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DMGO as Corrosion Inhibitor: A Mechanical, Electrical and Surface Study of Mild Steel in Acidic Environment

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Abstract : ***Mechanical, electrical and adsorption studies of mild steel in 0.5 M HCl solution with dimethylglyoxime (DMGO) as corrosion inhibitor were performed by using gravimetric analysis, adsorption isotherm analysis, resistance gradient analysis and analysis of different elastic constants like Young's modulus (Y), Bulk modulus (K) , Shear modulus (η) and Poisson's ratio (σ). It is found that DMGO shows very good corrosion inhibition action (Percentage corrosion inhibition efficiency more than 80%) at 30°C in HCl solution by its basic nature and adsorption action on mild steel surface due to presence of many lone pair donor sites and unsaturated π delocalized system in its structure. Electrical analysis reveals that the rate of increase of resistance gradient due to corrosion action of mild steel decreases significantly with the increased concentrations of inhibitor which support the retardation of loss in mechanical strength and surface erosion due to inhibition action of DMGO. Increased value of Poisson's ratio suggests the reduction in longitudinal strain which checks the loss of hardness and strength of mild steel by action of strong acidic environment. Type of adsorption (Langmuir Adsorption isotherm) and probable mechanism of the inhibition action of DMGO are also reported in this study.***

Index Terms: **Corrosion inhibitor, DMGO, Elastic constants, Langmuir adsorption isotherm, Poisson's ratio, Resistance gradient.**

I. INTRODUCTION

Corrosion has received considerable attention because of the staggering associated costs that result [1]-[7]. With large number of outdoor structures such as buildings, fences, bridges, towers, automobiles, ships and innumerable other applications exposed to the different environment, there is no wonder that so much attention has been given to the subject. Considerable amount of work has been carried out on corrosion in acidic medium [8]-[14] however there has been little work concerning the effect of corrosion on the elastic coefficients of metal and the effect of inhibitor on the mechanical and electrical nature of metal. Some reported literature shown that M. Fatmi, M.A. Ghebouli, B. Ghebouli, T. Chihi, S. Boucetta and Z.K. Heiba worked on structural elastic optical and thermal properties of Ni_3Al [15], H. Liu on mechanical properties and corrosion behavior of novel Cr2Ni low alloy construction steel with weight loss method [16], J.H. Hwang, D.W. Seo, K.T. Park and Y.J. You on mechanical properties of FRP bars by hybridizing with steel wire [17], P. Pokorny, D. Dobias and D. Citek, studied the influence of corrosion on zinc powder on mechanical properties of concrete by using compressive cubic strength and compression modulus of elasticity [18] and A. Mukherjee, M. Ghosh, K. Mondal, P. Venkitanarayanan, A. P. Moon and A. Varshney studied the mechanical properties, microstructures and corrosion behavior of Al 7075 and T651 alloy with varying strain rate [19]. Corrosion inhibition property of DMGO is investigated on mild steel in 0.5 M hydrochloride solution at 30°C by gravimetric analysis, adsorption isotherm analysis, resistance gradient analysis and analysis of In continuation to our earlier study on corrosion inhibition [20]-[27], in the present study, the corrosion different elastic constants like Young's modulus (Y), Bulk modulus (K), Shear modulus (η) and Poisson's ratio (σ).

II. MATERIALS AND METHODS

A. Materials

Mild steel (ASTM-283) wire (dimensions: 1.58 mm diameter and 60 cm length) of chemical composition: C–0.17, Si–0.35, Mn–0.42, S–0.05, P–0.20, Ni–0.01, Cu–0.01, Cr–0.01 and Fe-balance (w/w) were used. 0.5 M analytical grade HCl solution was used as aggressive acid environment, triply distilled water for solution preparation, Ethyl alcohol and acetone as drying agent, 0.01g/L, 0.02g/L, 0.03g/L, 0.04g/L and 0.05g/L DMGO as corrosion inhibitor in HCl solution.

B. Equipments

Weighing balance- Single pan analytical balance, Precision 0.01mg, Model AB 135-S/FACT, Source Mettler Toledo, Japan. *Air thermostat*- Nine adjustable chambered, electrically controlled, Accuracy ± 0.1°C. *Maxwell's Needle Apparatus*- Brass tube opened at both ends fitted with four cylinders of equal length and radii (two solid and two hollow), Needle carries a mirror and pin-vice fixed to center, timing measurement by digital stopwatch using telescope. *Searle's Apparatus*- Similar and equal bar of rectangular cross section suspended at middle points from rigid support by two torsion less vertical threads, timing measurement by digital stopwatch using telescope. *Carey Foster Bridge*- A meter long nichrome wire between thick copper strips fixed on wooden board, 1.5 V dry cell, and precision $10^{-4}\Omega$.

