Int. J. Electrochem. Sci., 13**(2018)** 11961 – 11973, doi: 10.20964/2018.12.52

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Investigation of some Porphyrin Derivatives as Inhibitors for Corrosion of N80 Steel at High Temperature and High Pressure in 3.5% NaCl solution containing carbon dioxide

Jinchang Wang[1,2], *Yuanhua Lin*[1,3,*], *Ambrish Singh*[1,3,*], *Wanying Liu*[4]

[1] State Key Laboratory of Oil and GasReservoirGeology and Exploitation, SouthwestPetroleum University, Chengdu, Sichuan 610500, China
[2] North China Oil and GasBranchCompany of SINOPEC, Zhengzhou, Henan 450006, China
[3]School of Materials Science and Engineering, SouthwestPetroleum University, Chengdu, Sichuan 610500, China
[4]CNPC Key Lab for TubularGoods Engineering (SouthwestPetroleum University), Chengdu, Sichuan 610500, China
[*]E-mail: vishisingh4uall@gmail.com; yhlin28@163.com

Received: 20 July 2018/ *Accepted:* 23 August 2018 / *Published:* 5 November 2018

Corrosion of N80 steelin 3.5% NaCl solution containingcarbondioxidewasinvestigatedwith and withoutPorphyrinderivativesusingelectrochemical, and gravimetric tests. Surface morphologywasexaminedusing contact angle, and scanning electronmicroscopy (SEM) techniques. The inhibition efficiencyof Porphyrinderivatives tend to increasewith concentration but decreasewithincrease in temperature. The surface studiesshowed the ruptering of the inhibitor film as the temperatureincreases. Among all the inhibitorsused P5 wasfound to show the best inhibition efficiency due to itswide structure and presence of heteroatomsattached to the rings.

Keywords: Porphyrins, Electrochemical; SEM-EDX, High temperature Autoclave, N80 steel

1. INTRODUCTION

Corrosion is a bane to the worldwide industries, refineries and plants wherever metals are used. It causes widespread economic losses, failures and accidents throughout the globe. High temperature corrosion is one of the leading problems in oil and gas refineries / plants. High temperature leads to high corrosion rates causing fatal failures of transportation pipes, reservoir casing, and storage tanks. N80 steel is one of the common steel to be used in oil and gas industries. The strength, resistivity and cost makeN80 steel to be used frequently all over the globe [1].

High temperature and high pressure in the NaCl solution saturated with carbon dioxide causes the rate of corrosion to increase quickly. The metal undergoes corrosion at a very fast rate and the surface becomes irregular and corroded with cracks and pits visible. So, to mitigate the corrosion rate an inhibitor is required that can cover the entire or most of the available metal surface. Porphyrin has a large structure with ample heteroatoms and this was the motivation to use this inhibitor. The planar structure of Porphyrin molecule contains four pyrrole subunits with heteroatoms attached to the rings. The metal is mostly present in the centre bonded to the pyrrole reaction group [2-4]. The presence of conjugated double bonds and cyclic rings make Porphyrins a very active group with several reaction sites. The existence of these reaction sites plays an important role during the adsorption process on the metal surface in various aggressive solutions. Porphyrin molecules are known to develop great bonding and interactions with the metal surface due to their wide structure and electronic active groups. Structured molecular layers can be formed by the Porphyrin molecules by reconfiguring the electron distribution of the aromatic ring and varying their properties [5]. Porphyrin molecules fulfill the criteria of an effective inhibitor as the wide structure can cover the active centers of the metal surface and the heteroatoms can bond with the empty orbitals of the metal avoiding the diffusion of corrosive media towards the metal. Although, the defensive barrier formed by the Porphyrin molecules can be affected by peripheral functional groups, steric hindrance and electron density at donor reaction sites [6]. The current paper aims to investigate the five Porphyrin compounds as affective corrosion inhibitor for N80 steel in 3.5% NaCl solution containing carbon dioxide.

