Int. J. Electrochem. Sci., 6 **(2011)** 4286 - 4295

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Inhibitive Effect of Imidazolium Based Aprotic Ionic Liquids on Mild Steel Corrosion in Hydrochloric Acid Medium

Sudhish K. Shukla, Lutendo C. Murulana, Eno E. Ebenso[*]

Department of Chemistry, School of Mathematical and Physical Sciences, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa
[*]E-mail: Eno.Ebenso@nwu.ac.za

Received: 20 July 2011 / *Accepted:* 6 August 2011 / *Published:* 1 September 2011

The inhibition performance of imidazolium based aprotic ionic liquids (ILs) $[C_4mim][NO_3]$, $[C_4mim][BF_4]$ and $[C_4C_1mim][BF_4]$ on mild steel corrosion in hydrochloric acid was studied at 303-313K using weight loss and hydrogen evolution techniques. Inhibition efficiency increased and corrosion rate decreased with increase in ILs concentration. The order of the inhibition efficiency is $[C_4mim][NO_3] > [C_4mim][BF_4] > [C_4C_1mim][BF_4]$. The adsorption of ILs follows Langmuir adsorption isotherm model. Physical adsorption is proposed from the values of ΔG_{ads} obtained.

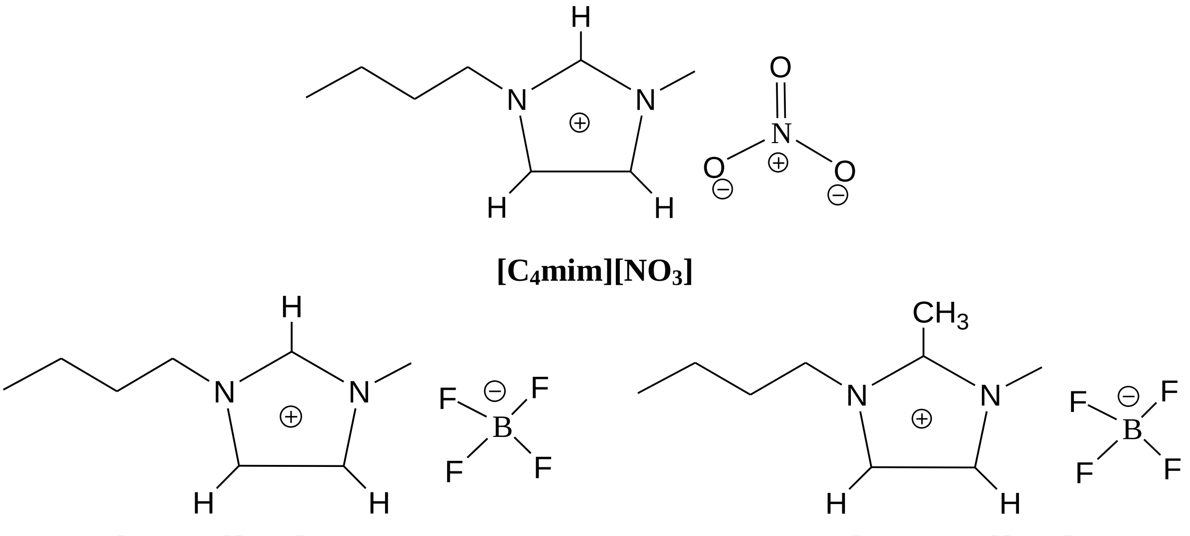
Keywords: Mild steel, corrosion inhibition, ionic liquids, adsorption.

1. INTRODUCTION

Mild steel is the most common constructional material for various industries due to its excellent mechanical properties. It is widely used in the industries as storage tanks, different machinery parts, pipelines of petroleum industries, reaction vessels and boilers [1, 2]. Acids are widely used in various industrial operations such as pickling, cleaning, descaling and acidisation of oil wells. Because of the aggressiveness of the acids inhibitors are used to reduce the rate of dissolution of the metal. Hydrochloric acid is most common acid used in all such industrial operations [3-6]. The use of inhibitors is the most economical and practical method of reducing corrosive attack on metal [7]. In the past few decades, the inhibition of mild steel corrosion in acid solutions by various types of organic inhibitors has attracted much attention [8-11].Inhibition properties of the organic compounds depends upon the functional group which adsorbed on the metal surface. Most of the efficient organic compounds that act as corrosion inhibitors have oxygen, sulphur, nitrogen atoms and multiple bonds through which they adsorb on the metal surface [12-16]. Most of the organic compounds used as corrosion inhibitors are highly toxic to human beings and the environment. Ionic liquids have attracted considerable attention in recent years because of their environment friendly nature [17-18].