C. Methods

Weight loss Measurements

The effects of immersion time and gravimetric experiments was conducted on mild steel wire polished successively with sand paper, washed in distilled water, degreased with ethyl alcohol and acetone and finally dried by hot air blower. Tests were conducted in 200ml acid solutions without and with different concentrations of DMGO inhibitor at 50^{o}C temperature for 36 hours immersion time. The cleaned sample wires were weighed before and after immersion time for weight loss measurements. Corrosion rate (CR), degree of surface coverage (θ) and Percentage corrosion inhibition efficiency (PCIE) was calculated by using equations 1, 2 and 3 respectively.

$$CR = \frac{534 \text{ X } W}{DAT} \tag{1}$$

Where, W is weight loss of wire in mg, D is density of wire in g/cm^3, A is surface area of wire in inch^2 and T is immersion time of test in hours.

$$\theta = \frac{Wo - W}{Wo} \tag{2}$$

Where, W_o is weight loss of mild steel wire without inhibitor treatment and W is weight loss of wire with inhibitor treatment.

$$PCIE = \frac{CRo - CR}{CRo} \text{ X } 100 \tag{3}$$

Where, CR_o is corrosion rate in absence of inhibitor and CR is corrosion rate in presence of inhibitor.

Mechanical Elastic Coefficient Measurements

To determine mechanical elastic coefficients, Maxwell's Needle experiment, Searle's experiments were carried out on sample wire after treatment without and with different concentrations of inhibitor. Modulus of rigidity (η) and Young's Modulus were determined by Maxwell's Needle experiment from equation 4 and Searle's experiment from equation 5 respectively.

$$\eta = \frac{8\pi\ell(m_1 - m_2)a^2}{(t_1^2 - t_2^2)r^4} \tag{4}$$

Where, *l* is length and r is radius of suspended sample wire, m_1 and m_2 are mass of each of solid cylinder and hollow cylinder respectively, t_1 is time period of oscillation when solid cylinder outside and t_2 is time period of oscillation when solid cylinder is inside.

$$Y = \frac{8\pi\ell I_1}{t_1^2 r^4} \tag{5}$$

Where, *l* is length and r is radius of suspended sample wire, I_1 is found from dimensions and mass of bar of Searle's apparatus and t_1 is time period of oscillations. Having determined η and Y, the value of bulk modulus (K) and Poisson's ratio (σ) was calculated from equations 6 and 7 respectively.

$$\frac{1}{Y} = \frac{1}{9K} + \frac{3}{\eta} \tag{6}$$

and

$$\sigma = \frac{1}{2}\left(1 - \frac{Y}{3K}\right) \tag{7}$$

Resistance Gradient Measurements

To determine the resistance gradient of sample wire using Carey Foster Bridge, first they are cut in equal lengths and tested for resistance using the formula

$$\rho = \frac{R + \sigma\left(x_1 - x_2\right)}{\ell} \tag{8}$$

Where, ρ is resistance gradient of sample wire of length ℓ, σ is resistance per unit length of bridge wire in Ω/cm, R is known resistance in Ω. x_1 and x_2 are balancing lengths before and after interchanging the known resistances in Carey Foster apparatus.

Adsorption Isotherm Measurements

For surface study and to determine the mechanism of adsorption of inhibitor on mild steel surface extent of adsorption i,e concentration of inhibitor per unit surface covered (C/θ) and surface coverage was related to the concentration of inhibitor. Different adsorption isotherms were tested from linear regression coefficients calculated by Fortran 2.0 software. Adsorption constant (K_{ads}) and Gibb's free energy change of adsorption (ΔG) was calculated by following equations 9, 10 and 11.

$$C/\theta = K_{ads} C^{\frac{1}{n}} \quad \text{(Freundlich)} \tag{9}$$

$$\theta = \frac{K_{ads} C}{1 + K_{ads} C} \quad \text{(Langmuir)} \tag{10}$$

$$\Delta G = -RT \ln K_{ads} \tag{11}$$

Where *n* is the degree of adsorption.

III. RESULTS AND DISCUSSIONS

A. *Gravimetric Study*

The variations of weight loss, corrosion rate and percentage corrosion inhibition efficiency of DMGO is function of concentration of inhibitor and their results are summarized in Table1.

