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New Schiff's bases as corrosion inhibitors for mild steel in HCl medium

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ABSTRACT

Corrosion inhibition effect of newly synthesized schiff's bases Formaldehyde methylene hydrazone, (FMH), N-N′-Dibenzylidene hydrazine, (NDBH), 4- (Dimethylamino) benzaldehyde {(1E) - [4-(Dimethy amino) methylene} hydrazone, (DMBH), and 2-furaldehyde [(1E)-2-furylmethylene] hydrazone, (FFMH) on mild steel in 2N HCl acid medium, were investigated through weight loss and galvano static polarization techniques. Effect of concentration and effect of time of immersion on corrosion inhibition efficiency were part of the investigation. The inhibiting performances of all the compounds were found to increase with the increase in concentration. The SEM images of protected steel samples with compounds were recorded for morphological assessment.

KEYWORDS

Schiff's base;
Weight loss;
Polarization;
SEM;
Corrosion.

INTRODUCTION

Mild steel is one of the most important widely used engineering materials particularly for the structural and automobile applications. However, it undergoes corrosion easily in the humid atmosphere and its rate of corrosion is quite high in acidic environment. Thus, protection of mild steel from corrosion is an important problem. Out of several methods, use of chemical inhibitors is one of the most practical methods for the prevention of corrosion particularly in acidic media. Acid solutions are widely used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid de-scaling and oil wet cleansing etc[1,2].

Corrosion resistance property of steel has been achieved by using suitable inhibitors that control the metal dissolution when added to the acid medium in small quantities. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulfur or oxygen atoms[3–7]. It has been found that most of the organic inhibitors adsorbed on the metal surface[8]. This phenomenon is influenced by structure of the organic compound, nature and surface charge of metal and type of aggressive electrolyte[9]. Many studies have been made on the corrosion and inhibition of steel in acid media[10–14]. Some Schiff's bases have been reported earlier as corrosion inhibitors for steel[15–17]. These compounds, in general are adsorbed on the metal surface by blocking the active corrosion sites. A few research reports[18,19] revealed that the inhibition efficiency of Schiff's bases is much higher than that of corresponding aldehydes and amines, and this may be due to the presence of >C=N- group in the molecules. The planarity (π) and lone pairs of electrons present on N at-

