International Journal of Innovative Technology and Exploring Engineering (IJITEE)
ISSN: 2278-3075 (Online), Volume-3 Issue-12, May 2014

Nano Analyses of Protective Film onto Carbon Steel

T.Kasilingam, C.Thangavelu

Abstract— The corrosion inhibition effect of cathodic surfactant, namely: dodecyl trimethyl ammonium bromide (DTAB) and zinc ions, have been used as corrosion inhibitor for carbon steel in well water. Surface analysis using SEM, EDAX and AFM shows a significant morphological improvement on the carbon steel surface with the addition of inhibitors. FTIR spectra revealed the interaction between inhibitor molecules and carbon steel surface.

Keywords: AFM, Inhibitor, SEM-EDAX, Weight loss,

I. INTRODUCTION

The corrosion of iron and carbon steel is a fundamental, academic and industrial concern that has received a considerable amount of attention [1]. Water distribution systems have been primarily composed of iron and steel pipes for over five centuries that are inevitably subject to corrosion and will cause hundreds of billions dollars expenditure on repairing and replacing corroded pipes over the next twenty years. Corrosion of system pipes has economic, hydraulic and aesthetic impacts, including water leaks, corrosion product build up, increase pumping costs, and water quality deterioration (red water). Minimization of corrosion problems mainly depends on the investigations on the pipe materials [2,3].

Surfactants are molecules composed of a polar hydrophilic group, the 'head' attached to a non polar hydrophobic group, the 'tail'. In generally, in aqueous solution the inhibitory action of surfactant molecules may also be due to physical (electrostatic) adsorption or chemisorptions onto the metallic surface, depending on the charge of the solid surface and the free energy change of transferring a hydrocarbon chain from water to the solid surface. the adsorption of the surfactant markedly changes the corrosion resisting property of a metal and for this reason, studies on the relation between adsorption and corrosion inhibition are of considerable importance[4,7]. The adsorption behaviour of surfactant at the solid-solution interface is described by many authors[8].

Ionic surfactant have been used for the corrosion inhibition of steel [9,20], copper[21-24], aluminium[25,28] and other metals[29] in different media.

The objective of this work is to study the effect of investigates inhibitor on the corrosion of carbon steel in well water with weight loss techniques. Investigate chemical bond interaction of the inhibitor molecule by using FTIR spectra. Another objective in this work is to study the surface morphology using SEM, AFM and EDX.

Manuscript published on 30 May 2014.
***Correspondence Author(s)**
Mr.T.Kasilingam, Department of Chemistry, Periyar E.V.R. College (Autonomous), Tiruchirappalli, Tamil Nadu, India.
Dr.C.Thangavelu, Department of Chemistry, Periyar E.V.R. College (Autonomous), Tiruchirappalli, Tamil Nadu, India.

II. EXPERIMENTAL DETAILS

A. Materials

The composition of carbon steel used for corrosion inhibition studies was (Wt %): 0.026% S, 0.06% P, 0.4% Mn, 0.1% C and balance being Fe. The specimens of size 1.0cm×4.0cm×0.2cm were press cut from the carbon steel sheet, were machined and abraded with a series of emery papers. This was followed by rinsing in acetone and bidistilled water and finally dried in air. Before any experiment, the substrates were treated as described and freshly used with no further storage. The inhibitors DTAB, molecular mass 308.30g mol^{-1}, Zn^{2+} ions were used as received. A stock solution of 1000ppm of DTAB was prepared in bidistilled water and the desired concentration was obtained by appropriate dilution. The concentration of DTAB used for the study ranges from 10 to 150ppm. All solutions were using well water (Tiruchirappalli, Tamil Nadu, India). The study was carried out at room temperature. The molecular structure of DTAB is given in Fig 1. The environmental chosen well water and the physico-chemical parameter of well water is given in Table 1.

