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N′-(4-Methoxybenzylidene)benzohydrazide as Effective Corrosion Inhibitor for Mild Steel in 1 M HCl†

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N′-(4-Methoxybenzylidene)benzohydrazide (MBBH) as inhibitor for the corrosion of mild steel in 1 M HCl was investigated by weight loss method and electrochemical techniques. Inhibition efficiency, corrosion rate and surface coverage have evaluated by varying temperature and immersion time. The inhibitor molecule might be adsorbed on the mild steel surface. Polarization curves revealed that, the synthesized *N′*-(4-Methoxybenzylidene)benzohydrazide inhibitor act as a mixed type inhibitor and the inhibition efficiency was about 93 %. The inhibitive action of *N′*-(4-methoxybenzylidene)benzohydrazide was discussed on the basis of Langmuir adsorption stable complex formed at the mild steel surface.

Key Words: *N′*-(4-Methoxybenzylidene)benzohydrazide, Corrosion inhibition, Langmuir adsorption, Tafel polarization.

INTRODUCTION

Acid solutions are widely used in industries for pickling, acid cleaning of boilers de-scaling and oil well acidizing[1]. One of the methods of corrosion prevention in acids is the addition of inhibitor. Effective inhibitors are organic compounds containing N, S, O hetrocyclic and aromatic ring[2-7]. Thermodynamic, electrochemical and quantum chemical studies were carried out on some Schiff bases for their use as corrosion inhibitors[8]. *N′*-(4-methoxybenzylidene)benzohydrazide was evaluated as corrosion inhibitor for mild steel corrosion in 1 M HCl solutions. The inhibiting performance of *N′*-(4-methoxybenzylidene)-benzohydrazide inhibitor was evaluated by weight loss, potentiodynamic polarization and electrochemical impedance method.

EXPERIMENTAL

A conventional three-electrode cell containing platinum foil counter electrode, saturated calomel electrode provided with the Luggin capillary as reference electrode and a mild steel specimen as working electrode were used. Experiments were performed using EG and G- electrochemical analyzer (Model-6310) at 303 K. The potentiodynamic polarization studies were carried out from the cathodic potential of -300 mV (SCE) to an anodic potential of + 300 mV (SCE) at a scan rate 0.5 mVs^{-1}. Electrochemical impedance spectroscopy measurements were carried out between 100 kHz-10 mHz frequency range at steady open circuit potential with an amplitude of 10 mV.

RESULTS AND DISCUSSION

Weight loss studies: Various concentrations of *N′*-(4-methoxybenzylidene)benzohydrazide (MBBH) inhibitor have decreased the % IE with exposure time. This is due to the attractive lateral interactions between the inhibitor molecules containing long hydrocarbon chains. Due to the van der Wall forces, which give stronger adsorption and higher inhibition efficiency of this inhibitor. The free energy of activation for corrosion was found to be 43.13 and 60.63 kJ mol^{-1} in the absence of inhibitor and in the presence of inhibitor respectively. The inhibitor *N′*-(4-methoxybenzylidene)benzohydrazide enhanced the free energy of activation for corrosion to occur. The calculated ΔG for adsorption values were 32.12, 32.5, 33.05, 34.31 and 34.63. The ΔG_{ads} values decrease with increase in temperature indicating that the adsorption was spontaneous with chemical interaction. This chemisorption may involves sharing or transfer of electrons from the transition metal (ion) with lone pairs of electrons on the N atom or *p*-electrons of the benzene rings.

Inhibition efficiency was decreased from 87.6 to 38.54 in the temperature range between 303 and 383 K. High inhibition efficiency of this compound may be attributed to the presence

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of extensively delocalized π electrons of the phenyl rings[9], planarity and presence of lone pair of electrons on *N*-atoms, which favoured greater adsorption of MBBH on the metal surface. The negative value of activation energy indicates (Fig. 1) the spontaneous adsorption of inhibitors on the metal surface. A decrease in inhibition efficiency with temperature is analogous to an increase in activation energy of corrosion in the presence of inhibitors. This is due to the formation of an adsorption film on the surface[10-12]. The effectiveness of a compound as corrosion inhibitor depends on the structure of the organic compounds[13] and the presence of (-C=C-) group in conjugation with aromatic ring plays a major role in increasing efficiency.

