Study of corrosion inhibition of mild steel in in 0.01M H_2SO_4 by corrosion inhibitors: A comparative Study

REETU AND HARDEEP ANAND

Department of Chemistry, Kurukshetra University, Kurukshetra-136119, Haryana, India
Corresponding author: reetusalyan@gmail.com

Abstract

Mild steel is the raw material for the construction and fabrication of weapons and equipments. In order to study synergistic effect, various combinations of caffeine, acetamide and benzalkonium chloride (BKC), ammonium ceric nitrate, myristic acid were investigated as corrosion inhibitors for mild steel. Corrosion rate and percentage inhibition efficiency of various combination of corrosion inhibitors(100, 200, 300 ppm of different concentration of caffeine, acetamide, benzalkonium chloride (BKC), ammonium ceric nitrate, myristic acid in 0.01 M H_2SO_4 at two different temperature 298K and 318K by weight loss method, SEM. The results obtained revealed that value of inhibition efficiency decreases to a large rate in case of myristic acid and acetamide but to a slight decrease in case of BKC with the increase in temperature. The protection of metals from corrosion is analyzed by many technologies such as weight loss, Scanning Electron Microscope (SEM).

Keywords: Corrosion inhibitors, Caffeine, Acetamide, Benzalkonium Chloride, Myristic acid, Ammonium Ceric Nitrate

Introduction

The corrosion of steel is the most common form of corrosion, especially in acid solution [1] Mild steel is widely used in many industrial applications. In most industrial processes, the acidic solutions are commonly used for the pickling, industrial acid cleaning, acid descaling, oil well acidifying etc. [2-6]. The aim of the present work is to study the behaviour of mild steel in 0.01N sulphuric acid in the absence and presence of caffine, acetamide, benzalkonium chloride (BKC), ammonium ceric nitrate and myristic acid as a corrosion inhibitor for mild steel using weight loss method and SEM. Further the study also focuses on the inhibition mechanism based on the adsorption isotherms, activation and thermodynamic parameters obtained.

The main advantage of this acid over the other acids in cleaning and pickling operations lies in its ability to form metal chloride, which is extremely soluble in aqueous medium, compared to sulphate phosphate and nitrate. The higher solubility of chloride salt causes the least polarizing effect and does not hinder the rate of corrosion [7-8]. Various protective methods have been adopted; one of the frequently used measures is the use of organic compounds containing nitrogen, oxygen and sulphur atoms **[9-13]**.

The use of organic compounds containing oxygen, sulfur and especially nitrogen to reduce corrosion attack on steel has been studied in some detail [14-16]. unsaturated bonds and/or aromatic rings [17-19] The compounds having the –C,N– group, electron donating groups, polar groups, and p electrons are reported to behave as effective inhibitors of mild steel in acid medium [20-22].

The adsorption of corrosion inhibitor depends mainly on physico-chemical properties of the molecule such as functional groups, steric factor, molecular size, molecular weight, molecular structure, aromaticity, electron density at the donor atoms and p-orbital character of donating electrons [23-27] and also on the electronic structure of the molecules [28-29]. Many studies have been made on the corrosion and inhibition of steels in acid media [30-34]. In the present work, the electrochemical behaviour of mild steel in 0.01 M H_2SO_4 in the absence and presence of benzotriazole derivatives has been investigated by potentiodynamic polarization, electrochemical impedance and weight-loss measurements.