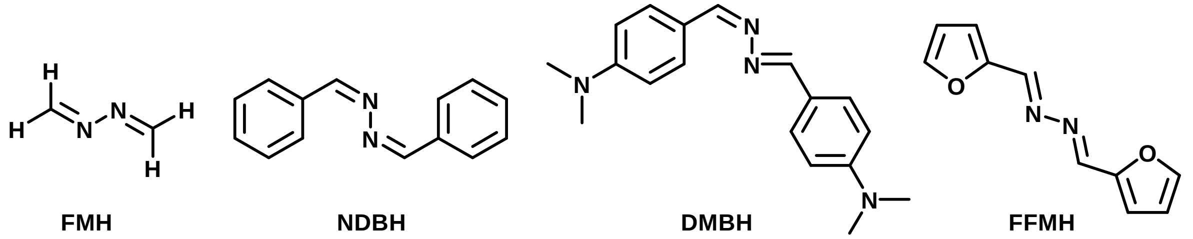

Figure 1 : Structure of Schiff's bases

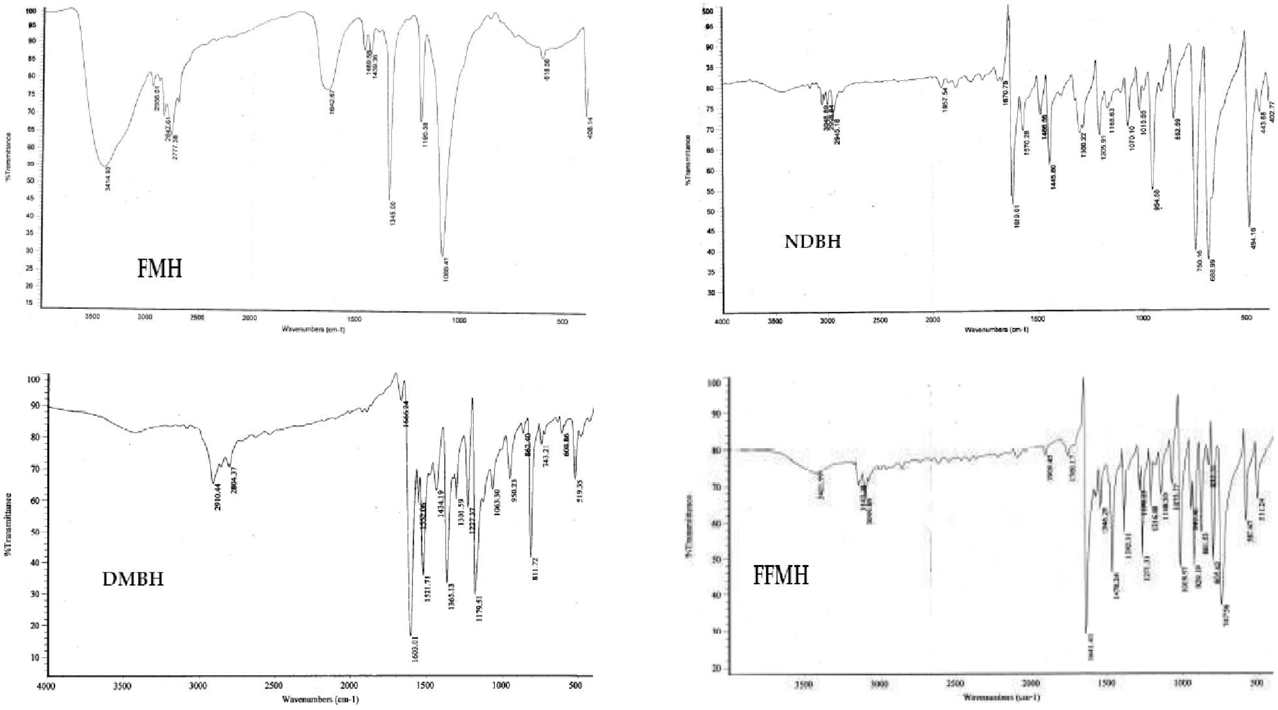

Figure 2 : IR spectra of Schiff's bases

oms are the important structural features that determine the adsorption of these molecules on the metal surface.

The present work involves synthesizing and evaluation of corrosion inhibiting efficiencies under insitu conditions of new schiffs bases generated using hydrazine, N_2H_4, as one of the precursors while varying the other reactant like Formaldehyde, for FMH, Benzaldehyde for NDBH, para dimethyl amino benzaldehyde for DMBH and Furfuraldehyde for FFMH. The substituted Hydrazine has been investigated for inhibiting ability in acidic medium by different research groups[20-23]. In the present work performances of the above said Schiff's bases are being evaluated as insitu inhibitors.

EXPERIMENTAL

Through out the synthesis of schiff's bases AR grade chemicals and demineralised water has been used. The Procedures as described in standard literature was followed in Toto or imitated on identical line, for product synthesis[24]. The prepared compounds were thoroughly washed with demineralised water and subjected to re crystallization in alcohol. The chemical structures of the compound are given in figure 1. The IR spectra of the compounds are given in figure 2.

Weight loss measurements

Metal coupons were taken through all preparative cleaning method and final mirror finish was obtained by mechanical polishing through different grades of emery paper. Metal coupon dimensions are 5×2×0.16 cm and they measured before and after each experiment. The following concentrations of the condensation products ranging from 200 to 800 ppm were dissolved in 25 ml polar solvent mixture containing DMF, DMSO and Alcohol in ratio of 3:1:1. The organic solutions prepared