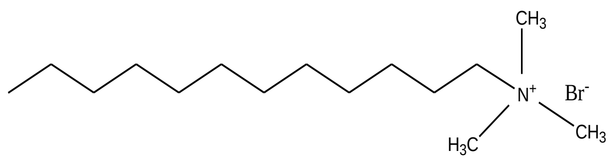

Figure 1 Molecular structure of DTAB

Table 1 physico-chemical parameter of well water

Parameters	Values
pH	8.0
TDS	1092ppm
Chloride	220ppm
Alkalinity	300ppm
Total Hardness	450ppm
Conductivity	1747μmhos/cm

B. Weight - loss Measurements

The freshly prepared carbon steel specimens were suspended in 150ml beakers containing 100ml of test solution maintained at room temperature with the aid of glass rods and hooks. The weight loss taken was the difference between the weight at a given time and the original weight of the specimens. The measurements were carried out for the uninhibited solution and the solution containing DTAB and DTAB - Zn^{2+} mixture.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

Weight loss experiments were performed for the duration of seven days. The specimens were immersed in triplicate and the average corrosion rate was calculated. These uncertainties or RSD for three replicate measurements were less than 5%. The corrosion rates (CR) were determined using the equation:

$$CR\left(\frac{mm}{y}\right) = \frac{87.6 \times w}{a\,t\,D}$$

where w = corrosion weight loss of carbon steel (mg)
a = area of the coupon (cm^2)
t = exposure time (h)
D = density of the carbon steel (g cm^{-3}).

The inhibition efficiency (IE) of DTAB - Zn^{2+} mixture was calculated by using the following equation:

$$\%IE = \frac{CRo - CRi}{CRo}$$

where CRo = corrosion rate of carbon steel in the absence of inhibitor
CRi = corrosion rate of carbon steel in the presence of inhibitor

C. Surface analysis by FTIR spectroscopy

After the immersion period of one day in various environments, the specimens were taken out of the test solution and dried. The film formed on the surface was scratched carefully and it was thoroughly mixed so as to make it uniform throughout. FTIR spectrum of the powder (KBr Pellets) was record using perkin-elmer-1600 FTIR spectrophotometer with resolving power of 4 cm^{-1}.

D. Scanning Electron Microscopy

The surface morphology of the corroded steel sample surface in the presence and absence of the inhibitors was studied using SEM (Model: TESCAN vega3 USA). To study the surface morphology of carbon steel, polished specimens prior to initiation of any corrosion reaction, were examined in optical microscope to find out any surface defect, such as prior noticeable irregularities like cracks etc. Only those specimens, which had a smooth pit-free surface, were subjected to immersion. The specimens were immersed for 24h at 30^0C. After completion of the tests specimens were thoroughly washed with bidistilled water and dried and then subjected to SEM examination.

E. Energy Dispersive Analysis of X-ray (EDAX)

EDAX (Model: BRUKER Nano Germany) system attached with Scanning Electron Microscope was used for elemental analysis or chemical characterization of the film formed on the carbon steel surface. As a type of spectroscopy, it relies on the investigation of sample through interaction between electromagnetic radiation and the matter. So that, a detector was used to convert X-ray energy into voltage signals. This information is sent to a pulse processor, which measures the signals and passed them into an analyzer for data display on the analysis.

F. Atomic Force Microscopy (AFM)

Atomic force microscopy is a powerful method for the gathering of roughness statistics from a variety of surfaces. This exciting new techniques that allows surface to be imaged at higher resolutions and accuracies than ever before. The protective films are examined for a scanned area. AFM is becoming an accepted technique of roughness investigation [30-33]. AFM provided direct insight into the changes in the surface morphology takes place at several hundred nanometers when topographical changes owing to the initiation of corrosion and formation of protective film on to the metal surface in the with and without addition of inhibitors respectively. All the AFM images were recorded on a Pico SPM2100 AFM instrument operating in contact mode in air. The scan size of all the AFM images are 40μm × 40μm areas at a scan rate of 0.20(H_z) lines per second.