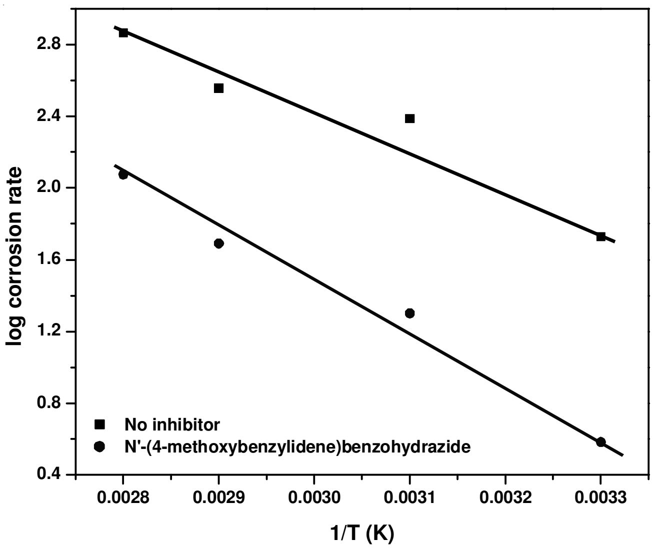

Fig. 1. Variation of log corrosion rate with 1/T in the absence and presence of *N'*-(4-methoxybenzylidene)benzohydrazide inhibitor

Tafel polarization studies: Corrosion parameters such as corrosion current density (I_{corr}), corrosion current potential (E_{corr}), Tafel slopes (b_a and b_c) and inhibition efficiency were calculated from Tafel plots of mild steel in 1 M HCl in the presence and absence of various concentrations of the inhibitors at 303 K (Fig. 2). Corrosion current density decreased with increasing inhibitor concentration is attributed to increase in surface coverage (Table-1). The presence of surface coverage coverage on the metal surface permitted the free access to H^+ ions[14] and metal dissolution took place subsequently by the desorption of the inhibitor film on the mild steel surface[15,16]. E_{corr} values were slightly shifted in nobler direction with increased concentration of inhibitors. These compounds acted as mixed inhibitor and the inhibitive action was due to blockage of active surface sites on mild steel surface[17,18]. The adsorption of inhibitors on the surface of mild steel was due to the presence of electron rich N atom and aromatic rings in the inhibitor molecule.

Electrochemical Impedance measurements: Table-2 summarizes the parameters such as charge transfer resistance, double layer capacitance (C_{dl}) and inhibition efficiency (IE) in presence and absence of different concentrations of inhibitors obtained from electrochemical impedance spectra. The observed single depressed semicircle was due to high frequency dispersion[19] (Fig. 3), the impedance of an inhibited substrate increased with increasing concentration of inhibitor[20,21]. The depressed semicircles in the Nyquist plots were probably due to the surface heterogeneity or the corrosion products of the metal substrate developing the defects in the film[22]. The presence of depressed semicircle was caused by the surface in-homogeneity of the solid surface and the adsorption of inhibitor[23]. R_p values increased with MBBH concentration. It was due to the formation of protective layer which acted as a barrier for both mass and the charge transfer. The inhibition efficiency values were almost equal to the values obtained from the weight loss measurement and Tafel polarization methods. The value of double layer capacitance (C_{dl}) and the charge transfer resistance (R_{ct}) were decreased and increased respectively in presence of inhibitors.

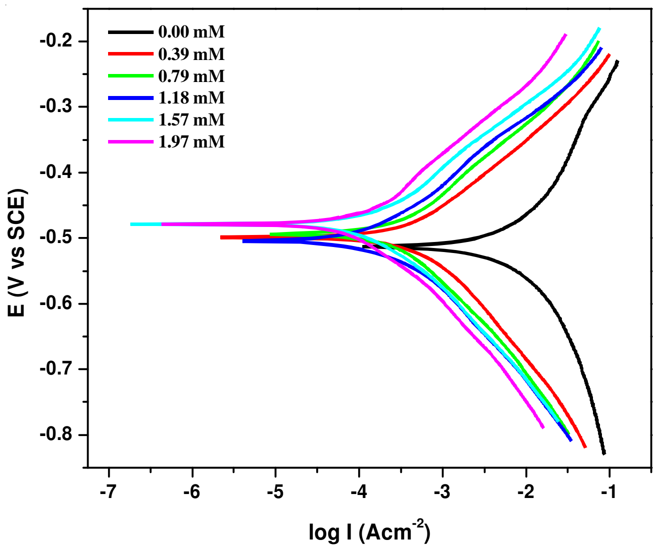

Fig. 2. Potentiodynamic polarization curves for mild steel in 1 M HCl with different concentrations of *N'*-(4-methoxybenzylidene)benzohydrazide at 303 K