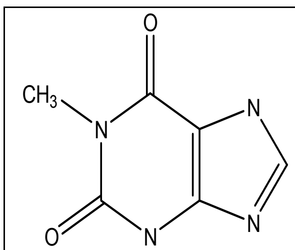
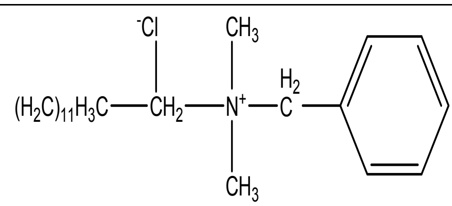
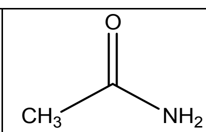
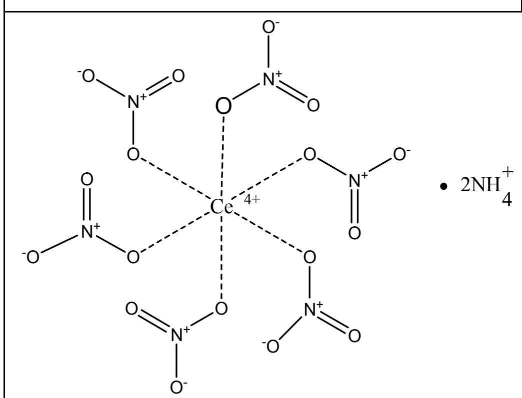
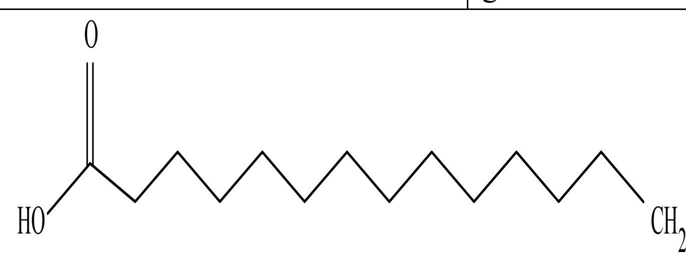
Experimental:

Mild steel used for the investigation was in the form of sheet (0.25mm thick) and had the following composition. C, 0.14;Si, 0.03;Mn, 0.32; P, 0.02; Ni, 0.01; Cu 0.01; Cr, 0.01; Fe, balance(w/w)

Sample Preparation:

For weight loss measurements, carbon steel specimen of 3cm × 2.0cm size were cut from the sheet were used. All the specimens were mechanically polished successively with the help of emery papers of grades 80, 100, 220, 320 and 400 and then thoroughly washed with distilled water and then acetone.The specimen were dried and stored in a desicator over silica gel. All the chemicals used were of A.R. grade and solution were prepared using double distilled water,Duplicate or in some cases triplicate experiments have been performed to verify the experimental data:

Table 1: Name and structure of four Vapour Phase Corrosion Inhibitors

 Caffine : Mol Wt. 194.19g/mol	 Benzalkonium Chloride(BKC): Mol Wt. 283.88g/mol	 Acetamide : Mol Wt. 59.07 g/mol
 Ammonium Ceric Nitrate : 548.26 g/mol	 Myristic Acid : 228.3709 g/mol	

The following techniques were employed for investigating the inhibition action and mechanism of inhibitor action on the metal surface. i) Weight Loss ii) Scanning Electron Microscopy (SEM)

Weight Loss Technique:

After recording the initial weights of mild steel specimens, they were immersed in tilted position in 100 ml beaker having 80 ml of corroding solution as corroding medium with or without the inhibitor. After exposing the specimen for 24 hours at 298 K, 308 K and 318 K, the specimens were taken out from the beaker and washed with water. Loosely adhering corrosion products were removed by rubbing the specimen surface with rubber cork and the specimens were again washed thoroughly with distilled water, acetone and dried and then weighed again. Corrosion rate in miles per year (mpy) and percentage inhibition efficiency were calculated using the following equations.

$$\text{Corrosion Rate (mpy)} = \frac{534 \times W}{D \cdot A \cdot T}$$

Where W = weight loss (mg) D = density of mild steel A = area of specimen (sq. inch) T = exposure time (hours)

$$\text{Percentage inhibition efficiency} \frac{B - A}{B} \times 100$$

Where B = Weight loss in absence of inhibitor, A = Weight loss in presence of inhibitor

Scanning Electron Microscopy (SEM) Technique:

SEM is used for the study of surface of mild steel coupons to know the nature and type of corrosion. The micrograph of the corroded specimens were taken after exposure of 24 hours. Micrographs of the blank mild steel were also taken for the comparison study.

Results and Discussion

Weight Loss Technique**:** The values of weight loss (mg), corrosion rate (mpy) and PCIE for all the five corrosion inhibitors are shown in Table 2 and Table 3 at temperature 25°C and 45°C. The corrosion rate is found to be decreased. PCIE of these three inhibitors are shown in figure 1 and 2 at temperature 25°C and 45°C respectively. It is clear from the figure 1 and 2 that PCIE of BKC is highest at 25°C and 45°C.