III. RESULTS AND DISCUSSION

A. Weight-loss measurements

The inhibition behaviour of surfactant in controlling corrosion of carbon steel immersed in well water for a duration seven days in the both without and with of DTAB and Zn^{2+} is given in Table 2. It can be seen from data that Zn^{2+} alone has some IE and DTAB alone is poor inhibitor and is found to be corrosive. For example 75ppm of DTAB has 23% IE and 25ppm of Zn^{2+} has 20% IE. However the combination of 75ppm of DTAB and 25ppm of Zn^{2+} has 78% IE. This is found to be the maximum IE obtained by the system. This clearly suggests that DTAB and Zn^{2+} mutually enhance the inhibition efficiency of each other in controlling the corrosion of carbon steel. The synergism is due to the formation of complex with DTAB and the role of Zn^{2+} is to transport the surfactant inhibitor from the bulk of the solution onto the metal surface.

Table. 2. Corrosion parameters for carbon steel in well water in without and with addition of inhibitors measured by using weight – loss technique

Conc. of Zn^{2+} ppm	Conc. of DTAB ppm	Corrosion Rate mmy^{-1}	IE (%)	Surface Coverage (θ)	Synergism (S_I)
Blank	-	194.4	-	-	-
25	-	155.5	20	0.20	-
-	10	196.4	-1	0.01	-
-	25	182.0	6	0.06	-
-	50	175.0	10	0.10	-
-	75	149.7	23	0.23	-
-	100	163.3	16	0.16	-
-	125	171.1	12	0.12	-
-	150	178.9	8	0.08	-
25	10	151.6	22	0.22	1.03
25	25	134.1	31	0.31	1.08
25	50	101.1	48	0.48	1.38
25	75	42.7	78	0.78	2.80
25	100	70.0	64	0.64	1.86
25	125	83.6	53	0.53	1.49
25	150	108.9	44	0.44	1.31

B. Analyses of FTIR spectra

The FTIR Spectrum of pure DTAB is shown in Fig 2a. The stretching frequency of C-Br appear at 530.42cm^{-1}. The FTIR spectrum of film formed on the carbon steel surface after immersion in the solution containing 75ppm of DTAB and 25ppm of Zn^{2+} are shown in Fig 2b.

Published By:
Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP)

The DTAB of C-Br stretching frequencies are shifted from 530.42cm^{-1} to 470.63cm^{-1}. This shift indicate that electron cloud density of DTAB and Zn^{2+} atoms is coordinated with Fe^{2+} on anodic sites of the metal surface.

The stretching frequency appear at 1381cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface[34,35]. Thus FTIR spectral analyses leads to the conclusion that the protective film consists of Fe^{2+} - DTAB complex and $Zn(OH)_2$.

