

Investigation of Piperazine and its Derivatives as Vapor Phase Corrosion Inhibitors for Mild Steel

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Abstract: Piperazine and its derivatives such as phosphates, carbonates, benzoates, cinnamate and maleate were developed and investigated as vapor phase corrosion inhibitors by weight loss, potentiodynamic polarization methods for mild steel. All of these compounds have shown good inhibition efficiency for mild steel after 30 days under continuous condensation test (CT). The potentiodynamic polarization studies have shown predominantly anodic behavior of all these compounds.

Keywords: Corrosion inhibition, vapor phase corrosion inhibitors, piperazine, mild steel.

1. INTRODUCTION

Vapor phase corrosion inhibitors are best known to protect metallic articles and equipments during storage and transportation [1-4]. There are numerous investigations on corrosion inhibition studies by aliphatic amines, salicylic amines and their salts as vapor phase corrosion inhibitors for various industrial metals and alloys [5-8]. However, investigations bearing Oxygen, Nitrogen or Sulphur atoms in the ring have received little attention. Benzotriazole has been reported as effective corrosion inhibitor for copper and its alloys [9,10]. Subramaian *et al.* [11] has recently studied the corrosion inhibition behavior of morpholine and its three salts, such as morpholine carbonate, borate and phosphate, of these, morpholine and its carbonate derivatives exhibited 90 percent and 85 percent inhibition efficiency, while other salts gave less than 40 per cent inhibition efficiency. Fifty-three products [12], mostly carboxylate salts of amines, were evaluated as vapor phase corrosion inhibitors for mild steel, among them, fifteen compounds showed effectiveness in excess of 90%. Morpholine was the most effective amine and caprylic acid as the most effective acid constituent. Daquan Zhang *et al.* [13] developed bis-piperidiniummethyl-urea as volatile corrosion inhibitor for temporary protection of carbon steel.

In the present study, the authors have studied the inhibiting properties of five vapor phase corrosion inhibitors, such as piperazine (P), piperazine dinitrobenzoate (PDNB), piperazine dimaleate (PDM), piperazine diphosphate (PDP) and piperazine dicarbonate (PDC) on corrosion of mild steel.

2. EXPERIMENTAL

Prior to all measurements, cold rolled mild steel samples of size 2 x 2.5 x 0.25 cm having composition (wt%): 0.14% C, 0.35%Mn, 0.17% Si, 0.025% S, 0.03% P and balance Fe.

The strips were polished by emery paper of 1/0, 2/0 and 3/0 rinsed with double distilled water, degreased and dried at room temperature. Piperazine and its derivatives such as carbonate, nitro benzoate, maleate and phosphate, were synthesized by reacting the piperazine with carbon dioxide, nitro benzoic acid, maleic acid and phosphoric acid respectively. The names, molecular structures of the compounds are given in Table 1.

Weight loss experiments were carried out in presence and absence of inhibitors at various concentrations, using tight fitting rubber cork jars (Fig. 1). The mild steel specimens was level mounted on the top of the beaker by transparent adhesive tapes and just below these specimens were kept vapor phase inhibitor samples in a small bottle. These jars were kept at 100% relative humidity at 40°C for 8 hours and then for 16 hours under the room temperature [14] in order to allow continuous condensation of moisture on metal specimen. This set up was kept for 30 days.

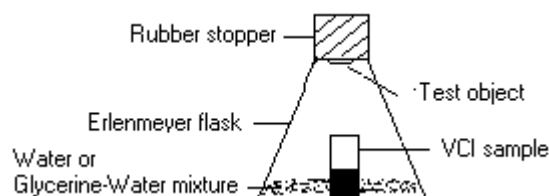


Fig. (1). Experimental setup for weight loss experiments.

The inhibition efficiency (IE %) was determined by the following equation:

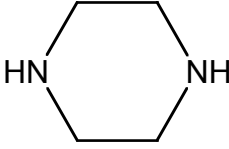
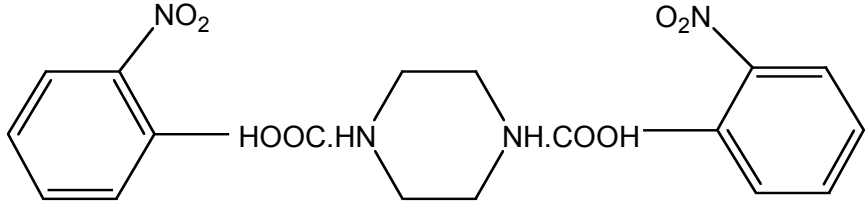
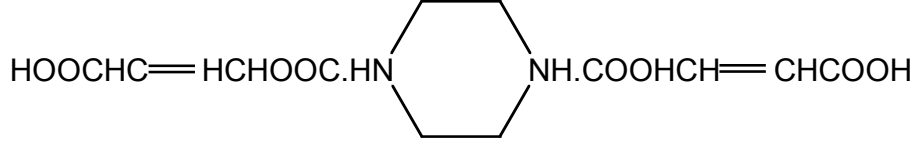
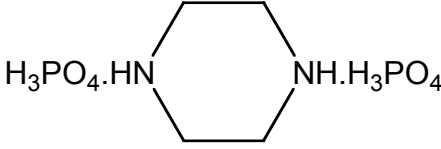
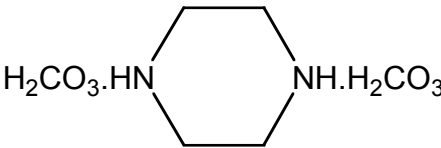
$$I.E.(%) = \frac{W_o - W_i}{W_o} \times 100 \quad (1)$$

where W_o and W_i is the weight loss value in the absence and presence of inhibitor

Potentiodynamic polarization studies were performed using EG&G PARC potentiostat / Galvanostat (model 173) and X- Y recorder (Model RE0089). The polarization was carried out at a sweep rate of 1 mVs⁻¹. The potential was carried out from OCP within the range of ±200 mV and the

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Table 1. Molecular Structures of the Inhibitors Used

S. No.	Molecular Structure	Names and Abbreviations
1.		Piperazine (P)
2.		Piperazine dinitrobenzoate (PDNB)
3.		Piperazine dimaleate (PDM)
4.		Piperazine diphosphate (PDP)
5.		Piperazine dicarbonate (PDC)

electrodes were polarized from cathodic to anodic direction. The cell assembly (Fig. 2) consisted of mild steel as a working electrode, platinum foil as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All the experiments were carried out in 1N Na₂SO₄ solution as electrolyte.

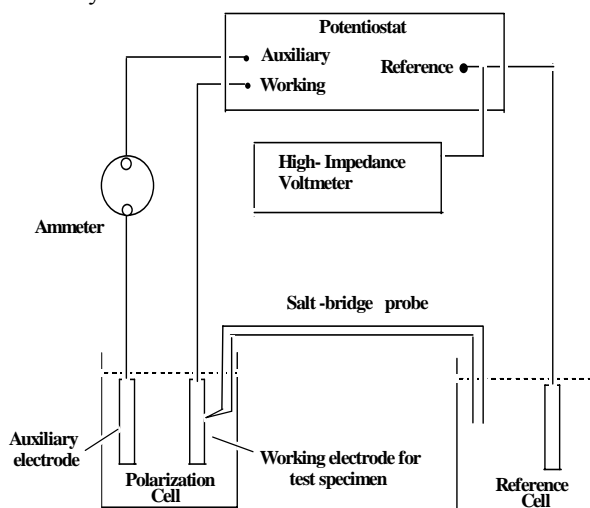


Fig. (2). Instrumental setup for electrochemical polarization experiments.

The corrosion inhibition efficiency (%IE) was evaluated from the measured i_{corr} values using the relationship:

$$I.E.(%) = \frac{i_{corr}^0 - i_{corr}^i}{i_{corr}^0} \times 100 \quad (2)$$

where, i_{corr}^0 and i_{corr}^i are the corrosion current densities in the absence and in presence of inhibitor.

3. RESULTS AND DISCUSSIONS

3.1. Weight Loss Studies

The values of inhibition efficiency (IE) and corrosion rate (CR) obtained at different concentrations of inhibitors are given in Table 2. All the VCI's have shown good inhibition efficiencies which may be attributed to the formation of physical barrier between metal and corrosive environment by the interaction of metal and inhibitor molecule. However, the difference in their inhibiting action can be explained on the basis of their molecular structure.