2. MATERIALS

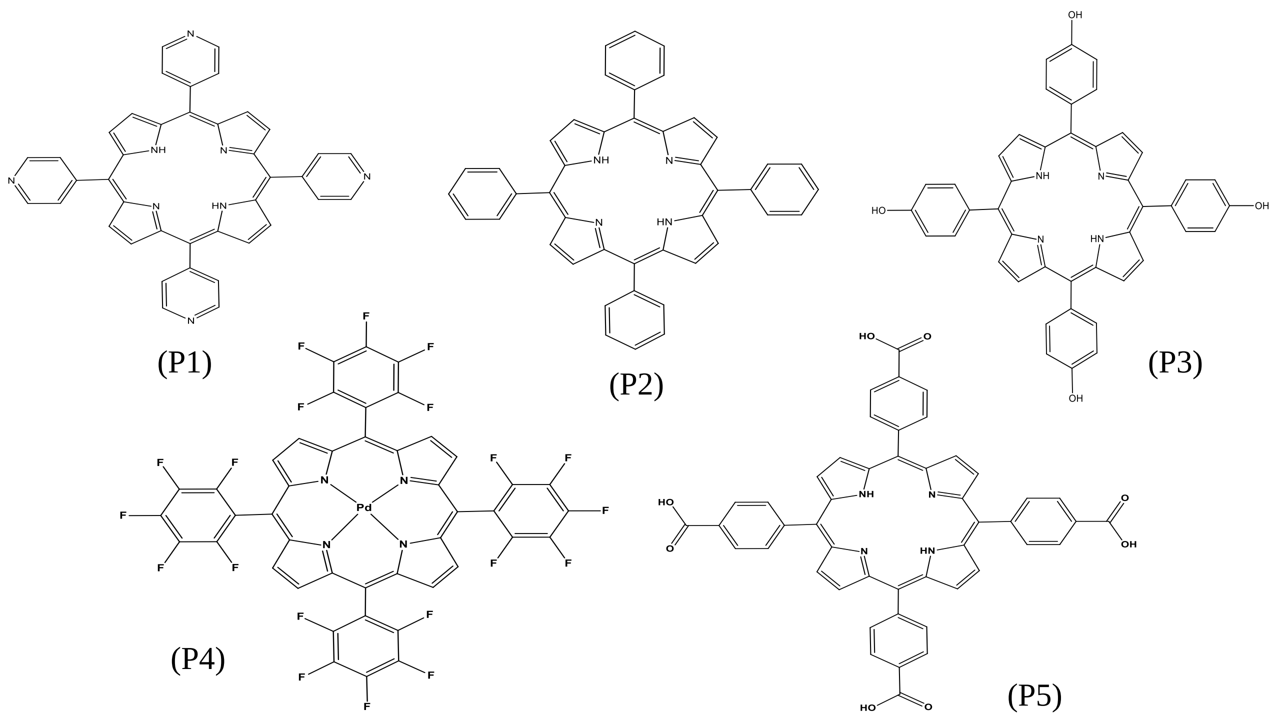


Figure 1. Structure of Porphines

The five Porphyrins (5,10,15,20-Tetra(4-pyridyl)-21H,23H-porphine (P1),5,10,15,20-Tetraphenyl-21H,23H-porphine (P2),5,10,15,20-Tetrakis(4-hydroxyphenyl)-21H,23H-porphine (P3), 4,5,10,15,20-Tetrakis(pentafluorophenyl)-21H,23H-porphinepalladium(II) (P4), 4,4′,4″,4‴-(Porphine-5,10,15,20-tetrayl)tetrakis(benzoicacid) (P5))used for gravimetric and electrochemical tests wereboughtfromMerck and Sigma Eldrichcompany [7]. The structure of all the five Porphyrinsused are shown in figure 1. The electrochemical and gravimetric tests wereperformed on N80 steelwith composition (wt.%): C 0.31; Si 0.19; Mn 0.92; P 0.010; S 0.008; Cr 0.2; and Fe remaining.The sampleswereabradedtill mirror finish with fine grade sandpapers [8].

2.1. Gravimetric tests

Gravimetricexperiments(weightloss) werecarried out at variedtemperatures to determinevariousthermodynamicproperties. The temperaturewasincreased to find out the performance of the Porphyrins at high temperature. All the experimentswereperformedusingstatic high temperature high pressure Autoclave in presence of 3.5% NaCl solution containingcarbondioxide. The pressure of carbondioxide in the autoclave was 10 Mpa and temperaturewasvariedfrom 40°C to 100 °C [9].

2.2. Electrochemicalmethods

The electrochemical tests werecarried out usingAutolabworkstation and FRC, GPES softwares wereused to fit and analyze the data.The conventionalcellwasusedwith four neck includingworkingelectrode, auxiliaryelectrode, referenceelectrode and fourth neck was use to saturate the solution withcarbondioxide. After saturation for 1 hour the neck wasproperlysealedwithepoxyresin.Impedance testswereperformedfrom 100 kHz to 0.00001 kHz understable open circuit potential. Immersion time of 30 minutes wasallowedbefore the start of each test at obtain a stable potential [10]. The efficiency of the inhibitorswerecalculatedusing the equationbelow

$$\eta\% = \frac{R_{\mathrm{ct}}^{'} - R_{\mathrm{ct}}^{0}}{R_{\mathrm{ct}}^{'}} \times 100 \qquad (1)$$

where, $R_{\mathrm{ct}}^{'}$ and R_{ct}^{0} are the charge transferresistance in presence and in the absence of an inhibitor, respectively [11].

Potentiodynamicpolarization figureswereobtainedusing the potentialfrom −300 to +300 mV at a scan rate of 1 mV s^{-1}. The anodic and cathodicpolarization (Tafel) curveswereanalyzed to get the corrosaion rate, corrosion currentdensity(I_{corr}) and otherparameters [12]. The efficiencyof the inhibitorswereevaluatedusing the relationship

$$\eta\% = \frac{I_{\mathrm{corr}}^{0} - I_{\mathrm{corr}}^{'}}{I_{\mathrm{corr}}^{0}} \times 100 \qquad (2)$$

where, I_{corr}^{0} and $I_{\mathrm{corr}}^{'}$ are the corrosion currents in absence and in the presence of an inhibitor, respectively.

2.3. Surface Characterization

To test the hydrophillic and hydrophobic nature of the metal surface contact angle measurementsweredoneusing the sessile drop method. All the tests wereperformedusingDSA100 Kruss instrument and prior to each test the sampleswerecleanedcarefully to avoid contaminations [13,14]. Surface of the metalsampleswereexposed to the corrosive solution with and withoutinhibitors for 24 hours. After 24 hours the sampleswerewashed, cleaned and driedbeforeexposing to the Zeiss instrument for SEM tests [15].

3. RESULTS AND DISCUSSION

3.1. Gravimetric tests

Gravimetric (weightloss) tests wereperformed at varyingtemperaturesfrom 40°C to 100°Cusingstatic high temperature high pressure autoclave. Prior to exposing the samples in autoclave a test to determine the optimum concentration wasdone and 500 ppm (mg/L) wasfound to be the optimum concentration for all the inhibitorsused. Above 500 ppm concentration therewas no significant change in the efficiency of the inhibitors. The inhibition efficiencywasfound to decrease for all the inhibitors [16].

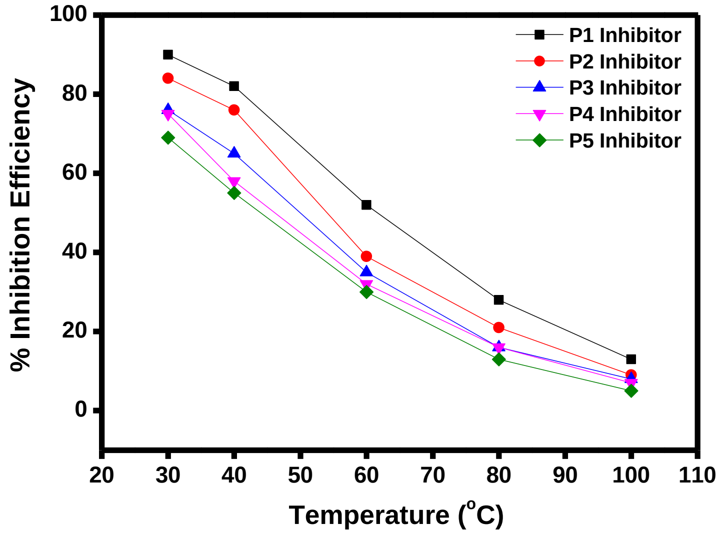


Figure 2. Weight loss data for N80 steel in 3.5% NaCl solution with 10 Mpa pressure of carbon dioxide in the absence and presence of Porphines at various temperatures .

