

Quantum and electrochemical studies of Ecofriendly and Green Corrosion inhibitor Ionic Liquid for Metal Surface in 0.5 M Sulfuric Acid

*Bhaskaran^{*a}, Gurmeet Kaur^b, Raj Kishore Sharma^a and Gurmeet Singh^{*a}*

^a*Department of Chemistry, University of Delhi, Delhi-110 007*

^b*SGTB Khalsa College, University of Delhi, Delhi-110007*

**(gurmeet123@yahoo.com), *(bhaskaryadav7@gmail.com)*

Abstract

An ionic liquid-like imidazolium was synthesized and characterized by ¹H, ¹³C, and I.R spectroscopy. Anticorrosion impacts of the 1-Butyl-3-Ethyl imidazolium bromide ionic liquid were studied. The analysis was observed by Tafel plot and Electrochemical Impedance Spectroscopy which show high mitigation efficiency in 0.5 M H₂SO₄ solution. Electrochemical studies revealed that the investigated compound is a mixed-type of inhibitor and Langmuir adsorption isotherm is observed. The mitigation efficiency was increased with an increase in concentration. The corrosion mitigation influence of 1-Butyl-3-Ethyl imidazolium bromide is observed due to the adsorptive interaction with the surface of mild steel which formed a protective layer against corrosion. The quantum chemical calculations supplement the results of polarization studies.

Introduction:

To achieve the optimum performance of industrial equipment and machinery, scale and oxide are isolated from the metallic surface to reduce the corrosive product formation. During the pickling procedure, acidic solutions are generally employed [1-3]. Carbon steel products are mostly treated with solutions of HCl and H₂SO₄. The exceedingly corrosive nature of these solutions, in turn, affect the physicochemical properties of the carbon steel materials. As a consequence of this, the corrosion inhibitors method is used for the protection of metallic materials against corrosion loss is employed. From the most recent years several organic compounds of nitrogen, such as pyridines, imidazolines [4-5], and azoles, have revealed high action for the inhibition of

corrosion. In spite, of this, the toxicity of these compounds is endangering the environment. Researchers have diverted *Corresponding Authors

their interest in ionic liquids as corrosion inhibitors because of their green nature towards the environment. Ionic liquids (ILs) are a captivating collection of solvents possessing a distinctive mixture of physicochemical properties, encountering extremely low vapor pressure at room temperature, low melting point, chemical, and thermal stability. They also hold the wide liquid range with the capability to dissolve both polar and non-polar inorganic and organic compounds. For this reason, in various chemical processes ionic liquids [6-8] can replace many volatile organic solvents, together with synthesis, extraction, catalysis, and separation. The cationic and anionic parts of ionic liquids are the deciding factor for the overall physical and chemical properties of a given ionic liquid. The variation of cationic and anionic part invariably affect the various physical properties of ionic liquid such as miscibility, solvation, viscosity, hydrophilicity. Ionic liquids can be categorized as "customized solvents" because they can be modified and adapted according to conditions.

In the current investigation, 1-Butyl-3-Ethyl Imidazolium Bromide Ionic Liquid [BEIM]Br has been read as corrosion mitigators for Mild steel (MS) in 0.5 M H₂SO₄. Electrochemical strategies including tafel plot and electrochemical impedance spectroscopy have been executed to find out corrosion inhibition properties of MS in presence of 0.5 M H₂SO₄. This IL examined has indicated anticorrosive properties. The hindrance efficiencies were affirmed by the electrochemical tests, which were additionally enhanced by quantum studies.

Galvanostatic Polarization Studies:-

The polarization parameters E_{corr} , I_{corr} , β_a , β_c are listed in Table 1. Tafel bends for MS in 0.5 M H₂SO₄ solution at various concentrations of [BEIM]Br have appeared in Fig.1. Through this examination, it is seen that the presence of [BEIM]Br IL caused a conspicuous decline in the consumption rate. Table 1. shows that the corrosion current thickness diminishes with an

expansion in the convergence of the inhibitor and [BEIM]Br while the relief productivity diminishes with the increment in temperature of the system [9-12].

Electrochemical Impedance Spectroscopy:-

Electrochemical impedance studies show that with an increase in the concentration of [BEIM]Br, charge transfer resistance (R_{ct}) increases which gives a clear indication that there is a formation of a protective layer between metal-solution interface. Moreover, C_{dl} value (Table 2) also decreases with an increase in the concentration of inhibitor which provides information that the thickness of the electric double layer has considerably increased thereby giving better corrosion inhibition. Nevertheless, the sizes of the capacitive loops are increased [13-14].