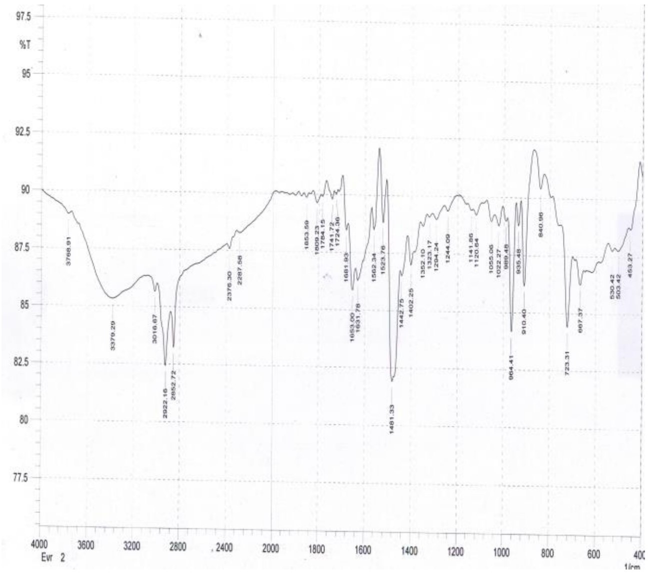

Fig.2a: Pure DTAB

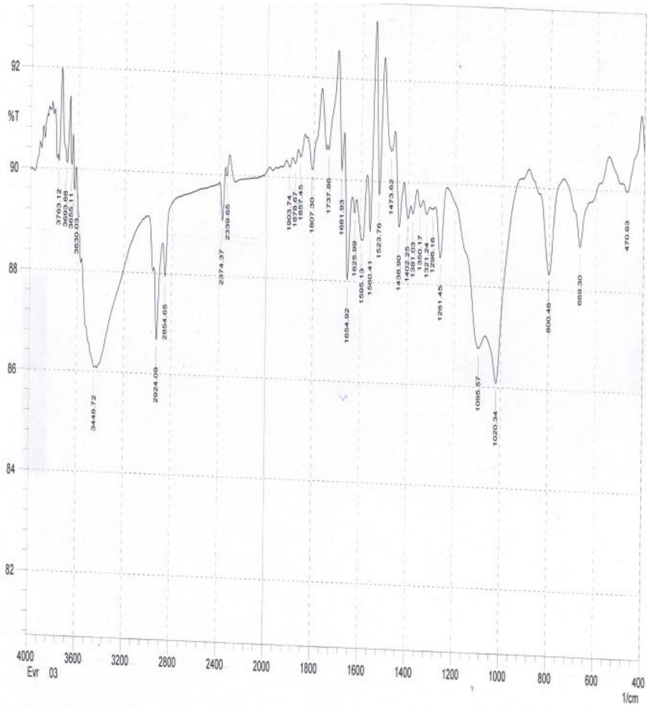

Fig.2b: 25ppm Zn^{2+} + 75ppm DTAB

C. Evidence of Surface Morphology

SEM micrographs for carbon steel in well water without and with inhibitor system have been presented in Fig.3. The morphology of the carbon steel specimen in without addition of inhibitor is very rough and the surface was damaged due to metal dissolution. Polished carbon steel surface (Fig. 3a) is good surface properties as compared to the blank material (Fig. 3b). At 25ppm Zn^{2+} + 75ppm DTAB, it has been found that the smoothness of the surface improved remarkably and the metal surface is almost free from corrosion due to the better coverage of the metal surface (Fig. 3c).

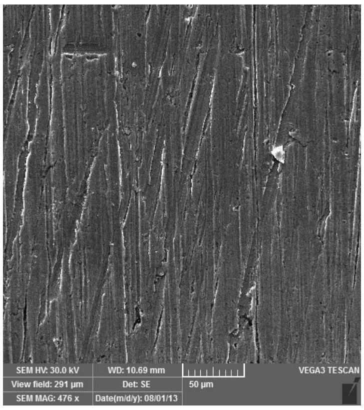

Fig.3a: Polished metal

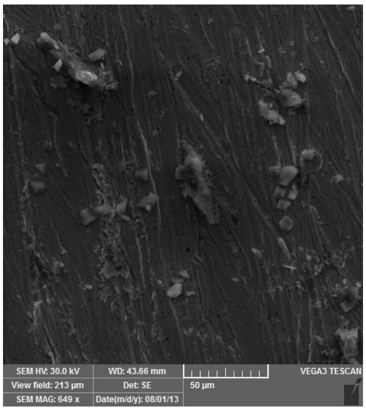

Fig.3b: After immersion in well water without inhibitor

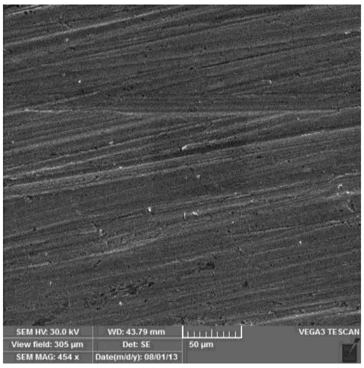

Fig.3c: After immersion in well water with inhhibitor 25ppm Zn^{2+} + 75ppm DTAB

Further, the surface morphology of carbon steel specimens was studied by atomic force microscopy which also predicts the same trend as in SEM micrographs. Fig.4.(a-c) show the 3D AFM micrographs of the carbon steel samples in well water containing without and with addition of inhibitor respectively. The relative roughness has been plotted in Fig.4d. which also indicates smoother surface for 25ppm Zn^{2+} + 75ppm DTAB. Average roughness factor have been calculated 133.1, 235.7 and 92.8 nm for polished carbon steel, After immersion in well water without inhibitor and after immersion in well water in the presence of25ppm Zn^{2+} + 75ppm DTAB, respectively.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

The smoothening of the surface was caused by the deposition of the inhibitor molecules on the surface which protects the surface from the attack of corrosive environment. Hence, both SEM and AFM studies of the metal surface coverage support the result obtained from other techniques.