3.2. ElectrochemicalImpedanceAnalysis

The Nyquist graphs of all the Porphyrinsused3.5% NaClcontainingcarbondioxide are shown in Figure 3. The Nyquist graphs show the capacitive loop in the high frequency and inductive loop in the lowfrequency zone.

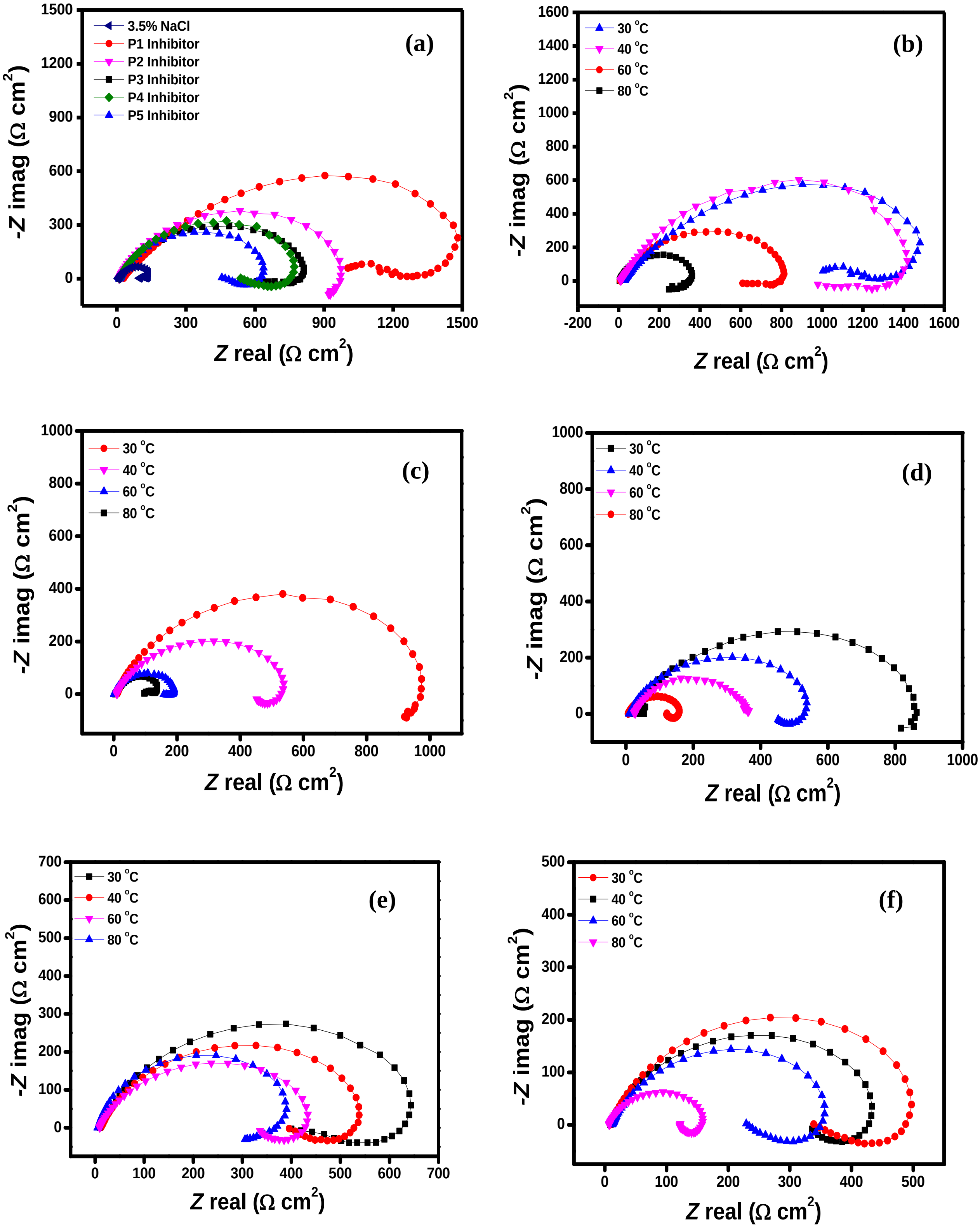


Figure 3. Nyquist plot for N80 steel in 3.5% NaCl solution in the absence and presence of Porphines with10 Mpa pressure of carbon dioxide.

This sort of action isrelated to the frequency dispersion whichiscaused due to the roughness and otherinhomogeneities of solid surface [17,18]. The presence of inductive loopisalsoattributed to the stabilizationprocess at the electrodeafter the reactionbetweenPorphyrins and theirproducts. Figure 3a shows the Nyquist graph of five Porphyrinderivatives at 500 ppm concentration. The shape of the graph isalmost the samewhichsuggests the overallmechanismis not affected by the addition of inhibitors in the solution. The diameter of the graph varies in presence of differentinhibitors and P1 inhibitor shows the best inhibition efficiencyamong the otherPorphyrins. This couldbe due to the availableheteroatomspresent in P1 moleculewhichform a metal-inhibitorcomplexwhileadsorbing on the surface and shielding the reaction of metalwith corrosive media [19].

Figure 3b, 3c, 3d, 3e, and 3f shows the Nyquist graphs of P1, P2, P3, P4 and P5 inhibitors at differenttemperatures (30 °C to 80 °C). The optimum concentration of 500 ppm (mg/L) wasused for all inhibitorswhiletestingthem at differenttemperatures. The diameter of the Nyquist graphs decreasedrapidly as the temperaturewasincreased for all the inhibitors. This phenomenoncanbe due to the ruptering of the metal-inhibitorcomplex at high temperature. The corrosive media can diffuse through the ruptured film and increase the corrosion rate of the system. The increase in the corrosion rate can lead to decrease in inhibition efficiency of the inhibitors [20].

