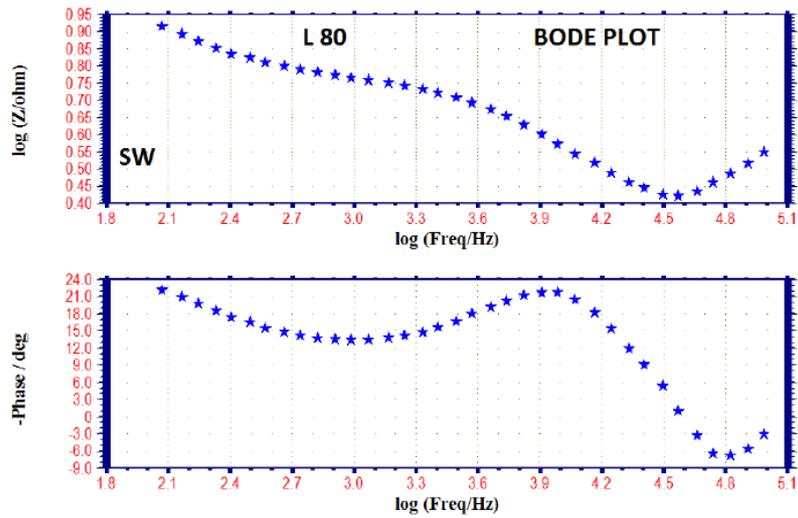


Figure 7. AC Impedance spectra (Bode plot) of L80 alloy immersed in sea water.

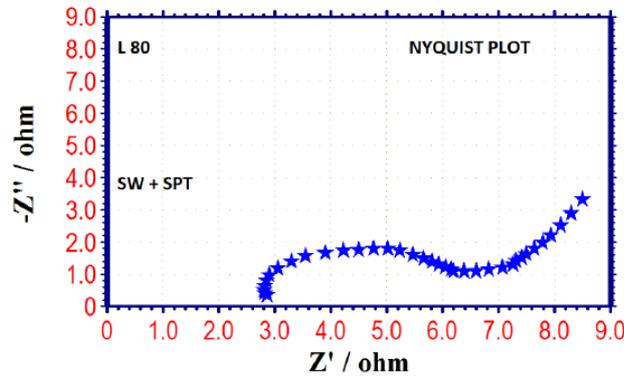


Figure 8. AC Impedance spectra (Nyquist plot) of L80 alloy immersed in sea water + SPT.

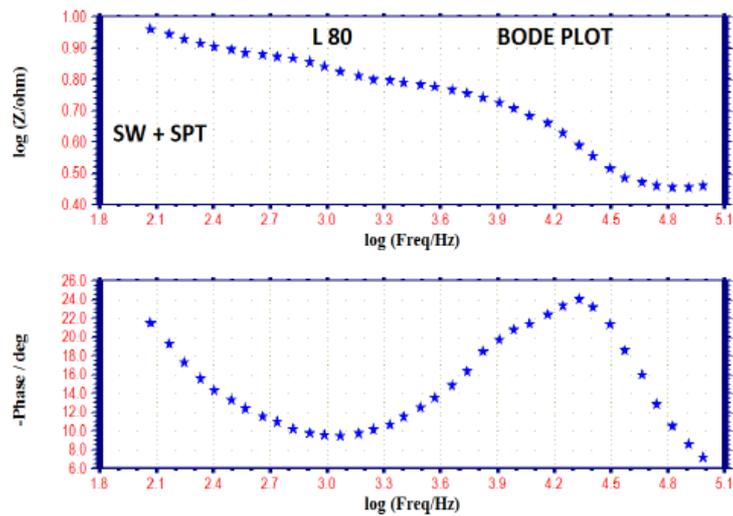


Figure 9. AC Impedance spectra (Bode plot) of L80 alloy immersed in sea water + SPT.