Ionic liquids are molten salts which are composed of the organic cation and various anions. Melting points of ionic liquids are at or below ambient room temperature. Ionic liquids possess large number of physicochemical properties mainly, good electrical conductivity, solvent transport, and a relatively wide electrochemical window [19-21]. One of the most important properties of ionic liquids is that of negligible vapour pressure [22], which leads it towards the eco-friendly, less hazardous inhibitor for metal corrosion. Ionic liquids consist of an amphiphilic group with long chain, hydrophobic tail and a hydrophilic polar head. Mostly, ionic liquids (ILs) have hetero atoms such as nitrogen, sulphur and phosphorus as the central atoms of cations such as imidazolium, pyrrodinium, pyridinium, sulphonium, quaternary phosphonium etc.

Imidazolium compounds are reported to show the corrosion protection tendency on mild steel and other metals [23-26]. The present work describes a study of the corrosion of mild steel in 0.5 M HCl without and with different concentrations of three imidazolium based aprotic ionic liquids using the hydrogen evolution and weight loss techniques. Molecular structures of the ILs used in study are given in Figure 1 below.



$[C_4mim][NO_3]$

$[C_4mim][BF_4]$

$[C_4C_1mim][BF_4]$

Figure 1. Structure of Ionic Liquids (ILs)

2. EXPERIMENTAL

The mild steel used in the study had the following composition (wt %), C (0.19), Si (0.26), Mn (0.64), S (0.05), P (0.06), Ni (0.09), Cr (0.08), Mo (0.02), Cu (0.27), and the remainder iron (Fe). The mild steel coupons were prepared, degreased and cleaned as previously reported [27-30]. The concentration of the blank corrodent, HCl (BDH Chemical Supplies Laboratory, England) prepared and used was 2M. The ionic liquids used, as inhibitors in the present study are all products of Sigma

Chemicals. All preparations were carried out using deionized water. All chemicals and reagents used were of analytical grade. They were used as sourced without further preparation.

The apparatus and procedure followed for weight loss and hydrogen evolution methods were similar to that earlier reported [27-30]. In the weight loss method, the progress of the corrosion reaction was monitored by determining the weight loss of the coupons (obtained as the differences in the weight of the coupons after immersion in different solutions of the system and the original weight of the coupons) and careful measurement of the volume of hydrogen gas evolved for weight loss and hydrogen evolution methods respectively at fixed time intervals. In both techniques, the experiments were conducted at 303 and 313K maintained in a thermostated bath.

3. RESULTS AND DISCUSSIONS

3.1. Hydrogen evolution technique

This technique is used to know the inhibitive properties of the ILs used in the study. The graph of the inhibition efficiency obtained from this technique against the concentration of inhibitors is shown in Figure 2. It is evident from the figure that inhibition efficiency increases with increase in the inhibitor concentration for all the ILs used in the study. Increase in the inhibition efficiency suggests that these ILs are good corrosion inhibitors for mild steel in hydrochloric acid environment. It is also shown from figure 1 that [C_4 mim][NO_3] gives the highest inhibition efficiency in all concentrations.