Thermodynamic Studies

Thermodynamic datas were determined to clarify the adsorption behavior of inhibitor on the metal surface. The Datas as given in Table 3 demonstrate that the adsorption cycle is for the most part by chemisorption[15,16]. which is ascribed to ΔG°_{ads} value - 82.35 kJ mol⁻¹. The estimation of R^2 i.e regression coefficient of the adsorption process shows that the Langmuir adsorption model is trailed by inhibitor. so Mitigation effectiveness turns into the capacity of the electrode surface secured by the inhibitor molecules [17,18]. The free vitality of adsorption can be determined from K_{ads} utilizing Eq. (1).

$$K_{ads} = \frac{1}{55.5} \exp \left[\frac{-\Delta G_{ads}}{RT} \right] \quad (1)$$

The following equation (2) represents the adsorption isotherm relationship for Langmuir Adsorption Isotherm

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + c \quad (2)$$

Quantum Chemical Studies:-

The streamlined structure of ILs, energies of HOMO and LUMO, absolute charge density, complete current potential, 3D isosurface of all out charge thickness on the inhibitors per unit area are given in Fig. 3 and the various quantum studied data are recorded in Table 4.

The distinction between EHOMO and ELUMO (the energy gap, ΔE) is a significant boundary in choosing the alleviation strength of the inhibitor particles. The lower the distinction in ELUMO and E_{HOMO} , the higher will be the relief proficiency which is because of the simplicity of adsorption on the metal surface. (19,20).

conclusion:-

(1) [BEIM]Br principally adsorbs on the MS surface through the emphatically charged N-heterocyclic particle in the imidazole ring, and it complies with the Langmuir isotherm dynamic model.

(2) [BEIM]Br displays a decent inhibitive exhibition because of the strong electron-donating effect of the alkyl group.

(3) Activation Energy(E_{act}) values are higher in the presence when contrasted with without inhibitors, showing that disintegration of MS is slow within [BEIM]Br .

Affirmation:-

The Authors appreciatively recognize University of Delhi for Research and Development grant and the Director of USIC for doing phantom investigations.

References

1. Q.B. Zhang, Y.X. Hua, *Electrochim. Acta* 54 (2009) 1881–1887.
2. A. Subramania, N.T. Kalyama Sundaram, R. Sathiya Priya, K. Saminathan, V.S.Muralidharan, T. Vasudevan, *J. Appl. Electrochem.* 34 (2004) 693–696.
3. D. Kuang, P. Wang, S. Ito, M. Zakeeruddin, M. Gratzel, *J. Am. Chem. Soc.* 128 (2006) 7732–7733.
4. D. Zhao, Z. Fei, T.J. Geldbach, R. Scopelliti, P.J. Dyson, *J. Am. Chem. Soc.* 126 (2004) 15876–15882.

5. K. M. Manamela, L. C. Murulana, M. M. Kabanda, E. E. Ebenso, *Int. J. Electrochem. Sci.* 9 (2014) 3029-3046.
6. O. Olivares-Xometl, C. Lopez-Aguilar, P. Herrastí-Gonzalez, N. V. Likhanova, I. Lijanova, R. Martinez-Palou, J. Antonio Rivera-Marquez, *Ind. Eng. Chem. Res.* 53 (2014) 9534–9543.
7. X. Zheng, S. Zhang, M. Gong, W. Li, *Ind. Eng. Chem. Res.* 53 (2014) 16349–16358.
8. D. Guzmán-Lucero, O. Olivares-Xometl, R. Martinez-alou, N. V. Likhanova, M. A. Dominguez-Aguilar, V. Garibay-Febles, *Ind. Eng. Chem. Res.* 50 (2011) 7129–7140.
9. L. C. Murulana, A. K. Singh, S. K. Shukla, M. M. Kabanda, E. E. Ebenso, *Ind. Eng. Chem. Res.* 51 (2012) 13282–99.
10. M. H. Wahdan, A. A. Hermas, M. S. Morad, *Mater. Chem. Phys.* 76(2) (2002) 111-118.
11. L. B. Tang, G. H. Liu, *Mater. Chem. Phys.* 95 (2006) 29–38.
12. Q. B. Zhang, Y. X. Hua, *Electrochim Acta.* 54 (2009) 1881-1887.
13. S. M. Tawfik, *J. Mol. Liq.* 207 (2015) 185-194.
14. H. Vashisht, I. Bahadur, S. Kumar, M. S. Goyal, G. Kaur, G. Singh, L. Katata-Seru, E. E. Ebenso, *J. Mol. Liq.* 224 (2016) 19-29.
15. J. H. Ha, J. H. Cho, J. H. Kim, B. W. Cho, S. H. Oh, *J. Power Sources* 355 (2017) 90-97.
16. P. Huanga, J. A. Lathama, D. R. MacFarlaneb, P. C. Howletta, M. Forsyth, *Electrochimica Acta.* 110 (2013) 501– 510.
17. P. Kannan, J. Karthikeyan, P. Murugan, T. S. Rao, N. Rajendran, *J. Mol. Liq.* 221 (2016) 368–380.
18. A. A. Olajire, *J. Mol. Liq.* 248 (2017) 775–808.
19. E. Heakal, A. S. Fouda, M. S. Radwan, *Mater. Chem. Phys.* 125 (2011) 26–36
20. L. C. Murulana, A. K. Singh, S. K. Shukla, M. M. Kabanda, E. E. Ebenso, *Ind. Eng. Chem. Res.* 51 (2012) 13282–13299.
21. G. Gece, *Corros. Sci.* 50 (2008) 2981–2992.
22. N.O. Obi-Egbedi, I. B. Obot, *Corros. Sci.* 53 (2011) 263–275