The results of weight loss studies clearly demonstrate the superior performance (> 99 percent inhibition efficiency) of Piperazine derivatives containing organic anions such as dinitrobenzoate (PDNB) and maleate (PDM) than those containing inorganic anions such as carbonate (PDC) and phosphate (PDP). In the present investigation, nitrobenzoate

salt of piperazine (PDNB) exhibited the best performance due to presence of nitro group, aromatic ring and carboxylate anion. Better inhibitive action of PDM is attributed to the presence of π -bond between carbon atoms ($-C=C-$) which facilitates greater adsorption of inhibitor molecule on the mild steel surface.

Table 2. Weight Loss Parameter Obtained from Different Concentration of Piperazine and its Derivatives at 40°C and 100% Relative Humidity for 30 Days

System	Weight Loss (mg)	Inhibition Efficiency (%)	Corrosion Rate (mmpy) X 10 ⁻³
Blank	38.5	--	5.95
Piperzine (P)			
250	6.6	82.86	1.20
500	2.1	94.55	3.25
750	1.2	96.88	1.85
1000	0.5	98.70	0.77
Piperazine Dinitrobenzoate (PDNB)			
250	2.3	94.03	3.56
500	1.9	95.06	2.94
750	0.4	98.96	0.62
1000	0.2	99.48	0.31
Piperazine Dimaleate (PDM)			
250	3.0	92.21	4.46
500	0.8	97.92	1.24
750	0.3	99.22	0.46
1000	0.2	99.48	0.31
Piperazine Diphosphate (PDP)			
250	2.0	94.81	3.09
500	1.6	95.84	2.48
750	0.8	97.92	1.24
1000	0.6	98.44	0.93
Piperazine Dicarboxylate (PDC)			
250	4.1	89.35	6.35
500	1.2	96.88	1.86
750	0.9	97.66	1.39
1000	0.7	98.18	1.08

3.2. Potentiodynamic Polarization Studies

The polarization behavior of mild steel in 1N Na₂SO₄ containing different concentrations of inhibitors is shown in Fig. (3a-e) and the electrochemical parameters derived from Tafel plots are summarized in Table 3. It is evident from the results that I_{corr} (Corrosion Current) values of all the inhibited mild steel coupons are low as compared to uninhibited mild steel, suggesting that all the Piperazine derivatives are effective corrosion inhibitors. It is also seen that all these samples shift

the corrosion potential significantly to noble direction therefore they are predominantly anodic inhibitors.

Table 3. Potentiodynamic Polarization Parameters Obtained from Different Concentration of Piperazine and its Derivatives

Concentration ppm	Corrosion Potential E _{corr} (mV)	Corrosion Current I _{corr} (mA cm ⁻²)	Inhibition Efficiency IE (%)
Blank	-562	0.25	--
Piperzine (P)			
250	-500	.064	74.4
500	-490	.060	76.0
750	-420	.052	79.2
1000	-480	.048	80.8
Piperazine Dinitrobenzoate (PDNB)			
250	-432	.074	70.4
500	-468	.068	72.8
750	-358	.056	77.6
1000	-346	.044	82.4
Piperazine Dimaleate (PDM)			
250	-510	.076	69.6
500	-370	.060	76.0
750	-360	.058	76.8
1000	-460	.050	80.0
Piperazine Diphosphate (PDP)			
250	-480	.058	76.8
500	-470	.055	78.0
750	-516	.045	82.0
1000	-460	.040	84.0
Piperazine Dicarboxylate (PDC)			
250	-490	.074	70.4
500	-390	.060	76.0
750	-470	.058	76.8
1000	-425	.048	80.8

3.3. Mechanism of Corrosion Inhibition

Vapor phase inhibitors can inhibit corrosion of metals in the following ways:

1. By saturating the space with their vapors and reducing the relative humidity below the critical value [15].
2. By alkalizing the medium to pH values at which the rate of corrosion becomes significantly low [8].
3. By producing a high ohmic resistance on the metal surface which reduces the corrosion current to a minimum value [16].