Table 1: CR ($x10^3$mpy) and PCIE of different concentrations of DMGO

Concentrations	CR	PCIE
Blank	0.2008	-
0.01g/L	0.0581	71.05
0.02g/L	0.0444	77.89
0.03g/L	0.0335	83.33
0.04g/L	0.0281 ``	86.02
0.05g/L	0.0273	86.40

It is observed that the PCIEs of sample wires increased with increase in concentration of DMGO. This behavior is the result of more adsorption of inhibitor on the mild steel surface due to interaction of lone pairs of N and O atoms and π electron systems of DMGO with the d-orbitals of metals present in mild steel according to Lewis acid-base interaction.

B. Mechanical Study

Results of different elastic coefficients were recorded to determine the inhibition action of DMGO on mild steel samples. Shear modulus and Young's modulus of each sample were recorded by measuring time period of 15 oscillations one by one on Maxwell's Needle apparatus and Searle's apparatus. From these elastic coefficients bulk modulus and Poisson's ratio were calculated. Results of all elastic constants ate summarized in Table 2 and Fig. 1, Fig. 2 and Fig. 3.

Table 2: Results of different Elastic coefficients and parameters in different concentrations of DMGO

Conc.	Y(GPa)	η(GPa)	K(GPa)	σ
Blank	186.5	69.8	189.2	0.3357
0.01g/L	210.7	77.9	238.2	0.3526
0.02g/L	213.8	78.6	249.5	0.3572
0.03g/L	216.2	79.5	257.0	0.3598
0.04g/L	218.9	80.3	265.2	0.3630
0.05g/L	220.7	80.9	270.9	0.3642

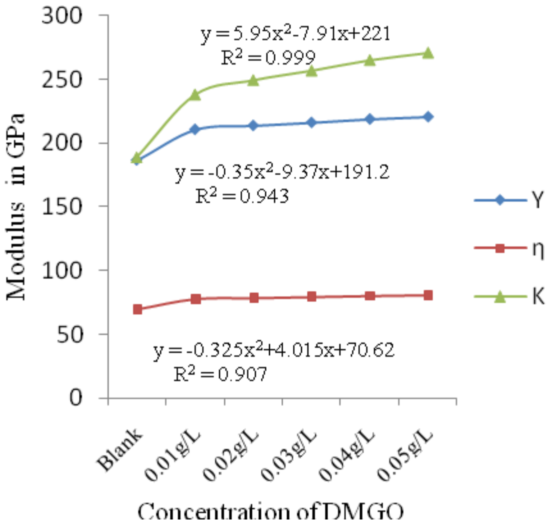

Fig. 1: Variation of Young's Modulus, Shear Modulus and Bulk Modulus of sample wires with different concentrations of DMGO in 0.5 M HCl solution.

Results of mechanical study revealed that the all elastic constants of mild steel sample wires decreased quadratically with the corrosion rate and increased with increased concentration of DMGO. A drastic decrease in volume elasticity was noticed at high corrosion rate due to high volumetric strain which is possibly due hydrogen gas embrittlement by action of acid to the mild steel.

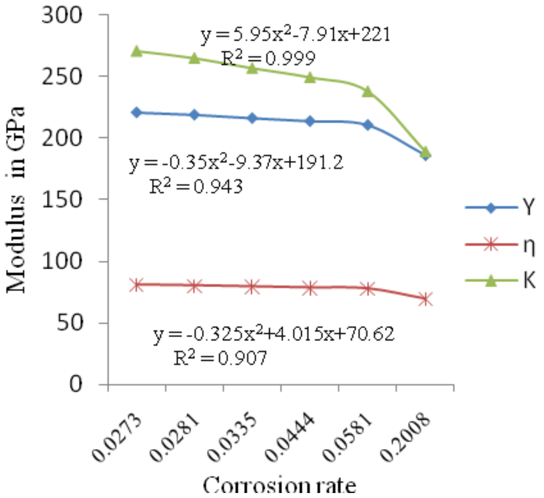

Fig. 2: Variation of Young's Modulus, Shear Modulus and Bulk Modulus of sample wires with Corrosion rate.