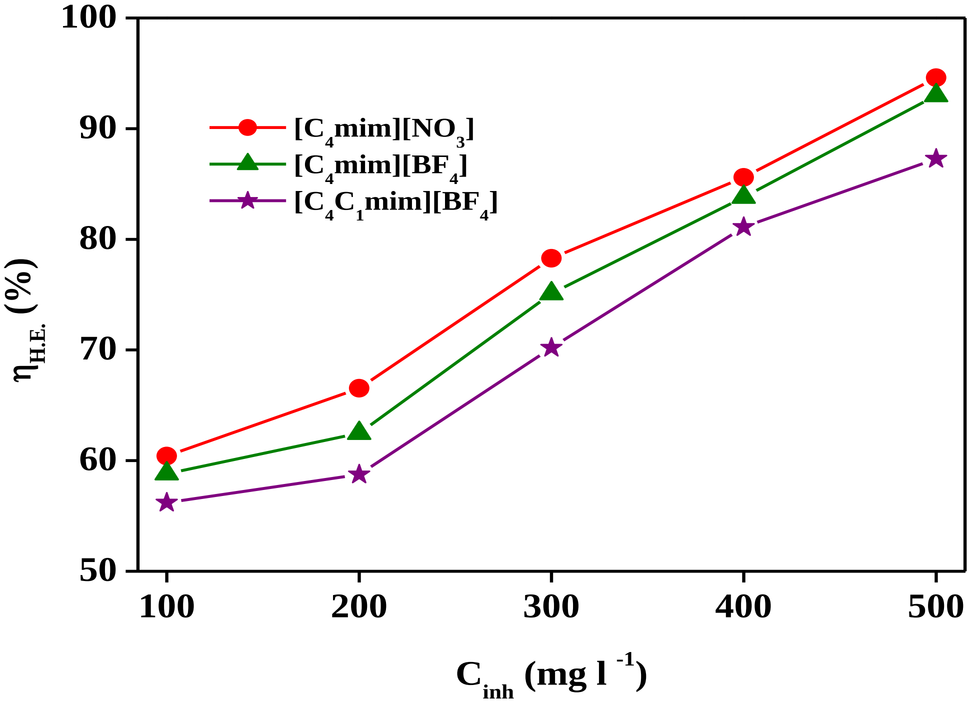


Figure 2. Plot of inhibition efficiency obtained from hydrogen evolution technique against inhibitor concentration for mild steel in 0.5M HCl solution at 303K.

3.2. Weight loss technique

The values of % inhibition efficiency and corrosion rate from weight loss method at different concentrations of ILs in 0.5 M HCl at 303K and 313K are presented in Table1.

Table1. Weight loss data for mild steel corrosion in the presence and absence of different concentrations of ILs in 0.5 M HCl at 303 and 313K.

Name of Inhibitor	Conc. (mg l^{-1})	303 K			313 K		
		IE (%)	C_r (mpy)	θ	IE (%)	C_r (mpy)	θ
-	Blank	-	35.42	-	-	56.38	-
$[C_4mim][NO_3]$	100	64.60	7.89	0.65	54.50	9.34	0.55
	200	70.98	6.26	0.71	61.02	7.28	0.61
	300	81.34	4.02	0.81	70.81	4.62	0.71
	400	87.80	2.55	0.88	76.42	2.94	0.76
	500	95.48	0.79	0.96	84.60	0.89	0.85
$[C_4mim][BF_4]$	100	61.20	9.29	0.61	50.81	11.20	0.51
	200	66.54	6.20	0.67	55.62	7.42	0.56
	300	77.28	4.05	0.77	68.41	4.58	0.68
	400	84.19	2.47	0.84	72.91	2.85	0.73
	500	92.48	1.20	0.93	80.24	1.38	0.80
$[C_4C_1mim][BF_4]$	100	60.41	9.17	0.60	48.24	11.48	0.48
	200	62.80	6.80	0.63	51.42	8.31	0.51
	300	74.11	4.67	0.74	63.84	5.42	0.64
	400	83.62	2.41	0.84	73.00	2.75	0.73
	500	89.74	1.76	0.90	78.94	2.00	0.79