Table 1 show the parametersobtainedfromNyquist graphs afterfitting the circuit. The charge transferresistance value withoutinhibitor shows lower value in the corrosive media. The value of charge transferresistanceincreases in presence of inhibitors[21]. The highest value of 1390 Ω cm^2 wasobserved for P1 inhibitorin 3.5% NaCl solution containingcarbondioxide. This couldbe due to the increase in the surface coverage by the inhibitorwhich blocks the active reaction sites on the metal surface [22].

Table 1. Electrochemicalimpedanceparameters at an amplitude of 10 mV for N80 steelin 3.5% NaCl solution in the absence and presence of Porphines.

30 °C	$\boldsymbol{R_s}$	$\boldsymbol{R_{ct}}$	$\boldsymbol{n}$	$\boldsymbol{Y_\circ}$	$\boldsymbol{L}$	$\boldsymbol{\eta}$	**Surf.coverage**
Solution	**(Ωcm^2)**	**(Ω cm^2)**		**($\Omega^{-1}s^n/cm^2$)**	**(H cm^2)**	**%**	$\boldsymbol{\theta}$
3.5% NaCl	9.6	128	0.755	298	-	-	-
P5	3.3	1390	0.757	121	113	78	0.78
P4	5.9	570	0.771	103	124	79	0.79
P3	2.7	556	0.787	92	99	83	0.83
P2	3.9	525	0.792	87	52	87	0.87
P1	3.2	430	0.812	65	37	91	0.91

3.2. PolarizationMeasurements

Anodic and cathodicpolarizationcurves of N80 steelwith and withoutinhibitorsin 3.5% NaCl solution containingcarbondioxide are shown in Figure 4. The corrosion currentdensity(I_{corr}), corrosion potential (E_{corr}) cathodic and anodicslopes(b_c, b_a)weredetermined by the extrapolation of polarizationcurves. Kinetics of both the anodic and cathodicslopes(b_c, b_a)wereequallyaffected due to the electrontransferprocess at the electrode surface [23]. Figure 4a shows the polarizationcurves of

N80 steel in presence of differentinhibitors at 500 ppm (mg/L) of optimum concentration. Figure 4b, 4c, 4d, 4e, and 4f shows the polarization graphs of P1, P2, P3, P4 and P5 inhibitors at differenttemperatures (30 °C to 80 °C). As canbeobservedfrom the graphs both the anodic dissolution and cathodichydrogenevolutionweremitigatedequally in the presence of inhibitors.

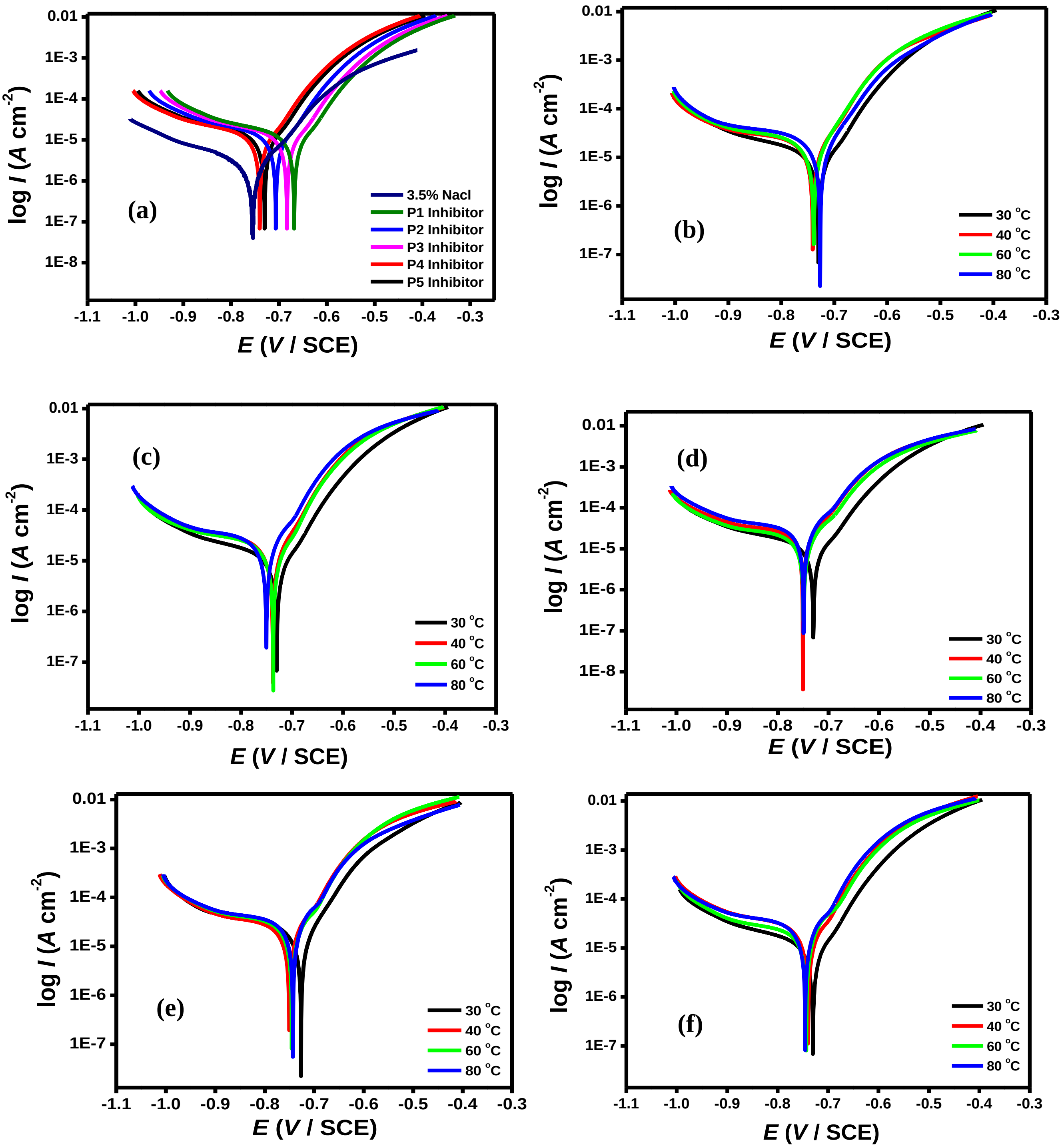


Figure 4. Tafel polarization plots for N80 steelin 3.5% NaCl solution with10 Mpa pressure of carbon dioxide in the absence and presence of Porphines.