Table 2 Weight loss, corrosion rate and percentage inhibition efficiency in 0.01 N H_2SO_4 at 25^0C

VPCI	Concentration (ppm)	Weight loss (mg)	CR (mpy)	PCIE
Blank		30.1	2.5183	
Caffine	200	28.8	2.4108	4.319
	300	24.6	2.0592	18.27
BKC	200	16.75	1.4021	44.35
	300	14.7	1.2305	51.16
Acetamide	200	21.2	1.7746	42.69
	300	16.7	1.3979	66.77
Ammonium Ceric Nitrate	200	23.0	1.9253	23.58
	300	20.5	1.7160	31.89
Myristic acid	200	15.8	1.3226	47.50
	300	11.0	0.9208	63.45

Table-3 Weight loss, corrosion rate and percentage inhibition efficiency in 0.01 N H_2SO_4 at 45^0C

VPCI	Concentration (ppm)	Weight loss (mg)	CR (mpy)	PCIE
Blank		31.75	2.6564	
Caffeine	100 300	28.8 21.2	2.4108 1.7746	9.29 33.23
Acetamide	100 300	29.1 20.5	2.4359 1.7152	8.34 35.43
BKC	100 300	14.6 12.5	1.2221 1.0464	54.01 60.63
Ammonium Ceric Nitrate	100 300	31.0 20.1	2.5950 1.6826	2.36 36.69
Myristic Acid	100 300	28.2 24.2	2.3606 2.0258	11.18 23.77

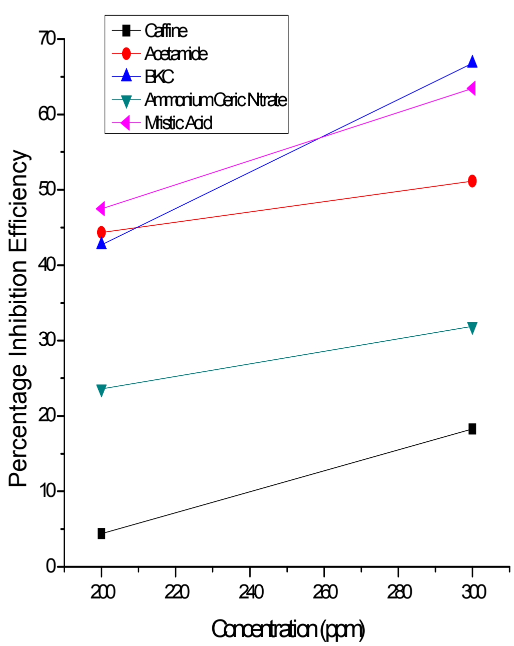


Figure 1: Percentage inhibition efficiency of Caffine, Acetamide, BKC, Ammonium Ceric Nitrate, Myristic Acid at 200,300 ppm concentration at 25^0 C

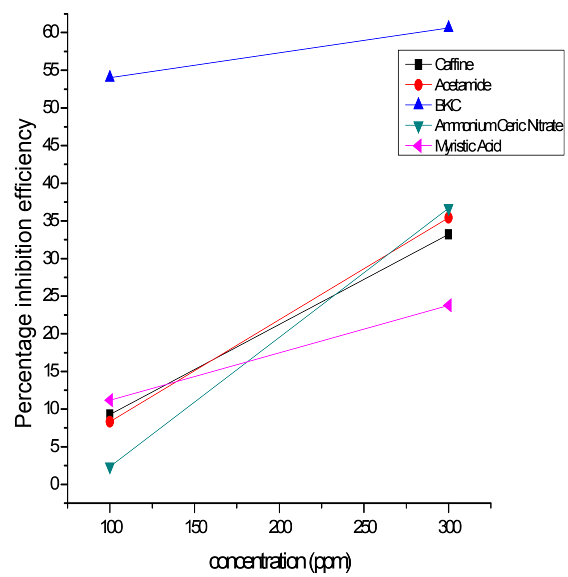


Figure 2: Percentage inhibition efficiency of Caffine, Acetamide, BKC, Ammonium Ceric Nitrate, Myristic Acid at 100,300 ppm concentration at 45^0 C

SEM: Scanning electron microscopy studies the SEM images of polished mild steel specimen in 0.01M H_2SO_4 solution and in the presence of caffine inhibitor at 45^0 C for 24 hours. Then they were washed with distilled water, dried in desicator and therefore subjected to SEM examination. The SEM photographs in figure 5 and 6 shows that the metal surface which in the presence of inhibitor (Caffeine) is more smooth than figure 3 and 4 in the absence of inhibitor. it conclude that the inhibitor form a protective layer on the metal surface and prevent from corrosion.