Table 3: AFM data for carbon steel immersed in without and with inhibitor systems

Samples	RMS(R_q) Roughness (nm)	Average(R_a) Roughness (nm)	Maximum Peak – to – valley Height (nm)
Without inhibitor system (blank)	310.0	235.7	914
Polished carbon steel (Reference)	168.5	133.1	480.0
With inhibitor system	117.2	92.8	339.3

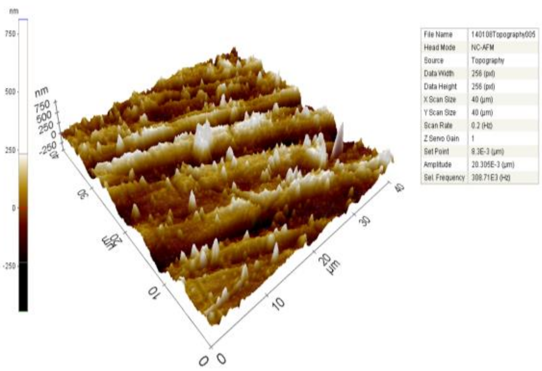

Fig.4a: Polished carbon steel surface

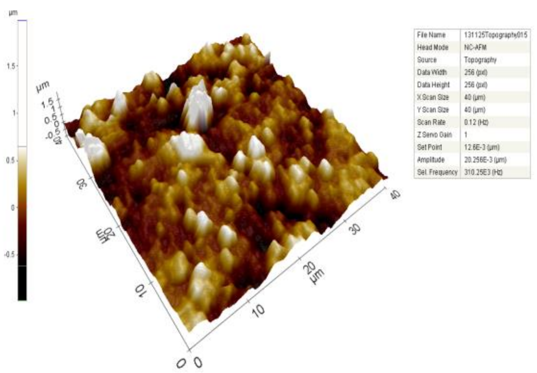

Fig.4b: Without inhibitor (Blank)

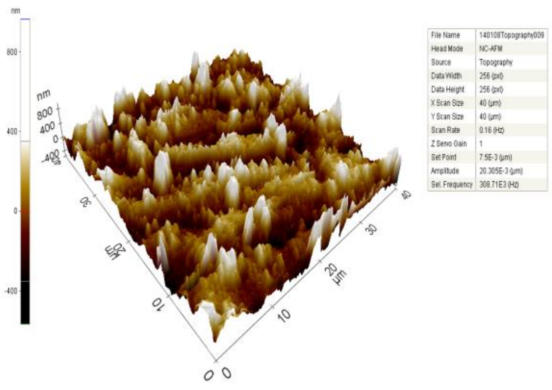

Fig.4c: With inhibitor (25ppm Zn^{2+} + 75ppm DTAB)

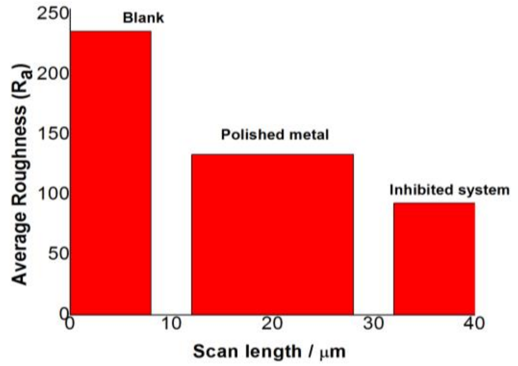

Fig.4d: Plot of Average Roughness

D. Energy dispersive X-ray analysis (EDX)

The composition of protective film formed on the carbon steel surface was analyzed using EDX as shown in Fig. 5. (a-c). The EDX spectrum of polished carbon steel sample in Fig.5a shows a unity of surface composition properties, while the spectrum in case of carbon steel sample immersed in well water absence of inhibitor molecules was failed because it is severely weakened due to the corrosion as shown in Fig.5b. by adding 25ppm Zn^{2+} + 75ppm DTAB the decrease of iron peak and appearance of carbon, bromide and zinc peak was observed due to the formation of a strong protective film of the inhibitor molecules on the surface of carbon steel sample. The action of inhibitor is related to adsorption and formation of a barrier film on the electrode surface. The formation of such a barrier film is confirmed by SEM, AFM and EDX examination of carbon steel surface.