Although, the shift is not much to the anodic or cathodicside at high temperaturewhichsuggests mixed action of inhibitors [24]. The values of I_{corr}, the corrosion potential (E_{corr}), cathodic and anodicTafelslopes and inhibition efficiency (η%) are given in Table 2.

Table 2. Polarizationparameters for N80 steelin 3.5% NaCl in the absence and presence of different concentrations of Porphines.

Tafel data						
Solution	**E_{corr} (V vs. SCE)**	**I_{corr} (mA cm^{-2})**	**b_a (mV d^{-1})**	**$-b_c$ (mV d^{-1})**	**η (%)**	**Surface coverage θ**
3.5% NaCl	-0.739	0.91	82	214	-	-
P1	-0.729	0.23	67	171	75	0.75
P2	-0.733	0.18	78	119	80	0.80
P3	-0.727	0.12	65	145	87	0.87
P4	-0.740	0.09	72	133	90	0.90
P5	-0.746	0.08	58	98	91	0.91

According to the studiesif the value of $E_{corr}$is>85 mV, the inhibitorcanbecategorizedintocathodic or anodic type. But, if the value of $E_{corr}$is<85 mV, the inhibitorcanbearrangedinto the mixed type group. Table 2 shows that the change in E_{corr} valuesis<85 mV for all inhibitorsused. This suggeststhat all the inhibitorsusedbelong to the mixed type category[25-28]. The maximum inhibition efficiency (91%) at 30 °C wasobserved for P1 inhibitorwithI_{corr}values of 0.08 mA cm^{-2}. The performance of P1 inhibitoris the best at high temperaturetoo due to the presence of ample heteroatoms and conjugated double bonds in the molecule. The double bonds and heteroatomsformscomplexwith the metal and the size helps to cover the entiremetal surface and block the reactioncenters.

3.3. Surface Characterization

3.3.1. Contact Angle

To determine the surface behavior of the metal in presence and absence of inhibitor at varioustemperatures contact angle tests werecarried out as shown in Figure 5. The gravimetric (weightloss) sampleswereused to test the contact angles. Prior to each test a standard baselinewasdetermined to keep all the parameterssame. The surface wascleanedcarefully to avoid contaminations. The solution wasdropped on to the metal surface using sessile drop technology. To ensurequalityresults the tests wererepeated for 3 times for eachtemperature. At lowtemperature (30 °C) the contact angle recordedwere high for all inhibitors. The inhibitor film on the surface prevents the droplet to meet the metal surface and henceforms a big angle. This phenomenonis due to the hydrophobic nature of the metal surface in presence of inhibitors[29]. As the temperatureincreases the contact angle begins to decrease. This is due to the deterioration of the inhibitor film whichallows the droplet to contact the metal surface directly. The direct contact of the droplet on the metal surface refers to the hydrophillic nature of the surface. All the inhibitorsshowedhydrophobic nature but P1inhibitorshowed the best resultwith an angle of 124.3°. In presence of Porphyrins the hydrophobic nature wasprominentwhichdeterioratedwithincrease in temperature.

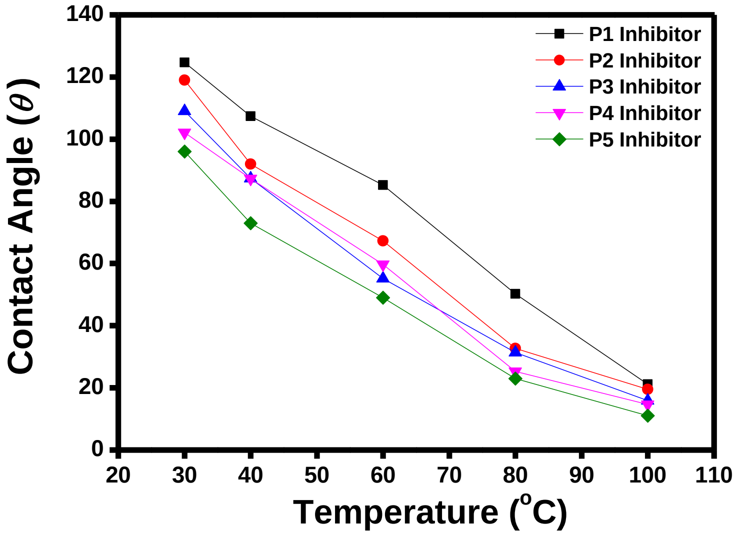
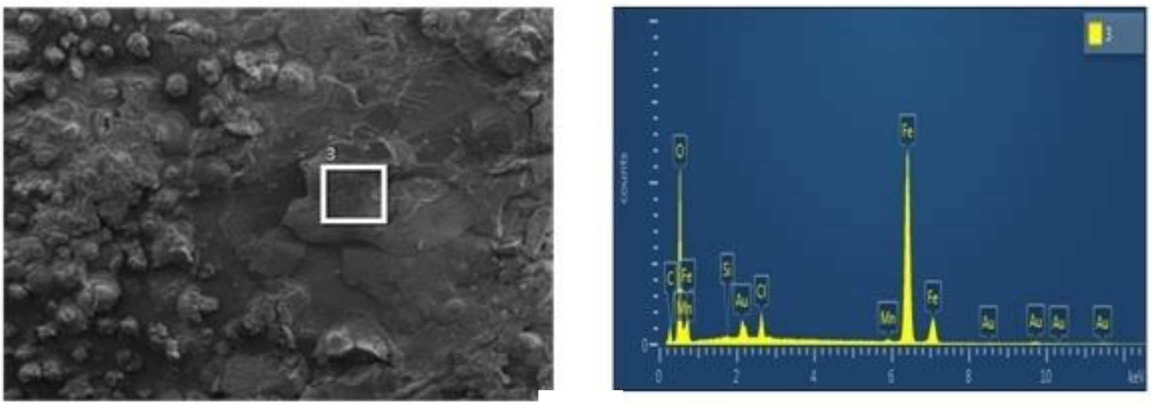
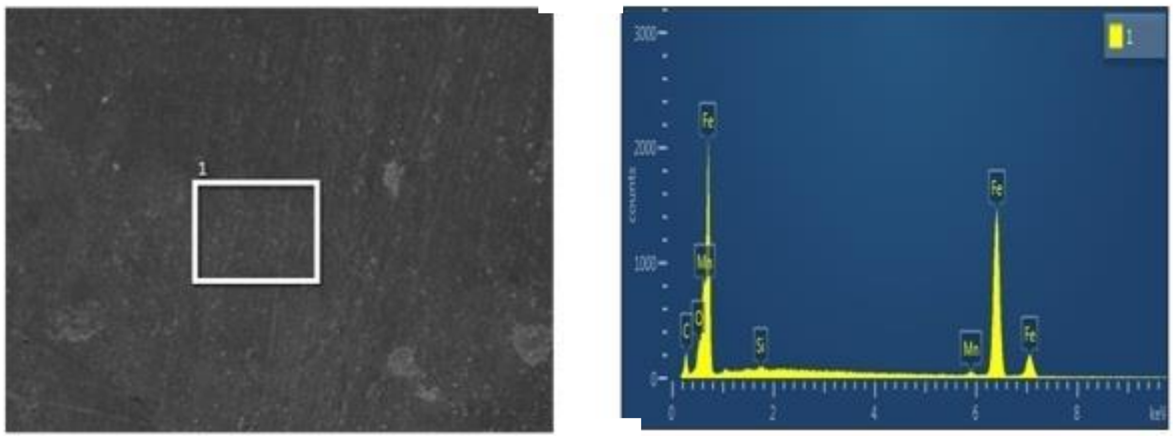