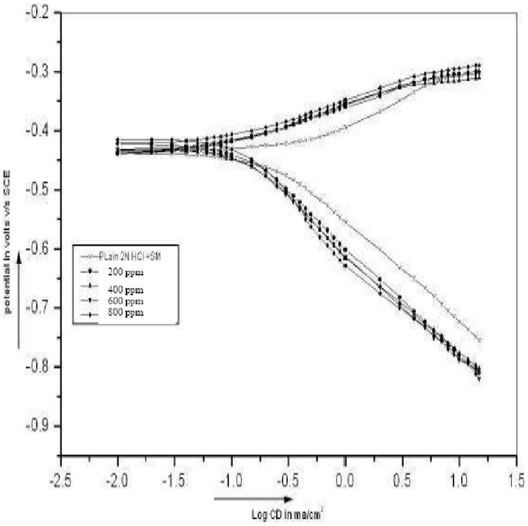

Figure 3 : Superimposed polarisation curves of FMH in corrosive medium

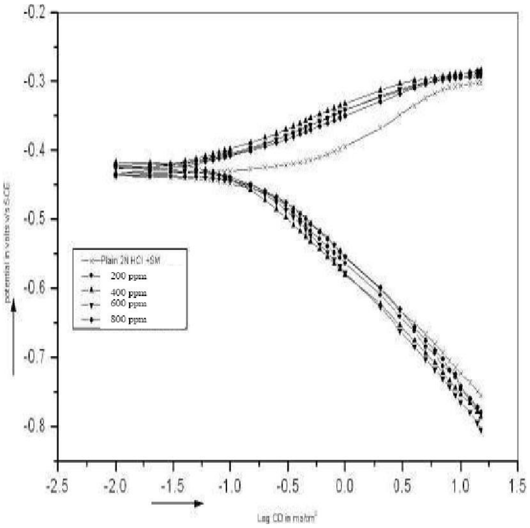

Figure 4 : Superimposed polarisation curves of NDBH in corrosive medium

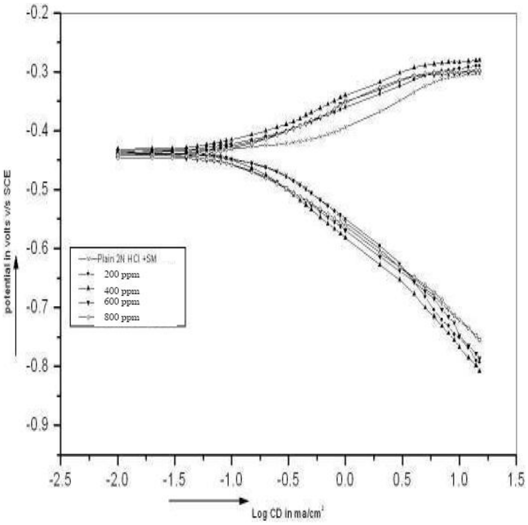

Figure 5 : Superimposed polarisation curves of DMBH in corrosive medium

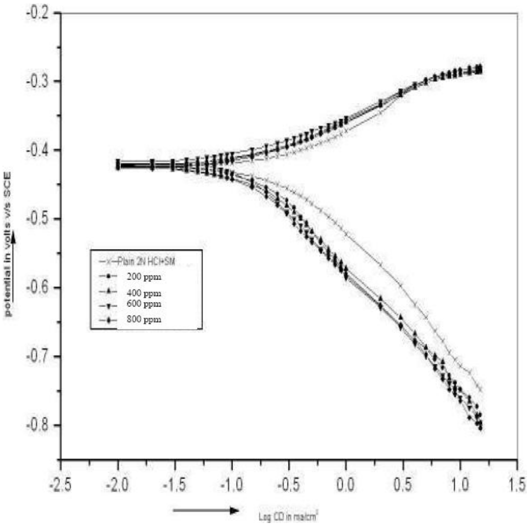

Figure 6 : Superimposed polarisation curves of FFMH in corrosive medium

as said above were added to a known volume standard volumetric flask containing concentrated HCl sufficient to make 2N corroding medium and rest of the volume in the flask was made up with demineralised water.