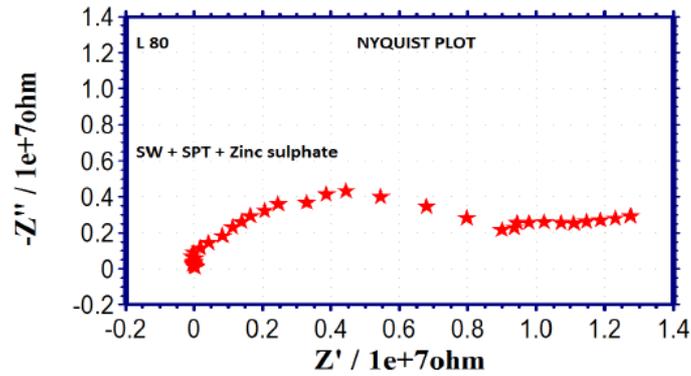


Figure 10. AC Impedance spectra (Nyquist plot) of L80 alloy immersed in sea water + SPT + Zinc Sulphate.

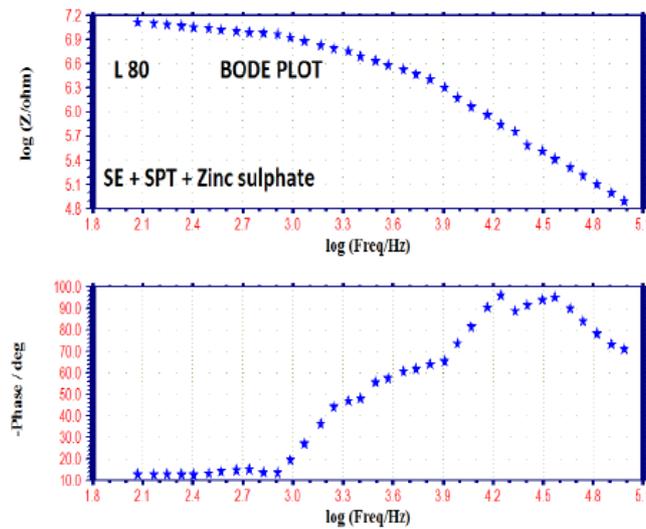


Figure 11. AC Impedance spectra (Bode plot) of mild steel immersed in sea water + SPT + ZnSO₄.

Influence of Zinc sulphate (ZnSO₄. 7H₂O)

When ZnSO₄.7H₂O is added to the above system, the corrosion resistance further increases (Fig. 12). This is revealed by the fact that there is an increase in R_t values and impedance value. There is a decrease in C_{dl}. Thus, electrochemical studies reveal that the corrosion resistance of L80 alloy in sea water decreases in the following order:

$$\text{Sea water} + \text{SPT} + \text{ZnSO}_4 > \text{Sea water} + \text{SPT} > \text{Sea water}.$$

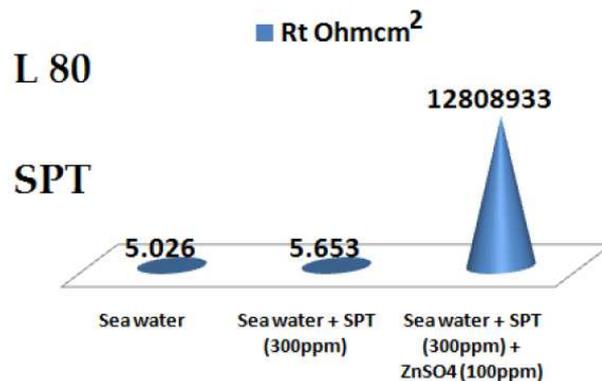


Figure 12. Comparison of R_t value.

L80 alloy – TSC system

Polarization study

It is seen from Table 5 that, when TSC is added to sea water, the corrosion resistance of L80 alloy increases. This is revealed by the fact that when TSC is added to sea water, LPR values increases and I_{corr} value decreases (Figs.13 and 14). There is the formation of a protective film on the metal surface. So, the transfer of electrons from anodic site to cathodic site is restricted. Hence, LPR value increases and, correspondingly, corrosion current value decreases.

Table 5. Corrosion parameters of L80 alloy immersed in sea water, in the absence and presence of TSC and zinc sulphate ($ZnSO_4 \cdot 7H_2O$), obtained by Polarization study.