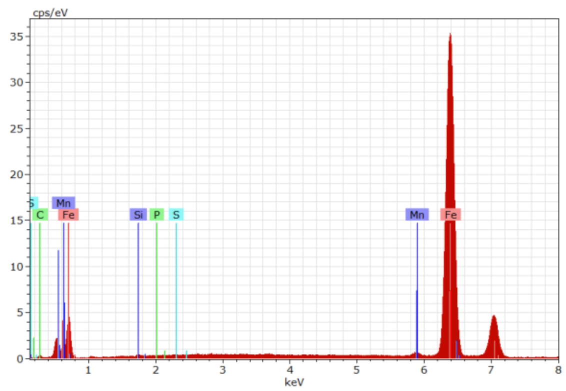

Fig.5a: Polished metal

Published By:
Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP)

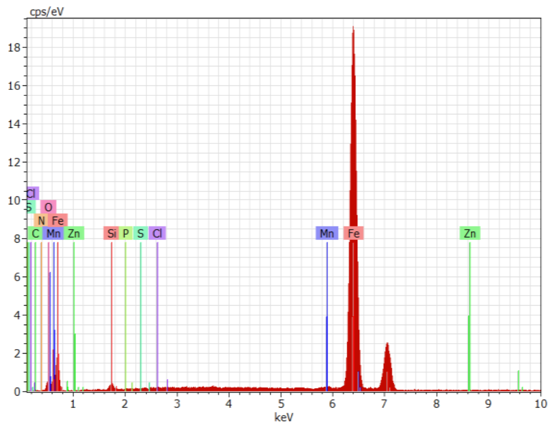

Fig.5b. After immersion in well water (without inhibitor)

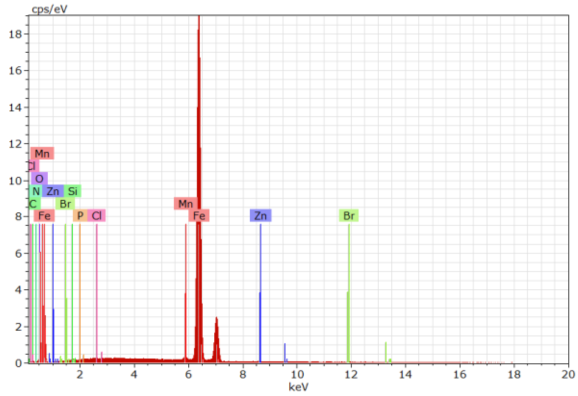

Fig.5c. After immersion in well water (with inhibitor)

IV. CONCLUSION

The result of weight – loss shows that 25ppm Zn^{2+} + 75ppm DTAB has an excellent inhibiting property and the inhibitor system has good synergistic effect in well water. Surface morphological studies such as FTIR, SEM, AFM and EDX analysis showed that a film of inhibitor is formed onto the surface of carbon steel.

ACKNOWLEDGMENT

The author is thankful to Principal of Periyar E.V.R. College (Autonomous) Tiruchirappalli – 23. The investigator sincerely thanks to Dr.M.M.Senthamil Selvi, Head of the Department & Control of Examination, Department of Chemistry, Periyar E.V.R. College(Autonomous) Tiruchirappalli – 23. Dr.K.Selvarani, Assistant Professor of Chemistry, Periyar E.V.R. College (Autonomous) Tiruchirappalli – 23, for their support and encouragement