Figure 5. Contact angle of Porphyrins for N80 steel at various temperature with10 Mpa pressure of carbon dioxide.

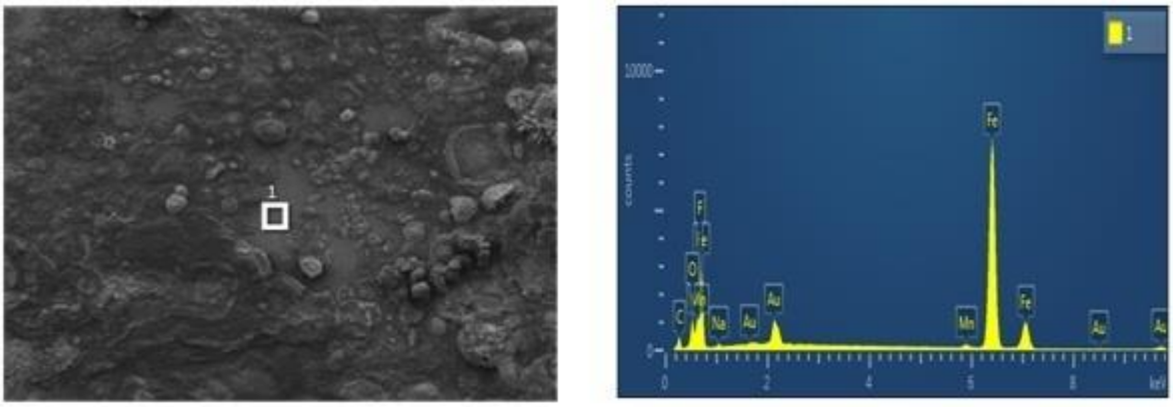
3.3.2. Scanning ElectronMicroscopy(SEM)



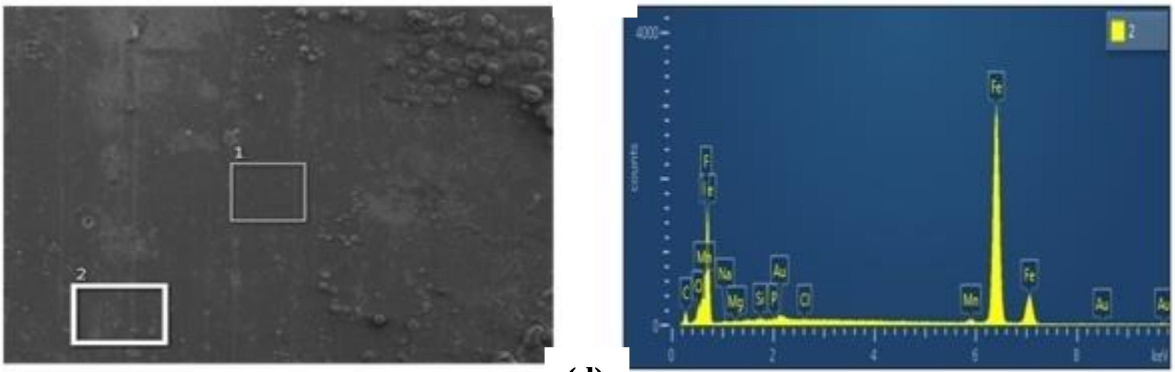
(a)



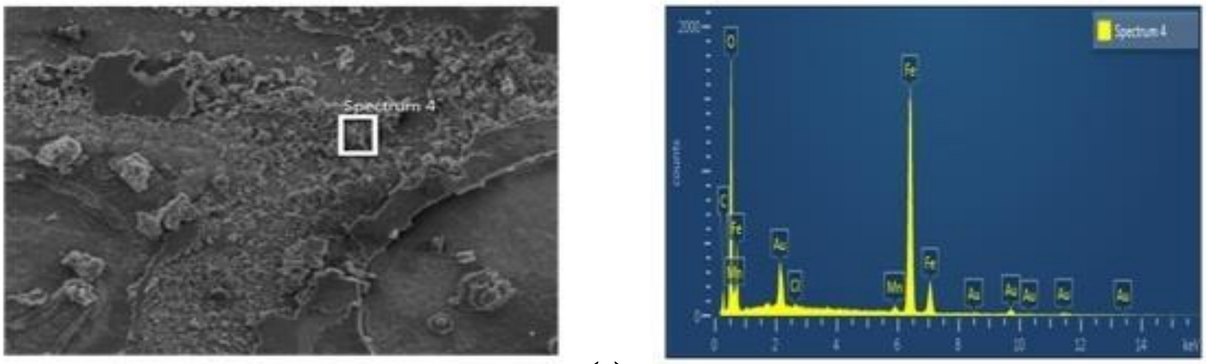
(b)