System	E_{corr} mV SCE	b_c mV/decade	b_a mV/decade	LPR Ohm cm^2	I_{corr} A/ cm^2
Sea water	-830	161	221	355	1.138×10^{-4}
Sea water + TSC (300 ppm)	-761	165	232	391	1.076×10^{-4}
Sea water + TSC (300 ppm) + $ZnSO_4$ (100 ppm)	-704	146	209	465	8.044×10^{-5}

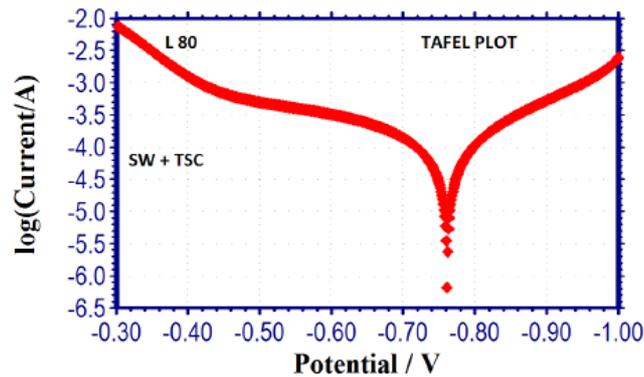


Figure 13. Polarization curve of L80 alloy immersed in sea water + TSC.

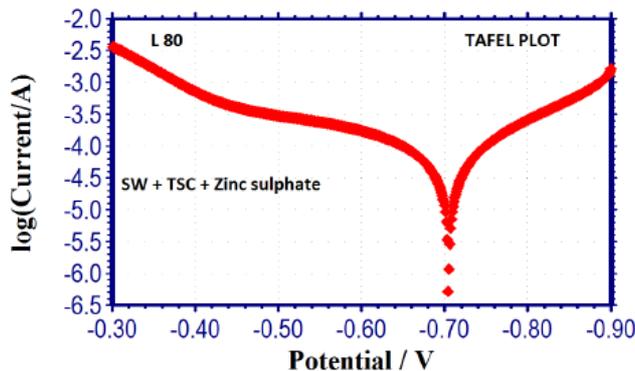


Figure 14. Polarization curve of L80 alloy immersed in sea water + TSC + zinc sulphate.

Influence of Zinc sulphate ($ZnSO_4 \cdot 7H_2O$)

When $ZnSO_4 \cdot 7H_2O$ is added to the above system, LPR value increases tremendously (Fig.15) and I_{corr} decreases very much. This indicates that, in the

presence of SPT - $ZnSO_4 \cdot 7H_2O$ system, the corrosion resistance of L80 alloy in sea water increases to a great extent.

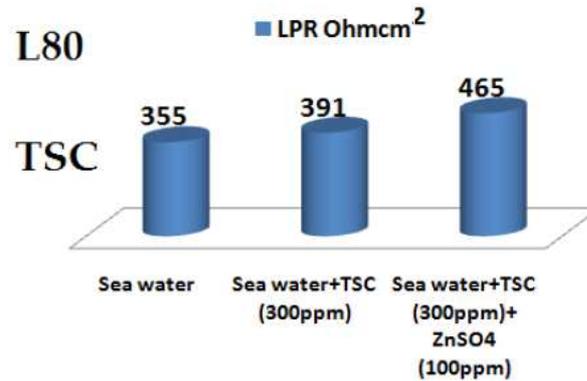


Figure 15. Comparison of LPR values.

AC impedance spectra

The AC impedance spectra (Nyquist plots, Bode plots) of L80 alloy immersed in various test solutions are shown in Figs. 16 to 19. The corrosion parameters are given in Table 6. It is observed from Table 6 that, when TSC is added to sea water, the corrosion resistance of L80 alloy increases. This is revealed by the fact that there is an increase in R_t value and impedance value and a decrease in C_{dl} value.