REFERENCES

1. P.R. Roberge, Handbook of corrosion engineering McGraw – Hill, 2000.
2. Melchers. E, Jeffery. R, "Corrosion Reviews", 1(2005) 84.
3. Melchers. R.E, Jeffery. R, "Corrosion Reviews", 6 (2005) 297.
4. J.M Bastidas, P.pinilla, J.L. Polo, S. Miguel, "Copper corrosion inhibition by triphenylmethane derivatives in sulphuric acid media" Corros. Sci. 45(2003) 427-449.
5. A.E. Bolzan, I.B. Wakenge, R.C.V. Pittai, R.C. Salvarezza, A.J. Arvia, "The behaviour of copper anodes in aqueous thiourea-containing sulphuric acid solutions. Open circuit potentials and electrochemical kinetics".J.Electroanal. Chem. 501(2001) 241-252.
6. E. Stipnisek-Lisac, A. Gazivoda, M. Madzarac, "Evaluation of non-toxic corrosion inhibitors for copper in sulphuric acid" Electrochim. Acta 47 (2002) 4189-4194.
7. M. Sahin, S. Bilgic, H. Yilmaz, "The inhibition effects of some cyclic nitrogen compounds on the corrosion of the steel in NaCl mediums" Appl. Surf. Sci.195 (2002) 1-7.
8. C.A. Miller, S. Qutubuddin, in: H.F. Eick, C.D. parfitt(Eds.), Interfacial Phenomena in Apolar Media, Surfactant Science Series, vol. 21, Markel Dekker Inc., New York, Basel, 1987, p. 166.
9. Elachouri, M.S. Hajji, M. Salem, S.Kertit, R. Coudert, E.M. Essassi, "Some surfactants in the series of 2-(alkyldimethylammonio) alkanol bromides as inhibitors of the corrosion of iron in acid chloride solution" Corros. Sci 37 (1995) 381-389.
10. M.A. Migahed, E.M.S. Azzam, A.M. Al-Sabagh, "Corrosion inhibition of mild steel in 1 M sulfuric acid solution using anionic surfactant" Mater ChemPhys 85 (2004) 273-279.
11. M.M. Osma. A.M. Omer, A.M. Al-Sabagh, "Corrosion inhibition of benzyl triethanol ammonium chloride and its ethoxylate on steel in sulphuric acid solution" Mater ChemPhys 50 (1997) 271-274.
12. F. Zucchi, G.Trabanelli, G.Brunoro, "The influence of the chromium content on the inhibitive efficiency of some organic compounds" Corros Sci 33 (1992) 1135.
13. M. Elachouri, M.S. Hajji, M. Salem, S.Kertit, R. Coudert, E.M. Essassi, "Some surfactants in the series of 2-(alkyldimethylammonio) alkanol bromides as inhibitors of the corrosion of iron in acid chloride solution" Corros. Sci 37 (1995) 381-389.
14. Z. Wei, P. Duby, P. Somasundram, "pitting inhibition of stainless steel by surfactants: an electrochemical and surface chemical approach" J Colloid Interface Sci 259 (2003) 97-102.
15. J.M. Bastidas, J.L. Polo, E. Cano, C.L. Torre, "tributylamine as corrosion inhibitor for mild steel in hydrochloric acid" J Mater Sci 35 (2000) 2637.
16. J.M. Bastidas, J.L. Polo, E. Cano, "Substitutional inhibition mechanism of mild steel hydrochloric acid corrosion by hexylamine and dodecylamine" J Appl Electrochem 30 (2000) 1173.
17. Z. Abdel Hamid, T.Y. Soror, H.A. El Dahan, A.M Omer, "New cationic surfactant as corrosion inhibitor for mild steel in hydrochloric acid solutions" Anti – Corros Methods Mater 45 (1998) 306.
18. M. Saleh, A.A. Atia, "Effects of structure of the ionic head of cationic surfactant on its inhibition of acid corrosion of mild steel" J Appl Electrochem 36 (2006) 899.
19. M.A. Migahed, "Electrochemical investigation of the corrosion behaviour of mild steel in 2 M HCl solution in presence of 1-dodecyl-4-methoxy pyridinium bromide" Mater Chem Phys 93 (2005) 48.
20. A.M. Al Sabagh, M.A. Migahed, H.S. Awad HS, "reactivity of polyester aliphatic amine surfactants as corrosion inhibitors for carbon steel in formation water (deep well water)" Corros SCi 48 (2006) 813.
21. R. Fuchs-Godec, V. Dolecek, "a effect of dodecylsulfate of the corrosion of copper in sulphuric acid media" Colloids Surf A 244 (2004) 73.
22. H. Ma, S. Chen, B. Yin, S. Zhao, X. Liu, "impedance spectroscopic study of corrosion inhibition of copper by surfactant in the acidic solutions" Corros Sci 45 (2003) 867.
23. A.A. Amin, "weight loss, polarization, electrochemical impedance spectroscopy, SEM and EDX studies of the corrosion inhibition of copper in aerated NaCl solutions" J Appl Electrochem 36 (2006) 215.
24. D.Q. Zhan, L.X. Gao, G.D. Zhou, K.Y.Lee, "undecyl substitution in imidazole and its action on corrosion inhibition of copper in aerated acid chloride media" J Appl Electrochem 38 (2008) 71.
25. T.P. Zhao, G.N. Mu,"the adsorption and corrosion inhibition of anion surfactant on aluminium surface n hydrochloric acid" Corros Sci 41 (1991) 1937.
26. S.S. Abd El Rehim, H.H. Hassaan, M.A. Amin, "corrosion inhibition of aluminium by 1,1(lauryl amido)propyl ammonium chloride in HCl solution" Mater ChemPhys 70 (2001) 64.
27. S.S. Abd El Rehim, H.H. Hassaan, M.A. Amin, "the corrosion inhibition study of sodium dodecyl benzene sulphonate to aluminium and its alloys in 1.0 M HCl solution" Mater ChemPhys 78 (2002) 337.
28. A.K. Maayta, N.A.F. Al-Rawashdeh, "inhibition of acidic corrosion of pure aluminum by some organic compounds" Corros Sci 46 (2004) 1129.
29. R. Guo, T. Liu, X. Wei, "effect of SDS and some alcohols on the inhibition efficiency of corrosion for nickel" Colloids Surf A 209 (2002) 273-278.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)