1
C
O
Fe
Na
Au
Mn
keV

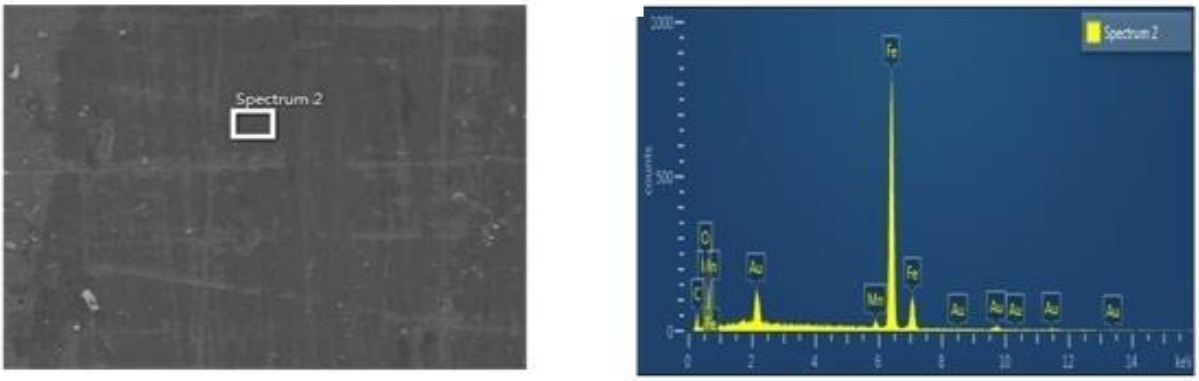
(c)


1
2
C
O
Fe
Na
Mg
Si
P
Cl
Au
Mn
keV

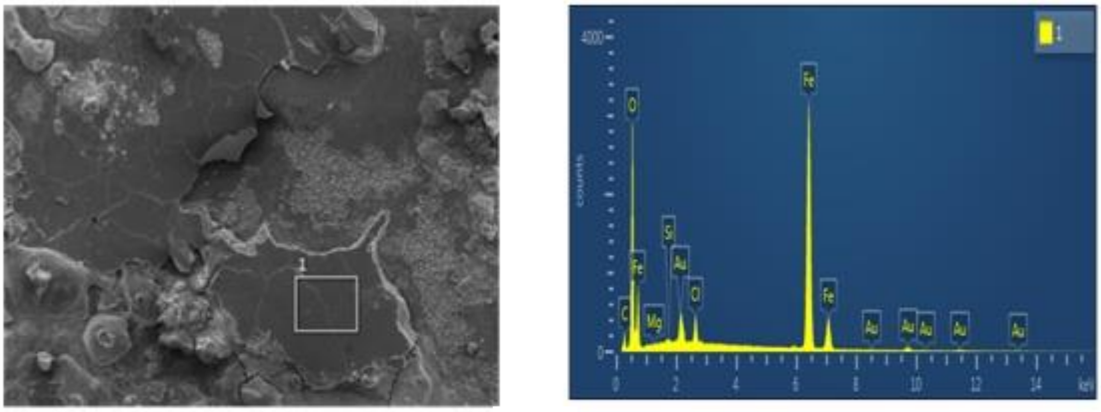
(d)


Spectrum 4
O
C
Fe
Mn
Au
Cl
keV

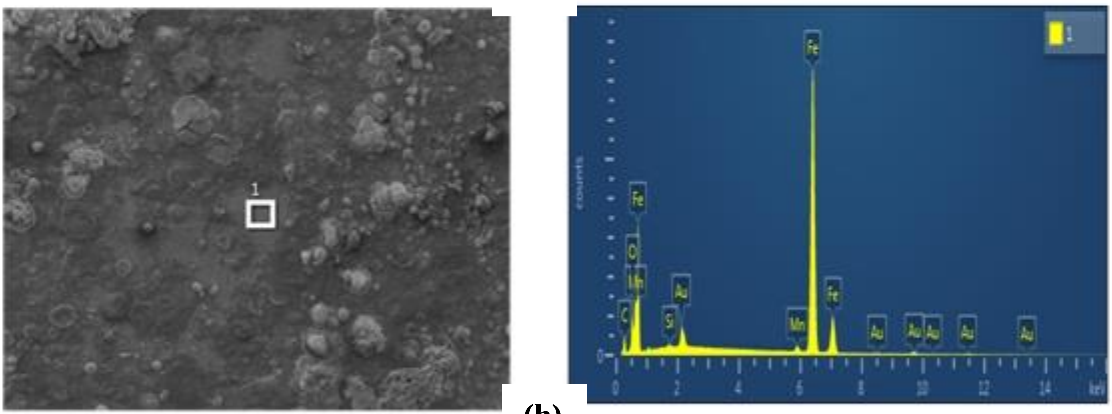
(e)


Spectrum 2
O
C
Mn
Au
Fe
keV

(f)



(g)



(h)

Figure 6.SEM images for (a) 3.5% NaCl at 30 °C (b) P1 inhibitor at 30 °C (c)3.5% NaCl at 40 °C (d) P1 inhibitor at 40 °C (e) 3.5% NaCl at 60 °C (f) P1 inhibitor at 80 °C (g) 3.5% NaCl at 30 °C (h) P1 inhibitor at 80 °C with10 Mpa pressure of carbon dioxide.

The surface of the metalwasexaminedthrough SEM-EDX to draw exclusive conclusion about the action of inhibitors. Figure 6 shows the images of electrode surface with and withoutPorphyrins at varioustemperatures. Figure 6a, 6c, 6e, and 6g shows the surface of metalwithoutinhibitor. As canbeobserved the surface isvery rough, cracked and deteriorated. The EDX peaksalso show various corrosion by-productpeaks. While in Figure 6b, 6d, 6f and 6h the surface of the metalisverysmooth, uniform and lessdeteriorated. The EDX peak show the heteroatomspresent in the inhibitormolecule and the by-productpeaks are supressed due to inhibitor film [30].