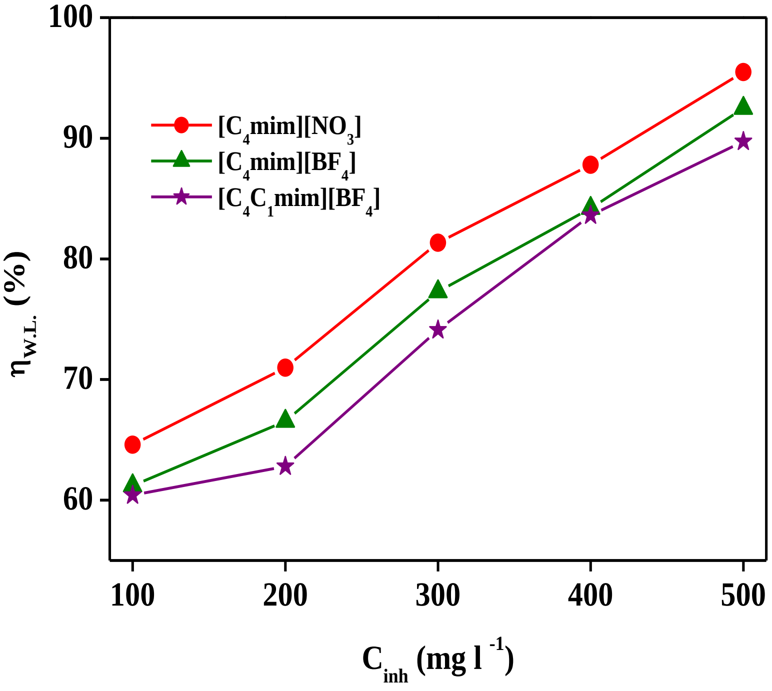


Figure 3. Plot of inhibition efficiency obtained from weight loss technique against inhibitor concentration for mild steel in 0.5M HCl solution at 303K.

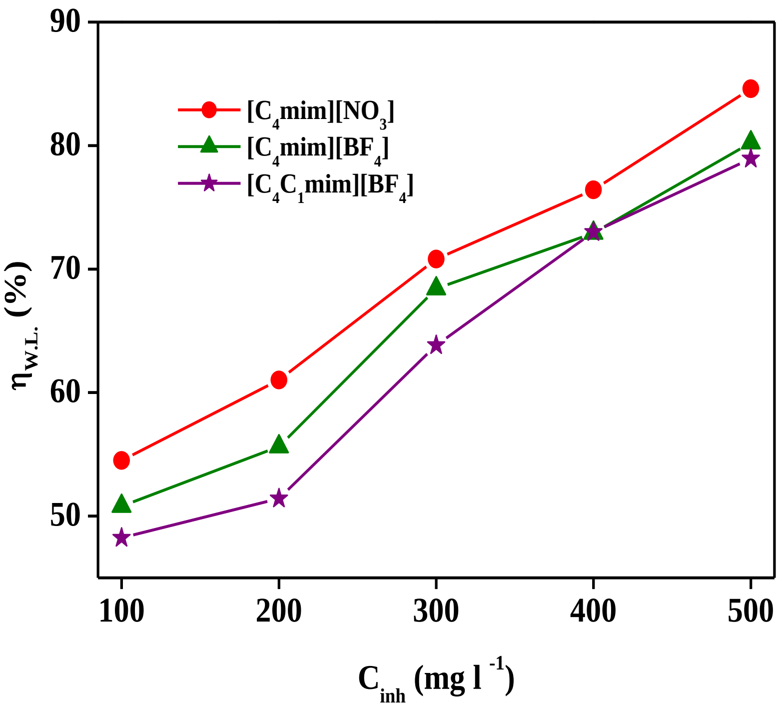


Figure 4. Plot of inhibition efficiency obtained from weight loss technique against inhibitor concentration for mild steel in 0.5M HCl at 313K.

Variation in inhibition efficiency with inhibitors concentrations at 303K and 313K are presented in Figures 3 and 4 respectively. It is observed from the figures that the inhibition efficiency increases with increase in the concentration of all three ILs used in study at both temperatures 303K and 313 K. It is found that all the ILs give maximum efficiency at 500 mg l^{-1}. In all among ionic liquids [C_4mim][NO_3] gave maximum inhibition efficiency. It is evident from the Table 1 that corrosion rate decreases and inhibitor efficiency increases with increase in ILs concentrations where as corrosion rate increases and inhibition efficiency decreases with increase in the ILs concentrations. Results obtained from the weight loss study are in good agreement with the hydrogen evolution technique.