30. Ph. Dumas, B. Butffakhreddine, C. Am, O.Vatel, E.Ands, R.Galindo and F.Salvan, "Quantitative microroughness analysis down to the nanometer scale, Europhys. Lett. 22 (1993)717-722.
31. J.M. Bennett, J. Jahannir, J.C.Podlesny, T.L. Baiter and D.T.Hobbs, "Scanning force microscopy as a tool for studying optical surface, Appl. Opt 43(1995)213-230.
32. A.Duparre, N.Kaiser, H.Truckenbrodi, M.Berger and A.Kohler, "Microtopography investigations of optical surfaces and thin films by light scattering, optical profilometry SPIE, 1995(1993)181-192.
33. C.Amra, C. Deumie, D.Torricini, P.Roche, R.Galindo, P.Dumas and F.Salvan Overlapping of roughness spectra measured in microscopic (Optical) and microscopic (AFM) bandwidths, Int. Symp. On Optical Interference Coatings, 6-10 June 1994. Grenoble, Proc. SPIE 2253(1994)614-630.
34. C.Thangavelu, P.Patric Raymond, S. Rajendran, M. Sundaravadivelu, "Influence of Chloride Ion on the Corrosion Inhibition Efficiency of the ATMP-Zn2+ System," Asian j. Research Chem. 4(3)(2011)402-405.
35. C.Thangavelu, M.Umarani, M. Sekar, "Eco- Friendly Inhibitor System for Corrosion Inhibition of Carbon Steel in High Chloride Media", RASAYAN.J.Chem. 4(2011)245-250.

AUTHOR PROFILE

T. Kasilingam Research Scholar, PG & Research Department of Chemistry, Periyar E.V.R. College (Autonomous), Affiliated to Bharathidasan University, Tiruchirappalli – 23, Tamil Nadu, India.

Dr. C. Thangavelu, Assistant Professor, PG & Research Department of Chemistry, Periyar E.V.R. College (Autonomous), Affiliated to Bharathidasan University, Tiruchirappalli – 23, Tamil Nadu, India.

Published By:
Blue Eyes Intelligence Engineering
and Sciences Publication (BEIESP)