4. CONCLUSIONS

- Porphyrinscannotbeused as effective corrosion inhibitor for N80 steel at high temperaturesin 3.5% NaCl solution containingcarbondioxide.
- The E_{corr} values (< 85 mV) suggeststhatall the inhibitorsusedbelong to mixed type category.
- The SEM and contact angle analyses confirmed the formation of metal-inhibitorcomplexwhichwaslaterruptured at high temperature.

ACKNOWLEDGMENTS
Authors are thankful for the Sichuan 1000 Talent fund, Sichuan Province project and Open Fund (PLN1411) of State Key Laboratory of Oil and GasReservoirGeology and Exploitation, SouthwestPetroleum University.

References

1. Ambrish Singh, K. R. Ansari, Yuanhua Lin, M. A. Quraishi, Hassane Lgaz, *J. Taiwan Inst. Chem. E.,* 000 (2018) 1.
2. A. Singh, Y. Lin, M. A. Quraishi, O. L. Olasunkanmi, O. E. Fayemi, Y. Sasikumar, B. Ramaganthan, I. Bahadur, I. B. Obot, A. S. Adekunle, M. M. Kabanda, E. E. Ebenso, Molecules, (2015) 2015122.
3. Ambrish Singh, K.R. Ansari, Jiyaul Haque, Parul Dohare, Hassane Lgaz, Rachid Salghi, M.A. Quraishi, *J. Taiwan Inst. Chem. E*., 82 (2018) 233.
4. A. Singh, K. R. Ansari, X. Xu, Z. Sun, A. Kumar, Y.Lin, (2017) *Sci. Report*., 7 (2017) DOI:10.1038/s41598-017-13877-0.
5. A. Singh, Yuanhua Lin, K. R. Ansari, M. A. Quraishi, E. E. Ebenso, Songsong Chen, W. Liu, *Appl. Surf. Sci.,* 359 (2015) 331.
6. B. Evgenij, J. R. Macdonald, Impedance Spectroscopy Theory, Experiment, and Applications, John Wiley& Sons, New Jersey, (2005).
7. A. Singh, K.R. Ansari, A. Kumar, W. Liu, C. Songsong, Y. Lin, *J. Alloys Comp.,*712 (2017)121.
8. A. Singh, Y. Lin, E. E. Ebenso, W. Liu, B. Huang, *Int. J. Electrochem. Sci*., 9 (2014) 5993.
9. A. Singh, E. E. Ebenso, M. A. Quraishi, Y. Lin, *Int. J. Electrochem. Sci*., 9 (2014) 7495.
10. M. A. Quraishi, A. Singh, V. K. Singh, D. K. Yadav, A. K. Singh, *Mater. Chem. Phys.,* 122 (2010) 114.
11. Hongwei Feng, Ambrish Singh, Yuanpeng Wu, Yuanhua Lin, *New J. Chem*., (2018) DOI: 10.1039/c8nj01676c.
12. A. Singh, Y. Lin, W.Liu, S. Yu, J.Pan, C. Ren, D. Kuanhai, *J. Ind. Eng. Chem*., 20 (2014) 4276.
13. Ambrish Singh, Mohd Talha, Xihua Xu, Zhipeng Sun, Yuanhua Lin, *ACS Omega*, 2 (2017) 8177.
14. I. Ahamad, R. Prasad, M. A. Quraishi, *Corros. Sci.,* 52 (2010) 1472.
15. A. Singh, I. Ahamad, V. K. Singh, M. A. Quraishi, *J. Solid State Electrochem.,* 15 (2011) 1087.
16. Ambrish Singh, K. R. Ansari, M. A. Quraishi, Hassane Lgaz and Yuanhua Lin, *J. Alloys Comp*., 762 (2018) 347.
17. K. F. Khaled, M. A. Amin, *Corros. Sci.,* 51 (2009) 1964.
18. A. Khamis, M. M. Saleh, M. I. Awad, *Corros. Sci.,* 66 (2013) 343.
19. A. Singh, I. Ahamad, M. A. Quraishi, *Arab. J. Chem.,* 9 (2016) S1584.
20. K. M. Ismail, *Electrochim. Acta.,* 53 (2008) 5953.
21. Xihua Xu, A. Singh, Z. Sun, K. R. Ansari, Y. Lin, *R. Soc. Open Sci*., 4 (2017) http://dx.doi.org/10.1098/rsos.170933.
22. Priyanka Singh, Ambrish Singh, M.A. Quraishi, *J. Taiwan Inst. Chem. E*., 60 (2016) 588.
23. Ambrish Singh, Y. Lin, W.Liu, S. Yu, J.Pan, C. Ren, D. Kuanhai, *J. Ind. Eng. Chem*. 20 (2014) 4276.
24. Ambrish Singh, Y. Lin, I. B. Obot, E. E. Ebenso, K. R. Ansari, M. A. Quraishi, *Appl. Surf. Sci*., 356 (2015) 341.
25. Ambrish Singh, Yuanhua Lin, Eno. E. Ebenso, Wanying Liu, Jie Pan, Bo Huang, *J. Ind. Eng. Chem.* 24 (2015) 219.
26. H. Keles, M. Keles, I. Dehri, O. Serindag, *Col. Surf.* A., 320 (2008) 138.
27. A. Singh, Y. Lin, I. B. Obot. E. E. Ebenso, *J. Mol. Liq*., 219 (2016) 865.
28. K.R. Ansari, M.A. Quraishi, A. Singh, *Corros. Sci*., 79 (2014) 5.
29. Yuanhua Lin, Ambrish Singh, E. E. Ebenso, Yuanpeng Wu, Chunyang Zhu,H. Zhu,*J. Tai. Inst. Chem. Eng*., 46 (2015) 214.

30. K.R. Ansari, M.A. Quraishi, A. Singh, *Corros. Sci.,* 95 (2015) 62.