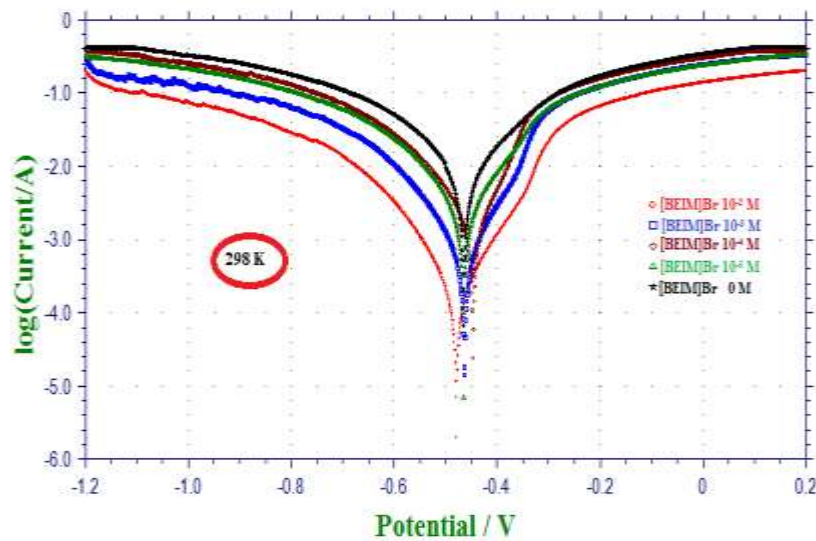


Fig.1. Tafel Polarization Values for the Corrosion of MS in 0.5 M H₂SO₄ with [BEIM]Br at 298 K

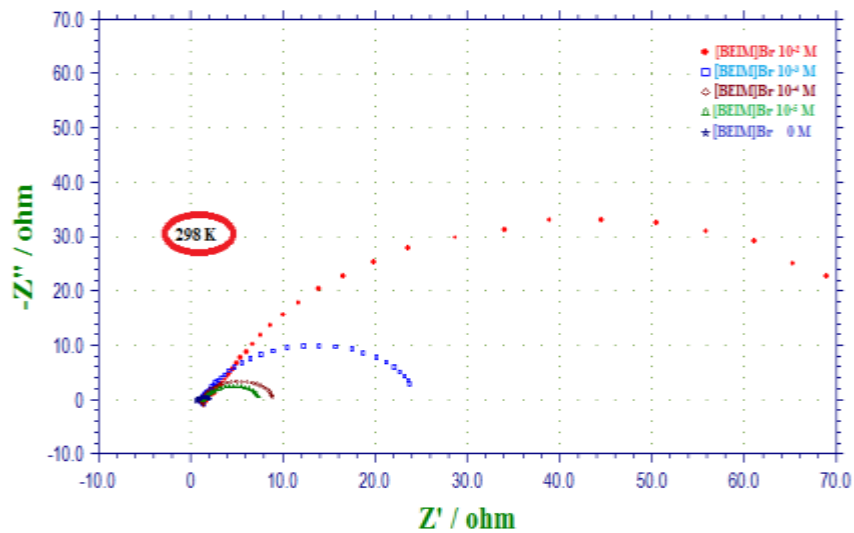


Fig.2. The nyquist curve for the Corrosion mitigation of MS in 0.5 M H₂SO₄ in the Presence and Absence of [BEIM]Br at 298 K