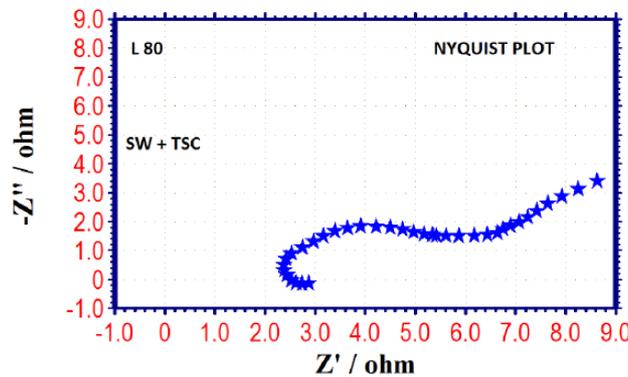


Figure 16. AC Impedance spectra (Nyquist plot) of L80 alloy immersed in sea water + TSC.

Table 6. Corrosion parameters of L80 alloy immersed in sea water, in the absence and presence of TSC and Zinc sulphate ($ZnSO_4 \cdot 7H_2O$), obtained by AC impedance spectra.

System	R_t $Ohm\ cm^2$	C_{dl} F/cm^2	Impedance $\log(z/ohm)$	Phase angle degree
Sea water	5.026	0.010×10^{-4}	0.9149	22.03
Sea water + TSC (300 ppm)	6.282	0.022×10^{-4}	0.9671	26.22
Sea water + TSC (300 ppm) + $ZnSO_4$ (100 ppm)	7.077	7.206×10^{-7}	1.021	28.84

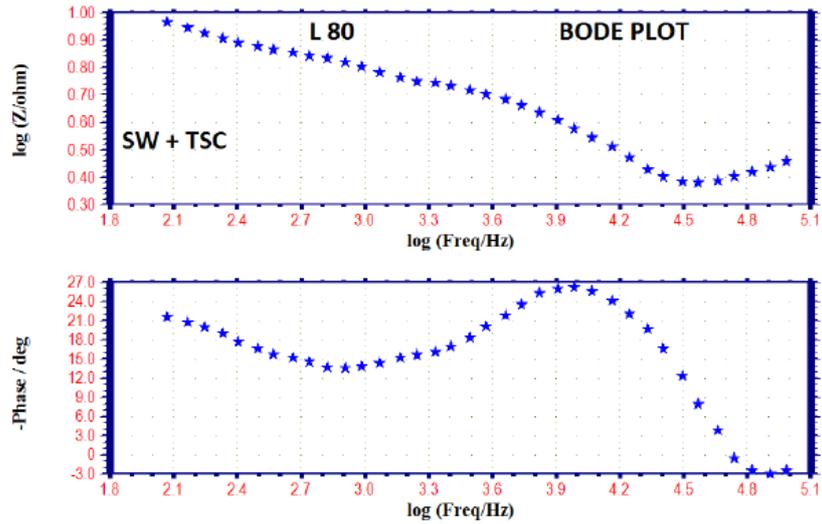


Figure 17. AC Impedance spectra (Bode plot) of L80 alloy immersed in sea water + TSC.

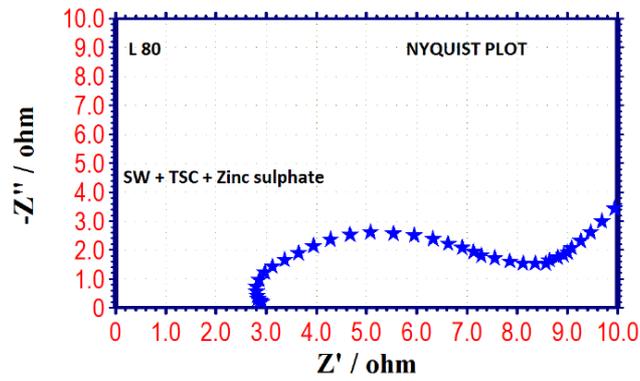


Figure 18. AC Impedance spectra (Nyquist plot) of L80 alloy immersed in sea water + TSC + ZnSO₄.