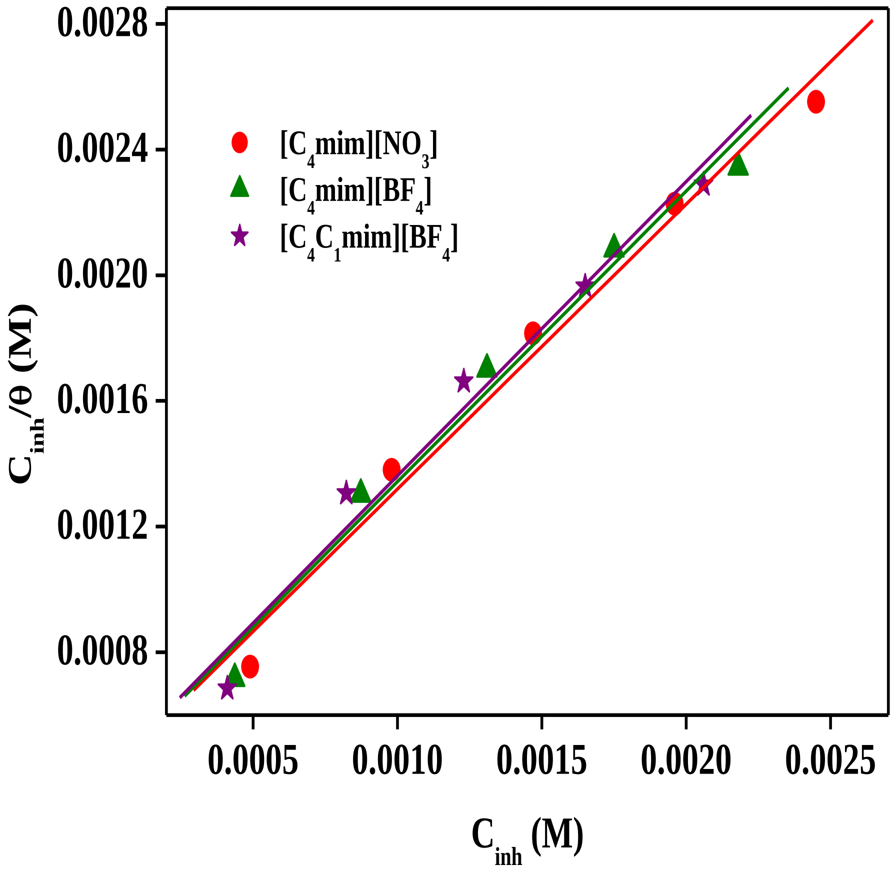
3.3. Adsorption isotherm

Adsorption of the inhibitor molecule mainly depends upon charge and nature of the metal surface, electronic characteristics of the metal surface, adsorption of solvent and other ionic species, temperature and electrochemical potential at solution interface [31]. Inhibitor molecules undergo two types of adsorption with the metal surface. One is the physical adsorption (physisorption) resulting due to electrostatic attraction between inhibiting organic ions or dipoles and the electrically charged surface of metal and the other, chemical adsorption (chemisorption) resulting when charge sharing or charge transfer from adsorbates to the metal surface atoms in order to form a covalent type of bond. Chemical adsorption has free energy of adsorption and the activation energy higher than the physical adsorption [32]. The adsorption isotherm describes the adsorptive behaviour of organic compounds in order to know the adsorption mechanism. The most frequently used adsorption isotherms are Langmuir, Temkin, Frumkin and Freundlich isotherms. To obtain the adsorption isotherm, the degree of surface coverage (θ) was calculated for various concentrations of ILs at 303K and 313K from the weight loss data and presented in Table1.