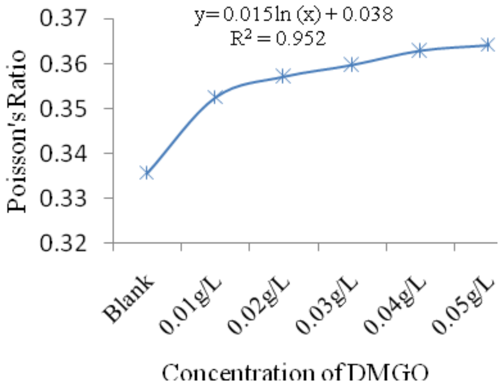

Fig. 3: Variation of Poisson's Ratio of sample wires with different concentration of DMGO in 0.5 M HCl solution.

Interaction of acid increased the porosity, weakened the metallic bond, decreased the strength and swallowed the mild steel specimen wires from which sample wires became soft. Poisson's ratio increased due to decrease in longitudinal strain and increased in lateral strain due to inhibition action of DMGO and reduction of loss of mechanical strength of mild steel.

C. Electrical Study

Results obtained by the study of electrical resistance gradient are shown in Table 3 and Fig. 4. It is observed that opposition offered by the sample wire to the flow of current through itself is decreasing with the increase in concentration of inhibitor in HCl solution. This might be due to the decrease in surface erosion of the wire occurring due to corrosion. High resistance of blank sample suggests that the corrosion products formed on the surface of wire are of poor electric conductivity and have decreased the effective cross section area and skin effect, which caused the high resistance of blank sample. Protective film formed by inhibitor on sample wire barred the entry of acid ions into the crystal structure and decelerated the rate of corrosion.

Table 3: Resistance Gradient (Ω/cm) of sample wire in different concentrations of DMGO

Concentration	Resistance Gradient
Blank	0.252
0.01g/L	0.148
0.02g/L	0.142
0.03g/L	0.138
0.04g/L	0.130
0.05g/L	0.127

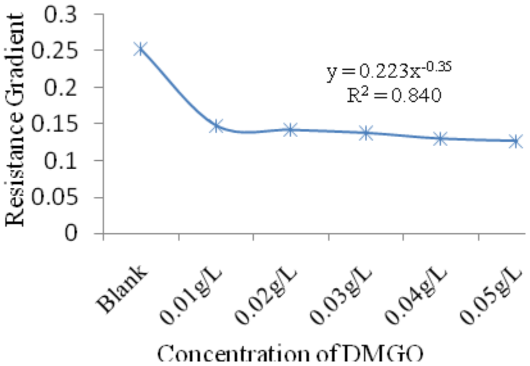

Fig. 4: Variation of Poisson's Ratio of sample wires with different concentration of DMGO in 0.5 M HCl solution.

D. Surface Study

From the result obtained from adsorption isotherm analysis, Freundlich and Langmuir adsorption isotherms were tested as given in Fig. 5 and Fig. 6 on the basis of regression coefficients calculated by Fortran 2.0 which were found to be best fit i,e found very close to unity. Adsorption constant (K_{ads}) and Gibb's free energy change of adsorption (ΔG) from both adsorption isotherms were calculated which are given in Table 4.

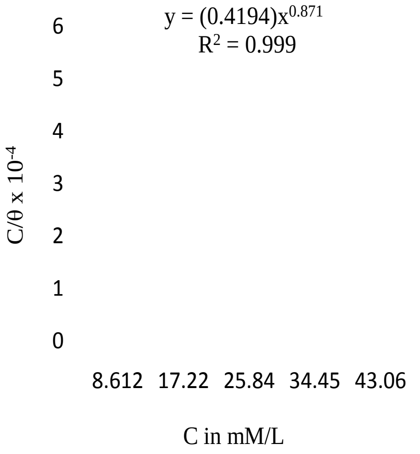

Fig. 5: Freundlich Adsorption Isotherm of DMGO onto mild steel surface in 0.5 M HCl solution at 30°C.

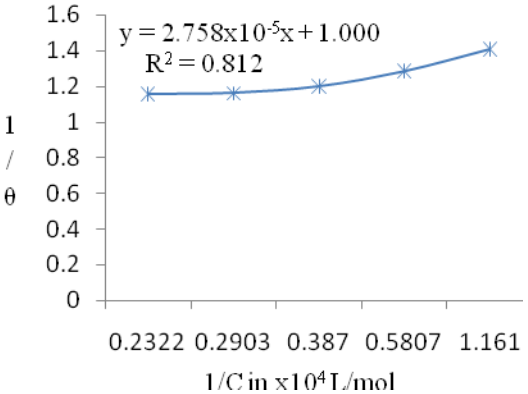

Fig. 6: Langmuir Adsorption Isotherm of DMGO onto mild steel surface in 0.5M HCl solution at 30°C.