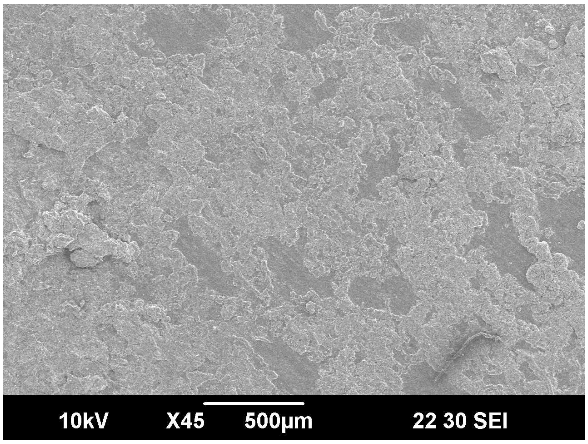


Figure 3: blank mild steel coupon SEM with 500μm resolution after treated with 0.01N H_2SO_4 for 24 hour at 25ºC

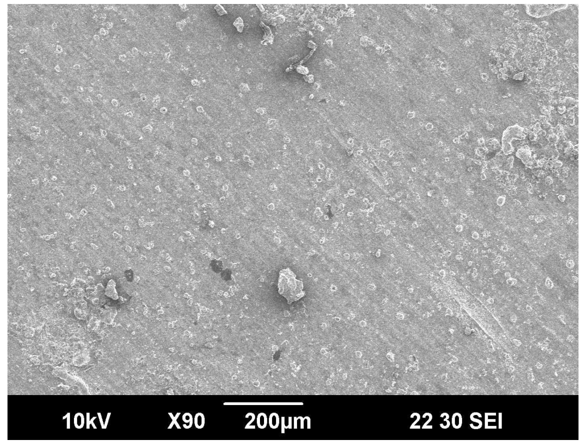


Figure 4: blank mild steel coupon SEM with 200μm resolution after treated with 0.01N H_2SO_4 for 24 hour at 25ºC

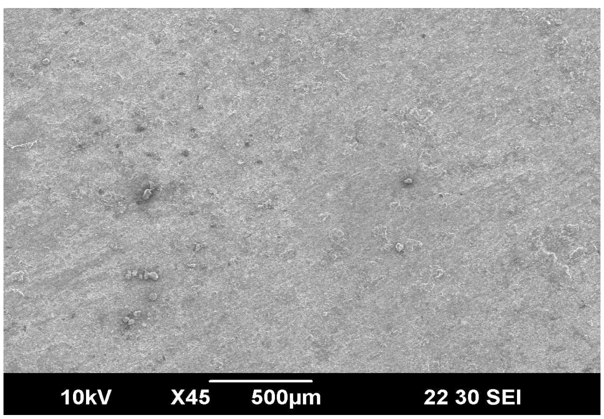


Figure 5: Mild steel coupon treated with Caffine at 500μm resolution after immersion for 24 hour in 0.01 N H_2SO_4 and Caffine (100ppm) at 25°C

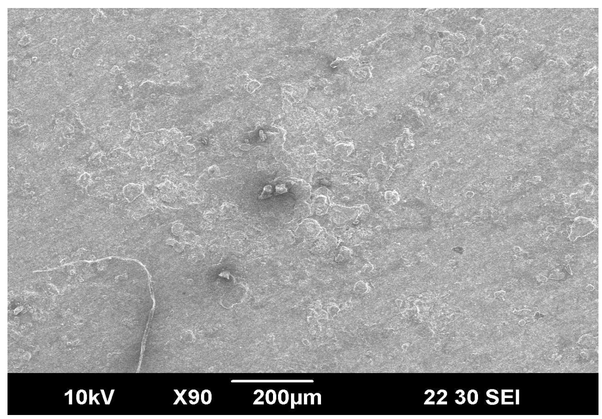


Figure 6: Mild steel coupon treated with Caffine at 200μm resolution after immersion for 24 hour in 0.01 N H_2SO_4 and Caffine (100ppm) at 25°C