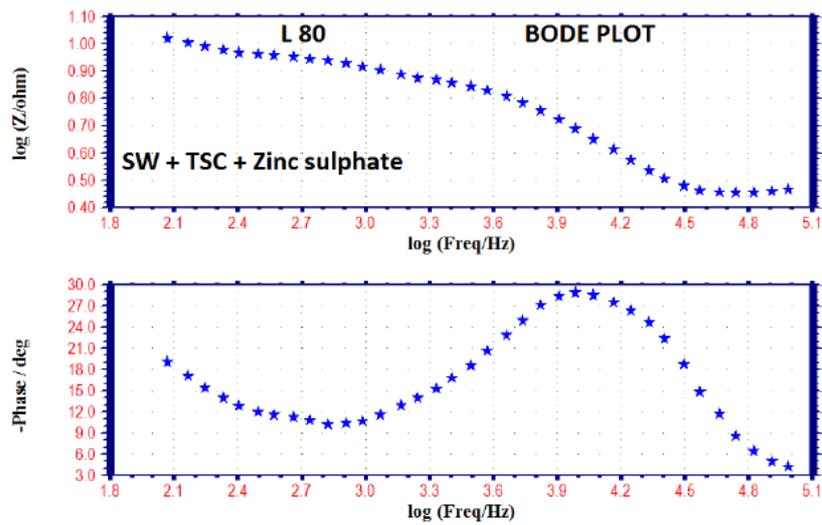


Figure 19. AC Impedance spectra (Bode plot) of L80 alloy immersed in sea water + TSC + ZnSO₄.

Influence of Zinc sulphate (ZnSO₄ .7H₂O)

When ZnSO₄.7H₂O was added to the above system, the corrosion resistance further increased. This is revealed by the fact that there is an increase in R_t values (Fig. 20) and impedance value. There is a decrease in C_{dl}. Thus, electrochemical studies [19-28] reveal that the corrosion resistance of L80 alloy in sea water decreases in the following order:

$$\text{Sea water} + \text{TSC} + \text{ZnSO}_4 > \text{Sea water} + \text{TSC} > \text{Sea water}$$

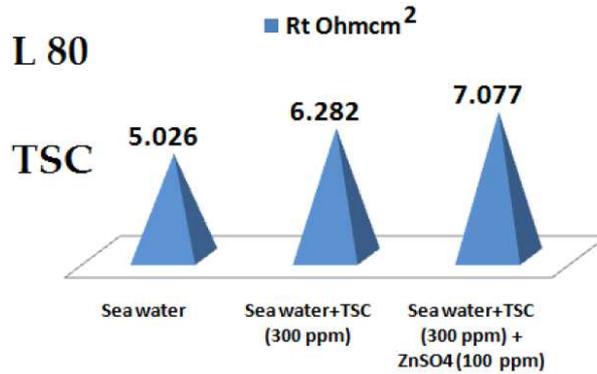


Figure 20. Comparison of R_t values.

Conclusion

The corrosion resistance of L80 alloy in sea water, in the absence and presence of sodium potassium tartate (SPT), trisodium citrate (TSC) and zinc sulphate (ZnSO₄ . 7H₂O), has been evaluated by electrochemical studies, such as polarization study and AC impedance spectra. The study led to the following conclusions:

L80 alloy – SPT system

Electrochemical studies revealed that the corrosion resistance of L80 alloy in sea water decreases in the following order:

$$\text{Sea water} + \text{SPT} + \text{ZnSO}_4 > \text{Sea water} + \text{SPT} > \text{Sea water}$$

L80 alloy – TSC system

Electrochemical studies revealed that the corrosion resistance of L80 alloy in sea water decreases in the following order:

$$\text{Sea water} + \text{TSC} + \text{ZnSO}_4 > \text{Sea water} + \text{TSC} > \text{Sea water}$$

Addition of Zinc sulphate improves the corrosion resistance of the TSC and SPT systems.

This study also led to the conclusion that the SPT-Zinc system offers better corrosion resistance than the TSC-Zinc system.

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