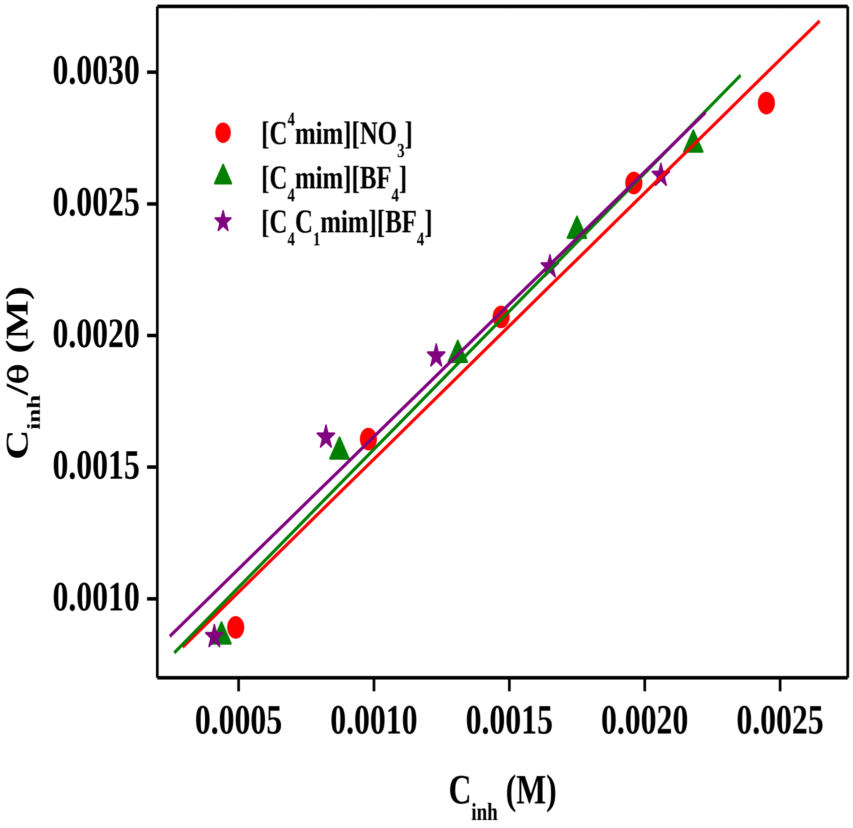
Langmuir adsorption isotherm was tested to fit with the experimental data. Langmuir adsorption isotherm is represented by equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (1)$$

where, K_{ads} = adsorption equilibrium constant, θ = degree of surface coverage and C_{inh} is molar concentration of the inhibitor used in acid solution. Straight lines were obtained by plotting the graph of C_{inh} /θ vs. C_{inh} for the three ILs at 303K and 313K (Figure 5a and b). The regression coefficient is almost unity. These results suggest that the Langmuir adsorption isotherm model gives the best description of the adsorption behaviour of ILs on the mild steel surface. The parameters calculated from the Langmuir adsorption isotherm model are reported in Table 2.



A



B

Figure 5. Langmuir adsorption isotherm plots for the ILs at (A) 303K and (B) 313 K

Table 2. Langmuir adsorption parameters

Inhibitor	Temp (K)	K_{ads} (mol^{-1})	Slope	R^2	ΔG_{ads} ($kJmol^{-1}$)
[C_4mim][NO_3]	303	2421.3	0.9068	0.9925	-29.75
	313	1926.8	1.0113	0.9904	-30.14
[C_4mim][BF_4]	303	2392.3	0.9252	0.9901	-29.72
	313	1926.8	1.0487	0.9907	-30.14
[C_4C_1mim][BF_4]	303	2352.9	0.9368	0.9871	-29.68
	313	1639.3	1.0056	0.9802	-29.72

3.4. Thermodynamic consideration

Equilibrium constant for the adsorption process is related to the standard free energy of adsorption by the following expression [33]:

$$K_{ads} = \frac{1}{55.5}\exp\left(\frac{-\Delta G^o_{ads}}{RT}\right) \quad (3)$$

This equation can also be expressed as:

$$\Delta G_{ads} = -2.303RT\log(55.5K_{ads}) \qquad (4)$$

where, ΔG_{ads} is Gibbs Free energy of adsorption, T is temperature in Kelvin and K_{ads} is the equilibrium constant for adsorption process and 55.5 is the molar concentration of water in solution. K_{ads} value was calculated from the intercept of Figure 5a and 5b and listed in Table 2. The negative values of ΔG_{ads} ensure the spontaneity of the adsorption process and the stability of the adsorbed species on the mild steel surface [34, 35]. Usually the values around -20kJ mol^{-1} or lower are consistent with physical adsorption, while those higher than -40kJ mol^{-1} involves chemical adsorption [36]. When charged species adsorbed on the metal surface, there is possibility of the columbic interaction between adsorbed cation and anion thereby causing increase in the ΔG_{ads} even if no chemical bonds are formed [37]. The values of ΔG_{ads} for the ILs are listed in Table 2. These values indicate the physical adsorption of the ILs on mild steel surface. The adsorption is enhanced by means of the presence of nitrogen atoms with lone pair of electrons in the ILs molecules that influence it to adsorb electrostatically on the mild steel surface forming the insoluble and stable inhibitor film on metal surface that decreases the metal dissolution.

3.5. Mechanism of inhibition

The imidazolium group as well as nitrogen atom in the hetero aromatic ring of imidazolium compounds can be protonated in acidic solutions. Li.*et al* [38] and Yurta *et al* [39] have reported the mechanism of corrosion inhibition for the dissolution of mild steel as follows;

The anodic dissolution of iron follows the steps:

$$Fe + Cl^- \rightarrow (FeCl^-)_{ads} \qquad (5)$$

$$(FeCl^-)_{ads} \rightarrow (FeCl)_{ads} + e^- \qquad (6)$$

$$(FeCl)_{ads} \rightarrow (FeCl^+)_{ads} + e^- \qquad (7)$$

$$FeCl^+ \rightarrow Fe^+ + Cl^- \qquad (8)$$

The cathodic dissolution of iron follows the steps:

$$Fe + H^+ \rightarrow (FeH^+)_{ads} \qquad (9)$$

$$(FeH^+)_{ads} + e^- \rightarrow (FeH)_{ads} \qquad (10)$$

$$(FeH)_{ads} + H^+ + e^- \rightarrow Fe + H_2 \qquad (11)$$

Cl^- anion is first adsorbed onto the positively charged metal surface by columbic attraction. The steps that follow involve the adsorption of inhibitor molecules through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. The adsorbed molecules interact with $(FeCl^-)_{ads}$ species to form monolayer on the surface. This is how the steel surface is protected from the attack by aggressive chloride ions.

4. CONCLUSIONS

All the measurements shows that the imidazolium based ionic liquids have excellent inhibition properties against the mild steel corrosion in hydrochloric acid solution. ILs showed their maximum inhibition efficiency at 500 mgl^{-1} concentration. $[C_4mim][NO_3]$ showed maximum inhibition efficiency among three studied ILs. Inhibition efficiency reported from hydrogen evolution and weight loss techniques are in good agreement. The inhibitors follow the Langmuir adsorption isotherm model. Results of Gibbs free energy indicate that the adsorption process is spontaneous and follow the physical adsorption mechanism.

ACKNOWLEDGEMENTS
SKS acknowledges the North-West University for a Postdoctoral Fellowship; LCM and EEE thanks the Corrosion Institute of South Africa and the National Research Foundation (NRF) of South Africa for funding the research.