Conclusion

The five investigated corrosion inhibitors show a high percentage corrosion inhibition efficiency toward mild steel at two different temperatures 25°C and 45°C. From these five different inhibitors at lower concentration Myristic acid shows the best corrosion inhibition efficiency and at higher concentration BKC shows the highest corrosion inhibition efficiency at 25°C and at 45°C BKC shows the highest corrosion inhibition efficiency both at lower and higher concentration. Percentage corrosion inhibition efficiency was found in the order of Myristic acid > Acetamide> BKC> Ammonium Ceric Nitrate>Caffine at lower concentration and BKC> Myristic acid>Acetamide> Ammonium Ceric Nitrate> Caffine at higher concentration of inhibitors at temperature 25° C and at temperature 45°C PCIE was found in the order of BKC> Myristic Acid> Acetamide> Caffine> Ammonium Ceric Nitrate and BKC>

Ammonium ceric nitrate> Acetamide> Caffine> Myristic Acid at ower and higher concentration respectively. These result obtained by weight loss technique are further supported by SEM technique.

References

[1] M. Benabdellah, A. Ousslim, B. Hammouti, A. Elidrissi, A. Aouniti, A. Dafali, K. Bekkouch, M. Benkaddour, 2-(o-Hydroxyphenyl) Benzimidazole as a New Corrosion Inhibitor for mild Steel in Hydrochloric Acid Solution, *J. Appl. Electrochem*., 2007, 37, 819-826.

[2] I. Ahamad, M.A. Quraishi, Bis (benzimidazol-2-yl) disulphide: an efficient water soluble inhibitor for corrosion of mild steel in acid media, Corros. Sci. 2009, 51, 2006–2013.

[3] Q. B. Zhang, Y. X. Hua, Corrosion inhibition of mild steel by alkyl imidazolium ionic liquids in hydrochloric acid," Electrochim. Acta, 2009, 54, 1881–1887.

[4] W. Li, Q. He, C. Pei, B. Hou, Experimental and theoretical investigation of the adsorption behaviour of new triazole derivatives as inhibitors for mild steel corrosion in acid media," Electrochim. Acta , 2007, 52, 6386–6394.

[5] R. Solmaz, G. Kardas_, B. Yazıcı, M. Erbil, "Inhibition effect of rhodanine for corrosion of mild steel in hydrochloric acid solution," Prot. Met. 41, 2005, 581– 585.

[6] G. Kardas_, The Inhibition effect of 2-thiobarbituric acid on the corrosion performance of mild steel in HCl solutions, Mater. Sci., 2005, 41, 337–343.

[7] Hudson, R.M., Warning, C.J., Influence of halide mixtures with organic compounds on dissolution and hydrogen absorption by low C-steel in H_2SO_4, Corros. Sci., 1970, 10, 121–134.

[8] Emregul, K.C., Hayval, M., Studies on the effect of a newly synthesized Schiff base compound from phenazone and vanillin on the corrosion of steel in 2M HCl, Corros. Sci., 2006, 48, 797–812.

[9] Hossini, S. M. A., Salari, M., Corrosion inhibition of stainless steel 302 by 1-methyl-3-pyridine-2-Y1-thiourea in acidic media, *Indian Journal of Chemical Technology*, 2009, 16, 480-485.

[10] Shetty, S. D., Shetty, P., Nayak, H. V. S., Assessment of caffeine adsorption onto mild steel surface as an eco-friendly corrosion inhibitor," *J. Serb. Chem. Soc.*, 2006, 71, 1073-1082.

[11] Gogoi, P.K., Barhai, B., Dimensional stability, thermal degradation and termite resustant studies of chemically treated wood, *Int. J. Chem.*, 2010, 2, 218-223.

[12] Adardour, K., Kassou, O., Touir, R., Ebn Touhami, M., El Kafsaoui, H., Benzeid, H., Essassi, M., Sfaira, M., Study of the influence of new quinoxaline derivatives on corrosion inhibition of mild steel in hydrochloric medium, *J. Mater. Environ. Sci.,* 2010, 1, 129-138.

[13] Quraishi, M. A., Rawat, " Inhibition of mild steel corrosion by some macrocyclic compounds in hot and concentrated hydrochloric acid", J., *Mat. Chem. Phys.*, 2002, 73, 118.

[14] J.M. Sykes, "Silver Jubilee review 25 years of progress in electrochemical methods", Brit. Corros. J., 1990, 25, 175-183.

[15] M. Elachouri, M.S. Hajji, S. Kertit, E.M. Essasi, M. Salem, R. Coudert, "Some surfactants in the series of 2-(alkyldimethylammonio) alkanol bromides as inhibitors of the corrosion of iron in acid chloride solution", Corros. Sci. 37, 381.