TABLE 1
PARAMETERS DERIVED FROM POTENTIODYNAMIC POLARIZATION CURVES FOR MILD STEEL IN 1M HCL CONTAINING DIFFERENT CONCENTRATIONS OF N'-(4-METHOXYBENZYLIDENE) BENZOHYDRAZIDE AT 303 K

Concen. (mM)	E_{corr} (mV Vs SCE)	Tafel slopes (mV dec^{-1})		I_{corr} (mA/cm^2)	I.E (%)
		Anodic (b_a)	Cathodic (b_c)		
0.00	-512	128	104	1.597	-
0.39	-498	122	96	0.264	83.46
0.79	-494	123	92	0.201	87.41
1.18	-504	122	89	0.178	88.85
1.57	-478	114	94	0.132	91.73
1.97	-479	119	97	0.104	93.48

TABLE-2
PARAMETERS DERIVED FROM IMPEDANCE MEASUREMENT FOR MILD STEEL IN 1 M HCl CONTAINING N'-(4-METHOXY BENZYLIDENE) BENZOHYDRAZIDE AT 303 K

Concentration	R_{ct} (Ω/cm^2)	C_{dl} (μF/cm^2)	IE (%)
0.00	20.02	147.65	-
0.39	132.14	97.2	84.84
0.79	240.05	56.5	91.66
1.18	323.41	46.2	93.72
1.57	403.15	33.4	95.03
1.97	583..25	21.2	96.56

Adsorption behaviour and corrosion inhibition mechanism: Adsorption isotherm is arrived at for organic molecule interaction with the metal surfaces. The value of surface coverage θ was measured from the weight loss data. The values of log (θ/1-θ) *Vs*. log C for different concentrations of the inhibitors were plotted (Fig. 4). The straight line obtained indicates that, the adsorption of MBBH inhibitor on the mild steel surface followed the Langmuir adsorption isotherm.

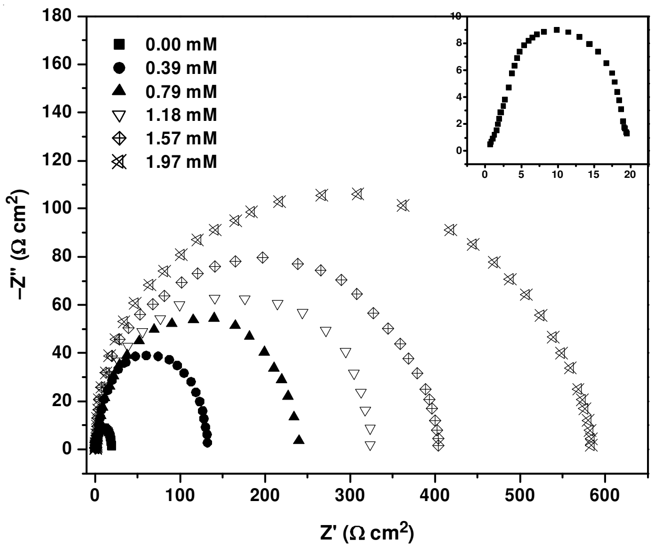

Fig. 3. Nyquist diagrams for mild steel in 1 M HCl with different concentrations of *N′*-(4-methoxybenzylidene)benzohydrazide) inhibitor

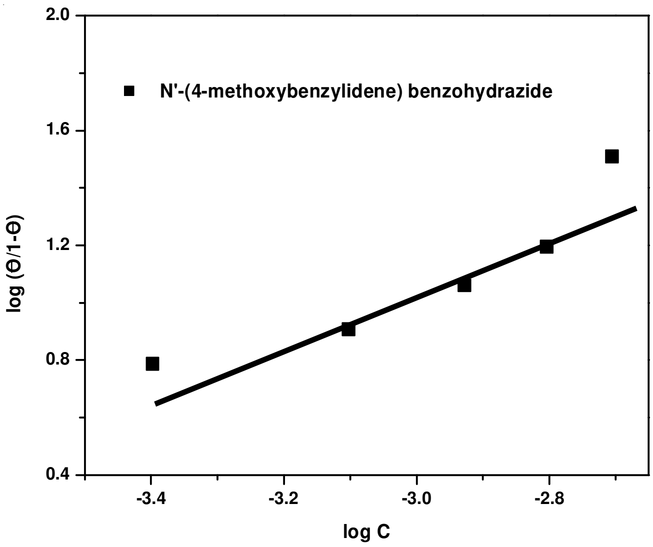

Fig. 4. log C *Vs* (θ/1- θ) plot for the adsorption of inhibitor containing 2.10 mM concentraion of *N′*-(4-methoxybenzylidene)benzohydrazide

The inhibitor had polar atoms or groups which adsorbed on the metal surface and interacted by mutual attraction and repulsion. The MBBH molecules adsorbed at cathodic sites in competition with hydrogen ions, which reduced H_2 gas evolution[24]. The chemical structure of inhibition[25] indicates the presence of carbonyl group (-C=O) and the π electrons of -C=N and phenyl groups.