References

1. J. Zhang, J. Liu, W. Yu, Y. Yan, L. You, L. Liu, *Corros. Sci*, 52 (2010) 2059.
2. I.B. Obot, N.O. Obi-Egbedi, A.O. Eseola, *Ind. Engg. Chem. Res.,* 50 (2011) 2098.
3. S.K. Shukla, M.A. Quraishi, *Corros. Sci.,* 51 (2009) 1007.
4. E.E.Ebenso, P.C.Okafor, U.J. Ibok, U.J.Ekpe and A.I. Onuchukwu, *Jour. Chem. Soc. Nig*. 29 (2004) 15.
5. S.K. Shukla, M.A. Quraishi, *J. Appl. Electrochem.* 39 (2009) 1517.
6. H.A. Sorkhabi, B. Masoumi, P. Ejbari, E. Asghari, *J. Appl. Electrochem.* 39 (2009) 1497.
7. M.A. Quraishi, S.K. Shukla. *Mater. Chem. Phys.* 113 (2009) 685.
8. A.Asan, S. Soylu, T. Kiyak, F. Yildirim, S.G. Oztas, N. Ancin, M. Kabasakaloglu, *Corros. Sci.* 48 (2006) 3933.
9. M. Lebrini, F. Bentiss, H. Vezin, M. Lagrenee, *Corros. Sci.* 48 (2006) 1279.
10. S.K. Shukla, A.K. Singh, I. Ahmad, M.A. Quraishi, *Mater. Letts.* 63 (2009) 819.
11. S.K. Shukla, M.A. Quraishi, *Mater. Chem. Phys.* 120 (2010) 142.
12. F. Bentiss, M. Lebrini, M. Traisnel, M. Lagrenee, *J. Appl. Electrochem.* 39 (2009) 1399.
13. H.A. Sorkhabi, M. Es'haghi, *Mater. Chem. Phys.* 114(2009) 267.
14. E.E. Ebenso, E.E. Oguzie, *Mater. Letts*. 59 (2005) 2163.
15. S.K. Shukla, M.A. Quraishi, *Corros. Sci.* 51 (2009) 1990.
16. S.K. Shukla, M.A. Quraishi, *Corros. Sci.* 52 (2010) 314.
17. Q. Zhang, Y. Hua, *Mater. Chem. Phys.,* 119 (2010) 57.
18. X. Zhou, H. Yang, F. Wang, *Electrochimica. Acta,* doi:10.1016/j.electacta.2011.01.081.

19. H. Zhao, *Chem. Eng. Comm*. 193 (2006) 1660.
20. A.Fernicola, B. Scrosati, H. Ohno, *Ionics*, 12 (2006) 95.
21. T. Tsuda, C.L. Hussey, *Interface*, 16 (2007) 42.
22. D.L. Boxall, J.J. O'Dea, R.A. Osteryoung, *J. Electrochem. Soc.* 149 (2002) E468.
23. S. Murlidharan, S.V. Iyer, *Anti Corros. Met. Mat.* 44 (1997) 100.
24. R. Gasparac, C.R. Martin, E. Stupnisek,-Lisac, *J. Electrochem. Soc.* 147 (2000) 548.
25. D.Q. Zang. L.X. Gao, G.D. Zhu, *Corros. Sci.* 46 (2004) 3031.
26. M.A. Quraishi, M.Z.A. Rafiquee, S. Khan, N. Saxena, *J. Appl. Electrochem.* 37 (2007) 1153.
27. S.A. Umoren, O. Ogbobe, E.E. Ebenso, U.J. Ekpe, *Pigment. Resin. Technol.* 35 (2006) 284.
28. S.A. Umoren, O. Ogbobe, E.E. Ebenso *Bull. Electrochem*. 22 (2006) 155.
29. E.E.Ebenso, U.J. Ekpe, S.A. Umoren, E.Jackson, O.K.Abiola and N.C. Oforka, *J. Appl. Polym. Sci.* 100 (2006) 2889.
30. S.A.Umoren and E.E.Ebenso, *Mater. Chem. Phys.* 106 (2007) 387.
31. A.K. Singh, S.K. Shukla, M. Singh, M.A. Quraishi, *Mater. Chem. Phys.* 129 (2011) 68.
32. G. Trabanelli, in: F.Mansfeld (Ed.), Corrosion Mechanism, Mercel Dekker, New York, 2006.
33. M. Schorr, J.Yahalom, *Corros. Sci.* 12 (1972) 867.
34. H. Keles, M. Keles, I. Dehri, O. Serindag, *Colloids Surf A: Physicochem. Eng. Aspects*, 320 (2008) 138.
35. A.S. Fouda, F.E. Heakal, M.S. Radwan, *J. Appl. Electrochem*, 39 (2009) 391.
36. S.A. Umoren, I.B. Obot, E.E. Ebenso, P.C. Okafor, O. Ogbobe, E.E. Oguzie, *Anti-Corros. Meth. Mat.* 53 (2006) 277.
37. A.K. Singh, M.A. Quraishi, *Corros. Sci.* 53 (2011) 1288.
38. W. Li, Q. He, C. Pei, B. Hou, *Electrochimica Acta.* 52 (2007) 6386.
39. A.Yurta, A. Balaban, S.U. Kandemir, B. Bereket, B. Erk, *Mater. Chem. Phys.* 85 (2004) 420.