Pre weighed steel coupons were hung in above prepared schiff's base solution for various duration (2hr-8hr) at 303 K under fully covered condition. A parallel observation without inhibitor compound and rest of the combination of corroding media remaining unaltered was also made. Experiments were duplicated every time for concurrency. The inhibiting efficiency (%η) of compound based on weight loss was calculated as per the formula

$$\%\eta = \frac{W_1 - W_2}{W_1} \times 100$$

where, W_1 is the weight loss of the coupon in blank experiment. W_2 is the weight loss of the coupon in corroding medium containing inhibitor to known concentration and for known time period. The result was normalized to unit area.

Polarization measurements

Polarization studies were carried on 1cm^2 exposed area of mild steel coupon. A three-compartment cell of 125 ml capacity was used for carrying out experiment. Platinum electrode was used as auxiliary electrode, while

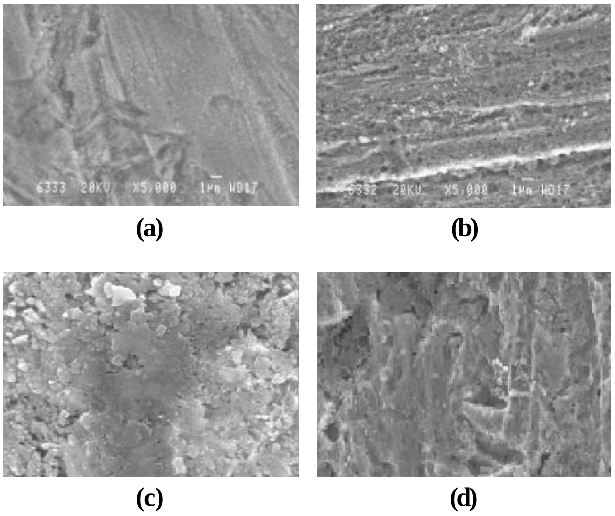

Figure 7 : SEM Micrograph of mild steel surface in acid medium in presence of different inhibitor (a) FMH (b) NDBH (c) DMBH (d) FFMH

standard calomel electrode (SCE) was used as reference electrode. The metal coupon formed the working electrode. For galvanostatic polarization experiment metal surface preparation methods were followed on identical lines to that of weight loss measurements. Corrosive medium containing different concentrations of inhibitor was prepared on the same lines as described in weight loss measurements. The corroding medium containing inhibitors was filled in three-compartment cell ensuring the expulsion of air bubble from the capillary tip. The working electrode was aligned with its exposed area lying very close to capillary tip.

A DC source (calibrator Rohnan make), which can provide a lowest current step of 10 micro amps, was used. Anodic and cathodic polarisation was established by reversing the polarities between Platinum electrode and working electrode. The polarization data was collected by scanning between 0.01mA to 15mA in each cycle. Before reversing the polarity the exposed surface was mildly polished to remove corrosion debris. The cathodic polarization was always started as first cycle followed by the anodic cycle. The open circuit potential, (OCP), was recorded after allowing sufficient time for the reading to stabilize.

The inhibiting efficiencies (%η) of inhibitors based on polarization studies was calculated using the formula

$$\%\eta = (1 - \frac{i}{i_0}) \times 100$$

where, i_0 is equivalent corrosion current without inhibitor and i is equivalent corrosion current with inhibitor.

SEM studies

For knowing the surface morphology of the inhibited steel surface square specimens of steel having dimensions 10mm×10mm×1mm were used. The procedures as described in weight loss studies were followed while preparing surfaces of the specimen steel coupons. The coupons were hung in 200 ppm inhibitor solutions for 2 hour duration. After the lapse of designated time duration the coupons were taken out, water washed carefully, hot air dried, desiccated and taken to SEM scanning (JOEL-JEM-1200, EX II electron microscope).

RESULTS AND DISCUSSIONS

TABLE 1 gives the inhibiting efficiency (%η) as a function of concentration and time of immersion of schiff's bases. Inhibition efficiency of all the compounds was increased with increase in concentration and immersion time. Inhibition efficiency was reached maximum value at 800 ppm and above this concentration almost same values were observed. Inhibition efficiency values are increased with immersion time upto 8 hours then remains almost same. Thin isolative layer of inhibitor on metal surface was formed and it is confirmed by SEM studies. Also the weight loss measurement revealed the excellent stability of the inhibitors in the acid medium. To assess the stability, the experiments were conducted by taking acid solution containing inhibitor which was kept for 10 days under air agitation and no change in inhibition efficiency values were observed.