Table 4: Freundlich and Langmuir adsorption isotherm parameters obtained from corrosion test in 0.5M HCl solution containing inhibitor

Parameters		Freundlich Isoth.	Langmuir Isoth.
Slope	-	-	$2.758X10^{-5}$
n	-	1.148	-
K_{ads}	-	$4.194 X 10^{-1}$	$3.626X10^{4}$
ΔG	-	+2.189KJ/mol	-26.45KJ/mol

Adsorption constants and Gibb's free energy change data obtained from both adsorption isotherms clearly indicated that the Langmuir adsorption isotherm was found to be best fit in adsorption of DMGO as corrosion inhibitor on mild steel sample wires. It is assumed that the mild steel surface contains a fixed number of adsorption sites and each site is chemically hold one inhibitor molecule by interaction of lone pair and π electron systems of DMGO with the d-orbitals of metals present in mild steel. Very high negative Gibb's free energy clearly indicates the spontaneous chemisorption of DMGO on mild steel surface. Almost independence of observed extent of adsorption at very high concentration is due to non-availability of adsorption sites on the mild steel surface for adsorption of inhibitor.

IV. CONCLUSIONS

Following conclusions are drawn from the study of corrosion inhibition of mild steel sample wires in different concentrations of DMGO:

1) DMGO show very strong corrosion inhibition action due to interaction of lone pairs of N and O atoms and π electron systems of DMGO with the d-orbitals of metals present in mild steel according to Lewis acid-base interaction.
2) CR is drastically decreased and PCIE is drastically increased with increase in the concentration of DMGO in HCl solution initially but this effect is poorly observed at very high concentration of inhibitor due to non-availability of adsorption active sites on the mild steel surface.
3) Young modulus, Shear modulus and Bulk modulus of mild steel sample wires decreased quadratically with the corrosion rate and increased with increased concentration of DMGO due to increase in the

porosity, weakening of metallic bond and swallowing the mild steel by action of acid.

4) Poisson's ratio increased due to decrease in longitudinal strain and increased in lateral strain due to inhibition action of DMGO and reduction of loss of mechanical strength of mild steel.
5) High resistance of blank sample suggests that the corrosion products formed on the surface of wire are of poor electric conductivity and have decreased the effective cross section area and skin effect, which caused the high resistance of blank sample.
6) Langmuir adsorption isotherm was found to be best fit in adsorption of DMGO as corrosion inhibitor on mild steel. Very high negative Gibb's free energy indicates the spontaneous chemisorption of DMGO on mild steel surface.

REFERENCES

[1] W.H. Ailor, "Atmospheric Corrosion", John Wiley, New York, 1982.

[2] S.W. Dean and T.S. Lee, "Degradation of Metal in the Atmosphere. American Society for Testing and Materials", Philadelphia, 1987.

[3] J. Tidblad, V. Kucera and A.A. Mikhailov, Report 30: UN/ECE International Cooperation Progress on Effects on Materials, Swedish Corrosion Institute, 1998.

[4] T.E. Graedel and C. Leygraf, "Scenarios for Atmospheric Corrosion in the 21st Century", The Electrochemical Society Interface, Vol. 10(4), pp. 24-30, 2001.

[5] X. Naixin, L. Zhao,C. Ding, C. Zhang, R. Li and Q. Zhang, Corrosion Science, Vol.-44, pp. 163-170, 2002.

[6] P.W. Brown, L.W. Masters, "Atmospheric Corrosion", John Wiley, NewYork, 1982.

[7] J.C. Scully, "The Fundamentals of Corrosion", 4th Edition, Pergamon Press, New York, 1994.

[8] G.A. Ijuo, H.F. Chahul and I.S. Eneji, "Corrosion inhibition and adsorption behavior of Lonchocarpus laxiflorus extract on mild steel in hydrochloric acid", European journal of Chemical Kinetics, Vol. 1, pp. 21-30, 2016.

[9] H.F. Chahul, C.O. Akalezi and A.M. Ayuba, "Effect of adenine guanine and hypoxanthine on the corrosion of mild steel in H_3PO_4", International journal of Chemical Science, Vol. 7, pp. 2006-3350, 2015.

[10] M.J. Reddy, C.B. Verma, E.E. Ebanso, K.K. Singh and M.A. Quaraishi, "Electrochemical and thermodynamic investigation on nitrofurantoin as effective corrosion inhibitor for mild steel in 1.0M hydrochloric acid solution", International Journal of Electrochemical Science, Vol. 9, pp. 4884-4899, 2014.