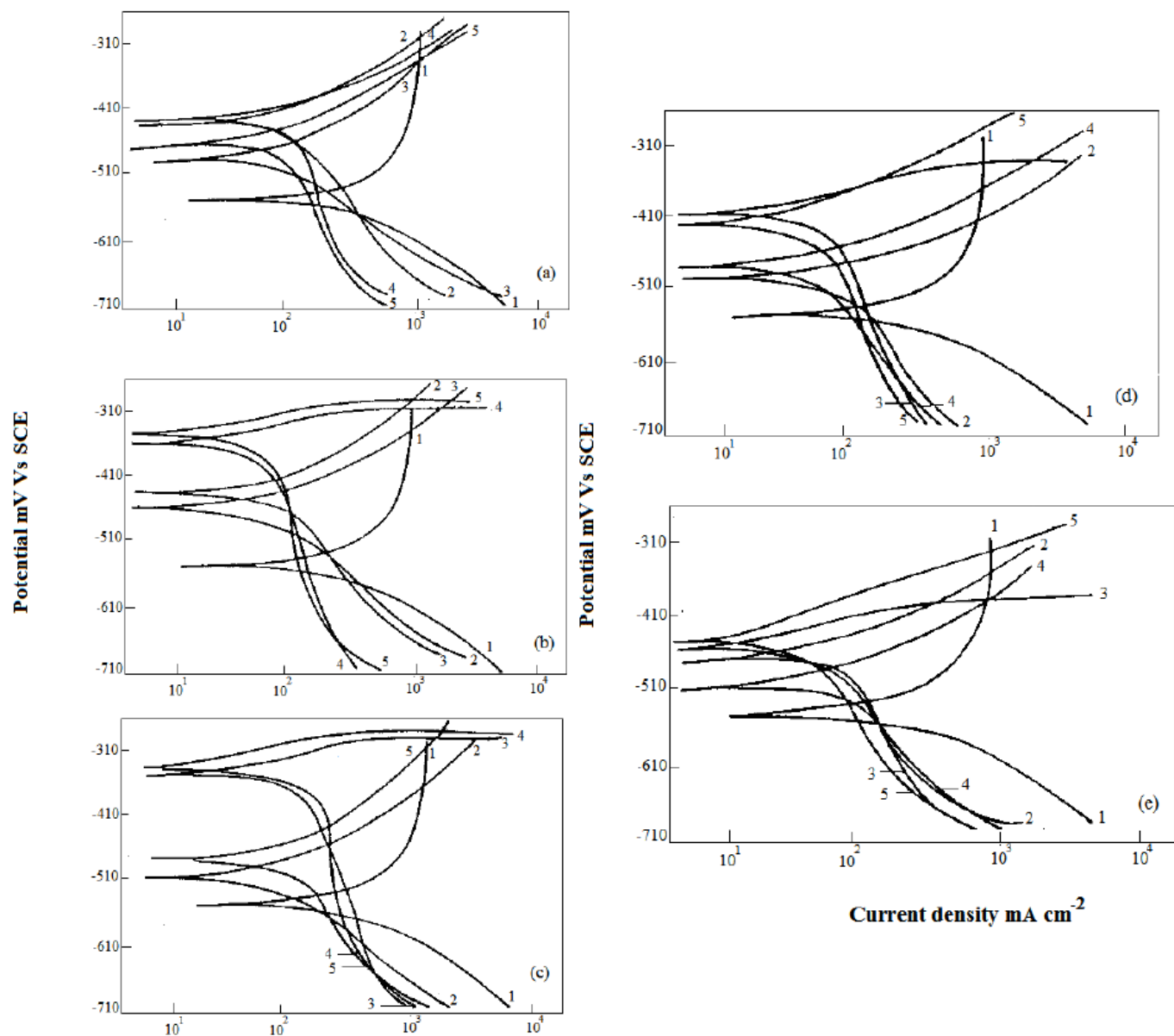


Fig. (3). Potentiodynamic polarization curves for mild steel inhibited with different concentration of: (a) Piperazine. (b) Piperazine dinitrobenzoate. (c) Piperazine dimaleate. (d) Piperazine diphosphate. (e) Piperazine dicarbonate. 1. Blank, 2. 250 ppm, 3. 500 ppm, 4. 750 ppm, 5. 1000 ppm.

- By rendering the metal surface hydrophobic thereby preventing the reaction of metal with the environment [17].

4. CONCLUSIONS

The vapor phase corrosion inhibition of mild steel carried out by using Piperazine and its derivatives shows good inhibition efficiency. Inhibition of corrosion is by the formation of physical barrier between metal and corrosive environment by the interaction of metal and inhibitor molecules. The inhibitive performance of all inhibitors increases on increasing the inhibitor concentration. PDNB gave the best performance among all compounds giving 99.48 percent inhibition efficiency at 1000 ppm concentration. All inhibitors have shown anodic behavior by retarding the anodic dissolution of mild steel by blocking the active sites on the mild steel surface.

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