Conclusion

The compound MBBH was acted as efficient corrosion inhibitor in 1 M HCl at various temperatures and immersion time. Inhibition efficiencies obtained from the electrochemical studies have agreed reasonably with weight loss method. The potentiodynamic polarization studies have revealed that, the inhibitors acted on both cathodic and anodic areas on the metal surface and offered mixed inhibition. The adsorption model obeys the Langmuir adsorption isotherm at ambient temperature and the negative values of free energy of adsorption indicated that the adsorption of the MBBH was spontaneous process.

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REFERENCES

1. G. Trabanelli, *Corrosion*, **47**, 410 (1991).
2. A. Chetouani, A. Aouniti, B. Hammouti, N. Benchat, T. Benhadda and S. Kertit, *Corros. Sci.*, **45**, 1675 (2003).
3. A.A. Ismail, S.H. Sanad and A.A. El-Meligi, *J. Mater. Sci. Tech.*, **6**, 397 (2000).
4. L. Wang, *Corros. Sci.*, **43**, 2281 (2001).
5. A. Popova, M. Christov, S. Raicheva and E. Sokolova, *Corros. Sci.*, **46**, 1333 (2004).
6. L.B. Tang, X.M. Li, Y.S. Si, G.N. Mu and G.H. Liu, *Mater. Chem. Phys.*, **5**, 29 (2006).
7. Y. Yan, W.H. Li, L.K. Cai and B.R. Hou, *Electrochim. Acta*, **53**, 5953 (2008).
8. Y. Tang, X. Yang, W. Yang, Y. Chen and R. Wan, *Corros. Sci.*, **52**, 242 (2010).
9. M. Lebrini, F. Bentiss, H. Vezin and M. Lagrenee, *Corros. Sci.*, **48**, 1279 (2006).
10. S.M.A. Hosseini and A. Azimi, *Mater. Corros*., **59**, 41 (2008).
11. M.J. Bahrami, S.M.A. Hosseini and P. Pilvar, *Corros. Sci.*, **52**, 2793 (2010).
12. E.E. Oguzie, *Corros. Sci.*, **50**, 2993 (2008).
13. M.A. Quraishi, S. Ahmad and M.Q. Ansari, *Br. Corros. J.*, **32**, 297 (1997).
14. A. Chetouani, B. Hammouti, T. Benhadda and M. Daoudi, *Appl. Surf. Sci.*, **249**, 375 (2005).
15. B. El Mehdi, B. Mernari, M. Traisnel, F. Bentiss and M. Lagrenee, *Mater. Chem. Phys*., **77**, 489 (2003).
16. M. El-Achouri, S. Kertit, H.M. Gouttaya, B. Nciri, Y. Bensouda, L. Perez, M.R. Infante and K. Elkacemi, *Prog. Org. Coat.*, **43**, 267 (2001).
17. G. Moretti, G. Quartarone, A. Tassan and A. Zlngales, *Electrochim. Acta*, **41**, 1971 (1996).
18. I. Ahamad and M.A. Quraishi, *Corros. Sci.*, **51**, 2006 (2009).
19. K. Jüttner, *Electrochim. Acta,* **35**, 1501 (1990).
20. T. Tüken, B. Yazici and M. Erbil, *Mater. Chem. Phys*., **99**, 459 (2006).
21. I. Dehri, H. Sozusaglam and M. Erbil, *Prog. Org. Coat.*, **48**, 118 (2003).
22. U. Rammelt, G. Reinhard and K. Rammelt, *J. Electroanal. Chem.*, **180**, 327 (1984).
23. A.P. Srikanth, T.G. Sunitha, S. Nanjundan and N. Rajendran, *Prog. Org. Coat.*, **56**, 120 (2006).
24. R. Solmaz, G. Kardas, M. Çulha, B. Yazici and M. Erbil, *Electrochim. Acta*, **53**, 5941 (2008).
25. S. Zhang, Z. Tao, S. Liao and F. Wu, *Corros. Sci.*, **52**, 3126 (2010).