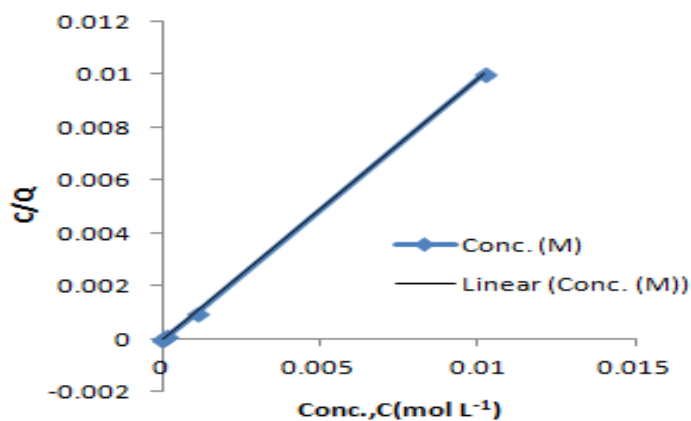


Fig.3. Adsorption behavior of [BEIM]Br on the mild steel surface in 0.5 M H₂SO₄

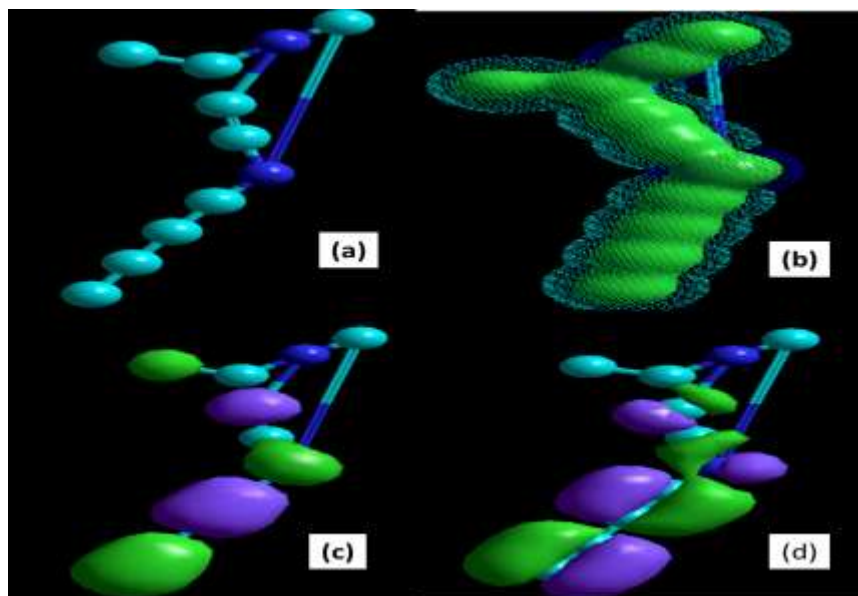


Fig. 4. (a) Structure of [BEIM]Br (b) Total Charge Density of [BEIM]Br (c) HOMO of [BEIM]Br (d) LUMO of [BEIM]Br

Table 1: Tafel polarization datas for the consumption of Metal surface in 0.5 M H₂SO₄ with presence and nonappearance of [BEIM]Br at 298 K

Temp. (K)	Conc. (mol/L)	I _{corr} (mA/cm ²)	-E _{corr} (mV)	b _a (mV/dec.)	b _c (mV/dec.)	IE%
298	Blank	9.679	465	70.59	60.89	-
	10 ⁻⁵	2.800	465	108.28	137.21	68.19
	10 ⁻⁴	1.545	447	63.19	129.29	82.45
	10 ⁻³	0.653	463	77.74	114.62	92.57
	10 ⁻²	0.199	478	92.62	103.46	97.74

Table 2: Impedance boundaries for the consumption of Metal surface in 0.5 M H₂SO₄ with presence and nonappearance of [BEIM]Br at 298 K

Solutions	Conc. (M)	R _{ct}	F _{max}	C _{dl}	IE
H ₂ SO ₄	0.5	1.65	21.23	4.54×10 ⁻³	-
[BEIM]Br	10 ⁻⁵	5.97	2.10	1.26×10 ⁻²	72.36
	10 ⁻⁴	7.63	14.36	1.45×10 ⁻³	78.37
	10 ⁻³	22.60	8.07	8.72×10 ⁻⁴	92.70
	10 ⁻²	67.35	3.09	7.65×10 ⁻⁴	97.55

Table 3: Thermodynamic parameters for the mitigation of Metal surface in 0.5 M H₂SO₄ with presence and nonappearance of [BEIM]Br at 298 K

Inhibitor	Temperature (K)	Log K _{ads}	R ²	-ΔG ^o _{ads} (kJ mol ⁻¹)
[BEIM]Br	298	10.41	0.9984	82.35

Table 4: Quantum Chemical parameters for [BEIM]Br

Quantum	Para Meters
Binding Energy (kcal/mol)	-35723
Heat of Formation (kcal/mol)	450.78
Dipole Moment (Debye)	1.54
E _{HOMO} (eV)	-9.581
E _{LUMO} (eV)	-2.925
E _{HOMO} - E _{LUMO} (eV)	-6.656