[11] E.A. Mohsin, M.K. Husamand and N.A. Rasha, "Inhibition of copper corrosion in H_2SO_4, NaCl and NaOH solution by Citrillus colocunthis fruit extract", Journal of Natural and Scientific Research, Vol. 4, pp. 60-73, 2014.

[12] A.M. Al- Fakih, M. Aziz and H.M. Sirat, "turmeric and ginger as green inhibitor of mild steel corrosion in acidic medium", Journal of Material and Environmental Science, Vol. 6(5), pp. 1480-1487, 2015.

[13] M.N. Rahuma, H. Amer and M. Alfergani, " Corrosion inhibition of mild steel in 11% hydrochloric acid solution by using black pepper, Chemical Science Transactions, Vol. 3(2), pp. 764-772, 2014.

[14] A.A. Al-Amiery, Y.K. Al-Majedy, A.A.H. Kadhum and A.B. Mohamad, "New coumarin derivative as an eco-friendly inhibitor of corrosion of mild steel in acid medium molecules", Vol. 20(1), pp. 366-383, 2014.

[15] M. Fatmi, M.A. Ghebouli, B. Ghebouli, T. Chihi, S. Boucetta and Z.K. Heiba, " Study of structural, elastic, electronic, optical and thermal properties of Ni_3Al", Romman Journal of Physics, Vol. 56(7-8), pp. 935-951, 2011.

[16] H. Liu, " Mechanical properties and corrosion behavior of novel Cr2Ni low alloy construction steel, "International Journal of Electrochemical Science, Vol. 10, pp. 2130-2140, 2015.

[17] J.H. Hwang, D.W. Seo, K.T. Park and Y.J. You, "Experimental study on the mechanical properties of FRP Bars by hybridizing steel wires", Engineering, Vol. 6, pp. 365-373, 2014.

[18] P. Pokorny, D. Dobias and D. Citek, "The influence of corrosion of zinc powder on mechanical properties of concrete", Ceramics-Silikaty, Vol. 60(3), pp. 195-199, 2016.

[19] A. Mukherjee, M. Ghosh, K. Mondal, P. Venkitanarayanan, A. P. Moon and A. Varshney, "Study of mechanical properties, microstructures and corrosion behavior of al 7075 t651 alloy with varying strain rate", IOP: Conference series, Material Science and Engineering, vol. 75, pp. 1-9, 2015.

[20] H. Kumar, V. Saini and V. Yadav, "Study of Vapour Phase Corrosion Inhibitors for Mild Steel under different Atmospheric Conditions". International Journal of Engineering & Innovative Technology, Vol. 3(3), pp. 206-211, 2013.

[21] H. Kumar and V. Yadav, "Corrosion Characteristics of Mild Steel under different Atmospheric Conditions by Vapour Phase Corrosion Inhibitors", American Journal of Materials Science & Engineering, Vol. 1(3), pp. 34-39, 2013.

[22] H. Kumar and V. Yadav, "CHA, BA, BTA & TEA as Vapor Phase Corrosion Inhibitors for Mild Steel under different Atmospheric Conditions", Journal of Corrosion Science & Engineering, Vol. 16(Preprint 4), 2013.

[23] H. Kumar and V. Saini, "Corrosion characteristics of vapor phase inhibitors for mild steel under different atmospheric condition. Journal of Corrosion Science & Engineering", Vol. 14(Preprint 5), 2012.

[24] H. Kumar and V. Saini, "DAPA, EA, TU and BI as Vapour Phase Corrosion Inhibitors for Mild Steel under Atmospheric Conditions", Research Journal of Chemical Sciences, Vol. 2(2), pp. 10-17, 2012.

[25] H. Kumar and V. Yadav, "BIA, DPA, MBTA and DMA as Vapour Phase Corrosion Inhibitors for Mild Steel under different Atmospheric Conditions", International Letters of Chemistry, Physics and Astronomy, Vol. 1, pp. 52-66, 2014.

[26] V. Saini and H. Kumar, "DAA, 1-BIZ and 5-ATZ as VPCI for mild steel under different aggressive atmospheric conditions at high temperature", International Letters of Chemistry, Physics and Astronomy, Vol. 17(2), 174-192, 2014.

[27] V. Saini and H. Kumar, "Synergistic effect of CTAB as VPCI for mild steel", International Journal of Chemical and Physical Sciences, Vol. 3 (5), pp. 52-69, 2014.