The Tafel curves of anodic and cathodic polarization of steel coupon in corroding medium with and without inhibitors superimposed over tafel curve of steel in corroding medium are given in figure 3-6. The corrosion parameters as arrived through interpretation of Tafel curves are given in TABLE 2. The compound FMH shifts corrosion potential to more positive than that of E_0 value of uninhibited steel surface. The percentage surface coverage θ, and also %η increased with the increase in concentration. The compound has in its structure conjugated unsaturated bonds along with unshared electrons on nitrogen atom, a prerequisite quality for adsorption/chemisorption on to the metal surface. The

TABLE 1 : Percentage inhibiting efficiencies of inhibitors through weight loss method

Compound	Concentration ppm	Inhibiting efficiency (%η)			
		2 hours	4 hours	6 hours	8 hours
FMH	200	50	58	63	68
	400	56	60	67	70
	600	57	61	69	72
	800	66	70	71	75
NDBH	200	45	48	51	55
	400	50	54	56	59
	600	54	58	60	64
	800	59	64	66	69
DMBH	200	52	58	60	63
	400	56	59	65	66
	600	60	61	67	69
	800	62	63	69	72
FFMH	200	26	30	36	40
	400	51	55	56	58
	600	52	57	58	60
	800	56	59	60	62

TABLE 2 : Corrosion parameters interpreted through polarization curves

Comp^{d}	Concentration	-E mv	i0µ amps/cm^2	θ degree coverage	ba mv	bc mv	Inhibition efficiency (%η)
	ppm	HCl 2N	446	178	63	114	
FMH	200	423	78	0.56	55	123	56
	400	428	65	0.63	58	133	63
	600	410	60	0.66	44	93	66
	800	425	49	0.72	55	177	72
NDBH	200	415	79	0.56	56	105	56
	400	415	71	0.60	65	116	60
	600	416	67	0.62	54	107	62
	800	418	61	0.66	48	88	66
DMBH	200	439	83	0.53	67	70	53
	400	441	77	0.57	75	86	57
	600	447	70	0.61	77	77	61
	800	450	58	0.67	82	79	67
FFMH	200	422	109	0.39	54	105	39
	400	427	83	0.53	74	117	53
	600	413	79	0.56	42	120	56
	800	426	73	0.59	55	91	59

adsorption of organic molecules on to the surface of metal proceeds with the displacement of aqua molecules and whose number is being guided by the size of organic molecules[25]. Absence of bulky groups on the matrix kinetically favors the molecule to bind on the metal in an orderly fashion as evidenced by the SEM figure 7a.

In case of NDBH compound also %η increased with the increase in concentration. The molecule has bulky aromatic ring in the matrix which could hinder in smooth deposition on to metal surface as evidenced through SEM figure 7b. Morphology reveals a spidery web like coverage all through the film. Also the SEM picture shows whitish spots at many locations indicating substrate getting corroded. The probable protonation of N atom in the molecule helps it to chemisorp on the cathodic sites of the substrate surface there by delaying the cathodic reduction consequently quenching the anodic dissolution rate.

The compound DMBH is more a mixed type inhibitor indicating the inhibitors ability to block both anodic as well as cathodic corrosion processes. The molecule has terminal aromatic rings with dialkyl amine substitution, which could inhibit molecule sterically in the process of adsorption a view supported well by SEM figure 7c. The SEM picture shows thick deposit of the compound interspersed with few corrosion product deposits here and there. The protonation across N atom perhaps helps the molecule to bind on to cathodic sites on the metal surface there by delaying the accompanying cathodic reduction.

The compound FFMH appears that it is anodic inhibitor. The surface coverage θ, gradually increases with the concentration of the inhibitor. The molecular matrix as shown in figure 1 indicates the extension of conjugation through heteroatom N. These attributes on the molecule favor a steric free, adhesion on to the metal, a view supported by electron micrograph figure 7d. The SEM picture shows few locations where corrosion product deposition taking place other wise picture reveals reasonably well-protected substrate.