[16] B. Mernari, H. Elattari, M. Traisnel, F. Bentiss, M. Lagrenee, Inhibiting effects of 3,5-bis (n-pyridyl)-4-amino-1,2,4-triazoles on the corrosion for mild steel in 1M HCL medium, Corrosion, 1998, 40, 391-398.

[17] Bentiss, F., Traisnel, M., Lagrenee, M., Influence of 2,5-bis (4- imethylaminophenyl)-1,3,4-thiadiazole on corrosion inhibition of mild steel in acidic media, J. Appl. Electrochem., 2001, 31, 41–48.

[18] Hosseini, M., Mertens, S. F. L., Ghorbani, M., Arshadi, M.R., Asymmetrical Schiff bases as inhibitors of mild steel corrosion in sulphuric acid media, Mater. Chem. Phys., 2003, 78, 800–808.
[19] Singh, A. K., Quraishi, M .A., Study of some bi dentate Schiff bases of isatin as corrosion inhibitors for mild steel in hydrochloric acid solution, Int. J. Electrochem. Sci., 2012, 7, 3222–3241.
[20] Fekry, A. M., Riham, R. M., Acetyl thiourea chitosan as an ecofriendly inhibitor for mild steel in sulphuric acid medium, Electrochim Acta, 2010, 55, 1933–193
[21] Nada, F. A., Fekry, A. M., Hamdi, M. H., Corrosion inhibition, hydrogen evolution and antibacterial properties of newly synthesized organic inhibitors on 316L stainless steel alloy in acid medium, Int. J. Hydrogen Energy, 2011, 36, 6462–6471.
[22] Hegazy, M. A., Ahmed, H. M., El-Tabei, A.S., Investigation of the inhibitive effect of p-substituted 4-(N,N,N-dimethyldodecylammonium bromide)benzylidene-benzene-2-yl-amine on corrosion of carbon steel pipelines in acidic medium, Corros. Sci., 2011, 53, 671– 678.
[23] E. Khamis, The effect of temperature on the acidic dissolution of steel in the presence of inhibitors, Corrosion, 1990, 46, 476-484.
[24] E. Stupnisek-Lisac and S. Podbrscek, Non-toxic organic zinc corrosion inhibitors in hydrochloric acid, Journal of Applied Electrochemistry, J. Appl. Electrochem., 1994, 24, 779-784.
[25] G. Schmitt and K. Bedbur, Investigations on structural and electronic effects in acid inhibitors by AC impedance, Werkst. Korros., 1985, 36, 273-296.
[26] I. L. Rosenfeld, Corrosion Inhibitors, McGraw-Hill, New York 1981,
[27] E. Stupnisek-Lisac and M. Metikos-Hukovic, Electrical study of substituted pyrroles for protection of iron during pickling, Brit. Corros. J., 1993, 28, 74-76.
[28] S.L.Granese, B.M. Rosales, C. Oviedo and J.O. Zerbino, The inhibition action of heterocyclic nitrogen organic compounds on Fe and steel in HCL media, Corros. Sci, 1992, 33, 1439-1453.
[29] S. L. Granese, Study of the Inhibitory Action of Nitrogen-Containing Compounds, Corrosion, 1988, 44, 322-327.
[30] B. Sathianandhan, K. Balakrishnan and N. Subramanyan, Triazoles as inhibitors of mild steel in acids, Br. Corros. J., 1970, 5, 270-274.
[31] F. Zucchi, G. Trabanelli and G. Brunoro, The influence of the chromium content on the inhibitive efficiency of some organic compounds, Corros. Sci., 1992, 33, 1135-1139.
[32] J. O'M. Bockris and B. Yang, The Mechanism of Corrosion Inhibition of Iron in Acid Solution by Acetylenic Alcohols, J. Electrochem. Soc., 1991, 138, 2237-2252.
[33] Benerijee, G. and Malhotra, S. N., Contribution to adsorption of aromatic amines on mild steel surface from HCl solutions by impedance, UV, and Raman pectroscopy, *Corrosion*, 1992, 48, 10–15.
[34] J. Uhrea and G. Aramaki, A Surface-Enhanced Raman Spectroscopy Study on Adsorption of Some Sulfur-Containing Corrosion Inhibitors on Iron in Hydrochloric Acid Solutions, J. Electrochem. Soc. 138, issue., 1991, 11, 3245-3251.