CONCLUSION

- The prepared Schiff's bases act as good insitu corrosion inhibitors in HCl medium.
- The solubility enhancement of the inhibitors in corroding media required prior dissolution of the compounds in polar solvent mixture.
- The inhibitive efficiencies increase with concentra-

tion and immersion time.

- Performance of the compounds are reproducible in both weight loss and polarization measurements.
- The SEM picturisation of the film surface adds weight to this view with respect to above results.

REFERENCES

[1] G.Schmitt; Br.Corros.J., **19**, 165 **(1984)**.

[2] M.Lagrenee, B.Mernari, M.Bouanis, M.Traisnel, F.Bentiss; Corros.Sci.J., **44**, 574 **(2002)**.

[3] S.Kertit, J.Aride, A.Ben-Bachir, A.Sghiri, A.Elkoly, M.Etman; J.Appl.Electrochem., **19**, 83 **(1989)**.

[4] Lin Wang; Corros.Sci., **43**, 1637 **(2001)**.

[5] J.M.Sykes; Brit.Corros.J., **25**, 175 **(1990)**.

[6] X.L.Cheng, H.Y.Ma, S.Chen, R.Yu, X.Chen, Z.M.Yao; Corros.Sci., **41**, 321 **(1999)**.

[7] Salih S.Al-Juaid; J.Electrochem.Soc.Ind., **50**, 99 **(2001)**.

[8] S.S.Abd EL-Rehim, M.A.M.Ibrahim, K.F.Khaled; J.Appl.Electrochem., **29**, 593 **(1999)**.

[9] J.G.N.Thomas; Some New Fundamental Aspects in Corrosion inhibitors, Ann.Univ., N.S.Ferrara, Sez.V.Suppl., University of Ferrara, Ferrara, Italy, **8**, 453 **(1981)**.

[10] B.Sathianandan, K.Balakrishnan, N.Subramanyan; Brit.Corros.J., **5**, 270 **(1970)**.

[11] F.Zucchi, G.Trabanelli, G.Brunoro; Corros.Sci., **33**, 1135 **(1992)**.

[12] J.O'M. Bockris, B.Yang; J.Electrochem.Soc., **138**, 2237 **(1991)**.

[13] G.Banergee, S.N.Malhotra; Corrosion., **48**, 10 **(1992)**.

[14] J.Uhrea, G.Aramaki; J.Electrochem.Soc., **138**, 3245 **(1991)**.

[15] K.C.Emeregul, O.Atakol; Mater.Chem.Phys., **82**, 188 **(2003)**.

[16] S.Bilgic, N.Caliskan; Appl.Surf.Sci., **152**, 107 **(1999)**.

[17] M.G.Hosseini, S.F.L.Mertens, M.Gharbani, M.R.Arshadi; Mater.Chem.Phys., **78**, 800 **(2003)**.

[18] M.N.Desai, M.B.Desai, C.B.Shah, S.M.Desai; Corros.Sci., **26**, 827 **(1986)**.

[19] H.Ashassi-Sorkhabi, B.Shaabani, D.Seifzadeh; Appl.Surf.Sci., **239**, 154 **(2005)**.

[20] M.A.Qureshi, Sardar R.Rana; Bull.Electrochem., **18**, 255 **(2002)**.

[21] M.A.Qureshi, Jamal, Danish; Anti.Corr.Meth.Mat., **47**, 233 **(2000)**.

[22] S.Sathiyanarayanan, C.Marikkannu, N.Palaniswamy; App.Surf.Sci., **241**, 477 **(2005)**.

[23] K.F.Khaled; App.Surf.Sci., **252**, 4120 **(2006)**.

[24] B.S.Furniss, A.J.Hannaford, P.W.G.Smith, A.R.Tatchell; Vogel's Practical Organic Chemistry, 5th Edition Thames Polytechnic, London, **(1989)**.

[25] M.Sahin, S.Biljic, H.Yilmaz; App.Surf.Sci., **195**, 1 **(2000)**.